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Insights into the corrosion mechanism and electrochemical properties of the rust layer evolution for weathering steel with various Cl\(^-\) deposition in the simulated atmosphere

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Abstract

This study aims to make clear the effect of various Cl\(^-\) deposition conditions on the changes of corrosion mechanism and electrochemical properties of the rust layer for weathering steel. The results indicate that the corrosion rate in presence of low Cl\(^-\) deposition is divided into three stages: sharp increase stage, rapid decrease stage and tending to be stable stage. While, the high Cl\(^-\) deposition process is divided into two stages: sharp increase stage and decrease stage. The increased of Cl\(^-\) deposition increase the contents of the β-FeOOH and decrease the contents of the α-FeOOH, and then to reduce the corrosion resistance. For the initial corrosion cycles, the increased of Cl\(^-\) deposition influence the oxygen supply, resulting in spatial heterogeneity of the potential distribution to promote the corrosion reaction. As the prolonged corrosion cycles, the weathering steel of low Cl\(^-\) deposition forms a protective rust layer to make the potential distribution become more uniform to reduce the corrosion rate, while the weathering steel of high Cl\(^-\) deposition of the potential distribution is more unevenly distributed with distinct low and high potential zones to promote corrosion reaction.

1. Introduction

Weathering steel (WS) is known as a low-cost steel without coating which can be maintained for decades [1]. The atmospheric service life of the WS depends on the phase composition generated from the corrosion products [2, 3]. At present, the unpainted WS is allowed to be used when the air-borne salinity concentration is below 0.05 (mg Cl\(^-\)/dm\(^3\)/d) [1]. As per the IOS.9233, the corrosivity of the atmosphere can be divided into six categories based on the Cl\(^-\) deposition, relative air humidity and so on. Hence, the Cl\(^-\) deposition is the major factor responsible for the formation of protective rust layer of WS.

It is well-known that under the condition of high Cl\(^-\) deposition, the formation of a protective rust layer on the WS is difficult. Previous studies have focused on the corrosion kinetics, generation process and electrochemical property of the WS rust layer under Cl\(^-\) deposition. Kamimura et al and Chico et al [4, 5] carried out atmospheric exposure test to find that the protective layer on the traditional WS could not be formed due to the corrosion of Cl\(^-\). The atmospheric exposure test can truly reflect the corrosion behavior of the actual steel in a specific atmospheric environment, but cannot reflect the atmospheric corrosion behavior of steel in presence of Cl\(^-\) due to the difficulties in controlling the conditions. Therefore, the simulated atmospheric corrosion tests were used to further study the influence of Cl\(^-\) on the corrosion behavior of WS. Elena Bernardi et al [6] pointed out that the Cl\(^-\) deposition facilitated metal dissolution with the weight loss tending to be linear with increasing Cl\(^-\) deposition. Fan et al [7] indicated that under high Cl\(^-\) deposition and humid atmospheric environment, γ-FeOOH and β-FeOOH were mainly located in the outer rust layer and the component of the inner rust layer of WS was mainly α-FeOOH. The rust layer containing γ-FeOOH and β-FeOOH became porous to allow the Cl\(^-\)
to penetrate the rust layer easily, which promoted corrosion reaction. Meanwhile, the β-FeOOH was formed unquestionably under high Cl\textsuperscript{−} deposition condition and as the Cl\textsuperscript{−} deposition increase, the content of β-FeOOH increase in rust layer [8]. Interestingly, it is hardly for the formation of protective rust layer for WS under the high Cl\textsuperscript{−} deposition, while the protective rust layer should be formed with a certain Cl\textsuperscript{−} deposition. Hence, the protective properties for the rust layer under the erosion of various Cl\textsuperscript{−} deposition are still unclear. Therefore, in order to predict the lifetime of WS, it is necessary to understand the corrosion mechanism and electrochemical properties of the rust layer of the WS in presence of various Cl\textsuperscript{−} deposition conditions.

The atmospheric corrosion of WS is always in wet and dry cycles which contributes the formation of a rust layer. Except for the WS composition, the atmospheric parameters determine the characteristics of the rust layer which is mainly composed of hydroxyl oxidize iron. In initial corrosion, corrosion products are composed of γ-FeOOH and more amorphous substances, which causes the rust layer to have a little protection ability. And then the γ-FeOOH spontaneously transforms into α-FeOOH which gradually enhances the corrosion resistance. The atmospheric exposure test can truly reflect the corrosion behavior of the actual steel in a specific atmospheric environment, and it is the most important method to evaluate the corrosion behavior for steel. However, it takes at least 4 years for an evaluation test. Due to the disadvantages of atmospheric exposure test, it springs out many simulated atmospheric corrosion tests to evaluate the corrosion behavior for steel. Especially for the Wet/dry cyclic corrosion test, based on solution spray followed by drying, is able to simulate regular wet and dry cycles in controlling RH and temperature [9, 10].

In addition, when the Cl\textsuperscript{−} is attached to the surface of WS, it could also accelerate the anodic oxidation reaction for WS to promote the electrochemical corrosion. As the Cl\textsuperscript{−} deposition increases, the electrochemical corrosion is even more intense. Hence, it springs out some electrochemical measurements to characterize the electrochemical properties of the rust layers of WS in the presence of various Cl\textsuperscript{−} deposition conditions. Gan et al[11] used the occluded corrosion cavity cell and measurements of short-circuited current to analyze the electrochemical properties of low alloy steels. They indicated that the presence of locally occluded surface was an essential factor affecting the localized corrosion. Vignal et al[12] carried out local electrochemical probes to study the electrochemical behavior of stainless steel. However, those methods are too complex to investigate the electrochemical properties of the rust layers of WS. Hence, it requires a new method to characterize the electrochemical properties for WS. The Wire Beam Electrode (WBE) has been applied to study the metal corrosion which can provide information about the mechanism of atmospheric corrosion of metal [13]. This method provides the distributions of potential/current under complex surface conditions. Tang et al[14] studied the electrochemical properties of the corrosion behavior and electrolysis mechanism of the Ni-P coatings by using WBE, which is beneficial for investigating the electrochemical properties of the surface coatings. The WBE method can be further used to study the influence of various Cl\textsuperscript{−} deposition on the electrochemical behavior of WS.

