Corrosion evolution of electric power equipment metal materials under industrial pollution environment with high heat and high humidity

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Abstract. To investigate the atmospheric corrosion characteristics of metal materials of electric equipment in the atmospheric environment with high humidity and high chlorine industrial pollution, atmospheric accelerated corrosion tests of a typical power metal Q235 carbon steel and galvanized steel were carried out by the salt spray method. The corrosion kinetics, corrosion products, and morphology of both materials were investigated by the weight loss method, scanning electron microscopy (SEM), and X-ray diffraction (XRD). The corrosion rate of carbon steel is larger than that of galvanized steel, and both drop with time. NaHSO₃ promotes the formation of α-FeOOH in the corrosion process of carbon steel. The high-humidity and high-chlorine environment is not conducive to the formation of Fe₃O₄. The interaction of NaHSO₃ and NaCl promotes the generation of corrosion products, mainly NaZn₄SO₄(OH)₈Cl·6H₂O, in galvanized steel by pitting corrosion.

1. Introduction

With the construction of UHV projects, China’s power grid covers a wider range of areas, including hilly areas, plains and desert areas, and some areas are even highly corrosive areas such as severe industrial pollution and high heat. However, because the complexity of terrain was not taken into account in the early design of the project, uniform design standards were adopted for the metal materials of power equipment, which led to the failure of the actual material life to meet the actual environmental requirements, resulting in serious potential safety hazards [1]. According to statistics, the overwhelming majority of power safety accidents are caused by tower inversion and line breakage of transmission network [2].

The main corrosion factors in a typical industrial city climate environment are SO₂, SO₃, H₂S, and others. SO₂ and Cl⁻ in the atmosphere are the main pollution factors affecting the atmospheric corrosion of metals [3]. When they exist alone, they will cause serious corrosion of metals. If both exist simultaneously, their corrosion amount will be greater [4]. Therefore, it is of great significance to study the corrosion characteristics of power equipment materials in high chlorine and high pollution environments for guiding the construction and protection of power transmission and transformation projects.

Based on high-temperature and humidity climate conditions in Chongqing, the corrosion kinetics, product characteristics and corrosion morphology evolution of carbon steel and galvanized steel, which
are metal materials of common power equipment, under extremely harsh environments of high chlorine and high pollution, are studied in this paper. At the same time, the corrosion characteristics of carbon steel and galvanized steel are compared. The difference and corrosion mechanism under this environment are discussed, which provides theoretical support for the engineering design and protection of metal materials for power transmission and transformation equipment.

2. Experimental

The typical power transmission and transformation equipment engineering materials Q235 low-carbon steel and hot-dip galvanized steel were selected as experimental materials. The chemical composition of carbon steel is shown in Table 1. The thickness of zinc layer was 100-140μm. The experimental material was first cut into 150mm×100mm×4mm large samples for corrosion weight loss test, and the other part was cut into 20mm×20mm×4mm small samples for surface morphology and product observation experiments. The small pieces were sanded with 180#~1200# sandpaper, and the oil and impurities on the surface were washed with alcohol and acetone and dried.

Table 1. Q235 low-carbon steel elemental composition.

| Element | C  | Si  | Mn  | P   | S   | Cr  | Ni  | Cu  | Fe  |
|---------|----|-----|-----|-----|-----|-----|-----|-----|-----|
| Percentage (%) | 0.14 | 0.21 | 0.26 | 0.017 | 0.010 | 0.03 | 0.05 | 0.05 | Other |

The accelerated corrosion test was carried out by the salt spray method to simulate high-temperature and high-humidity environment. The temperature in the box was controlled at 47 °C (±0.5 °C), and the spray amount was controlled in the range of 1~2ml/80cm2·h. The corrosion solution was mixed with NaHSO3 and NaCl to simulate high chlorine and industrial pollution environment, and the solution concentrations were 12.5 and 50g/L, respectively.

