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Experimental design of Cu content in weathering resistance steel for industrial atmosphere application

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Abstract

In this paper, the effect of sulfur dioxide (SO\textsubscript{2}) on the corrosion behavior of weathering steel with different copper (Cu) contents in a simulated industrial environment was studied. The results showed that the corrosion occurred in three distinct stages with the corrosion kinetics characterized via the parameter of ‘n’. For the first and second stage with n > 1 and n < 1, the corrosion of weathering steel was accelerated and reduced, respectively. The third stage witnessed the minimum value of n, indicating a lowest corrosion rate. As the Cu content increased from 0.15% to 0.50%, the corrosion weight gained and corrosion rate remarkably decreased. In contrast, when the Cu contents increased from 0.50% to 0.70%, the corrosion rate began to slightly decrease. With the Cu addition, the stable \(\alpha\)-FeOOH phase in the rust layer was refined, which increased the electrochemical impedance accordingly lowered the electrochemical reaction rate and ultimately enhanced the corrosion resistance. In this work, we have studied the corrosion mechanism of Cu element on the weathering steel in the industrial atmosphere, and studied the effect of Cu content on the corrosion resistance of weathering steel. The research shows that the content of the effect is not great, so the recommended amount of Cu in weathering steel is not more than 0.50%.

1. Introduction

Weathering steel normally with the addition of Ni, Cr, Cu, and other alloying elements, can produce a dense surface rust layer which acts as a physical protection barrier. Additionally, it can also enhance the electrochemical properties of the rust layer, thereby reducing the corrosion rate of the steel. The weathering steel possesses 2–8 times corrosion resistance of an ordinary carbon steel\cite{1} and has been widely used to fabricate various important steel structure facilities such as buildings, bridges, etc\cite{2–7}.

Cu has been added to steel as a good weathering-proof element, and there are many explanations for why Cu can improve the weather resistance. Inouye et al\cite{8} proposed that Cu\textsuperscript{2+} has a Jahn-Teller effect. It can also refine the cotton globular \(\alpha\)-FeOOH grain via inhibiting their growth, and thus increase the compactness of the rust layer. Hao et al\cite{9} performed some laboratory experiments of accelerated corrosion of Cu-bearing steels in simulated environment, and the results show that Cu can hinder the entry of O\textsubscript{2}, slow the growth and reduce the conductivity of the rust layer. They also assumed that Cu (I) would be involved in the formation of reverse spinel oxide Fe\textsubscript{3}O\textsubscript{4}, whose crystal structure contains one Fe (II)-centered octahedron (FeO\textsubscript{6})\textsuperscript{2-}, one Fe (III)-centered octahedron (FeO\textsubscript{6})\textsuperscript{2-}, and one Fe (III)-centered tetrahedron (FeO\textsubscript{4}). One Cu (I) might displace one Fe (III) and occupy the tetrahedral center of the FeO\textsubscript{4} crystal, creating an electronegative molecular. Therefore, this rust structure can reduce the penetration of SO\textsubscript{4}\textsuperscript{2-}, contributing to the cation-selectivity of the rust layer with respect to SO\textsubscript{4}\textsuperscript{2-}. Suzukiand et al\cite{10} demonstrated that Cu reduced the porosity of the rust layer and accordingly
increased its density. Simultaneously Cu promoted the crystalline magnetite formation via a redox reaction. All these impacts increased the barrier function of rust layer. Kimura et al [11] proposed that Cu could provide preferential nucleation sites for the formation of FeO(OH)₉, on the early stage of corrosion. This made the nucleation rate of FeO(OH)₉ exceed the growth rate, thus forming a fine-grained and tight protective rust layer. It is widely accepted that under a long-term exposure, weathering steel forms crystalline α-FeOOH, γ-FeOOH, β-FeOOH and Fe₃O₄. Among these crystalline phases, the rust layer consisting of α-FeOOH can act as a strong physical barrier to O₂ and other corrosive media, prevent the matrix from being heavily corroded, and improve the corrosion resistance [7, 12, 13]. Suzuk et al [14] studied the electrochemical properties of the rust layer on weathering steel and proposed an ‘overlapping dual electrode’ model. This study showed that γ-FeOOH in the rust layer was reduced to Fe₃O₄ during the cathode reaction, but α-FeOOH failed. Kamimura et al [15] used XRD and Mossbauer spectroscopy to analyze weathering steel and carbon steel exposed to industrial environments for 15 years and 32 years. The rust formed on weathering steel and mild steel exposed to an environment for a long time was characterized by means of Mössbauer spectroscopy. The rust consists of the crystalline α-FeOOH, γ-FeOOH, γ-Fe₂O₃ and an X-ray amorphous phase. γ-Fe₂O₃ is found only in the rust formed on mild steel Some researchers have pointed out that the addition of Cu could improve the corrosion resistance by decreasing Fermi energy from −9.276 to −12.365 eV [16].

