



# Influence of outer rust layers on corrosion of carbon steel and weathering steel during wet–dry cycles



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## ABSTRACT

The influence of the rust layers of carbon steel and weathering steel on the corrosion were investigated. It was found that corrosion of carbon steel slows down when its outer rust layer is removed. This phenomenon might be attributed to the shortening of the wetting time in wet–dry cycles when the outer rust layers are removed. What is more, growth time of the corrosion products is shortened as well, which results in the formation of the fine corrosion products. However, the behavior of corrosion of weathering steel is not obviously influenced by the outer rust layer and the wetting time.

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## 1. Introduction

Weathering steel shows higher corrosion resistance than carbon steel, which is owed to the addition of some alloy elements such as Cu, P, Cr and Ni [1–3]. These alloy elements are enriched in the inner rust layer which makes the inner rust layer of weathering steel obviously more compact than that of carbon steel [4–6]. Okada et al. [7,8] pointed out that the rust layer of weathering steel is composed of a loose outer layer and a compact, adhesive inner layer. Mizoguchi et al. [9] found that divalent Ni ions in the inner rust layer have the electrochemical effect of repelling Cl<sup>-</sup> from the steel/rust interface. In addition, the inner rust layer is composed of grains which can be densely packed because of their particular volume distribution. Yanlei Zhou et al. [10] reported that the addition of Cr and Cu is beneficial to the formation of the inner dense rust layer. Although there is no alloy elements in the rust layer of carbon steel, the outer layer is somewhat discontinuous and loose, while the inner layer is relatively dense and almost crack free [11]. So far, most researches have focused on the inner rust layer, and the influence of outer rust layer on corrosion was rarely reported. However, the effect of outer rust layer on corrosion cannot be simply ignored. For example, the outer rust layer normally contains the oxidizer [12], the mechanical removing of the oxidizer might influence the behavior of corrosion. In an atmospheric corrosion environment, rust layer acts as a strong oxidant that promotes electrochemical reaction under wet conditions [13]. Meanwhile, the cathodic reduction of oxygen must be consid-

ered, which involves electron transfer in the rust layer (ferric oxyhydroxides are also good electronic conductors [14,15]) and oxygen diffusion through rust layer, in addition to the reduction of the corrosion products in the rust [13,16]. The oxygen diffusion distance is obviously related to thickness of the rust layer, i.e. related to the outer rust layer.

The typical condition for the atmospheric corrosion is the alternating of the wetting and drying of the metal surface [17]. Due to the variation in thickness of the electrolyte layer during the wet and dry transition, the rate of oxygen reduction varies periodically and this result in a periodic variation of the corrosion potential. The high corrosion rate is possible only if the metal surface has been kept wet for a considerable time [17]. As corrosion goes on, the thickness of the rust layer increases continuously. When the rust layer becomes thicker, water in the rust layer needs more time to evaporate and the surface of metal keeps wet for a longer time. Therefore, the wetting time of the metal surface is influenced by the outer rust layer directly.

In this paper, we focused on the outer rust layers of carbon steel and weathering steel. These two kinds of steel were exposed for a certain time, and then removed the outer rust layer. This was done for half the samples. In the following corrosion process, the influence of the outer rust layer on corrosion could be investigated.

## 2. Experimental

### 2.1. Materials

The chemical compositions of the weathering steel and carbon steel are listed in Table 1. The steels tested were cut into three dif-

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ferent sizes for the wet–dry cyclic corrosion test (CCT). Three parallel samples of 40 mm × 40 mm × 4 mm were used to measure the weight gain in the corrosion process. The rust powder for X-ray diffraction (XRD) and N<sub>2</sub> adsorption test was collected from the rusted samples of 40 mm × 40 mm × 4 mm. In order to evaluating the hydration–dehydration capability of the rusted samples, other samples of 40 mm × 40 mm × 4 mm were used. Samples of 20 mm × 10 mm × 4 mm were used for rust layer analysis by scanning electron microscopy (SEM) and energy dispersive X-ray spectrometer (EDS). For electrochemical impedance spectroscopy (EIS) measurements, samples of 15 mm × 15 mm × 4 mm were used, and the wires for the electrical connections were soldered on the samples. All the samples were embedded in epoxy resin and only the largest surfaces were exposed for corrosion. The exposed surfaces of each sample were mechanically ground with 600 grit SiC paper.

## 2.2. Wet–dry cyclic corrosion test (CCT)

After being cleaned with ethanol, all the samples were subjected to the CCT [18]. The setup of the test consisted of [19–21]: (1) weighing the initial samples; (2) wetting the sample surfaces with 40 μL cm<sup>-2</sup> of 0.5% NaCl solution (mass%); (3) drying the samples in a chamber maintained at 25 °C and 60% RH for 12 h; (4) re-weighing the samples after drying; (5) washing the samples with deionized water to prevent the accumulation of progressive salt; (6) repeating the above steps from (2) to (5).