The solution of 500 mL HCl (38% concentrated hydrochloric acid), 500 mL distilled water, and 20 g C6H12N4 was used to remove rust from large-scale corroded carbon steel samples at room temperature. NH2CH2COOH and distilled water were used to prepare a saturated solution for rust removal of large-scale galvanized steel at room temperature. After rust removal, samples were washed with distilled water and alcohol, and weighed after drying. Sampling time was 2, 4, 6, 10, and 15 days.

A JEOL JSM-7800F field emission scanning electron microscopy (SEM) was used to observe the morphology of the corroded metal surface for 2 and 6 days, and PANalytic Empyrean X-ray diffractometer (XRD) was used to qualitatively analyze the composition of corrosion products.

3. Results and discussion

3.1. Corrosion kinetics behavior

The corrosion kinetic behavior of metals is generally expressed by corrosion weight loss [5]. The relationship between corrosion weight loss and time conforms to the classical power function equation:

\[ \Delta W = AT^n \]  

where \( \Delta W \) is the mass loss per unit surface area at different time, \( g/m^2 \), \( A \) is constant, \( T \) is corrosion exposure time, and \( n \) is a constant characterizing protective properties of corrosion products on the metal surface. At \( n > 1 \), the rust layer accelerates the metal matrix corrosion, while at \( n < 1 \), the rust layer has a certain protective effect.

Figure 1(a) shows the corrosion kinetics curves of Q235 carbon and galvanized steels under high-temperature and high-chlorine industrial pollution. It can be seen in the above figure that the corrosion weight loss of both materials increases with time, and the weight loss of carbon steel is higher than that of galvanized steel. By fitting the weightlessness data with a power function equation, we can get that \( n_1=0.759 \) for carbon steel and \( n_2=0.415 \) for galvanized steel. The results show that the rust products of both coatings have certain protective properties, which are better in the galvanized steel.
Formula (2) can be used to calculate the instantaneous corrosion rate $V_{\text{corr}}$ of metals as follows:

$$V_{\text{corr}} = \frac{dW}{dT} = A T^{n-1}$$

Figure 1(b) shows that corrosion rates of Q235 carbon steel and galvanized steel vary with time at high-temperature and high-chlorine industrial pollution environment. It can be seen that the corrosion rate of carbon steel is higher than that of galvanized steel during the whole corrosion process, and the corrosion rates of both steels show a downward trend, which is consistent with the analysis of $n$.

3.2. Analysis of composition change of rust layer

The products of carbon and galvanized steels corroded for 6 and 15 days were analyzed by the XRD spectrum and standard peak position. As shown in figure 2, the characteristic peaks of $\alpha$-FeOOH, $\gamma$-FeOOH, and Fe$_3$O$_4$ exist in the corrosion process of carbon steel. Among them, the peak values of $\alpha$-FeOOH at 21, 33, and 36° are strong, as well as those of $\gamma$-FeOOH at 14, 27, and 36°, but peak values vary in different periods. At the early stage of corrosion, the peak value of $\gamma$-FeOOH in the rust layer is the highest, while at the later stage, the peak value of $\gamma$-FeOOH decreased significantly, while the peak value of $\alpha$-FeOOH increased.

This indicates that the content of $\gamma$-FeOOH first increases and then decreases, and is gradually transformed to such corrosion products as $\alpha$-FeOOH. This is due to the strong reducibility of $\gamma$-FeOOH and strong stability of $\alpha$-FeOOH relative to $\gamma$-FeOOH, which is a protective rust component. The content of $\alpha$-FeOOH in the corrosion process is relatively high. This may be because the simulated environment is highly chlorine-polluted and NaHSO$_3$ is easily oxidized to Na$_2$SO$_4$, which promotes the formation of $\alpha$-FeOOH. The results are consistent with those of Yamashita et al [6]. The content of Fe$_3$O$_4$ increases.

**Figure 2.** XRD analysis of corrosion products of Q235 carbon steel for different corrosion periods.
less during corrosion, which may be related to the excessive solubility of chloride ions in corrosion solution [7].

