

Article

Research on Atmospheric Corrosion of 45# Steel in Low-Latitude Coastal Areas of China

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Abstract: Urgent action is required to mitigate the severe corrosion of carbon steel in low-latitude regions. The combination of high humidity, temperature, and salinity in these areas significantly accelerates steel corrosion, posing a substantial threat to the service safety of offshore engineering equipment. This study aims to elucidate the atmospheric corrosion mechanisms of 45# steel in low-latitude coastal areas. Samples of 45# steel were exposed to atmospheric conditions over various durations in the following three geographically distinct regions: Guangzhou, Wanning, and the South China Sea. The corrosion rates were calculated using weight loss tracking and potentiodynamic polarization measurements, while surface corrosion products were examined using X-ray diffraction (XRD) tests. The findings indicate a clear correlation between the corrosion rate of 45# steel and the latitude and specific location of the test area, with the highest to lowest rates observed in the South China Sea, Wanning, and Guangzhou, respectively. Similarly, the extent of corrosion rust penetration in defective coatings followed the same order. Moreover, the protection ability index (PAI) calculations revealed that none of the tested samples formed a protective corrosion film.



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1. Introduction

The corrosion of metallic materials, especially carbon steel, has long been a challenge in the marine industry, particularly at low latitudes. This issue is especially critical in the development of tropical offshore oil and gas fields, where property losses due to corrosion are substantial [1–4]. Therefore, understanding the atmospheric corrosion mechanisms of carbon steel in these regions is crucial to guide the application of steel-based materials effectively.

Atmospheric corrosion, a specific form of electrochemical corrosion, occurs when a metal surface under a thin water film reacts at certain humidity levels [5]. The water film, formed by the condensation of atmospheric moisture, and the diffusion of oxygen through this film to the metal surface, are essential for initiating atmospheric corrosion [5–7]. The formation of this film is strongly influenced by the relative humidity. The higher the humidity, the more readily a water film forms and persists on the metal surface, increasing the corrosion rate [8]. The lowest relative humidity required to form a water film on a metal surface is called corrosion critical relative humidity. Typically, the critical relative humidity of iron corrosion is about 65% [9]. Temperature is another critical factor affecting atmospheric corrosion. When the temperature is below the dew point, the corrosion rate of metals increases with the increase in temperature [10]. In low-latitude marine environments, the relative content of Cl^- in the air is another significant factor that affects the corrosion rate of metals [11–13]. A. Askey et al. found that, in a Cl^- containing acid environment,

Fe can directly react with Cl^- to form a soluble corrosion product (FeCl_2) [14]. Typically, the deposition rate of Cl^- in the marine atmosphere ranges from 5 mg/m² to 300 mg/m² per day (ISO 9223 [15]) [16]. When Cl^- is deposited on the metal surface, it will reduce the critical relative humidity and increase the conductivity of the film. The electrochemical reaction process will be promoted, thus accelerating corrosion [10]. Studies have shown that the farther away from the coastline, the less Cl^- in the air, and the smaller the corrosion rate [17]. M. Morcillo et al. studied the relationship between Cl^- and the corrosion rate of steel in different marine atmospheric regions [18]. The research demonstrated that, when the Cl^- concentration in the atmosphere is lower than 100 mg/m² per day, the corrosion rate of steel increases slowly with the increase in Cl^- concentration. However, when the Cl^- concentration increases to 400 mg/m² per day, the corrosion rate increases rapidly with the increase in Cl^- concentration. As the Cl^- concentration continues to increase, the corrosion rate does not change much and stabilizes [18]. Yoo et al. claimed that the color change in carbon steel is another critical factor that relates to the exposure period [19]. The color difference and glossiness of carbon steel observed using the 10-year outdoor exposure tests in Korea are discussed based on the corrosion rate and the environmental factors. Therefore, it can be easily concluded that the high humidity, temperature, and salinity of low-latitude coastal areas can greatly accelerate the rate of steel corrosion, posing a great threat to the service safety of offshore engineering equipment.

To further explore the atmospheric corrosion of carbon steel in these challenging conditions, this study employed commercial 45# steel plates. Samples were placed in different areas and on different days under an atmospheric exposure test. In descending order of latitude, the three regions are Guangzhou, Wanning, and the South China Sea. Weight loss tracking and potentiodynamic polarization measurements were employed to calculate the corrosion rate. Surface corrosion morphology observation and X-ray diffraction (XRD) tests were utilized to analyze the corrosion mechanisms. Additionally, the corrosion rust properties were analyzed through the protection ability index (PAI). This research may provide valuable insights into the deployment of 45# steel in low-latitude coastal regions.

2. Materials and Methods

2.1. Materials

The material 45# steel, also known as AISI 1045, contains the following: 0.45 wt.% C, 0.22 wt.% Si, 0.72 wt.% Mn, 0.02 wt.% S, 0.03 wt.% P, 0.20 wt.% Cr, 0.18 wt.% Cu, and 0.20 wt.% Ni, with the balance being Fe. The steel plates were cut into dimensions of 200 mm × 100 mm × 3 mm. Prior to the atmospheric corrosion tests, all samples underwent sandblasting and surface cleaning with ethanol.

2.2. Corrosion Test

The samples of 45# steel were exposed to atmospheric conditions over various durations in the following three geographically distinct regions: Guangzhou, Wanning, and the South China Sea. Detailed information is listed in Table 1.