Herein, we have investigated the effect of three different Cl\textsuperscript{−} concentrations on the rust layer of WS using Weight gain, SEM, XRD, Raman and electrochemical measurements. The above characterization methods evaluated the effect of various Cl\textsuperscript{−} depositions on the changes of the corrosion mechanism and the electrochemical properties of the rust layer of WS, and accordingly provide guidance for the selection of WS in the atmospheric environment.

2. Experimental procedure

2.1. Sample preparation

In this manuscript, the composition of the WS samples contained (in mass %): 0.058 C, 0.34 Si, 1.27 Mn, 0.34 Ni, 0.045 Cr, 0.31 Cu and Fe balance. It was machined into 20 mm × 20 mm × 4 mm samples and 100 wires (1.2 mm in diameter). The 20 mm × 20 mm × 4 mm samples were embedded in epoxy resin, the schematic diagram of which is shown in figure 1(a). The 100 weathering steel wires were arranged in order as a 10 × 10 matrix and embedded in epoxy resin, the schematic diagram of which is shown in figure 1(b). The total area of 100 wires was 2.0 cm\textsuperscript{2}. All the samples were wet-polished down to 600 #, 800 # and 1000 # grade emery paper, and then cleaned by ethanol. They were divided into three parts and stored in desiccator for 24 h prior to use.

2.2. Wet-dry cyclic corrosion test

As the ref shown [4, 15], the coastal atmosphere is classified by the Cl\textsuperscript{−} deposition which was performed by the dry gauze method according to JIS Z 2382 [16]. When the Cl\textsuperscript{−} deposition is lower than 0.2 mdd (mg/dm\textsuperscript{2}/day), it is considered as a seashore region. When the Cl\textsuperscript{−} deposition is higher than 0.5 mdd (mg/dm\textsuperscript{2}/day), it is considered as a severe seashore region. Hence, three Cl\textsuperscript{−} concentrations (0.01 mol l\textsuperscript{−}1, 0.05 mol l\textsuperscript{−}1 and 0.10 mol l\textsuperscript{−}1) were used to simulate the actual coastal atmosphere in this study. And then the Cl\textsuperscript{−} concentrations of 0.01 mol l\textsuperscript{−}1, 0.05 mol l\textsuperscript{−}1 and 0.10 mol l\textsuperscript{−}1 are corresponding to 0.1 mdd, 0.5 mdd and 1.0 mdd in the simulated
atmosphere, respectively. Three of the samples having dimensions of 20 mm × 20 mm × 4 mm were used for weight gain measurement as parallel samples. There is an approximate quantitative correspondence between weight gain and weight loss, satisfying the power function. Therefore, the corrosion kinetics are characterized by weight gain. Other samples with the dimensions of 20 mm × 20 mm × 4 mm and WBE were taken regularly for analysis of the rust layers. The wet-dry cyclic corrosion test was divided into six steps: (1) Weighing the samples; (2) Dropping 40 μl cm⁻² of the 0.01 mol l⁻¹, 0.05 mol l⁻¹ and 0.10 mol l⁻¹ NaCl solution on three parts of the samples surface as the wetting stage, respectively, using pipette; (3) Placing all the samples in constant temperature and humidity test chamber (25 ± 2°C, RH 60 ± 5%) as the drying stage for 24h; (4) Re-weighing all the samples after the step (3); (5) Cleaning all the samples with distilled water to prevent the accumulation of NaCl and then dry the samples before applying new corrosive electrolyte; (6) Repeating the steps (2)–(5) for each cycle.

2.3. Characterization and analysis of the corrosion products
A host of spectroscopic methods were used to characterize the corrosion products. The microstructure of the corrosion products was measured by SEM which was operated at 40 mA current and 15 kV voltage. The elemental composition was measured by EDS. XRD spectra of the rust powders were observed after grounding them into fine powders. The scanning angle (2θ) range during the XRD measurement was 10°–75° with a step size of 0.02° employing Cu Kα as the target. In order to compare the intensity of the corrosion products, the amount of corrosion products was maintained as the same mass for each analysis. The intensity of certain phase reflects its relative quantity semi-quantitatively [17]. The quantitative analysis was carried out by the reference intensity ratio (RIR) method and the Rietveld method.

The phase composition of the corrosion products was measured by Raman spectroscopy employing HR800 model from Horiba Jobin Yvon. The excitation wavelength of the laser was 532 nm, with the beam diameter and the output power being 40 μm and 80 μW, respectively. The common peak positions of the corrosion products are listed in Table 1 for [18–20].

| Phase                  | Peak position (cm⁻¹)         |
|------------------------|------------------------------|
| Lepidocrocite (γ-FeOOH)| 166, 217, 251, 310, 350, 378, 529, 655, 713, 1300 |
| Goethite (α-FeOOH)     | 203, 244, 300, 387, 399, 415, 480, 552, 684, 1002, 1113, 1304 |
| Akaganetic (δ-FeOOH)   | 139, 308, 389, 420, 499, 559, 609, 720, 1410 |
| Magnetite (Fe₃O₄)      | 306, 538, 666                |
| Hematite (Fe₂O₃)       | 228, 250, 294, 414, 502, 625, 670, 1330 |
| Maghemite (γ-Fe₂O₃)    | 339, 386, 461, 512, 671, 717, 1430 |
| Ferrihydrite (Fe₅HO₈·4H₂O)| Broad band between 700 and 710 |

Figure 1. (a) Schematic diagram for samples in epoxy resin; (b) dimension graphs of WBE.
2.4. Electrochemical measurements
The electrochemical measurements were carried out by classical three electrode cell set up at room temperature (25 °C) in 3.5% NaCl solution. The rusted steel samples with an exposed area of 1 cm², a platinum sheet and a saturated calomel electrode were applied as the working electrode, auxiliary electrode and the reference electrode, respectively. Before each test, the open–circuit potential (OCP) was monitored for an hour to obtain the stable potential. For potentiodynamic polarization, the voltage was scanned from $-1.0 \text{v}$ to $-0.1 \text{v}$ versus the reference electrode at a scan rate of 10 mV/min. The EIS measurement was conducted in the frequency range of $10^5 \text{Hz}$ to $10^{-2} \text{Hz}$ with an amplitude of ±10 mV at OCP.