With the rapid industrialization, SO₂ has appeared in many places. An industrial area with major pollutants has implemented increasing requirements for the large-scale application of steel. Therefore, it is necessary to study the corrosion behavior of Cu-bearing weathering steel in industrial environments and understand its corrosion mechanism. In particular, the content of Cu in weathering steel is limited by both the ASTM 709 and the Chinese GB 1836 standard and the Chinese GB 714 standard [17]. Namely, the content of Cu in W50 Type A and W50 Type B steels specified by ASTM709 is 0.25%–0.40% and 0.20%–0.40%, respectively, while the content of Cu in HPS50W/HPS70W steel is 0.34%–0.70%. By contrast, the Cu content specified by GB /714 is 0.25%–0.50%. In addition, ASTM G101–04 standard [18] provides a guideline for the evaluation of the atmospheric corrosion resistance of low alloy steels. The weather resistance index (I index) is used to determine the weather resistance of low alloy steels. However, the upper limit of Cu in this formula is 0.51%.

In order to investigate the upper content limit of Cu element in weathering steel, four weathering steels with differing Cu content from 0.15 to 0.70 wt% were prepared in this attempt, aiming to clarify the role of Cu in enhancing the weathering-proof rust layer formation in an industrial environment, optimize the Cu content in the weathering steel, and accordingly provide a guidance for industrial application.

### 2. Experimental

#### 2.1. Materials

Experimental steel was refined in a vacuum smelting furnace and rolled it to a thickness of 18 mm. The chemical compositions of the four experimental steels are shown in Table 1. The optical micrographs of the experimental steel are shown in figure 1, and show that it consists mainly of bainite and ferrite.

#### 2.2. Sample preparation

The experimental steel plate was cut into slices of 20 mm × 20 mm × 4 mm for the dry-wet alternating acceleration tests. Each specimen was mounted in cured epoxy resin, and the slices of 10 mm × 10 mm × 4 mm for electrochemical testing. One side was welded with a wire, the other sides were sealed with epoxy resin, with only the working face exposed. The sealed samples were dried for 48 h (figure 2). After being dried, the samples were ground with SiC paper down to 1500 grade emery paper, cleaned successively with ultrasonic acetone (for removing oil) and deionized water, then dehydrated with alcohol. Subsequently, the samples were stored in a desiccator for 24 h.

| Steel  | C   | Si   | Mn   | P    | S    | Ni  | Cr  | Mo  | Cu  | Nb  | V   | Ti  | Al  |
|--------|-----|------|------|------|------|-----|-----|-----|-----|-----|-----|-----|-----|
| WS0.15Cu | 0.051 | 0.16 | 1.12 | 0.0077 | 0.0018 | 0.37 | 0.41 | 0.21 | 0.15 | 0.019 | 0.021 | 0.007 | 0.014 |
| WS0.35Cu | 0.054 | 0.13 | 1.15 | 0.0076 | 0.0031 | 0.31 | 0.43 | 0.23 | 0.35 | 0.020 | 0.028 | 0.006 | 0.012 |
| WS0.50Cu | 0.052 | 0.13 | 1.11 | 0.0080 | 0.0050 | 0.35 | 0.45 | 0.22 | 0.50 | 0.023 | 0.023 | 0.06 | 0.017 |
| WS0.70Cu | 0.057 | 0.16 | 1.18 | 0.0084 | 0.0025 | 0.37 | 0.46 | 0.24 | 0.70 | 0.021 | 0.022 | 0.05 | 0.015 |

Table 1. Chemical compositions of the test materials.
2.3. Accelerated corrosion test

NaHSO₃ solution was used to simulate the corrosion of weathering steel in an industrial environment. The experiment was divided into the following steps:

1. 0.01 mol l⁻¹ NaHSO₃ solution to the surface of the sample with 40 μl cm⁻² to simulate an industrial environment [19];
2. the sample was stored in a dry and wet alternating test box for 12 h at 30 °C and 60% RH. When the relative humidity of the atmosphere is higher than the critical value (RH > 60%), the water in the air forms a thin liquid film on the surface of the steel due to the surface tension. At this time, electrochemical corrosion occurs on the surface of steel. The relative humidity of the atmosphere is lower than the critical humidity, the surface of steel is in a dry state, and the electrochemical corrosion on the surface is stopped. 30 °C is used to simulate indoor temperature [20];
3. 12 h later, the surface deposited corrosive medium was cleaned by deionized water to prevent crystallization;
4. after drying in an oven at 30 °C for 2 h, the sample was weighed with an analytical balance with an accuracy of 0.001 g;
5. repeat the above steps for 120 cycles, with 12 h for each cycle.