Table 1. Detailed information about the atmospheric corrosion test areas.

Location	Guangzhou	Wanning	South China Sea
Latitude	23° N	18° N	16° N
Climatic type	Subtropical monsoon climate	Tropical Rainforest climate	Tropical Marine climate

The weight loss experiment was conducted under a standard process [9]. The rust removal solution was prepared by adding 3.5 g $\text{C}_6\text{H}_{12}\text{N}_4$ and 500 mL HCl into deionized (DI) water (18.2 M Ohm) to achieve a total volume of 1000 mL. The steel plates were then placed in the above solution in an appropriate period. After the sample was taken out of the solution, the plates were cleaned with a brush and rinsed with DI water. Before

the measurement of weight, the plates were dried in air for 24 h. Each measurement was repeated at least three times.

Potentiodynamic polarization measurements were employed to study the corrosion rate and mechanism of 45# steel under exposure in different areas and on different days. A traditional three-electrode vertical cell with an exposure area of 1 cm² was applied for the electrochemical experiments. A saturated calomel electrode (SCE) was used as the reference electrode, and a platinum plate served as the counter electrode. Electrochemical characterization was carried out using a potentiostat (1010E, Gamry, Warminster, PA, USA), and all experiments were tested in a 3.5 wt.% NaCl solution. The scan rate was set to 1 mV/s after a 15-min open circuit delay. The short cathodic branch was utilized to estimate the corrosion current density.

2.3. Characterization

Surface macro-morphology observation was obtained with a CCD microscope digital camera (GP-431H, KSGAPPIN, Shenzhen, China). The crystal structures of the steel corrosion products were confirmed by X-ray diffraction (XRD, D/Max-2200V, Empyrean, Malvern, UK) with Cu K α radiation. The scan angle was from 10 degrees to 70 degrees, with a scan rate of 1 degree/min. The MAUD (Materials Analysis Using Diffraction) software version 2.999 was employed to fit the XRD results.

3. Results and Discussion

This study examined the atmospheric corrosion of 45# steel in three distinct low-latitude coastal areas. In descending order of latitude, the areas are Guangzhou, Wanning, and the South China Sea.

3.1. Atmospheric Corrosion of 45# Steel

Corrosion weight loss is calculated by subtracting the original mass of the sample from the mass after rust removal and dividing it by the surface area. It can be expressed by the following formula:

$$w = (w_0 - w_t) / S \quad (1)$$

In the above formular, w represents the corrosion weight loss, in g/m²; w_0 represents the mass of the sample before the test, in g; w_t represents the mass of the tested sample after rust removal, in g; and S represents the surface area of the samples, in m².

According to the results shown in Figure 1, corrosion weight loss correlates strongly with exposure time. The corrosion weight loss in the three different areas increased with the increase in test time. Comparing the corrosion weight loss of the three areas, it can be found that the corrosion at the South China Sea is the most serious, followed by Wanning and Guangzhou. It is worth noting that the initial weight loss in Guangzhou was slightly higher than that in Wanning, which may be associated with the urban atmospheric environment [10]. Overall, the above results obviously relate to the latitude and location of the test area.

Figure 2 displays the potentiodynamic polarization curves for 45# steel exposed in different locations. This test allows us to determine the corrosion rate of each sample by comparing the corrosion current densities. Except for the samples from Guangzhou, significant differences in corrosion current density and corrosion potential were observed at the same location over the different days. These variations in corrosion potential could be due to differences in the states of the surface passivation films or rust layers. To evaluate the corrosion rates, the values of the corrosion current densities were collected and summarized, as shown in Figure 3.