The potential distribution was measured with the WBE test. The WBE test were still carried out by classical three electrode cell set up at room temperature (25 °C) in 3.5% NaCl solution. Each of the WS wires was connected with copper wire and insulated from each other to ensure the exact electrical signal. When the test began, each individual electrode was disconnected from the other electrodes, and the local potential between this single electrode and other connected electrodes was measured. Once the potential data was obtained, the electrode was reconnected to other electrodes, and the next electrode was separated from the other electrodes and repeated for the same monitoring procedure until the electrodes were all measured.

3. Results

3.1. Corrosion kinetics
In general, the atmospheric corrosion kinetics of steel satisfies the power function [21–23] which can be expressed by equation (1) [24]:

$$\Delta W = AN^n$$

where, $\Delta W$ is the weight gain (mg), $A$ is a constant, and the exponent $n$ represents the power function index and $N$ is the corrosion cycles. Equation (2) is obtained from the logarithm of equation (1).

$$\log \frac{\Delta W}{N} = \log A + (n - 1) \log N$$

Equation (3) is gotten by taking the differential of equation (1). Combining equations (1)–(3) is obtained which could calculate the instantaneous corrosion rate $V_i$ (mg/cm²·d):

$$V_i = \frac{d\Delta w}{dN} = AnN^{n-1}$$

where, the exponent $n$ represents the corrosion kinetics. The value of $n > 1$, $n < 1$ or $n = 1$ means that the corrosion stage is in an acceleration stage, a deceleration stage or in a dynamic balance, respectively [1].

The corrosion kinetics of the samples in the presence of three different Cl⁻ deposition concentrations are shown in figure 2(a) and it is evident that the weight gain of the samples is in gradually increasing trend with prolonged cycles in the presence of three different Cl⁻ deposition concentrations. For 0.01 mol l⁻¹ and 0.05 mol l⁻¹ Cl⁻ concentration, the weight gains are basically similar at the initial stage ($N < 16$) and at the later stage ($16 \leq N \leq 30$) it is slightly higher for 0.05 mol l⁻¹ in comparison to the 0.01 mol l⁻¹. However, the weight gain in the presence of 0.10 mol l⁻¹ Cl⁻ concentration is significantly higher than the other two concentration values during the corrosion cycles. It indicates that high concentration of Cl⁻ deposition may promote the corrosion reaction of WS. A logarithmic mathematical model is used to analyze the data of figure 2(a) and the results are shown in figure 2(b). The linear fitting equations of the data obtained by Formula (2) are listed in table 2.

Figure 2(c) shows the instantaneous corrosion rates calculated by Formula (3). In the presence of 0.01 and 0.05 mol l⁻¹ Cl⁻ concentrations, the whole process can be divided into three stages. As evident from the figure 2(c), initial stage shows sharp increase in the corrosion rate followed by a decrease in the second stage whereas in the last stage the corrosion rate tends to be more or less stable. It is 5 cycles that is required for the 0.01 mol l⁻¹ Cl⁻ concentration before the second stage, while 6 cycles for the 0.05 mol l⁻¹ Cl⁻ concentration. Thus, in the initial stage, the corrosion kinetics for the two concentrations is basically similar. But in the presence of 0.10 mol l⁻¹ Cl⁻ concentration, the whole process is divided into two stages. In the initial stage, the corrosion rate increases sharply followed by slight decrease of the corrosion rate in the second stage. For 0.10 mol l⁻¹ Cl⁻ concentration, the first stage is continued for large number of cycles ($N \leq 16$). During the whole corrosion process, the change from one stage to another may give rise to the evolution of rust layer. Therefore, it is evident that WS entering into the next stage of corrosion process will be dependent on the concentration of Cl⁻ deposition.
3.2. Morphological studies of corrosion products

The morphological structures of various corrosion products have been identified by SEM. Flowery structure in the SEM micrographs indicate the presence of $\gamma$-FeOOH\footnote{25}, whereas the existence of cotton ball and rosette morphologies confirm the formation of $\alpha$-FeOOH and $\beta$-FeOOH, respectively\footnote{1, 26}. Antunes et al\footnote{25} reported that the $\gamma$-FeOOH has an open structure which caused the corrosive species to attack the metallic substrate easily. However, the $\gamma$-FeOOH transforms spontaneously to the $\alpha$-FeOOH which is identified as the protective structure and form a physical barrier impeding the corrosive species to attack the metallic substrate.

Figure 3 shows the microscopic corrosion morphology of the samples in the presence of three different Cl$^-$ concentrations for 6 and 24 cycles. As shown in figures 3(a), (c) and (e), the content of $\gamma$-FeOOH and $\beta$-FeOOH increase with the Cl$^-$ deposition increase while the content of $\alpha$-FeOOH decrease. As the prolonged corrosion cycles, the surface for 0.01 and 0.05 mol l$^{-1}$ Cl$^-$ concentration are very smooth and dense, consisting of $\alpha$-FeOOH, as shown in figures 3(b) and (d). Although it has some pores and cracks on the surface, some corrosion products could be attached to the periphery which could form a physical barrier to prevent the entry of corrosive

| Sample | Stage I | Stage II | Stage III |
|--------|---------|----------|-----------|
|        | Log$\Delta W/N = -0.05 + 1.34N$ (N $\leq 3 R^2 = 0.98$) | Log$\Delta W/N = 0.307 + 0.786N$ (5 $< N \leq 16 R^2 = 0.99$) | Log$\Delta W/N = 0.827 + 0.376$ (16 $< N \leq 30 R^2 = 0.99$) |
| 0.01 mol l$^{-1}$ | | | |
| 0.05 mol l$^{-1}$ | Log$\Delta W/N = -0.262 + 1.53N$ (N $\leq 6 R^2 = 0.98$) | Log$\Delta W/N = 0.251 + 0.843N$ (6 $< N \leq 16 R^2 = 0.99$) | Log$\Delta W/N = 0.628 + 0.552N$ (16 $< N \leq 30 R^2 = 0.99$) |
| 0.10 mol l$^{-1}$ | Log$\Delta W/N = 0.329 + 1.05N$ (1 $< N \leq 17 R^2 = 0.97$) | Log$\Delta W/N = 0.849 + 0.485N$ (17 $< N \leq 30 R^2 = 0.99$) | — |