During the corrosion process of galvanized steel (figure 3), there are many characteristic peaks of NaZn$_4$SO$_4$(OH)$_6$Cl·6H$_2$O at the early stage of corrosion, such as 6, 13, 32°, etc., and peaks are strong. At the same time, there is a thin zinc layer at the surface. At the later stage of corrosion, the exposed zinc layer disappeared, and the corrosion product Zn$_4$SO$_4$(OH)$_6$·5H$_2$O was formed at the surface, besides NaZn$_4$SO$_4$(OH)$_6$Cl·6H$_2$O. Because Cl$^-$ and SO$_4^{2-}$ exist simultaneously in the corrosion solution and Cl$^-$ concentration is higher than SO$_4^{2-}$ ion concentration, NaZn$_4$SO$_4$(OH)$_6$Cl·6H$_2$O is the main corrosion product, and there is no Zn$_3$(OH)$_6$Cl$_2$, which is consistent with the results of Odnevall et al [8].

**Figure 3.** XRD analysis of corrosion products of galvanized steel for different corrosion periods.

### 3.3. Microscopic corrosion morphology analysis of corrosion products

Figure 4 shows the surface morphology of Q$_{235}$ carbon steel for different corrosion periods. The surface structure of the rust layer of specimens that was corroded for 2 days (a1, a2) is loose, and the corrosion products are petal-like or layered. At this time, the corrosion products are mainly γ-FeOOH, which is reductive and has no protective effect on the matrix. There are many cracks on the surface of the rust layer, and Cl$^-$ easily penetrates into cracks and enters the matrix surface. The surface structure of specimens corroded for 6 days (b1, b2) is denser than that of the specimens corroded for 2 days. The corrosion products are gradually continuous, there are more flake products, and a certain amount of spherical products appears.

The surface products of Q$_{235}$ carbon steel specimens (c1), (c2), and (c3) corroded for 15 days were mainly spherical and dense massive products. According to the morphology of the spherical product, it is determined to be α-FeOOH, which is formed by dissolving γ-FeOOH into amorphous FeOOH and then transforming into a solid state [9]. It can be seen from (c3) that the rust layer is thicker and denser, and its protective performance increases accordingly. However, the corrosion of corrosive ions Cl$^-$ on the matrix cannot be prevented because of the existence of cracks.

Figure 5 shows the variation of SEM corrosion morphology of galvanized steel surface. It can be seen that there are numerous flake products on the surface of zinc layer after 2 and 6 days of corrosion, and the overall structure is reticular. The surface of zinc layer corroded for 6 days has some flower-like and block-like products, besides flake-like ones. The overall structure of the rust layer is relatively loose. The corrosion structure of the steel corroded for 15 days is more compact. There are many flake products on the surface of the corroded samples, but the corrosion products are thicker and caked.

Table 2 lists the EDS analysis results of products with different morphologies in Figure 5. In this paper, only the mass percentages of Zn, O, S, and Cl were selected for analysis and comparison. Table 3 shows the mass percentage of four elements of typical corrosion products on the surface of zinc layer calculated by the chemical formula.
Figure 4. Microscopic corrosion morphology of Q235 carbon steel surface with different corrosion time: (a1) (a2) 2 days, (b1) (b2) 6 days, (c1) (c2) (c3) 15 days.

Table 2. Elemental mass percentage of corrosion products with different corrosion periods and morphology.

| Products | Zn (wt%) | O (wt%) | S (wt%) | Cl (wt%) |
|----------|----------|---------|---------|---------|
| A        | 53.26    | 40.34   | 5.26    | 1.18    |
| B        | 53.21    | 39.40   | 4.24    | 3.15    |
| C        | 53.94    | 30.07   | 10.25   | 5.74    |
| D        | 51.65    | 28.18   | 18.40   | 1.77    |
| E        | 51.72    | 37.34   | 10.03   | 0.89    |
| F        | 53.34    | 35.56   | 11.1    | —       |