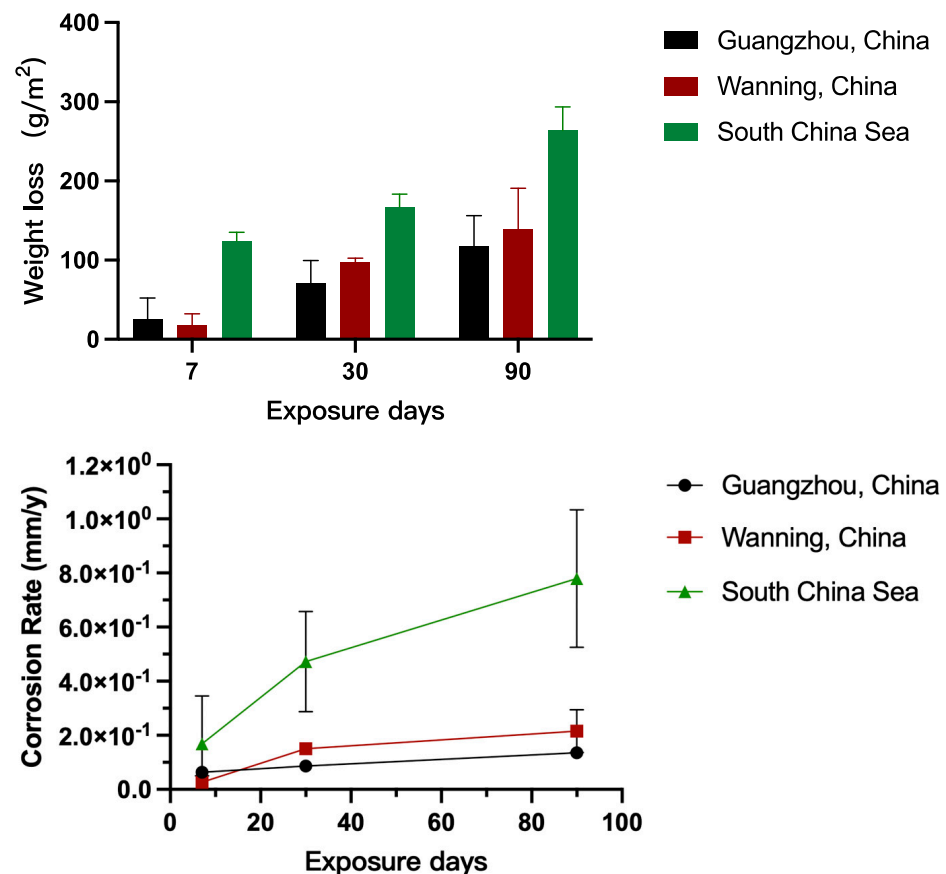


Figure 1. Weight loss and corrosion rate of 45# steel under exposure in different areas and on different days.

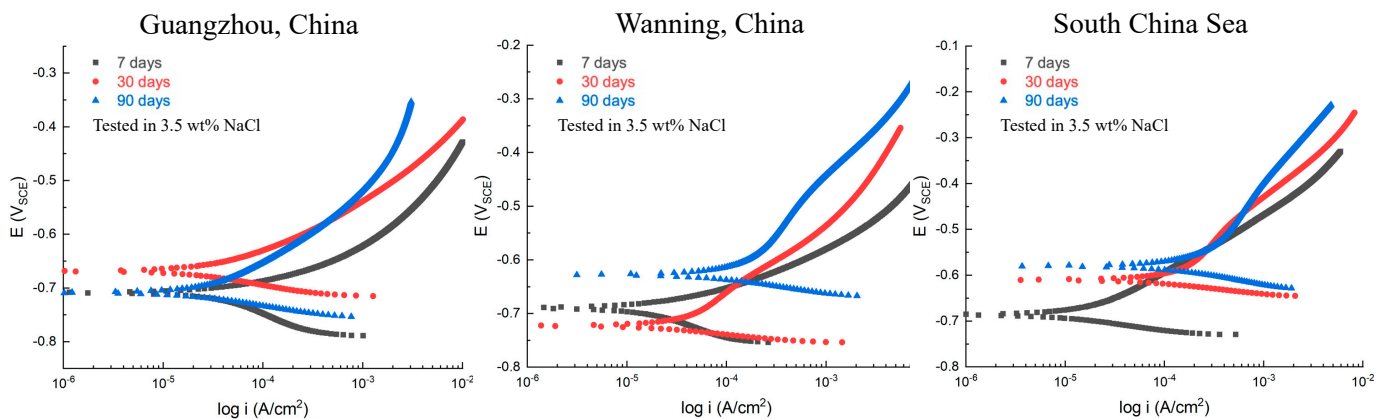


Figure 2. Potentiodynamic polarization curves of 45# steel under exposure in different areas and on different days.

Unlike the weight loss evaluation, the corrosion current density values provide more insight into how atmospheric conditions affect the surface state of 45# steel. As the exposure time increases, so does the corrosion current density, indicating a faster corrosion rate with longer exposure periods. This may be due to the rust layer on the samples still growing and not yet reaching a stable state. Overall, the corrosion in the South China Sea was found to be the most severe, followed by Wanning and Guangzhou. Similar to the weight loss results, the differences in corrosion current density are significantly related to the latitude and location of the test areas.

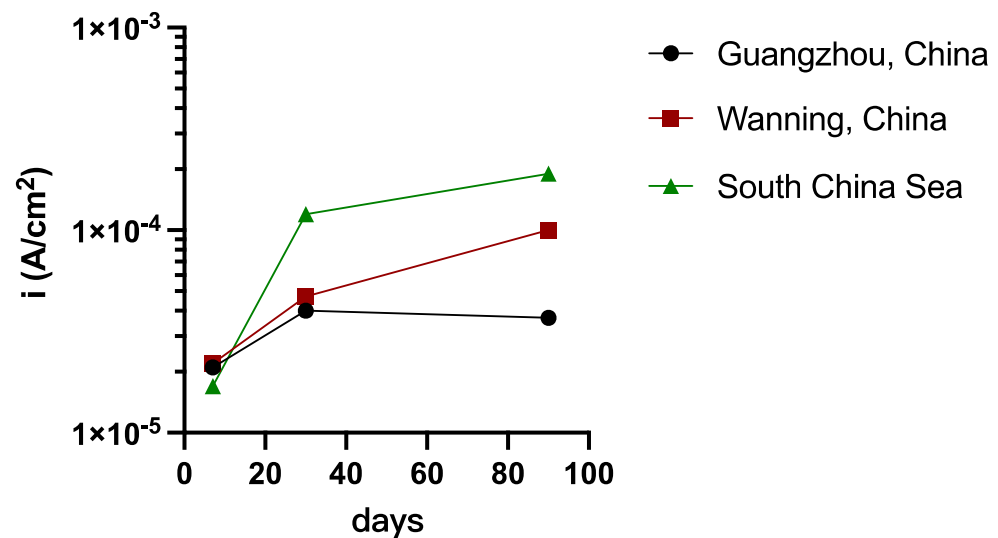


Figure 3. Summary of corrosion current density of 45# steel under exposure in different areas and on different days.