After 60 days of exposure, all the samples of weathering steel and carbon steel were divided into two groups. One group was exposed to the CCT for another 60 days. Meanwhile, the outer rust layers of the other group were removed, and then the samples were also subjected to CCT for another 60 days. The method for removing the outer rust layer is explained as following. At first, the surfaces of the samples were coated with acrylate adhesive (type HL-302 from Geliahao Chemical Factory, Fushun, China). After solidification of the adhesive, the outer rust layer adhered tightly to the acrylate adhesive. Then, the acrylate adhesive together with the outer rust layer was completely removed. The “X-weathering steel” and “X-carbon steel” are used to denote the weathering steel and carbon steel whose outer rust layers were removed.

## 2.3. Rust layer analysis

The rust powder was gathered from the surfaces of the 40 mm × 40 mm × 4 mm samples. Then the rust powder was subjected to an internal standard X-ray diffraction (XRD) using a Cu target. The scan speed was 2.0°/min and the 2θ angle ranged from 10° to 50°. ZnO was used as an internal standard matter. The diffraction intensities of (011) reflection of α-FeOOH, (110) reflection of β-FeOOH, (020) reflection of Fe<sub>3</sub>O<sub>4</sub> were measured and compared with (100) reflection of ZnO powder. The ratio of the corrosion products to ZnO was 7:3 [22].

The cross-sections of rust layers were analyzed by SEM. Also, Cr, Na and Cl contents in the 10 different regions of the outer rust layers and the inner rust layers on each sample were measured by EDS. The averaged values were taken from each sample.

## 2.4. N<sub>2</sub> adsorption test

The N<sub>2</sub> adsorption isotherms of the corrosion products were measured at 78 K using an AUTOSORB-6B. All the N<sub>2</sub> adsorption samples were degassed at 100 °C under 10<sup>-3</sup> Torr for 2 h before the tests. The specific surface areas (SSA) of the samples were determined by fitting the BET equation to the adsorption isotherms using the cross sectional area (0.162 nm<sup>2</sup>) of the N<sub>2</sub> molecule.

## 2.5. Hydration–dehydration test

The rusted steels were measured by hydration–dehydration test in order to obtain the amount of water adsorption and the water evaporation rate of the rusted samples: (1) weighing the rusted steels; (2) immersing the rusted samples in deionized water; (3) taking the rusted samples from the water and re-weighing them immediately; (4) repeating the above steps from (2) to (3) in 60 min; (5) drying the water saturated samples in a hermetic oven held at 25 °C and 60% RH; (6) weighing the samples at regular intervals during 1340 min.

## 2.6. Electrochemical impedance measurement

The electrochemical impedance spectroscopy (EIS) measurement was carried out using a three electrodes cell with platinum as the counter electrode, saturated calomel electrode (SCE) as the reference electrode, and the rusted samples with an exposed area of 2.25 cm<sup>2</sup> as the working electrode. All the samples were tested at room temperature using a Solartron 1255B frequency response analyser in combination with a PAR 1287A potentiostat. The frequency range for EIS was from 10<sup>5</sup> Hz to 10<sup>-2</sup> Hz with a sinusoidal potential perturbation of 10 mV. The corrosive electrolyte was 0.1 M aqueous NaCl solution. The impedance data was taken after measuring the open circuit potential for 1800s, and the change rate of the open circuit potential was less than 0.1 mV/s.

## 3. Results

### 3.1. Weight gain curves

The weight gain values of the weathering steel, carbon steel, X-weathering steel (initial outer layer removed) and X-carbon steel (initial outer rust layer removed) are shown in Fig. 1. The weight gain curves of the weathering steel and carbon steel are overlapping during the first 35 days. In the following corrosion process, the weight gain of the weathering steel slows down, while the weight gain curve of the carbon steel rises significantly. For further corrosion from day 60 to day 120, there is little difference between the weight gain curves of weathering steel and X-weathering steel. However, the weight gain of X-carbon steel obviously slowed down compared to that of carbon steel. This indicates that the corrosion of carbon steel was accelerated by the outer rust layer.

It can be seen from Fig. 1 that each weight gain curve can be divided into two stages and the weight gain increase linearly with the corrosion time in each stage. Therefore, the weight gain curves in Fig. 1 can be fitted by segmental linear functions (Table 2). The fitting results show that the slope of the second stage is lower than that of the first stage for all curves except that of carbon steel. The

**Table 1**  
Chemical compositions of weathering steel and carbon steel (mass%).

Sample	C	Si	Mn	P	S	Ni	Mo	Cu	Cr
Weathering steel	0.064	0.25	1.5	<0.01	<0.005	0.48	0.18	0.39	0.38
Carbon steel	0.028	0.21	1.48	–	–	–	–	–	–

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