Figure 1. Optical micrographs of the four experimental steel groups: (a) WS0.15 Cu, (b) WS0.35 Cu, (c) WS0.50 Cu, (d) WS0.70 Cu.

Figure 2. Schematic diagram of electrochemical sample preparation.
Figure 3. Corrosion kinetics evolution of three experimental steel groups in simulated industrial environment: (a) Weight gain curve, (b) corrosion rate curve. (c) Corrosion rate curve of 0 to 30 cycles, (d) corrosion rate curve of 31 to 80 cycles, (e) corrosion rate curve of 81 to 120 cycles.

Table 2. Corrosion weight gain fitting equations.

| Steel   | Part one (1–30) | Part two (31–80) | Part three (81–120) |
|---------|-----------------|------------------|---------------------|
| 0.16% Cu| $y = -3.9605 + 1.2935x$ | $y = -2.7660 + 0.4780x$ | $y = -2.4059 + 0.3846x$ |
| 0.35% Cu| $y = -3.9942 + 1.2966x$ | $y = -2.37485 + 0.4217x$ | $y = -2.4733 + 0.3634x$ |
| 0.50% Cu| $y = -5.06447 + 1.2343x$ | $y = -2.8576 + 0.4058x$ | $y = -2.6954 + 0.3265x$ |
| 0.70% Cu| $y = -3.3388 + 1.2497x$ | $y = -2.1276 + 0.3178x$ | $y = -2.0056 + 0.3029x$ |

1 ≤ N ≤ 30 R² = 0.99
31 ≤ N ≤ 80 R² = 0.99
81 ≤ N ≤ 120 R² = 0.99
2.4. Corrosion product analysis
The corrosion products were scraped off and ground to a particle diameter of less than 45 μm. XRD spectra were collected using a Cu-Kα target on a Rigaku D/max-2500/PC XRD instrument using an experimental voltage of 40 kV, a scanning current of 200 mA, a test angle range of 10°–70°, with step scan and of 1 s per 0.02°. The surface morphology of samples were observed by a Hitachi S-5000 SEM with a test voltage of 5 kV and current of 50 μA, respectively. Raman spectra were recorded using a HR800 Horiba Yvon spectrometer with an excitation wavelength of L1/4532 nm, a beam diameter of 40 μm, and an output power of 0.3 MW. The alloying element oxides precipitated from the surface of the steel After the corrosion, the rust layer of the sample near the substrate was scraped off and ground, and then the valence of the Cu element in the rust layer was analyzed by x-ray photoelectron spectroscopy (XPS, EscaLab 250xi, EscaLab, MA,USA).

2.5. Electrochemical experiments
The polarization curves and electrochemical impedance spectra were measured using a three-electrode system. Namely, A platinum plate were taken as the counter electrode, a saturated calomel as the reference electrode, and the sample as the working electrode. The rust samples contained a rust layer surface which was used as the working surface. Prior to the electrochemical tests, the solution was filled with N2 to avoid the influence of oxygen on the cathodic reaction. The samples were immersed in a room-temperature (25 °C) 0.01 mol l⁻¹ NaHSO₃ solution for 1 h to measure the open circuit potential. Electrochemical impedance spectroscopy (EIS) was measured within a frequency range of 10 mHz to 100 kHz. The amplitude of perturbed AC potential applied to the test was 10 mV. The scanning potential for polarization curve ranged from −1.3 V to −0.3 V, and the scanning speed was 0.0001667 V s⁻¹. All the measurements were carried out at room temperature.

3. Results
3.1. Corrosion kinetics
Figure 3(a) shows the weight gain due to accelerated corrosion for different experimental steels, and figure 3(b) shows the accelerated corrosion rate of different experimental steels. As shown in figure 3(a), when the Cu content increased from 0.15% to 0.50%, the weight gain was relatively large. When the Cu content increased from 0.50% to 0.70%, the corrosion weight gain is small. As the Cu content increased, it showed a reduced effect on the weatherability of the steel. As shown in figure 3(b), the corrosion rate of the four experimental steels increased with the increase of the corrosion cycle N at the initial stage of corrosion (N < 30); the corrosion rate decreased at an intermediate number of corrosion cycles (31 < N < 80) compared with the previous period. At the third stage of corrosion (81 < N < 120), the corrosion rate was reduced. It can be seen from the corrosion rate diagram in figure 2(b) that the corrosion rate was the lowest at any stage of the W0.70 steel.