3.2. Surface Characterization and Mechanism Analysis of 45# Steel

The surface macro-morphology of 45# steel is illustrated in Figure 4. Typically, the color of the corrosion rust deepens with the increase in exposure time. All of the samples were covered with a rust layer after 7 days of exposure. Initially (7 days), the color of the rust in Guangzhou and Wanning was yellow. After a longer exposure, all of the samples turned brown. This color change is related to the transformation of corrosion products during the electrochemical reaction and the relative content of Fe_3O_4 on the surface [20]. It is worth noting that the color of the sample in the South China Sea had already turned brown after 7 days of exposure, indicating environmentally accelerated corrosion. After an even longer exposure (90 days), a loose layer of rust appeared on the surface of each sample. It flaked off with a light touch. The surface of each sample failed to form a dense and protective rust layer.

It is challenging to avoid coating defects in the long-term service of engineering equipment. In high-latitude dry areas, these defects typically do not severely impact the system. However, in low-latitude coastal regions, such defects can lead to the rapid failure of the entire coating system. The measurement of corrosion rust delamination on defective coatings is crucial for evaluating the service life of marine engineering equipment.

Typically, the coating delamination rate is related to the rate at which the corrosive contents penetrate from the defective areas. The penetrated corrosive contents will react with the metal substrate and generate corrosion rust. The relatively larger amount of rust will lead to the peeling of the coating. Therefore, another set of 45# steel samples covered with a cross-scratched epoxy coating (approximately 150 μm) was employed in this test (Figure 5). The rust color trends were similar to those observed in the bare sample test, turning from yellow to brown with exposure. The corrosion rust penetration depth depended heavily on the exposure time and location. In Guangzhou, no significant corrosion rust penetration or severe coating failure was observed. In Wanning, corrosion rust penetration was noticeable after 90 days of exposure, with an easily peelable coating indicating severe delamination. The corrosion was more severe in the South China Sea, where significant corrosion rust penetration was observed after only 30 days. Filiform corrosion, mainly caused by high humidity and salinity, was also noted. After 90 days, extensive corrosion rust penetration and a delamination depth exceeding 0.6 cm were observed. Thus, corrosion rust penetration was most severe in the South China Sea, followed by Wanning and Guangzhou. The above results indicate a high correlation between corrosion rust penetration and the latitude of the test area.