**Figure 2.** The corrosion kinetics of WS in the three Cl$^-$ concentration as the corrosion cycles prolonging. (a) weight gain (b) The log-log pot for weight gain (c) instantaneous corrosion rate.

**Table 2.** Linear fitting results of corrosion kinetics data.
medium. However, the surface for 0.10 mol l\(^{-1}\) Cl\(^{-}\) concentration consists of many broken zones and carks which causes the Cl\(^{-}\) likely to aggregate at these zones and permeate into the rust layer, thereby reducing the corrosion resistance.

### 3.3. Composition of the rust layer

Figures 4(a), (b) show the XRD patterns of WS in the presence of three different Cl\(^{-}\) concentrations after 6 and 24 cycles. The results indicate that the peaks corresponding to \(\alpha\)-FeOOH, \(\gamma\)-FeOOH, \(\beta\)-FeOOH and Fe\(_3\)O\(_4\) are all detected after 6 as well as 24 cycles. In order to determine the proportion of these phases, the quantitative analysis was carried out by the reference intensity ratio (RIR) method and the Rietveld method. The results are shown in figure 4(c). In the initial corrosion stage with the increasing Cl\(^{-}\) concentration, the contents of the \(\gamma\)-FeOOH and \(\beta\)-FeOOH increased, especially the contents of \(\beta\)-FeOOH which is reported to be detected only in the presence of Cl\(^{-}\)\[27\]. In the later corrosion stage, the types of corrosion products remain unchanged but the relative content of different phases changed. With prolonged corrosion cycles, the relative contents of \(\gamma\)-FeOOH and \(\beta\)-FeOOH gradually decrease for the Cl\(^{-}\) concentrations of 0.01 and 0.05 mol l\(^{-1}\) while the \(\alpha\)-FeOOH gradually increase. However, there is still large content of \(\gamma\)-FeOOH and \(\beta\)-FeOOH in the presence of 0.10 mol l\(^{-1}\) Cl\(^{-}\) concentration even after 24 cycles. C R’emazeilles et al\[8\] indicated that the high Cl\(^{-}\) concentrations is necessary for the formation of \(\beta\)-FeOOH. Ma et al\[28\] also suggested that the higher the Cl\(^{-}\) concentration, more the \(\beta\)-FeOOH is produced. Hence, the XRD analysis show that the phase composition of
rust layer may be affected by the increase of Cl\(^{-}\) concentration and higher the Cl\(^{-}\) concentration, more the \(\beta\)-FeOOH would be produced which leads to the increase of corrosion rate.

In addition, Kamimura et al\(^{[4]}\) proposed the concept of \(\alpha/\gamma^*\) (the mass ratio of \(\alpha\)-FeOOH to the total mass of \(\gamma\)-FeOOH, \(\beta\)-FeOOH and Fe\(_3\)O\(_4\) in the rust), which is considered as an index for evaluating the protective rust layer with higher ratio indicating better corrosion resistance. Figure 4(d) shows that the ratio of \(\alpha/\gamma^*\) for three Cl\(^{-}\) concentrations generally increase with prolonged corrosion cycles. Furthermore, with increasing Cl\(^{-}\) concentration, the value of \(\alpha/\gamma^*\) decrease which indicates the reduction of the corrosion resistance of the rust layer. These results are in agreement with the corrosion kinetics.

Figure 5 shows the results of Raman spectra of the samples for three different Cl\(^{-}\) concentrations after 6 and 24 cycles. The results of the Raman spectra are consistent with that of the XRD. The corrosion products with different Cl\(^{-}\) contents basically contain \(\alpha\)-FeOOH, \(\gamma\)-FeOOH, \(\beta\)-FeOOH and Fe\(_3\)O\(_4\). With the increasing Cl\(^{-}\) concentration, the contents of \(\gamma\)-FeOOH and \(\beta\)-FeOOH increase, especially the content of \(\beta\)-FeOOH. With prolonged corrosion cycles, the types of corrosion products remain unchanged, but the relative content of the different phase changes. It indicates that the \(\gamma\)-FeOOH and \(\beta\)-FeOOH spontaneously transforms to \(\alpha\)-FeOOH, but the rate of transformation decreases with the increase of Cl\(^{-}\) concentrations.

### 3.4. Electrochemical properties of the rust layer

Figure 6 shows the polarization curves of the samples in presence of three Cl\(^{-}\) concentrations after 6 and 24 cycles in 3.5% NaCl solution. Generally, for the samples in presence of three Cl\(^{-}\) concentrations from figures 6(a), (b), they present almost the similar evolution behavior in OCP, cathodic current density and anodic current density. The OCP of all samples gradually move to positive position, indicating that the corrosion resistances are enhanced as the prolonged corrosion cycles. The changes of cathodic current density are caused by the formation of protective rust layer with an increasing content of \(\alpha\)-FeOOH. Moreover, the stabilized anodic current densities are due to the rust layer with physical barrier to restrain the penetration of Cl\(^{-}\). Figure 6(a) shows that the cathodic current density is almost similar for the three Cl\(^{-}\) concentrations, but the
anodic current density increases with the increasing Cl$^-$ concentration after 6 corrosion cycles. It may cause by the increasing Cl$^-$ concentration make the rust layer rougher to promote the anodic reaction. Figure 6(b) shows that the cathodic current density for 0.10 mol l$^{-1}$ Cl$^-$ concentration is slightly higher than that of two others.