In the early accelerated corrosion stage, the corrosion rate of different Cu contents in weathering steels was nearly the same, but as the corrosion cycles progressed, the corrosion rate of weathering steels with Cu contents of 0.50% and 0.70% were significantly lower than that of the 0.15% weathering steel. To better understand the corrosion process of weathering steel with different Cu contents in a simulated environment, the weight gain curve was mathematically treated using the following equation (1) [21, 22]:

\[ \Delta W = AN^n \]  

where \( \Delta W \) (g) is the corrosion weight gain per unit area, \( N \) is the number of corrosion cycles, \( A \) is the corrosion weight gain of the sample per unit area and per unit time, reflecting the corrosion rate in the first dry/wet alternate corrosion cycle and \( n \) is the power and usually a constant. Using logarithmic coordinates, (1) can be converted to (2), and the results of the linear fit are shown in table 2.

\[ \log w = \log A + n \log N \]  

Equation (2) can be used to determine the instantaneous rate of corrosion by differentiation. The formula is as shown in equation (3), and the instantaneous rate map of corrosion weight gain can be obtained (figure 2(b)).

\[ V_i = \frac{d\Delta W}{dN} = An^{n-1} \]  

\[ \log \left( \frac{d\Delta W}{dN} \right) = \log A + \log n + (n - 1)\log N \]  

\[ \log \left( \frac{d\Delta W}{dN} \right) = A + (n - 1)\log N \]
It can be shown from equation (5) that when \( n - 1 > 0 \) or \( n > 1 \), the corrosion rate increases with \( N \), that is, the experimental steel is in the accelerated corrosion phase. When \( n = 1 \), the corrosion rate is constant, and when \( n < 1 \), the corrosion rate decreases as \( N \) increases, i.e., the smaller the value of \( n \), the lower the corrosion rate.

Table 2 is the corrosion weight gain data using figure 3, and the linear software has been used to form a linear function using the origin software, which conforms to the corrosion gain function formula (2). It can be seen from figure 3(b) that the corrosion rates of the four weathering steels increased during the initial stage of corrosion \((1 \leq N \leq 30)\). The pre-\( n \) is greater than 1, that is the corrosion rate of the four experimental steels increased as the period \( N \) increased during the initial stage of corrosion. The corrosion rates of the four weathering steels were fairly similar. In the middle period of corrosion \((31 < N \leq 80)\), the corrosion rate decreased. When \( n \) was less than 1 the corrosion rate of weathering steel decreased as \( N \) increased. During the later stage of corrosion \((81 < N \leq 120)\), the corrosion rate of the four weathering steel was lower, and \( n \) was less than 1. The corrosion rate decreased with the Cu content, and the decrease was the lowest at a Cu content of 0.70%. The corrosion rates of the three experimental steels all first increased, then decreased, and finally stabilized. This process may be related to the conversion of corrosion products.

**Figure 4.** X-ray diffraction patterns of four experimental steel groups after (a) 30 cycles, (b) 80 cycles, and (c) 120 cycles (d) X-ray patterns of corrosion products of WS0.70Cu steel in different cycles, (e) The proportion of \( \alpha \)-FeOOH of different Cu contents in 120 cycles (f) The proportion of \( \alpha \)-FeOOH of different cycles.
3.2. Phase composition of the rust layer

The XRD pattern of corrosion product in each Cu-bearing sample exposed for 30, 80, and 120 dry and wet alternating cycles is shown in figures 4(a)–(c), respectively. Figure 4(d) shows the XRD pattern of corrosion product in WS0.70Cu steel exposed for differing cycle, typically as 30, 80, and 120. Figure 4(e) summarizes the quantified proportion of $\alpha$-FeOOH in the corrosion products of four experimental steels at 120 cycles. As figures 4(a)–(c) indicate, the corrosion products were mainly composed of $\alpha$-FeOOH, $\gamma$-FeOOH, and Fe$_3$O$_4$. In addition, as displayed in figure 4(d), the XRD peak of $\alpha$-FeOOH, $\gamma$-FeOOH, and Fe$_3$O$_4$ increased with the

Figure 5. Distribution of element in experimental steel sections after 120 cycles: (a) WS0.15Cu, (b) WS0.35Cu, (c) WS0.50Cu, (d) WS0.70Cu.
extending corrosion cycle, indicating the continuously accumulated corrosion products. However, as demonstrated in figure 4(e), the proportion of $\alpha$-FeOOH in corrosion products of weathering steel at the same cycle of 120 increased with the increasing Cu content. Figure 4(f) shows that the proportion of $\alpha$-FeOOH gradually increases with the increase of the corrosion cycle, indicating that $\alpha$-FeOOH is gradually accumulated during the corrosion process. Therefore, the amount of $\alpha$-FeOOH increased with the accumulated corrosion products. This would maintain a compact rust layer, serving as a shield and reducing the corrosion rate [23].