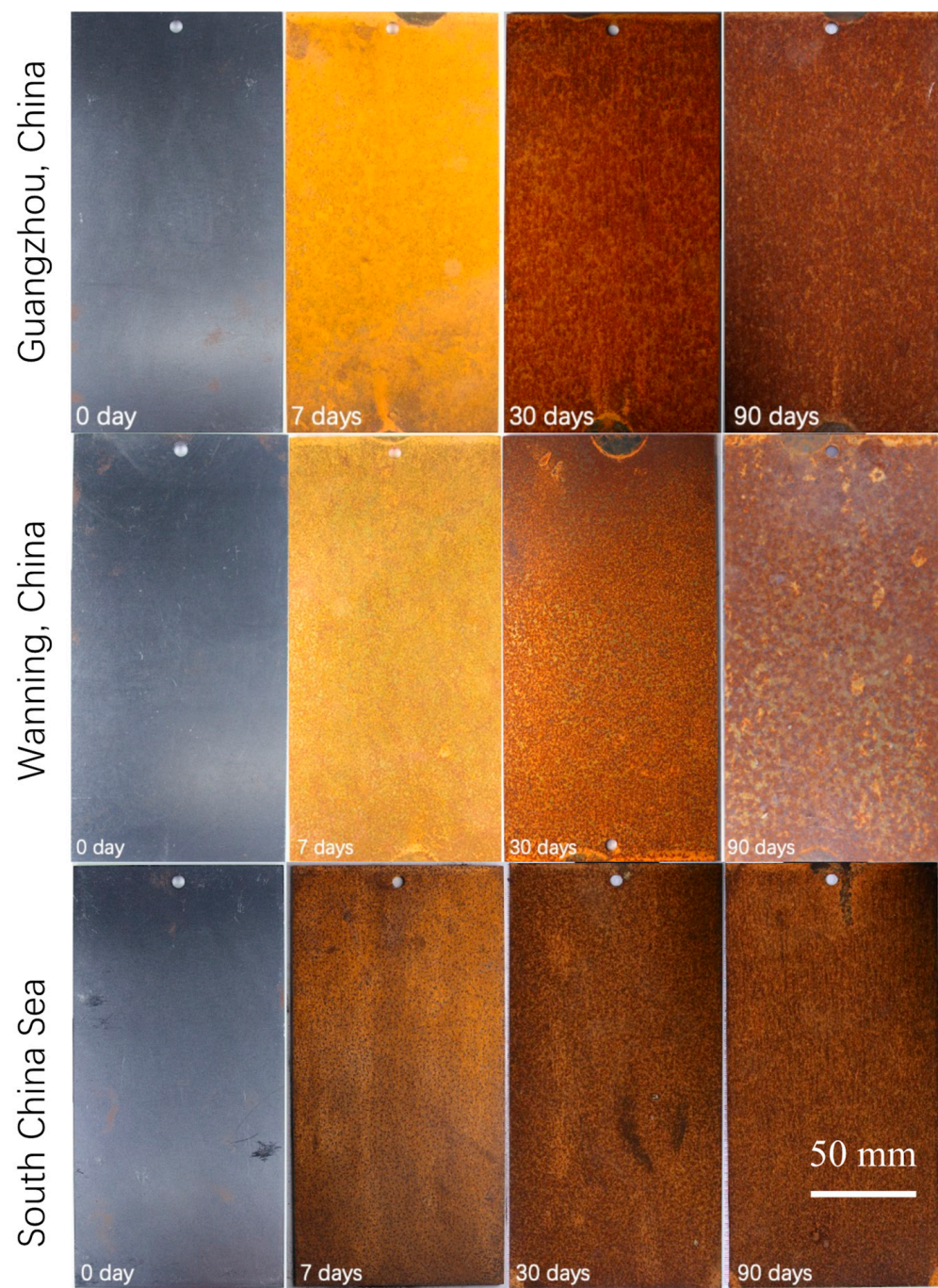


Figure 4. The surface corrosion morphology of 45# steel under exposure in different areas and on different days (the dimension of each plate is $200 \times 100 \times 3$ mm).

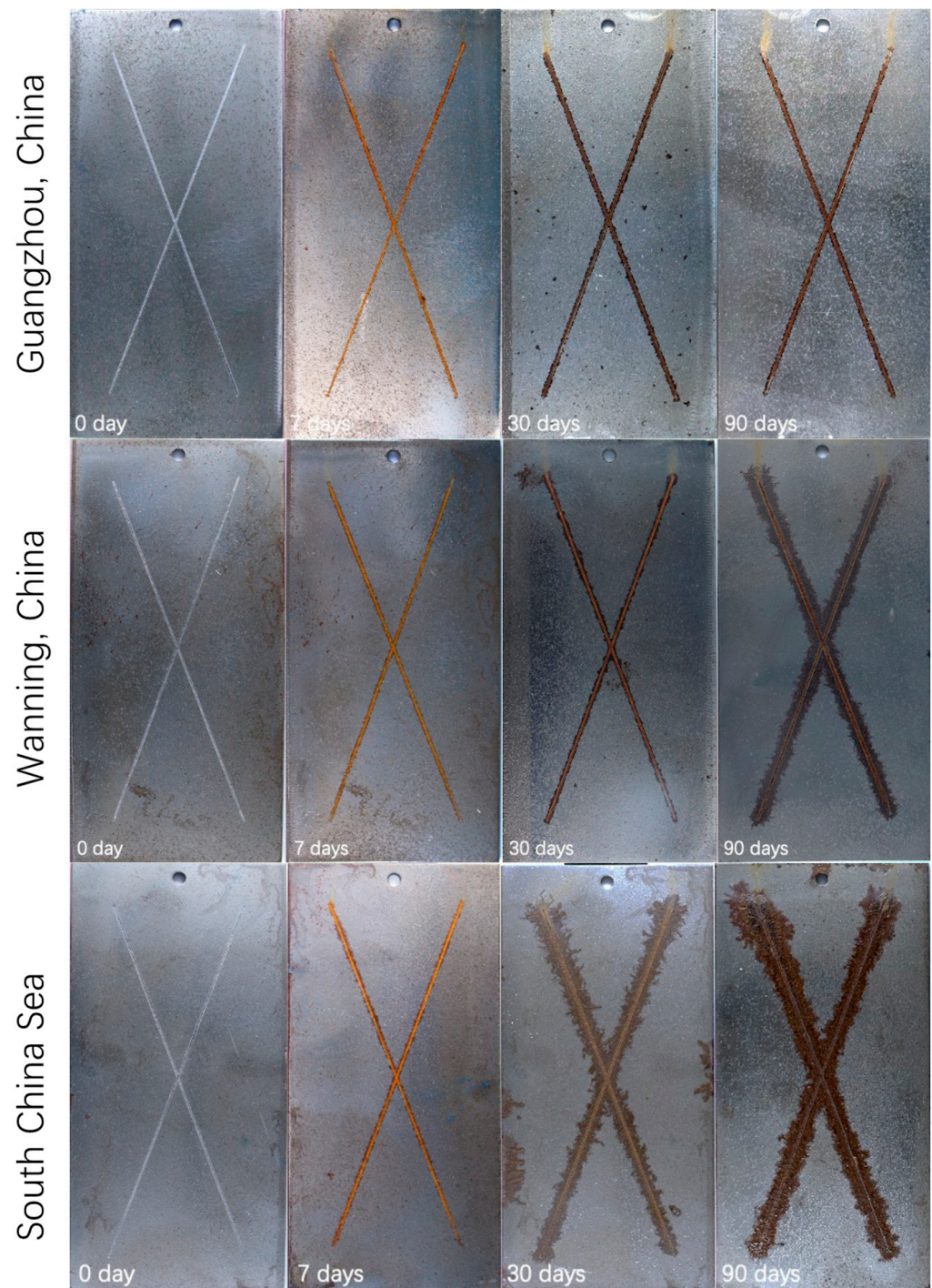


Figure 5. The surface corrosion morphology of 45# steel with coating defects under exposure in different areas and on different days (the dimension of each plate is $200 \times 100 \times 3$ mm).