The electrochemical parameters including Corrosion potential ($E_{corr}$) and Corrosion current density ($I_{corr}$) obtained from the polarization curves shown in figure 7. It is widely known that a lower $I_{corr}$ and a higher $E_{corr}$ for the polarization curves illustrated a lower corrosion rate. As the corrosion process prolonged, the $E_{corr}$ show a positive shift trend, and the $I_{corr}$ gradually decrease which indicates that the corrosion resistance are enhanced. In initial corrosion process, as the increased Cl$^-$ concentration, the variation of $E_{corr}$ is not obvious, while the $I_{corr}$ decreases. Meanwhile, in later corrosion process, the $E_{corr}$ show a positive shift trend, and the $I_{corr}$ gradually decrease as the increased Cl$^-$ concentration. The corrosion properties of rust layer are depending on the phase compassion and microstructure. As mentioned above, the relative contents of $\gamma$-FeOOH and $\beta$-FeOOH gradually increase and the $\alpha$-FeOOH gradually decrease as the increased Cl$^-$ concentration. It means that the increased Cl$^-$ concentration is harmful to enhance the corrosion resistance of rust layer according to the polarization curves.

Figure 8 shows the EIS results for the samples in the presence of three Cl$^-$ concentrations after 6 and 24 cycles. For the 6 and 24 cycles, the Nyquist curves are composed of unfinished semi-circle arcs and the impedance module. All the Nyquist curves contain a straight line with a slope closed to 1 in the low-frequency region which is described as the Warburg impedance at the low-frequency region [28, 29]. It reveals that the mass transport process corresponds to the diffusion process of the oxidized and reduced species [30, 31]. Hermas et al reported that the Warburg impedance represented for the dissolution kinetics of the film which was
limited by the diffusion of oxidation products [32]. Hence, it is reasonable for the occurrence of Warburg impedance tail due to the formation of rust layer for WS. Figures 8(a) and (b) present Bode plots, containing phase angle plot and the modulus plot, for the three Cl$^-$ concentrations as the prolonged corrosion cycles. The maxima phase angle in all curves are much lower than 90° which may be recognized as a deviation from ideal capacitor characteristic resulting from the inhomogeneities in the electrodes, porosity, mass transport and

Figure 7. Change trend of corrosion potential ($E_{corr}$) and corrosion current density ($I_{corr}$) of three Cl$^-$ concentration for 6 and 24 cycles.

Figure 8. The evolution of the EIS results for the samples of three Cl$^-$ concentration for 6 and 24 cycles. (a) for 6 cycles (b) for 24 cycles.
relaxation effects [33]. According to the modulus plot, the $|Z|$ value at high impedance ($|Z|_H$) corresponds to the solution resistance ($R_s$) and the sum of the solution resistance ($R_s$) and polarization resistance ($R_p$), respectively [34]. For the 6 cycles, the $|Z|_H$ values of the three Cl$^-\text{o}$ concentrations are almost the same about 15 $\Omega \cdot \text{cm}^2$, while the $|Z|_l$ values gradually decrease from 140 to 80 $\Omega \cdot \text{cm}^2$ as the Cl$^-\text{o}$ concentrations increase. It indicates that the lower $|Z|_l$ values are caused by the Cl$^-\text{o}$ promoting the corrosion reaction to generate $\gamma$-FeOOH and $\beta$-FeOOH during initial corrosion process. For the 24 cycles, the $|Z|_l$ values gradually increase as the corrosion process prolong which caused by the proportion of $\alpha$-FeOOH increases with subsequent decrease of the $\gamma$-FeOOH and $\beta$-FeOOH. However, the $|Z|_H$ values of the high Cl$^-\text{o}$ concentration are always lower than other two concentration which indicates that the high Cl$^-\text{o}$ concentration reduce the corrosion resistance for the WS. The effects of Cl$^-\text{o}$ deposition on the electrochemical properties of the rust layers are analyzed in the next section.

Figure 9 shows the potential distribution of the WBE for three Cl$^-\text{o}$ concentrations after 6 and 24 cycles. Figures 9(a), (c), and (e) presents the spatial heterogeneity of the potential for three Cl$^-\text{o}$ concentrations after 6 cycles. It can be seen that in the initial corrosion stage, the potential is gradually decreasing with the increasing Cl$^-\text{o}$ concentrations which indicates that the corrosion resistance of the samples are gradually
decreasing, which is consistent with the results from the weight gain [35]. Figures 9(b), (d), and (e) show that the potential corresponding to the 0.01, 0.05 and 0.10 mol l\(^{-1}\) Cl\(^-\) concentrations move towards positive after 24 cycles. In addition, the potential distribution for the Cl\(^-\) concentrations of 0.01 and 0.05 mol l\(^{-1}\) become relatively uniform and show little change between the low and high potential values. However, the potential distribution for the Cl\(^-\) concentration of 0.10 mol l\(^{-1}\) is more unevenly distributed with distinct low and high potential zones after 24 cycles. This phenomenon shows that the three Cl\(^-\) concentrations have significant effect on the electrochemical properties of the rust layers.

4. Discussion

4.1. The effect of Cl\(^-\) deposition on the corrosion kinetics

The formation process of the rust layer formed on the WS in the presence of low and high Cl\(^-\) deposition is briefly described in figure 10. The corrosion mechanism of the three Cl\(^-\) concentrations in the first stage is similar, while at the later stage it has a different corrosion mechanism for low and high Cl\(^-\) deposition.