Table 3. Elemental mass percentage of typical corrosion products of galvanized steel.

| Compounds                                      | Zn(wt%) | O(wt%) | S(wt%) | Cl(wt%) |
|-----------------------------------------------|---------|--------|--------|---------|
| Zn₅(OH)₆Cl₂·H₂O                               | 60.19   | 26.67  | —      | 13.14   |
| NaZn₄SO₄(OH)₆Cl·6H₂O                          | 44.55   | 43.87  | 6.08   | 1.77    |
| Zn₅SO₄(OH)₆·5H₂O                              | 48.87   | 45.11  | 6.01   | —       |
| Zn(OH)₂                                       | 67.01   | 32.99  | —      | —       |
| Zn₅(CO₃)₂(OH)₆                               | 62.86   | 37.13  | —      | —       |
| Na₂Zn(SO₄)₂·4H₂O                              | 20.24   | 59.81  | 19.94  | —       |
| ZnSO₄·H₂O                                     | 36.72   | 45.19  | 18.07  | —       |

Products A, B, C, D, and E all contain four elements: Zn, O, S and Cl. According to table 2 and XRD analysis, only NaZn₄SO₄(OH)₆Cl·6H₂O meets the requirements, and the mass ratios of various elements are similar to those of these products. Therefore, it can be inferred that the flake products A, B, C, E and petal products E are sodium zinc sulfate chlorinated alkali NaZn₄SO₄(OH)₆Cl·6H₂O. According to the element ratio of F, it can be judged that F is Zn₅SO₄(OH)₆·5H₂O. Therefore, in the early stage of galvanized steel corrosion, the main surface product is NaZn₄SO₄(OH)₆Cl·6H₂O. With the corrosion
occurring, the rust layer will gradually become thicker. Some \( \text{NaZn}_4\text{SO}_4(\text{OH})_6\text{Cl} \cdot 6\text{H}_2\text{O} \) will transform into plate-like compact basic zinc sulfate \( \text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O} \).

**Figure 5.** Microscopic corrosion morphology of galvanized steel surface with different corrosion periods: (a1) (a2) 2 days, (b1) (b2) (b3) (b4) 6 days, (c1) (c2) (c3) 15 days.

Figure 6 shows the cross-sectional corrosion morphology of carbon and galvanized steels corroded for different periods. The overall corrosion of carbon steel is uniform, while that of galvanized steel is mainly pitting corrosion. At the initial stage of corrosion (6 days), the surface of carbon steel was mainly composed of loose rust layer, which contained flake products. The surface of galvanized steel was thin, and it was a loose network structure. During the corrosion process, the rust layer became thicker, and a denser protective layer (15 days) was formed at the surface, which implied that the rust layer had a relatively high corrosion resistance.

**Figure 6.** Microscopic corrosion morphology of sample cross section at different corrosion time: Q235 carbon steel, (a1) 6 days, (a2) 15 days; galvanized steel, (b1) 6 days, (b2) 15 days.
3.4. Analysis of corrosion mechanism

Atmospheric corrosion of Q235 carbon and galvanized steels belongs to electrochemical corrosion under a thin liquid film. This study simulated the atmospheric corrosion in a corrosive environment with high chlorine and high pollution under high humidity and heat conditions.

At the initial stage of corrosion, more flake-like γ-FeOOH particles were formed on the surface of carbon steel, but during the corrosion process, they quickly transformed into spherical α-FeOOH, which may be related to the existence of NaHSO₃. The HSO₃⁻ dissolved in the liquid film adsorbed on the steel surface can be oxidized to H₂SO₄ by oxygen in the air, thus promoting the formation of α-FeOOH. Fe₂O₄ was also found in the corrosion process, but its content was not high. As the corrosion proceeded, the rust layer on the corrosion surface became thicker and denser, and the corrosion rate decreased. Therefore, the corrosion process of Q235 carbon steel under the condition of high humidity, heat and chlorine industrial pollution is described by equations (3) ~ (8).