As shown in Figure 6, the XRD analysis revealed characteristic peaks for the main corrosion products α -FeOOH, β -FeOOH, γ -FeOOH, and Fe_3O_4 [21]. The rust layer's structure on the 45# steel surfaces, regardless of exposure duration or environmental conditions, was consistently composed of these four corrosion products. Notably, even after a brief exposure period of 7 days, all four corrosion products were already detectable. Prolonged exposure did not significantly alter the composition of the corrosion products on the surface, which remained predominantly α -FeOOH, β -FeOOH, γ -FeOOH, and Fe_3O_4 .

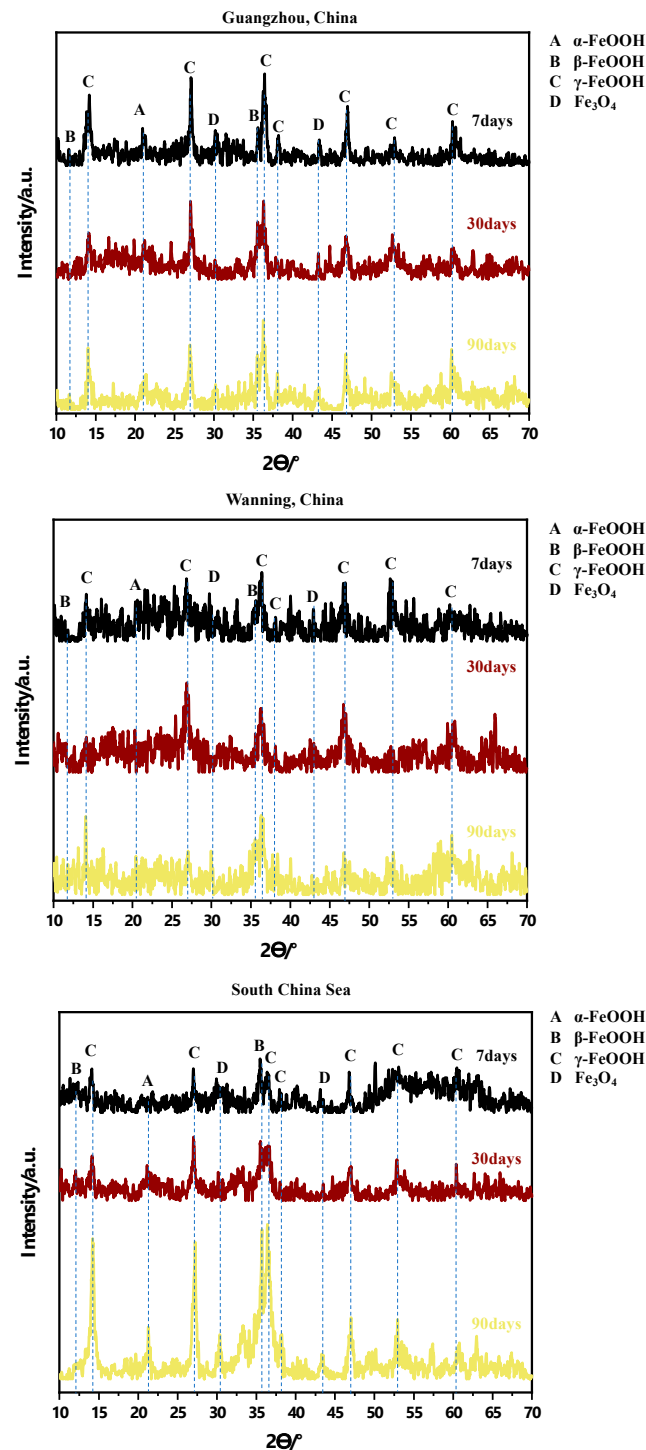


Figure 6. The XRD pattern of 45# steel under exposure in different areas and on different days.

To better compare the corrosion products, the XRD peaks were analyzed using MAUD software. Figure 7 illustrates the relative content changes in α -FeOOH, β -FeOOH, γ -FeOOH, and Fe_3O_4 . These variations potentially reflect differences in the corrosion rate and mechanisms affecting 45# steel. In Guangzhou, there were no significant changes in the relative content of each corrosion product, suggesting a relatively lower corrosion rate. Conversely, in comparison with the initial states, in Wanning and the South China Sea areas, some changes in the content of α -FeOOH, β -FeOOH, and γ -FeOOH were observed after 30 days of exposure, indicating alterations in the surface corrosion processes. A more detailed discussion of these mechanisms is provided in Section 3.3.