In the initial stage (N < 6), the corrosion rate of samples all increased for three Cl\(^-\) concentrations, while that increase with the increasing of Cl\(^-\) concentrations. The cathodic and anodic processes are mainly controlled by the reduction of oxygen and ferric hydroxyl-oxide, and the dissolution of steel, respectively [36]. The reactions occurring at the anode and cathode are:

\[
\text{Anode reaction: } \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad \text{and} \quad \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \quad (4)
\]

\[
\text{Cathode reaction: } \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (5)
\]

When the electrolyte is covered on the surface of the samples, the accumulation of Cl\(^-\) accelerate the dissolution of steel. The rust constituents are not well crystallized yet, and it mainly contain Fe(OH)\(_2\) and Fe(OH)\(_3\) on the samples surface [37]. The presence of large amounts of Cl\(^-\) in the electrolyte accelerates the rapid dissolution of Fe(OH)\(_2\) and Fe(OH)\(_3\).

At this time, the Cl\(^-\) not only plays the role of conductor, but also accelerates the partial dissolution of the Fe(OH)\(_2\) film layer, resulting in the appearance of cracks and holes in the rust layer which have been observed by figure 3 [37, 38]. Cracks and holes allow the corrosive medium to penetrate into the substrate, thereby promoting the anodic dissolution which has been observed by the increasing anodic current density with the increase of Cl\(^-\) during the initial reaction for the Tafel. In the absence of \(\beta\)-FeOOH, \(\gamma\)-FeOOH is the main factor affecting the corrosion resistance of WS [39]. Antoy et al [40] suggested that \(\gamma\)-FeOOH and \(\beta\)-FeOOH exhibit high reduction reactivity in the order \(\gamma\)-FeOOH < \(\beta\)-FeOOH. When the \(\gamma\)-FeOOH and \(\beta\)-FeOOH coexist, \(\beta\)-

![Figure 10. Corrosion mechanism diagram of WS in low and high Cl concentration electrolyte.](image-url)
FeOOH plays a dominant role in accelerating the corrosion rate \([28]\). As the evidence for the results of XRD and Raman, the rust layer of three \(\text{Cl}^-\) concentrations are mainly composed of \(\gamma\)-FeOOH and \(\beta\)-FeOOH in the initial corrosion process. Therefore, the composition of rust layer with a higher content of \(\gamma\)-FeOOH and \(\beta\)-FeOOH would accelerate the corrosion rate which is reflected in the corrosion rate sharp increase stage after 6 cycles. Meanwhile, the high \(\text{Cl}^-\) deposition produces more \(\beta\)-FeOOH than that of low \(\text{Cl}^-\) deposition on the basis of evidence gleaned from the XRD and Raman results leading to high corrosion rate.

With the prolonged corrosion process \((6 < N \leq 16)\), the corrosion rate for \(\text{Cl}^-\) concentrations of 0.01 and 0.05 mol l\(^{-1}\) gradually decreases, while that of 0.10 mol l\(^{-1}\) \(\text{Cl}^-\) concentration still increases. At this moment, the corrosion mechanisms are different between the low and high \(\text{Cl}^-\) deposition. Figure 11 shows the cross-sectional morphologies for three different \(\text{Cl}^-\) deposition concentrations and line scan of the elemental \(\text{Cl}^-\) distribution. As figure 11 shows, with increasing \(\text{Cl}^-\) concentration, the thicknesses of the rust layers are 55 \(\mu m\), 50 \(\mu m\) and 64 \(\mu m\), respectively. It can be seen that the rust layer is not compact and has some cracks for three of
steel. Meanwhile, that for the 0.01 and 0.05 mol l$^{-1}$ Cl$^{-}$ concentrations, Cl element is basically concentrated on the side near the substrate and the Cl$^{-}$ concentrate in the inner rust layer may be caused by the initial reaction products remaining in the rust layer, while for the concentration of 0.10 mol l$^{-1}$, the Cl element is evenly distributed in the whole rust layer. It indicates that the formation of rust layer for the 0.01 and 0.05 mol l$^{-1}$ Cl$^{-}$ concentrations act as the physical barrier to inhibit the entrance of Cl$^{-}$ effectively.

In the presence of low Cl$^{-}$ deposition, the $\gamma/\beta$-$\text{FeOOH}$ spontaneously transforms into $\alpha$-$\text{FeOOH}$ during the reaction followed by subsequent partial dehydration to produce $\text{Fe}_3\text{O}_4$. The relevant reactions are as follows:

$$\gamma/\beta-\text{FeOOH} \rightarrow \alpha-\text{FeOOH}$$

$$\text{Fe}^{2+} + 8\text{FeOOH} + 2\text{e}^- \rightarrow 3\text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O}$$

The $\alpha$-$\text{FeOOH}$ and $\text{Fe}_3\text{O}_4$ make the rust layer more compact to enhance the corrosion resistance of the rust layer and then reduce the corrosion rate. The compact and dense rust layer may form a physical barrier against the corrosive medium at a low concentration of Cl$^{-}$ that is reason for the turning point of corrosion rate in the corrosion kinetics.

In the presence of high Cl$^{-}$ deposition, large amounts of Cl$^{-}$ are concentrated in the micro-anode region resulting in the formation of FeCl$_2$ in the rust layer, followed by the hydrolysis reaction of FeCl$_2$ and FeCl$_3$ occurring as follows:

$$\text{(Fe}^{2+, \text{Fe}^{3+}) + \text{Cl}^- + \text{OH}^- \rightarrow \text{FeOCl} + \text{HCl}}$$

The micro-anode area and pits are filled with a large amount of acidified FeCl$_2$. Since the metal cations and H$^+$ need to be neutralized, a large amount of Cl$^{-}$ is attracted to the micro-anode and pit, further accelerating the corrosion reaction. This phenomenon is fed by the corrosion products themselves and referred to as ‘autocatalytic’ [15]. This reaction makes Cl$^{-}$ easily enter the rust layer. And it is observed that the Cl element is evenly distributed in the whole rust layer in figure 11(c). The Cl$^{-}$ of the rust layer promote the formation of $\beta$-$\text{FeOOH}$ and the accumulation of $\gamma$-$\text{FeOOH}$ and $\beta$-$\text{FeOOH}$ form a loose rust layer which may not form a physical barrier, and then accelerate the corrosion rate.

