Sensing the Instant Corrosivity of Haze Using Electrochemical Probes by Electrochemical Noise Technique

Chao MA, a Da-Hai XIA, a,b,* Yingying ZHANG, c Shizhe SONG, a,b Jihui WANG, a Zhiming GAO, a,b,* and Wenbin HU a

a Tianjin Key Laboratory of Composite and Functional Materials, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, People’s Republic of China
b CAS Key Laboratory of Nuclear Materials and Safety Assessment, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, Liaoning, People’s Republic of China
c CNPC Research Institute of Engineering Technology, Tianjin, 300451

*Corresponding authors: dahaixia@tju.edu.cn, gaozhiming@tju.edu.cn

ABSTRACT

Electrochemical noise (EN) was used to study the corrosivity of haze under Tianjin’s urban atmosphere by using two electrochemical corrosion probes made by T91 and Q235B steels. Experimental results indicate that temperature, relative humidity and concentrations of pollutants (PM10, PM2.5, SO2, NO2 and O3) can affect the corrosion of T91 and Q235B atmospheric corrosion monitoring probes. However, the atmospheric humidity has a major effect on corrosion activities. The corrosivity of haze under low temperature and high relative humidity has a high level, which can promote the corrosion of T91 and Q235B probes; the effect of atmospheric pollutant concentration on atmospheric corrosivity is not apparent due to theirs low concentrations. T91 probe is suitable for long term corrosion monitoring, while Q235B probe is suitable for short time monitoring and has high detection precision.

Keywords: Corrosivity, Sensor, Atmosphere, Electrochemical noise

1. Introduction

In recent years, haze has been widely recognized due to its significant impact on visibility, human health, cloud formation, and even global climate.1-5 Haze is a weather phenomenon that ranges from slight transient haze episodes to severe haze episodes, especially during the cold winter and spring seasons.5 Previous studies on the basic characteristics of haze have been carried out: Haze is related both to the meteorological conditions and air pollution, especially a sharp increase in airborne fine airborne particulate matters due to anthropogenic emissions and gas-to-particle conversion.4 The vertical structure of haze may complicate the radiation transfer process and it would alter the vertical profile of atmospheric heating rate, and thus facilitate the establishment of an extremely high concentration of airborne particulate matters near the surface layer.5

Airborne particulate matter (PM) is a complex mixture of ammonium, sulfates, nitrate, mineral dust, trace elements, and organic and elemental carbon (OC and EC), and it has become an important air quality indicator of ambient air because of its closely linked to air quality, human health problems, regional visibility, and global climate change.6-10 and much research has been done on PM.11-17 Tianjin has been facing the serious PM2.5 pollution especially in winter. Sulfate, nitrate, ammonium, organic, and element carbon have been found to comprise the major fraction of PM2.5.18,19 Han et al.18 investigated a heavy haze episode occurred in Tianjin and analyzed many characteristics associated with this episode, they pointed out that the concentrations of particulate and gaseous pollutants increased continuously during this haze period and the high layer transport of the pollutants and the secondary formation of aerosols were important mechanisms for causing the formation of this haze episode. Acide aerosols are considered not only detrimental to the public health, but also affect the metal corrosion in atmospheric condition. Large arrays of metal structures are directly exposed to haze environment. However, little information about sensing the instant corrosivity of haze has been studied.

Atmospheric corrosion of metal is an electrochemical corrosion process under an electrolyte film which is mainly determined by the relative humidity, wetting time, temperature, impurity ions, acid fog, and other factors.21,22 Therefore, haze will have a certain impact on the corrosion of the metal due to its height humid of meteorological conditions and air pollution. The pronounced contribution of sulfate and nitrate to this haze episode formation through the aqueous phase oxidation of their gas precursors (such as SO2, NOx) under higher RH condition during haze days might enhance the acidity of PM2.5.19,23-25 In addition, it was recently found that high concentration of NO2 promotes the conversion of SO2 to SO42- on heavy pollution days.26 Therefore, there is a need to develop new in-situ methods to sensing the corrosivity of haze.