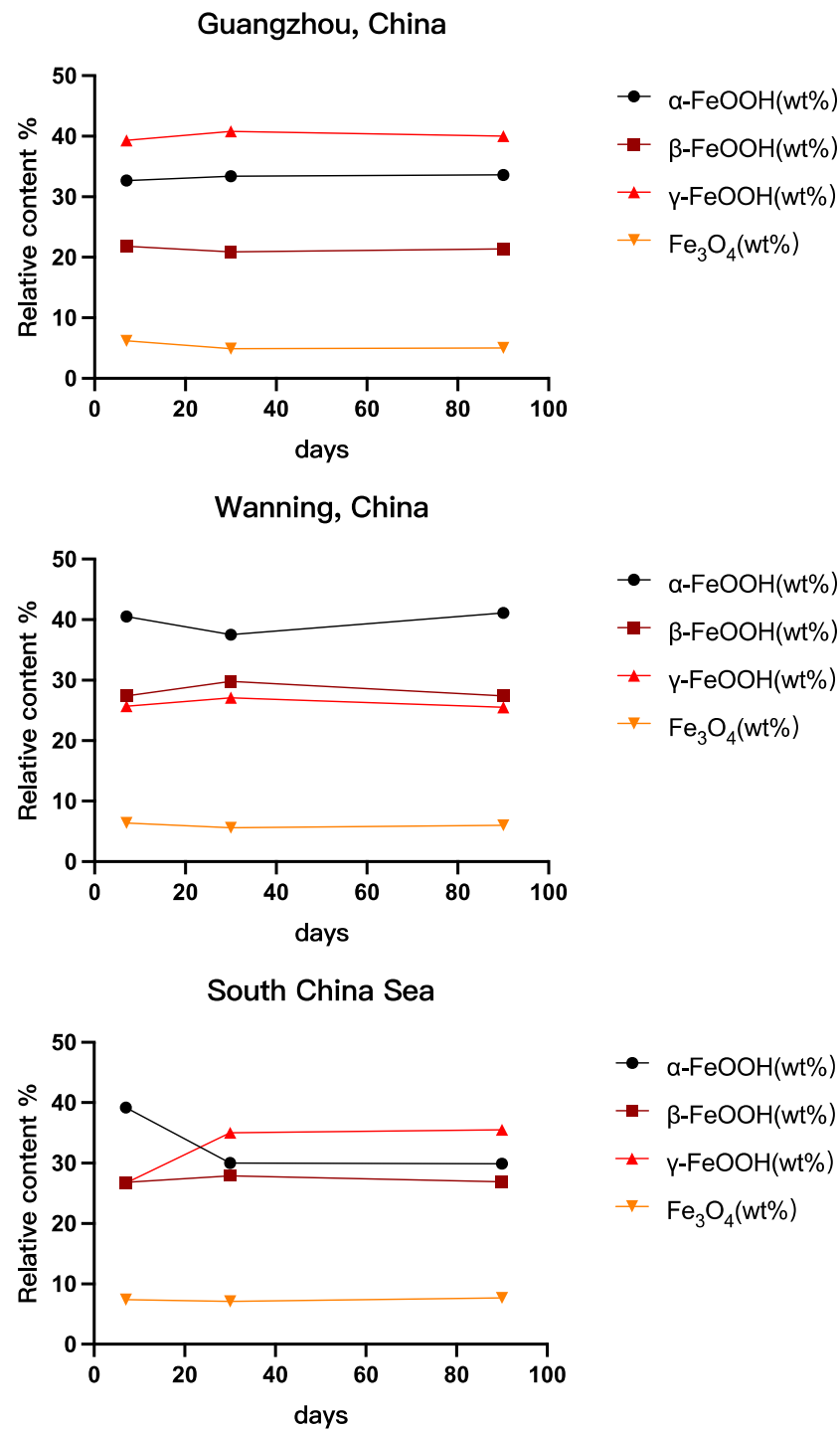


Figure 7. The corrosion product changes in 45# steel under exposure in different areas and on different days.

The changes in the relative content of the corrosion products are further analyzed and summarized in Figure 8. The protection ability index (PAI) is employed to evaluate the protective effect of the rust layer on the substrate [22–24]. The PAI of the rust layer is defined as the ratio of the more electrochemically stable product α^* (the sum of the relative contents of α -FeOOH and Fe_3O_4) to the more electrochemically reactive product

γ^* (the sum of the relative content of γ -FeOOH and β -FeOOH). It can be expressed by the following formula:

$$PAI = \alpha^* / \gamma^* = (\alpha + Fe_3O_4) / (\gamma\text{-FeOOH} + \beta\text{-FeOOH}) \quad (2)$$

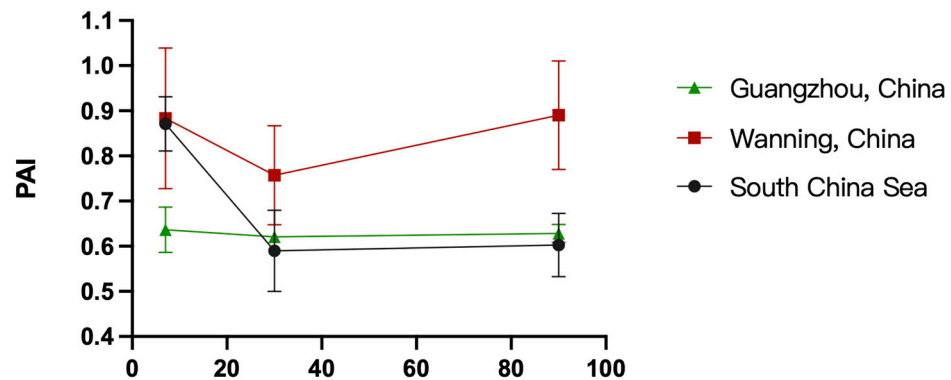
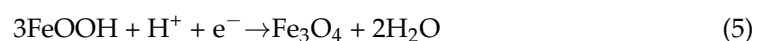
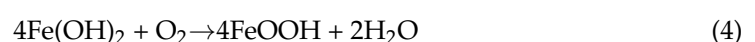


Figure 8. The change in PAI value of 45# steel under exposure in different areas and on different days.