In the later corrosion stage ($17 < N \leq 30$), the corrosion rate tends to be stable at low Cl$^{-}$ deposition and the corrosion rate slightly reduce at the high Cl$^{-}$ deposition. It can be seen from the results of XRD and Raman that the proportion of $\alpha$-$\text{FeOOH}$ increases with subsequent decrease of the $\gamma$-$\text{FeOOH}$ and $\beta$-$\text{FeOOH}$. In addition, many small $\alpha$-$\text{FeOOH}$ are attached around the cracks and holes as evident from the SEM. It makes the rust layer more compact and thus acting the role of physical barrier to improve the corrosion resistance. However, at higher Cl$^{-}$ deposition, due to continuous accumulation of the corrosion products, the inner rust layer has less contact with Cl$^{-}$ and the transformation reaction of $\gamma/\beta$-$\text{FeOOH}$ into $\alpha$-$\text{FeOOH}$ would occur, so that the formed rust layer led to slight reduction of the corrosion rate in the later stage. Thus, it suggests that it is difficult to form a protective rust layer on the WS under high Cl$^{-}$ deposition.

### 4.2. The effect of Cl$^{-}$ deposition on the electrochemical properties of the rust layers

The Cl$^{-}$ deposition has an obvious influence on the composition of the rust layer which would affect the thickness and the electrochemical properties with the gradually increasing Cl$^{-}$ deposition as the results of electrochemical measurements shown.

Based on the results of EIS and the related literatures [28, 29], an equivalent electrical circuit is shown in figure 12. In this figure, $R_s$ represents the electrolyte resistance, $R_{\text{rust}}$ and $Q_{\text{rust}}$ represent the resistance and constant phase element of the rust layer, respectively. $R_{\text{ct}}$ represents the charge transfer resistance and $Q_{\text{dl}}$ represent constant phase element. $W_1$ represents the Warburg impedance.
The total $Z$, shown in figure 12, can be written as:

$$Z = R_y + \frac{1}{Z_{Q_{rust}} + \frac{1}{R_{ct} + \frac{1}{Z_{Q_{dl}} + \frac{1}{Z_{rust}}}}} \tag{9}$$

The values of $Q_{rust}$ and $Q_{dl}$ are often used to explain the surface roughness which is caused by the corrosion reaction and it leads to inhomogeneities and disturbances (such as porosity) on the microscopic surfaces [42]. However, the double-layer capacitor is not an ideal part because of the rough rust layer. The impedance of a capacitor is expressed as follows:

$$Z^{-1} = Q(j\omega)^n \tag{10}$$

where, $Q$ is the proportionality constant with dimensions of $\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^n$, $j$ and $n$ are the angular frequency, the imaginary number and the CPE power, respectively. The Warburg impedance can be expressed as follows:

$$Z_w^{-1} = Y\sqrt{(j\omega)} \tag{11}$$

where, $Y$ is the Warburg capacitance which is related to the diffusion coefficient and the surface states.

It can be seen from table 3 that the values of $n$ are much less than 1, which suggests that the corrosion products are highly heterogeneous. The values of $R_y(R_y = R_{rust} + R_{ct})$ represents the resistance of the rust layer which has been widely used in the study of electrochemical corrosion kinetics [43]. Figure 13 shows that the $R_y$ values for the three different Cl$^-$ concentrations are basically similar in the 6 cycles. However, the $R_y$ value corresponding to the Cl$^-$ concentrations of 0.01 and 0.05 mol l$^{-1}$ after 24 cycles increase to 30.63 and 24.30 $\Omega \cdot \text{cm}^2$, respectively, while for the Cl$^-$ concentration of 0.10 mol l$^{-1}$, the corresponding value is 14.72 $\Omega \cdot \text{cm}^2$. Meanwhile, the Warburg capacitance $Y$ always corresponds to diffusion resistance which suggests the lower the $Y$ values, the more compact the rust layer it has. Table 3 shows that the $Y$ values decrease as the prolonged corrosion cycles for each Cl$^-$ concentration. And the $Y$ values of low Cl$^-$ concentration is lower than that of high Cl$^-$ concentration which indicates that the rust layer have a better corrosion resistance in lower Cl$^-$ concentration. This phenomenon is good consists with the result of corrosion kinetics. As the prolonged corrosion process, the accumulation of produced corrosion products and an increasing content of corrosion products yield the appearance of anodic potential valley presented in figure 9. In the oxygen-rich region, plenty of oxygen accelerate the oxygen reduction reaction resulting in the appearance of cathode potential peak. As the Cl$^-$ concentration increases from 0.01 to 0.10 mol l$^{-1}$, the local Cl$^-$ concentration is increased to promote the metal dissolution reaction in the anoxic area, and plenty of oxygen accelerate the oxygen reduction reaction in the oxygen-rich region which leads to accelerate electrochemical reaction at the micro anode and micro cathode.

During the electrochemical corrosion of metals, when the anodic and cathodic current density of the metal surface are unbalanced, there will be a flow of electric current from one area to another area, resulting in the migration of ions in the solution [44]. The evolution of interface in the presence of Cl$^-$ is briefly described in figure 14. When the surface is covered with electrolyte, the tendency of Cl$^-$ is preferentially adsorbed at defective sites yields non-homogeneous adsorption on the bare metal surface resulting in unbalanced current density of the cathode and the anode on the metal surface [45]. In addition, large amounts of Cl$^-$ gather in one area to make it equip with electronegative called anoxic area. While the cations get together in other area to form the oxygen-rich area. In the anoxic area, large amounts of Cl$^-$ promote the metal dissolution reaction resulting in the appearance of the anodic potential valley presented in figure 9. In the oxygen-rich region, plenty of oxygen accelerate the oxygen reduction reaction resulting in the appearance of cathode potential peak. As the Cl$^-$ concentration increases from 0.01 to 0.10 mol l$^{-1}$, the local Cl$^-$ concentration is increased to promote the metal dissolution reaction in the anoxic area, and plenty of oxygen accelerate the oxygen reduction reaction in the oxygen-rich region which leads to accelerate electrochemical reaction at the micro anode and micro cathode.