The method of determining the weight loss of metals is frequently used but does not reflect the real-time corrosion rate and is not suitable for assessing non-uniform corrosion and early corrosion.27 Electrochemical methods have been used to monitor the corrosivity of atmosphere: Su et al.28 used potentiodynamic polarization studied the corrosion process of pure copper in corrosive atmosphere. Electrochemical impedance spectroscopy (EIS) has proven to be an effective technique for monitoring the corrosivity of haze and related mechanisms of steel. Nishikata et al.29-36 used EIS to study the corrosivity of atmosphere to different types of steels, and the effects of electrolyte concentration and pH value on the atmospheric corrosivity of metal were also studied. EIS was used to study the atmospheric corrosion of steel under an electrolyte film in wet-dry cycles by Dong et al.31 Leygraf et al.32-36 used situ X-ray transmission spectromicroscopy, infrared reflection absorption spectroscopy (IRAS) and a quartz crystal microbalance to investigate the atmospheric corrosivity of metals.

Most of the methods described above used readily in the laboratory, however, they are hardly used to measure instant corrosivity of haze. Therefore, electrochemical noise (EN) technology has
2. Experimental

2.1 Electrochemical probes

Two electrochemical probes were used in the atmospheric corrosivity monitoring, one of which is shown in Fig. 1. Each probe contained three nominally identical Q235B or T91 electrodes, as shown in Fig. 1(a). The chemical compositions of Q235B and T91 steels are shown in Table 1. During EN measurement, the electrode on the left was reference electrode (RE), and the other two electrodes were used as working electrodes (WEs), marked as WE1 and WE2, which was used to constitute the zero resistance ammeter (ZRA) test circuit as shown in Fig. 1(b). Each Q235B or T91 electrode had an exposed area of 4.2 cm². Two electrochemical probes were used to monitor the atmospheric corrosivity of Q235B and T91 steels.

Figure 1. (Color online) (a) Electrochemical probe for atmospheric corrosivity monitoring (the three electrodes are made of Q235B or T91); (b) a schematic diagram of EN measurement using a zero resistance ammeter (ZRA). (WE = working electrode, RE = reference electrode, “E” means potential, “I” means current) have been developed and widely used in atmospheric corrosion testing. EN is the stochastic unbalanced fluctuation of the electrical state parameters during the evolution of the electrochemical power system and it is a non-destructive and in-situ monitoring technique that can achieve long-term monitoring. It is usually conducted at the EN measurement system which electrochemical potential noise (EPN) and electrochemical current noise (ECN) can be recorded simultaneously. It is generally accepted that EPN is related to the type of corrosion whereas ECN is associated with corrosion intensity.

This work aims to establish a suitable electrode system to study the corrosivity of haze and the effect of gaseous air pollutants and climatic parameters on the corrosivity. Two electrochemical probes were used to monitor the atmospheric corrosivity of Q235B and T91 steels.

### Table 1. Chemical composition of Q235B and T91 steels (wt.%).

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Mo</th>
<th>P</th>
<th>V</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Si</th>
<th>Nb</th>
<th>S</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q235B</td>
<td>0.21</td>
<td>—</td>
<td>0.017</td>
<td>—</td>
<td>0.58</td>
<td>—</td>
<td>—</td>
<td>0.21</td>
<td>—</td>
<td>0.036</td>
<td>0.020</td>
<td>98.927</td>
</tr>
<tr>
<td>T91</td>
<td>0.10</td>
<td>0.89</td>
<td>0.20</td>
<td>0.40</td>
<td>8.90</td>
<td>0.12</td>
<td>0.24</td>
<td>0.08</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>89.07</td>
</tr>
</tbody>
</table>

The two atmospheric corrosion probes were exposed to outdoor atmosphere without a cover in Tianjin. Tianjin is located at east longitude 117°38’, latitude 38°98’, and 5 meters above sea level. The probes were placed at 45 degree angles to the floor during the atmospheric corrosion monitoring experiments. The experiment of Q235B and T91 were carried out simultaneously from December 21th of 2016 to January 9th of 2017.

2.2 Measurement system and data analysis

A cRIO module, a lithium ion battery, a DC power supply, two zero resistance ammeter (ZRA) modules (as shown in Fig. 2) were used to constitute the EN measurement system. The measurement system is connected to the probe for sensing the instant corrosivity of haze. The power supply of the system can be powered by the lithium-ion battery or DC power supply. The EN data were recorded automatically for every 15 minutes interval by the cRIO module, and each recording lasted for 512 s. The test frequency of EN was set at 2 Hz, because EN in corrosion reaction is considered as noise at low frequency, as claimed by Cottis in his review paper. The meteorological parameters, including temperature and relative humidity were recorded every 10 minutes with a DL-WS20 data recorder.