Typically, a PAI value greater than two indicates a rust layer with a good protective effect [24]. However, according to the PAI results of 45# steel under exposure in different areas and on different days, none of them were higher than one. Since all samples in this work do not have a protection effect, the PAI comparison in this work may not be used to evaluate the corrosion rate of those samples. It can be concluded that the corrosion products that generate in low-latitude coastal areas cannot provide a protection effect on 45# steel. Therefore, the actual corrosion rates should be determined based on the polarization measurements that are detailed in Figure 3.

3.3. Atmospheric Corrosion Mechanism of 45# Steel

The atmospheric corrosion mechanism of 45# steel in low-latitude coastal areas can be ascribed to the following procedures:



In low-latitude coastal areas, the high relative humidity leads to the rapid adsorption of water vapor on the steel surface, forming a thin liquid film. As this film thickens, electrochemical reactions accelerate, promptly oxidizing iron (Fe) into ferrous ions (Fe^{2+}), as shown in Equation (3).

In the presence of sufficient oxygen, Fe^{2+} is quickly transformed into ferrous hydroxide ($Fe(OH)_2$) or hydroxyiron ($FeOH^+$). $FeOH^+$ is preferentially oxidized to gamma iron oxyhydroxide (γ -FeOOH) by dissolved oxygen within the liquid film [20,25,26]. Early in the exposure, the concentration of γ -FeOOH is particularly high, especially in samples from the Guangzhou area, which experiences milder environmental conditions compared to the other studied locations. Notably, the γ -FeOOH content remains high, even after 90 days, indicating that corrosion in Guangzhou is still in its early stages.

When chloride ions (Cl^-) from the air are absorbed into the liquid film, they react to produce iron chloride ($FeCl^+$), which quickly converts into beta iron oxyhydroxide (β -FeOOH), as detailed in Equation (4) [27]. According to Figure 8, the relative amount of β -FeOOH in Wanning and the South China Sea was higher than that observed in Guangzhou, which indicates that the concentration of Cl^- content in Guangzhou was lower than that seen in the other two area. The presence of β -FeOOH was more pronounced in Wanning and the South China Sea, highlighting higher Cl^- concentrations than those observed in

Guangzhou. This aligns with Guangzhou's relatively higher latitude and urban coastal environment, which generally exposes it to lower levels of chloride.

Over time, the surface's electrochemical dynamics evolve. The strong reducing properties of γ -FeOOH lead to its gradual transformation into either alpha iron oxyhydroxide (α -FeOOH) or magnetite (Fe_3O_4), as indicated in Equation (5). This reaction will gradually increase the content of α -FeOOH or Fe_3O_4 in the rust layer. The increase in the relative content of β -FeOOH in the rust layer may also be caused by the recrystallization of FeOOH in other crystal forms [28]. When β -FeOOH reacts with Fe in the matrix to form Fe_3O_4 , the relative content of β -FeOOH gradually decreases. In addition, the relative content of Fe_3O_4 gradually increases. This phenomenon can be observed in Figure 8. In Wanning and the South China Sea, the relative contents of β -FeOOH and Fe_3O_4 were negatively correlated. However, in the Guangzhou area, this phenomenon was not observed, which could relate to differences in the atmospheric component content in the urban environment [10].

A comprehensive analysis of corrosion rates, surface morphology, and rust layer composition reveals that the corrosion of carbon steel is strongly influenced by both the geographical latitude and the specific location of the test area.

4. Conclusions

This comprehensive analysis of the atmospheric corrosion behaviors of 45# steel in three distinct low-latitude coastal areas—Guangzhou, Wanning, and the South China Sea—has led to the following conclusions:

1. Corrosion Rate and Geographical Influence:

The corrosion rate of 45# steel is significantly influenced by both the latitude and the specific location within the test area. The South China Sea exhibits the highest corrosion rate, followed by Wanning and Guangzhou.

2. Corrosion Rust Penetration in Defective Coatings:

The extent of corrosion rust penetration in coatings with defects corresponds directly to the overall corrosion rates. This sequence, from most to least affected, is the same as the order of corrosion rates, as follows: the South China Sea, Wanning, and Guangzhou.

3. Predominant Corrosion Products:

The primary corrosion products identified in all regions are α -FeOOH, β -FeOOH, γ -FeOOH, and Fe_3O_4 . These compounds dominate the corrosion landscape across the different coastal environments.

4. Protection Ability Index (PAI):

The PAI calculations reveal that none of the tested samples succeeded in forming a protective corrosion film on 45# steel. This indicates an overall lack of effective natural protective barriers against corrosion under the conditions studied here.

These findings underscore the critical impact of environmental variables on the corrosion processes of carbon steel in coastal settings, highlighting the need for tailored protective strategies in different geographical areas. For future further investigations, the influence of UV, exposure temperature, wind speed, and salinity of the atmosphere can be included.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to some of the data are classified.

Conflicts of Interest: Authors Lihong Liu and Bo Zhang were employed by the company CEPREI, author Guoqiang Liu was employed by the company CCCC Fourth Harbor Engineering Institute Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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