3.3. Elemental distribution in rust layer cross-sections
Figures 5(a)–(d) show the EDS spectra of WS0.15Cu, WS0.35Cu, WS0.50Cu, and WS0.70Cu steel Cu in the layer after 120 accelerated corrosion cycles. Figures 5(b) and (c) show that the Cu element enriches in the inner rust and S element enriches in the outer rust, while the other element evenly distributes in the rust. It indicates that the Cu and S element may be mutually exclusive. In order to better analyze the distribution relationship between Cu and S element. The line scan is used to analyze distribution of Cu and S in different experimental steel sections after 120 cycles: (a) WS0.15 Cu, (b) WS0.35 Cu, (c) WS0.50 Cu, and (d) WS0.70Cu which are shown in figure 6. The line scan range is shown as the yellow arrow in figure 6(a). The figure 6 shows that the Cu element has a higher content and the S element has a less content in the inner rust. It indicates that the Cu element has an exclusive relationship with S element. The line scan results are consistent with the distribution of Cu and S element for EDS.

3.4. Microscopic morphology of the rust layer
Figures 7(a)–(d) show the microscopic topography of the corrosion products of four weathering steels WS0.15, WS0.35, WS0.50, and WS0.70 after 80 accelerated corrosion cycles. It is generally believed that the formation of a protective rust layer on the surface of weathering steel is the main reason for its improved corrosion resistance [24–26]. It can be seen that the corrosion products of the experimental steel after 80 corrosion cycles were mainly $\alpha$-FeOOH, $\gamma$-FeOOH. The cotton globules are $\alpha$-FeOOH, and the flower cluster is $\gamma$-FeOOH [27, 28]. The cotton globular $\alpha$-FeOOH structure is relatively tight, which can serve as a physical barrier and block the
penetration of corrosive media, and reduce the corrosion rate. The main corrosion product of figure 7(a) is γ-FeOOH, and when the Cu content increased to 0.35%, a small amount of cotton spherical α-FeOOH appeared in the corrosion products. When the Cu content increased to 0.50%, the corrosion product was mainly α-FeOOH. There was a small amount of γ-FeOOH, and when the Cu content increased to 0.70%, the corrosion products were nearly all α-FeOOH.

3.5. Rust layer cross-section phase distribution

The Raman micro-point method was used to analyze the corrosion products of the weathering steel rust layer sections with a Cu content of 0.70% after 120 accelerated corrosion cycles. Table 3 lists the shifts of all Raman peak positions. In figure 8, four points were selected from the side closest to the substrate for Raman phase analysis, and the corresponding results are shown in figure 8(b). It can be seen from figure 8(b) that the corrosion product was mainly α-FeOOH on the side closest to the substrate, and γ-FeOOH was mainly present on the side closest to the hot insert. The relative α-FeOOH content is an important index for evaluating the corrosion resistance of weathering steel [29–31]. Combined with the cross-sectional EDS spectrum, Cu was obviously enriched near the side close to the substrate. Cu can promote the formation of α-FeOOH, so when Cu is added to the weathering steel, it will form Cu and enrich the rust layer near the substrate during corrosion and promote the formation of α-FeOOH. A large amount of dense α-FeOOH is formed near the iron matrix, which makes

Table 3. Raman spectra peak positions corresponding to the phases present in the corrosion products [2, 28].

| Phase                        | Peak position (cm⁻¹)                      |
|------------------------------|-------------------------------------------|
| Lepidocrocite (γ-FeOOH)      | 166, 217, 251, 310, 350, 378, 529, 655, 713, 1300 |
| Goethite (α-FeOOH)           | 203, 244, 308, 387, 399, 415, 480, 532, 684, 1002, 1113, 1304 |
| Akaganite (β-FeOOH)          | 139, 308, 331, 389, 420, 499, 539, 609, 720, 1410 |
| Magnetite (Fe₃O₄)            | 306, 338, 666                              |
| Hematite (Fe₂O₃)             | 228, 250, 294, 414, 502, 625, 670, 1330    |
| Maghemite (γ-Fe₂O₃)          | Broad band between 339 and 366, 461 and 512, 671 and 717, 1430 |
| Ferrihydrite (Fe₅HO₈·4H₂O)   | Broad band between 700 and 710             |

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the structure of the rust layer more dense, hinders the penetration of the corrosive medium, and reduces the corrosion rate of the weathering steel.