For the EN data were recorded by the cRIO module, the direct current (dc) component should be removed from original EN data by a 5-order polynomial fitting. The standard deviation is given by:

\[
\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (X_i - \mu)^2}
\]

where \( \sigma \) is the standard deviation, \( N \) is the number of data points, \( X_i \) is the \( i \)-th data point, \( \mu \) is the average value of the overall data. The noise resistance \( R_n \) is defined as the ratio of the standard deviation of the EPN divided by the standard deviation of the ECN.

In the present paper, the cumulative probability, \( p \), was plotted as a function of the EN. To obtain the cumulative probability, the parameter values were sorted into ascending order and \( p \) was derived as \( n/(N + 1) \), where \( n \) is the value rank in the sorted list, and \( N \) is the frequency of occurrence of the value. The results have been presented to clearly show the distribution of the values and allow for easy comparisons with previous results.

Hourly mean concentrations of air pollution data including AQI, PM2.5, PM10, SO2, NO2, O3 for Tianjin were obtained from an online database (https://www.aqistudy.cn/) were used in this study to...
characterize the pollution level. The Air Quality Index (AQI) is based on the principle of the Pollution Standard Index (PSI) used by the US Environmental Protection Agency (EPA). PM2.5 is an aerosol particle with aerodynamic diameter less than 2.5 µm which can penetrate into human lungs. PM10 is the fraction of aerosol particles with aerodynamic diameter less than 10 µm. PM is the most dominant air pollutant with the highest concentrations during hazy days and determines the daily PSI readings.

3. Results and Discussion

3.1 EN spectra at dry and haze environment

Figure 3 show the ECN and EPN measured by a Q235B probe that was exposed in dry condition and haze condition respectively. During dry condition: the ECN and EPN amplitudes are very small and fluctuate around 0 mV and 0 nA, respectively. The ECN ranges from −0.63 to 0.57 nA and the EPN ranges from −0.29 to 0.30 mV, indicating that the corrosion rate is extremely low because there is no continuous thin electrolyte on metal surface. In Fig. 3, under the haze condition (relative humidity increases to 96%), the ECN ranges from −12.81 to 12.85 nA and the EPN ranges from −12.26 to 10.86 mV. Comparing Figs. 3(a, b) with (c, d), the amplitudes of ECN and EPN are significantly increased under haze condition, indicating that a significant increase in corrosion rate. This is mainly ascribed to the increased relative humidity and air pollutants which promote the corrosion of Q235B steel. In general, haze had high corrosivity to Q235B steel, as it promotes Q235B steel corrosion.

Figure 4 show the ECN and EPN of T91 probe that was exposed in dry and haze conditions. When T91 probe is exposed in dry condition, the fluctuation amplitudes of the ECN and EPN are around 0 and very small: the ECN ranges from −1.04 to 1.12 nA and the EPN ranges from −0.34 to 0.48 mV. ECN and EPN amplitudes remain basically unchanged during an 512 s time period in dry condition. Under this condition, the corrosion rate is significantly low. When the T91 probe is exposed under haze condition, the amplitude values of the ECN and the EPN are 5.54 nA and 6.81 mV, respectively. The increased ECN amplitude indicates that the corrosion rate of T91 probe in the haze condition is accelerated. In other words, the haze plays a role in promoting the corrosion of T91 probe.

Comparing of Fig. 3 with Fig. 4: in the case of drying, both of the corrosion rate of Q235B and T91 is low and basically equal, corrosion reactions almost do not occur. When they are exposed to the haze condition, the corrosivity of haze accelerates the corrosion rates of these two steels, and the corrosion rate of Q235B increases more remarkably. EPN values of Q235B and T91 probes in the form of a function of time is distinctive: EPN values of Q235B randomly distributed around 0 mV, but time-varying EPN of T91 in haze present some transient peaks. This is mainly due to the corrosion form of Q235B and T91 steel is different. Comparison of ECN for the two steels under dry and haze, their corrosion rates are significantly increased under haze. In addition, corrosive of Q235B steel under haze is more serious than that of T91 steel.