\[
\begin{align*}
\text{HSO}_3^- + 1/2\text{O}_2 &= \text{H}^+ + \text{SO}_4^{2-} \quad (3) \\
\text{Fe}^{2+} - 2\text{e}^- &= \text{Fe}^{2+} \quad (4) \\
\text{Fe}^{2+} + 2\text{Cl}^- &= \text{FeCl}_2 \quad (5) \\
4\text{FeCl}_2 + 6\text{H}_2\text{O} + \text{O}_2 &= 4\text{FeOOH} + 8\text{HCl} \quad (6) \\
2\text{FeSO}_4 + 3\text{H}_2\text{O} + 1/2\text{O}_2 &= 2\text{FeOOH} + 2\text{H}_2\text{SO}_4 \quad (7) \\
8\text{FeOOH} + \text{Fe} + 2\text{e}^- &= 3\text{Fe}_2\text{O}_3 + 4\text{H}_2\text{O} \quad (8)
\end{align*}
\]

No Zn₅(OH)₆Cl₂·H₂O was detected in the galvanized steel during corrosion. The main corrosion product was NaZn₅SO₄(OH)₆Cl·6H₂O. This may be because in the high-humidity and high-chlorine industrial pollution conditions, Cl⁻ and HSO₃⁻ are simultaneously present, and NaZn₅SO₄(OH)₆Cl·6H₂O has higher stability and is more likely to exist than Zn₅(OH)₆Cl₂·H₂O. Because NaZn₅SO₄(OH)₆Cl·6H₂O is a sheet-like network structure, the ability to inhibit corrosion is poor, resulting in corrosion of the surface of galvanized steel. In the later stage of corrosion, the rust layer on the surface of galvanized steel is gradually dense, and some NaZn₅SO₄(OH)₆Cl·6H₂O is transformed into Zn₅SO₄(OH)₆·5H₂O. The corrosion process of galvanized steel is shown in equations (9) to (14).

\[
\begin{align*}
\text{Zn}^{2+} + 2\text{e}^- &= \text{Zn} \quad (9) \\
\text{HSO}_3^- + 1/2\text{O}_2 &= \text{H}^+ + \text{SO}_4^{2-} \quad (10) \\
\text{O}_2 + 4\text{e}^- + 2\text{H}_2\text{O} &= 4\text{OH}^- \quad (11) \\
\text{Zn}^{2+} + 2\text{OH}^- &= \text{Zn(OH)}_2 \quad (12) \\
\text{Zn(OH)}_2 + 3\text{Zn}^{2+} + 4\text{OH}^- + \text{SO}_4^{2-} + 6\text{H}_2\text{O} + \text{NaCl} &= \text{NaZn}_{10}\text{SO}_{14}(\text{OH})_6\text{Cl}·6\text{H}_2\text{O} \quad (13) \\
\text{NaZn}_{10}\text{SO}_{14}(\text{OH})_6\text{Cl}·6\text{H}_2\text{O} &= \text{Zn}_{5}\text{SO}_{4}(\text{OH})_6·5\text{H}_2\text{O} + \text{NaCl} + \text{H}_2\text{O} \quad (14)
\end{align*}
\]

4. Conclusion

(1) In the high-humidity and high-chlorine industrial pollution environment, the corrosion rate of carbon steel is larger than that of galvanized steel, especially in the rust layer, and the corrosion rates of both steels decrease with time.

(2) The presence of NaHSO₃ in the corrosive solution promotes a relatively high content of α-FeOOH in the corrosion process of carbon steel. The high-humidity and high-chlorine environment is not conducive to the formation of Fe₂O₃, and its content is relatively small.

(3) The joint action of NaHSO₃ and NaCl implies that the corrosion products of galvanized steel in the corrosion process are mainly flaky NaZn₅SO₄(OH)₆Cl·6H₂O. The structure of the rust layer is loose, and the corrosion form is mainly pitting corrosion.
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