Hence, for initial corrosion process, various concentrations of Cl$^-$ cause uneven distribution of dissolved oxygen on the surface, leading to appear the nonuniform potential distribution. Therefore, the potentials for three different Cl$^-$ concentrations show spatial heterogeneity at the initial cycles as shown in figure 9(a). In addition, the potential differences between the highest and the lowest potential for three Cl$^-$ concentrations are 0.110 v, 0.113 v and 0.148 v after 6 cycles, respectively. The presence of a potential difference demonstrates an inhomogeneous electrochemical property and promote an accelerated localized corrosion. The increase of Cl$^-$ concentrations results in the appearance of a potential difference which indicates that the rust layer have a better corrosion resistance in lower Cl$^-$ concentration. This reason is that corrosion rate increases as the increase of Cl$^-$ concentration in the initial stage. With the prolonged corrosion process, the potential distribution decrease should be caused by the cathodic property of the rust layer. The rust layer at low Cl$^-$ concentration is mainly composed of $\gamma$-FeOOH, while the rust layer at high Cl$^-$ concentration is mainly composed of $\beta$-FeOOH as discussed in section 4.1. For these corrosion products the $\gamma$-FeOOH is the most thermodynamically stable phase which enables to enhance the corrosion resistance of rust layer [46].
### Table 3. Fitting results of EIS spectrum of three Cl\textsuperscript{−} concentration for WS.

| Concentration (mol l\textsuperscript{−1}) | Cycles | Rs (\(\Omega\) \cdot cm\textsuperscript{2}) | Q\textsubscript{rust}(Y\textsubscript{0}) \times 10\textsuperscript{−3} (\(\Omega\textsuperscript{−1} \cdot cm\textsuperscript{2} \cdot s\textsuperscript{n})) | \(n\)\textsubscript{rust} | R\subscript{rust} (\(\Omega\) \cdot cm\textsuperscript{2}) | Q\textsubscript{dl}(Y\textsubscript{0}) \times 10\textsuperscript{−3} (\(\Omega\textsuperscript{−1} \cdot cm\textsuperscript{2} \cdot s\textsuperscript{n})) | \(n\)\textsubscript{dl} | R\textsubscript{ct} (\(\Omega\) \cdot cm\textsuperscript{2}) | Y (cm\textsuperscript{2} \cdot s\textsuperscript{0.5}) |
|------------------------------------------|--------|------------------------------------------|-------------------------------------------------|----------------|----------------|-------------------------------------------------|----------------|----------------|----------------|
| 0.01                                     | 5      | 12.49                                    | 1.48                                            | 0.73          | 2.26          | 15.05                                           | 0.61           | 15.34          | 0.023          |
|                                          | 20     | 12.33                                    | 0.03                                            | 0.81          | 8.04          | 2.62                                            | 0.56           | 22.59          | 0.011          |
| 0.05                                     | 5      | 11.10                                    | 1.74                                            | 0.88          | 2.07          | 11.71                                           | 0.57           | 10.25          | 0.033          |
|                                          | 20     | 12.12                                    | 1.95                                            | 0.75          | 6.21          | 1.82                                            | 0.49           | 18.09          | 0.016          |
| 0.10                                     | 5      | 14.71                                    | 1.98                                            | 0.57          | 1.39          | 65.3                                            | 0.63           | 10.60          | 0.138          |
|                                          | 20     | 11.71                                    | 1.08                                            | 0.48          | 7.41          | 14.61                                           | 0.60           | 7.31           | 0.033          |
shown in figures 9(b) and (d). However, γ-FeOOH and β-FeOOH exhibit high reduction reactivity to promote the electrochemical reaction causes the potential distribution to be more unevenly distributed with distinct low and high potential zones as shown in figure 9(f). The increased of α-FeOOH forms a protective rust layer to promote the uniform potential distribution in presence of low Cl⁻ concentration. However, in case of 0.10 mol l⁻¹ Cl⁻ concentration, the presence of γ-FeOOH and β-FeOOH led to the high potential difference, promoting the corrosion reaction, which cause the nonuniform potential distribution. The potential differences between the highest and the lowest potential for three Cl⁻ concentrations are 0.067 v, 0.071 v and 0.123 v after 24 cycles, respectively. Under the Cl⁻ concentrations of 0.01 and 0.05 mol l⁻¹, the potential difference is significantly reduced compared with that after 6 cycles due to content of α-FeOOH increased to form a protective rust layer. However, in case of 0.10 mol l⁻¹ Cl⁻ concentration, the presence of γ-FeOOH and β-FeOOH led to the high potential difference, promoting the corrosion reaction, which later inhibit the formation of the protective rust layer to reduce the corrosion resistance.

5. Conclusions

(1) The corrosion process of WS in presence of Cl⁻ deposit at the concentrations of 0.01 and 0.05 mol l⁻¹ can be divided into three stages: (i) at the first stage, the corrosion rate sharply increases; (ii) at the second stage, the corrosion rate rapidly decreases; (iii) at the third stage, the corrosion rate tends to be stable. However,


Cl⁻ deposit at a concentration level of 0.10 mol l⁻¹ can be divided into two stages: (i) sharp rise at the first stage and (ii) slightly decrease at the second stage.

(2) During whole corrosion process, α-FeOOH, β-FeOOH, γ-FeOOH are all observed by SEM, XRD and Raman spectra. With the increase of Cl⁻ concentration, the contents of the γ-FeOOH and β-FeOOH in the corrosion products increased, especially the contents of β-FeOOH.

(3) The Cl⁻ concentration has significant effect on the electrochemical properties of the rust layers. The potentials for three different Cl⁻ concentrations influence the oxygen supply resulting in spatial heterogeneity of the potential distribution during the initial cycles. With prolonged corrosion process, the decrease in the difference should be caused by the cathodic property of the rust layer. The enhancement of α-FeOOH content causes the potential distribution to be evenly distributed, while the enhancement of γ-FeOOH and β-FeOOH content causes the potential distribution to be more unevenly distributed with distinct low and high potential zones.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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