Figure 5 shows a comparison of the probability distribution of ECN and EPN for Q235B and T91 probes after exposure to haze or dry condition. The values of ECN and EPN of Q235B and T91 exposed in dry condition are mainly concentrated near the 0 value, the range of distribution is very narrow because the density in the center is the largest. When the probe is exposed to haze, the fluctuation amplitudes of EPN and ECN becomes larger, therefore the distributions are wider. The increased ECN amplitudes indicates that the corrosion rate is accelerated. This reveals that haze plays an important role in the corrosion of Q235B and T91 probes. Furthermore, the ECN distribution of Q235B is wider than that of T91, which proves that the corrosion rate of Q235B is faster than T91 under the same haze condition. The probability density curve of EPN for T91 presents several peaks, indicating that the EPN distribution of T91 steel is dispersed. Meanwhile, the probability density curve of EPN for Q235B is concentrated in the center. This reveals that the corrosion types of the two materials are different under haze.

3.2 A continuous monitoring results

Figures 6(c, d) shows the calculated standard deviation of ECN and EPN of Q235B over 400 h respectively. Figures 6(e, f) shows the relative humidity and temperature values during the exposure experiment. The relative humidity and temperature fluctuate in opposite: when the temperature drops, the humidity rises; when the temperature is high, the humidity is low. The evolution of ECN...
standard deviation is closely linked to the relative humidity, as the relative humidity increases, the standard deviation of ECN also increase, illustrating that the corrosion reaction proceeded fast. It is indicating that the corrosion rate increases with the increase of humidity; humidity plays a decisive role in the metal corrosion. Figures 6(a, b) show the calculated ECN and EPN standard deviations of T91 steel probe exposed to the Tianjin outdoor atmospheric environment. The fluctuation trend of EPN and ECN standard deviation is less affected by relative humidity and temperature fluctuations, and the values of EPN and ECN standard deviation are relatively small, and there are some transient peaks in the EPN. Because T91 steel mainly occurs pitting corrosion and has a strong corrosion resistance; the corrosion reaction is insensitive to the relative humidity. Compare Figs. 6(a, b) with (c, d), haze has a strong corrosivity for the Q235B steel, while has weak corrosivity for T91 steel.

3.3 Impact of relative humidity and haze on noise resistance
Figure 7 shows the noise resistance ($R_n$) of Q235B and T91 steel exposed to Tianjin urban atmosphere. $R_n$ is defined as the ratio of the standard deviation of the EPN divided by the standard deviation of the ECN, and it is inversely proportional to the corrosion rate when both working electrodes have the same activity and the corrosion process is uniform. Figure 8 shows a comparison of the cumulative probability distribution of noise resistance for T91 and Q235B probes in Tianjin urban atmosphere. As shown in Figs. 7 and 8, the $R_n$ of T91 is a little bit higher than the $R_n$ of Q235B, indicating that the impact of the corrosivity of the atmosphere on the Q235B steel corrosion is relatively strong than that on T91 steel corrosion.

In Tianjin, the concentrations of pollutants (PM10, PM2.5, SO2, NO2 and O3) during exposure experiment from December 21th of

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**Figure 5.** (Color online) Probability distribution plot of EN data for T91 and Q235B probes in haze or dry: (a) ECN, (b) EPN.

**Figure 6.** (Color online) EN monitoring results of probe exposed to Tianjin urban atmosphere: (a) EPN standard deviation of T91 steel, (b) ECN standard deviation of T91 steel, (c) EPN standard deviation of Q235B steel, (d) ECN standard deviation of Q235B steel, (e) relative humidity, (f) temperature.

**Figure 7.** (Color online) Noise resistance of Q235B and T91 steel exposed to Tianjin urban atmosphere.

**Figure 8.** (Color online) Cumulative probability distribution of noise resistance data for T91 and Q235B probes in Tianjin urban atmosphere.
At 100 or 300 h, when the SO2 or NO2 concentration is higher, the quality environment is low and they have good corrosion resistance. The noise resistance of Q235B and T91 is value is low and the main air pollutants such as PM10, PM2.5 soluble compounds are also possible pathways for the formation of sulfate and nitrates, thereby promoting the occurrence of corrosion, absorption by the electrolytic liquid

Then HSO\textsubscript{3} \textsuperscript{-} is oxidized to produces SO\textsubscript{3} and produces H\textsubscript{2}SO\textsubscript{4}.