These data were analyzed by XPS Peak 4.1 software to fit each element on the area scanning spectra, depending on the NIST x-ray Photoelectron Spectroscopy Database. The results as shown in figure 9. The Cu 2p3/2 spectrum composed of two fitted peaks at 932.6 ± 0.1 eV and 531.4 eV which are attributed to CuFeO2 and CuO. The O 1 s spectrum is displayed in (b). According to the XPS data, the fitted peaks located at 529.9 eV and 531.3 eV correspond to the O²⁻ and OH⁻ states, respectively.

3.6. Electrochemical properties

The corrosion mechanism was further investigated by electrochemically testing different periodic electrochemical corrosion properties of rust samples. Figures 10(a), (c), (e) shows the Tafel plots of four weathering steels after 30, 80 and 120 cycles. The polarization R (Rp) is obtained by calculating the Tafel region figures 10(b), (d) and (f). The graph shows that the RP value increases gradually with the increase of content for the Cu element in the same period, it indicates that the addition of Cu in weathering can significantly improve the corrosion resistance. The polarization resistance (Rp) value was obtained from the linear polarization [32]:

\[
R_p = \frac{\beta_a \beta_c}{2.3i_{\text{corr}}(\beta_a + \beta_c)}
\]

where \(\beta_a\) and \(\beta_c\) are the anodic and cathodic Tafel slopes respectively, and \(i_{\text{corr}}\) is the corrosion current density for each specimen.

Figure 11 shows the corresponding corrosion current density \(i_{\text{corr}}\) (\(\mu A/cm^2\)) which is calculated by extrapolating the Tafel line for both the cathodic and anodic branches of these electrochemical polarization.
curves. It can be seen that the curve of the corrosion current density of various weathering steel in figure also presents two stages: when the alloyed Cu is less than 0.50 wt%, the $i_{\text{corr}}$ of weathering steel decreases sharply with the increased of Cu content in weathering steel; however, after the alloyed Cu in weathering steel exceeds 0.50 wt%, the $i_{\text{corr}}$ almost remains stable, which means that the influence of additional Cu in weathering steel on their corrosion resistance becomes insignificant after the alloyed Cu content exceeds 0.50 wt%.

Figure 12 shows the Nyquist plot of accelerated corrosion after 30, 80, and 120 cycles. Electrochemical impedance tests were performed on samples of different experimental periods. The Nyquist plot mainly fits a semi-arc curve of the high frequency region and the narrow curve of the low-frequency region and shows that there are two electric double layers in the electrochemical reaction of the electrolytic solution and the corrosion sample. An electric double layer exists between the solution and the corrosion sample, and a double-electrode layer exists between the solution and the rust layer, as represented by the capacitive anti-arc in the high-frequency region, reflecting the rapid response of the electrode. The greater the radius, the better the corrosion resistance. In the high-frequency range, the electric field changes rapidly, and the concentration change could be neglected during this process. At this time, the electrochemical reaction is dominant. When the corrosion increased later, the radius of the capacitive anti-arc gradually increases, indicating that the maximum capacitive
reactance arc is present in each cycle of WS0.70Cu. This suggests that the presence of Cu prevented charge transfer, reduced the electrochemical reaction rate, and thus increased its weathering resistance.

Figure 11 shows the circuit diagram fitted by resistance data, where $R_s$ is the solution impedance, and $R_r$ is the rust layer resistance. The magnitude of the resistance and the thickness of the rust layer and composition are

![Figure 11](image_url_11)

**Figure 11.** Variations of the corresponding instantaneous corrosion current density of difference cycles and four experimental steel.

![Figure 12](image_url_12)

**Figure 12.** Nyquist plots of four experimental steel groups after (a), (b) 30 cycles, (c), (d) 80 cycles, and (e) (f) 120 cycles.
related to the CPEr as a constant phase element, including the rust layer and the capacitance of the electrolyte solution. Rc is the charge transfer resistance of the redox process, CPEc represents the double-layer capacitance structure of the inner rust layer, and W is the resistance caused by concentration polarization [33, 34]. The relationship between the sample steel and the rust resistance of different Cu contents after 30, 80, and 120 cycles is shown in figure 14. During the various corrosion cycles, the resistance of the rust layer increases as the Cu content increases because the addition of Cu increases the resistance of the rust layer. After more corrosion cycles, the resistance of the rust layer also increased, indicating that the corrosion medium gradually accumulated. As the number of corrosion cycles increased, the physicochemical properties of the rust layer changed, increasing the resistance of the weathering steel rust layer.

4. Discussion

4.1. Corrosion dynamics

Figure 15 shows a schematic of the corrosion of weathering steel in an industrial atmosphere where atmospheric SO₂ dissolves in the water film on the surface of weathering steel to form HSO₃⁻. During the dry-wet alternating experiments, when the surface of the weathering steel is wet, the HSO₃⁻ in the corrosive medium is oxidized first.

\[
\frac{1}{2}O_2 + HSO_3^- = SO_4^{2-} + H^+ \tag{7}
\]

H⁺ is generated to raise the pH of the solution.
The iron matrix participates in the following reactions:

$$\text{Fe} + \frac{1}{2} \text{O}_2 + 2\text{H}^+ = \text{Fe}^{2+} + \text{H}_2\text{O}$$  \hspace{1cm} (8)

The anode reacts:

$$\text{Fe} = \text{Fe}^{2+} + 2e^-$$  \hspace{1cm} (9)

At this time, the cathode reacts:

$$\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2e^- = \text{H}_2\text{O}$$  \hspace{1cm} (10)

As corrosion proceeds, the continuous dissolution of the iron matrix occurs as follows:

$$4\text{FeSO}_4 + 6\text{H}_2\text{O} + \text{O}_2 = 4\alpha/\gamma \text{FeOOH} + 4\text{H}_2\text{SO}_4$$  \hspace{1cm} (11)

As the reaction proceeds, $\text{H}_2\text{SO}_4$ accumulates step-by-step, and the generated $\text{H}_2\text{SO}_4$ continues to dissolve the iron matrix and react as follows to accelerate the corrosion of the iron matrix:

$$\text{H}_2\text{SO}_4 + \text{Fe} + \frac{1}{2} \text{O}_2 = \text{FeSO}_4 + \text{H}_2\text{O}$$  \hspace{1cm} (12)

Therefore, in the early stage of corrosion, as the $\text{H}^+$ increases, the pH of the liquid film decreases, which accelerates the corrosion rate. As can be seen from figures 3(a) and (b), during the initial stage of corrosion of WS0.15Cu, the corrosion rates of WS0.35Cu, WS0.50Cu, and WS0.70Cu are very rapid, likely because more $\text{H}^+$ was generated during the initial stage. Since the corrosion rate is so fast, the Cu content has little effect on the corrosion resistance of weathering steel, which also explains why the weight gain and corrosion rate of the four weathering steels are similar during the initial stage of corrosion. However, as corrosion continues, the concentration of $\text{H}^+$ in the liquid film continually increases, resulting in a decrease in the pH of the liquid film. Formula (11) shows that inhibition slows the dissolution of the iron matrix. From figures 3(a) and (b), it can be seen that the corrosion rate is lower during the middle and late stages of accelerated corrosion than that during the first stage.

The simultaneously produced $\text{Fe}^{2+}$ reacts with the unstable $\gamma$-FeOOH phase to form stable $\alpha$-FeOOH.

$$\text{Fe}^{2+} + 8\gamma - \text{FeOOH} + 2e^- = 3\alpha\text{FeOOH} + 4\text{H}_2\text{O}$$  \hspace{1cm} (13)

However, during the dry-wet accelerated corrosion process, the generated $\gamma$-FeOOH changes to $\alpha$-FeOOH, resulting in a relatively stable and dense $\alpha$-FeOOH. Therefore as corrosion continues, $\text{H}^+$ was generated, and the Fe matrix continues to dissolve and as the corrosion increases, the amount of $\text{H}^+$ in the liquid film gradually increased, causing the pH to decrease. Reaction (11) is suppressed, the dissolution of the iron matrix is slower, and the generated $\gamma$-FeOOH is converted to $\alpha$-FeOOH and $\text{Fe}_2\text{O}_4$, while the $\alpha$-FeOOH and $\text{Fe}_2\text{O}_4$ are compacted. This can block the penetration of the corrosive medium and slow the weathering of the steel, thereby reducing its corrosion rate. Therefore, when the weathering steel is in an industrial environment, the corrosion rate is as shown in figure 3(b), and the corrosion rate increases during the early stage, and the corrosion rate decreases during the later stage [35].
4.2. Effect of Cu on corrosion resistance