The gaseous SO\textsubscript{2} is hydrolysed according to Eq. (2) after absorbed by the electrolytic liquid film on the surface of the probe. Then HSO\textsubscript{3} \textsuperscript{-} oxidized to produces SO\textsubscript{3} and produces H\textsubscript{2}SO\textsubscript{4}.

Corrosion is autocatalytic with a rapid dissolution of iron and production of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} cations and forms a sulfate. Sulfate anions enter the electrolyte as part of a component of precipitation to enhance the sulfate-induced corrosion of iron thus creating more dissolved iron cations, accelerate the corrosion rate.

NO\textsubscript{2} is oxidized to nitric acid

\[
\begin{align*}
\text{NO}_2 + O_3 & \rightarrow \text{NO}_3 + O_2 \\
\text{NO}_2 + \text{NO}_2 & \rightarrow \text{N}_2\text{O}_5 \\
\text{N}_2\text{O}_5 + H_2O & \rightarrow 2\text{HNO}_3
\end{align*}
\]

The gaseous NO\textsubscript{2} is oxidized to produces NO\textsubscript{3} according to Eq. (5). NO\textsubscript{3} and NO\textsubscript{2} react to produce N\textsubscript{2}O\textsubscript{5} and then dissolved in water generation HNO\textsubscript{3}. The presence of HNO\textsubscript{3} favors the corrosion of metals.

The apparent contribution of haze to atmospheric corrosion may be related to the high oxidation rate of SO\textsubscript{2} and NO\textsubscript{2}. SO\textsubscript{2} and NO\textsubscript{2} are converted to sulphate and nitrates in haze that occur by SO\textsubscript{2} and NO\textsubscript{2} through aqueous phase oxidation. The increase of relative humidity of haze is beneficial to the oxidation of SO\textsubscript{2}. Nitrate formation occurs through heterogeneous hydrolysis processes.

Strong synergistic effects between SO\textsubscript{2} and NO\textsubscript{2} were observed. The strong synergism of the two gases was attributed to the formation of an electrolyte containing nitrate on the surface, which enhances the subsequent uptake of sulphur dioxide. The large amounts of nitrates formed with ozone might be explained by the oxidation of nitrogen dioxide by ozone in the surface water film allowing further deposition of nitrogen dioxide.

As shown in Figs. 6, 7 and 9, the corrosion rate of Q235B is faster than T91. ECN, ECP and noise resistance have a higher sensitivity to the change of meteorological conditions and air pollution. Therefore, these parameters of Q235B are suitable for the short time and high precision detection of haze corrosivity. T91 has a strong corrosion resistance even in haze condition, and the corresponding electrochemical parameters are not sensitive to environmental factors. However, it is suitable for long periods sensing of the corrosivity of haze.

Figure 10 shows the morphology of T91 and Q235B after exposure to an outdoor atmosphere for 20 d. Q235B with a layer of compact corrosion product formed on the surface of the steel. Comparatively, T91 surface has little corrosion products. It is indicates that T91 probe has a low corrosion rate.
4. Conclusions

In the present work, the corrosivity of haze were monitored by two electrochemical probes by using electrochemical noise technique, and the conclusions are summarised as follows:
1. Standard deviations of EPN and ECN, and noise resistance can be used as corrosivity indicators of haze. Corrosion resistance of T91 probe is better than Q235B probe. The corrosion rate of T91 and Q235B in haze is faster than that in dry environment, the corrosively of haze plays a key role in promoting the corrosion behavior of both T91 and Q235B steel.
2. The probability density distributions of EPN and ECN can be used to illustrate a corrosion process visually. The probability density distribution curves of EPN and ECN plots for Q235B and T91 probes become wider when the probes were exposed in haze, compared with probes in dry conditions.
3. Temperature, relative humidity and concentrations of pollutants (PM10, PM2.5, SO2, NO2 and O3) can affect steel corrosion. Humidity plays a major role of the haze and the apparent contribution of haze to atmospheric corrosivity is possibly related to the high oxidation rate of SO2 and NO2.
4. Q235B is suitable for the short time and high-precision detection of the haze corrosivity due to its high sensitivity to environmental factor changes. The T91 probe has a low corrosion rate in haze and therefore it is suitable for long-term sensing of the corrosivity of haze.

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