4.2.1. Cu-contained rust layer acting as a chemical barrier

As shown in the EDS spectrum of the rust layer in figure 6, during corrosion, Cu is enriched in the rust layer near the iron matrix during corrosion, and Cu may change the electronegativity of the rust layer \([9]\). The chemical states of Cu elements in the rust, XPS analysis in figure 15 have been conducted. The result of Cu 2p3/2 peak around 932.6 ± 0.1 eV indicates its univalent state Cu(I) corresponding to the presence of CuFeO\(_2\). During corrosion, Cu exists as free Cu(I). Figure 16(b) shows a schematic diagram of Fe\(_3\)O\(_4\), where Fe(III) is located at the center of the regular tetrahedron. Fe(III) and Fe(II) are located at the center of two regular octahedrons, but the free Cu(I) occupies the center of the regular tetrahedron and replaces one Fe(III). Therefore, a certain number of electron holes are generated at some lattice points of the Fe\(_3\)O\(_4\) partially substituted by Cu(I) \([9]\). This may hinder the corrosive SO\(_4^{2-}\) from penetrating the rust layer (figure 16(a)), thereby slowing the corrosion rate.

4.2.2. Cu-contained rust layer as a physical barrier

By analyzing the equivalent impedance circuit of the rust layer (figure 13) and the rust layer resistance (figure 14), it can be found that the resistance of the rust layer increases with the Cu content, regardless of the corrosion period. This indicates that enrichment of Cu in the rust layer increases the electrical resistance of the rust layer and changes the chemical properties of the rust layer on the weathering steel. This indicates that enrichment of Cu in the rust layer increases the electrical resistance of the rust layer and changes the chemical properties of the rust layer on the weathering steel and reduce its electrochemical corrosion rate which is found that the Tafel line move to positive \([36]\) and increase its corrosion resistance. The enriched Cu contacts the surface of the iron matrix to passivate the steel and reduce its electrochemical corrosion rate and increase its corrosion resistance.

Cu also changes the physical properties of the rust layer. According to figure 4, which shows the XRD patterns of the microscopic corrosion products, the α-FeOOH content of the corrosion products of WS0.70Cu was the highest at each stage of corrosion. It can be seen from the microtopography of the corrosion products in figure 7 that WS0.50Cu weathering steel contained a large amount of α-FeOOH, while WS0.70Cu weathering steel was comprised almost entirely of α-FeOOH. This can be explained by noting that the addition of Cu in weathering steel promotes the formation of α-FeOOH and helps the weathering steel form a dense rust layer, which slows the corrosion rate. At the same time, the Cu enrichment increases the density of the generated α-FeOOH. It can be seen from the Raman spectrum (figure 8) of the rust layer that α-FeOOH was concentrated on the side closest to the iron matrix, and Cu refined α-FeOOH. The resulting rust layer became denser, which changed the physical barrier function of the weathering steel rust layer, to better prevent the intrusion of the corrosive medium. In this way, it protected the iron matrix from continuing to corrode, and reduced the corrosion rate and extended the service life of the weathering steel.

5. Conclusions

The following conclusions in this investigation can be drawn from the results on weathering steels with different Cu contents in a simulated industrial atmosphere:
1. When the Cu content in the weathering steel reached 0.50%, the weather resistance became saturated. Therefore, from the weather resistance and economic points of view, the Cu content should not exceed 0.50%, as there are no additional benefits of higher contents.

2. During accelerated corrosion in a simulated industrial environment, the corrosion products mainly included $\alpha$-FeOOH, $\gamma$-FeOOH, and Fe$_3$O$_4$. The $\alpha$-FeOOH corrosion product increased with the number of corrosion cycles. At the same number of corrosion cycles, $\alpha$-FeOOH increased with the Cu content.

3. During accelerated corrosion in of a simulated industrial environment, as the number of corrosion cycles increased, the resistance of the weathering steel rust layer increased, and the reaction rate decreased. As the Cu content increased, the resistance of the rust layer gradually increased, and the self-corrosion potential moved forward, slowing the electrochemical reaction and improving the weathering resistance.

4. Cu in the weathering steel was obviously enriched near the substrate during the corrosion process. Refining $\alpha$-FeOOH made the rust layer denser, blocking the penetration of corrosive media, slowing the electrochemical reaction, and reducing the corrosion of weathering steel.

Author Contributions

Methodology, Xuqiang Yan and Qiang Yu; formal analysis, Rui Sun.; investigation, Kai Guo; data curation, Siyuan Zhu; writing—original draft preparation, Xuqiang Yan and Qingfeng Wang; writing—review and editing, Xuqiang Yan and Qingfeng Wang; project administration, Yuwei Gao.

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Conflicts of Interest

The authors declare no conflict of interest.

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