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# Corrosion Science

# Effect of the direct current electric field on the initial corrosion of steel in simulated industrial atmospheric environment

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## ARTICLE INFO

## ABSTRACT

The effects of the direct current (DC) electric field on the initial corrosion of steel in simulated solution were investigated using measurements of weight loss and polarization curves, XRD and SEM techniques. The major constituents of the corrosion products are $\alpha$- and $\gamma$-FeOOH in $SO_4^{2-}$ solution. It was found that the corrosion rate of steel increased with the increase of DC electric field intensity. And the DC electric field suppresses the growth of $\alpha$-FeOOH and the transformation of $\gamma$-FeOOH to $\alpha$-FeOOH. All these lead to the reduction of the protective ability of rust layer and accelerate further corrosion of steel.

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## 1. Introduction

As a vital metal material, steel has attracted much attention from researchers in recent years, especially as concerns its atmospheric corrosion. Considerable efforts have been made to investigate the corrosion process of steel, as well as the corrosion products generated on the surface of steels [1–5]. Basically, the corrosion rate of iron is primarily governed by the type of oxide layers formed on the surfaces, and the initial stages of exposure of their virgin surface are important in predicting the long-term performance of steels [5–6]. The major atmospheric corrosion products of steel consist of goethite ($\alpha$-FeOOH), akaganeite ($\beta$-FeOOH), lepidocrocite ($\gamma$-FeOOH), magnetite ($Fe_3O_4$) and poorly crystallized iron oxides, the composition of which strongly depends on the exposure environment [7]. It is reported that $\alpha$-FeOOH is the most thermodynamically stable phase out of all these oxide products [8]. During the initial stages, as a main constituent, $\gamma$-FeOOH is formed and subsequently transformed into $\alpha$-FeOOH, and once a stable layer of $\alpha$-FeOOH proceeds on an iron surface, the corrosion rate of the steel is considerably reduced [2]. Some researchers reported that the factors which facilitate the transformation of $\gamma$-FeOOH to $\alpha$-FeOOH are the chemistry of the steels and the atmosphere at the

exposure site [2]. Moreover, $\beta$-FeOOH and $\gamma$-FeOOH are metastable with respect to $\alpha$-FeOOH, and they can transform into $\alpha$-FeOOH. It is also reported that the presence of salinity encourages the formation of $\beta$-FeOOH [9]. The stability and structure of the various corrosion products reflect the protective ability of the layer. Tanaka et al. studied the reaction between $Fe_3O_4$ and FeOOH, and when the iron powder was treated with $\gamma$-FeOOH, $\alpha$-FeOOH and $\beta$-FeOOH to generate $Fe_3O_4$, the results showed that the amount of $Fe_3O_4$ particles formed was in the order of $\beta$-FeOOH > $\gamma$-FeOOH » $\alpha$-FeOOH [10]. Hao et al. investigated the atmospheric corrosion of MnCuP weathering steel in simulated coastal and coastal-industrial atmospheres and found that the corrosion resistance of the rust layer was improved by the increase of $\alpha$-FeOOH content and decrease of $Fe_3O_4$ [11].

The morphology of the oxide layer formed on steels has been observed by several authors [12–14]. For instance, $\gamma$-FeOOH appears like small crystalline globules (sandy crystals) or like fine plates (flowery structures). $\alpha$-FeOOH looks like globular structures, called cotton balls (semicrystalline $\alpha$-FeOOH), interconnected by formations like nests or even like acicular structures (crystalline $\alpha$-FeOOH). $Fe_3O_4$ exhibits as dark flat regions, with circular disks. It is reasonable to believe that the structure determines the properties of the products. The more compact and dense the structure of the product, the more protective and stable the product is.

Furthermore, in terms of the various atmospheric environments in which metal parts worked, it is necessary to point out that most

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of the studies for characterization of corrosion products reported in the literature pertain to the oxides formed only in some simulated solution, but ignore other typical environments where metal is put to work. For the applications of steels, many steel-made devices are used under the DC electric field in the atmospheric environment. As an example, steel parts were employed in high voltage transmission lines which generate a high DC electric field, as well as electronic components were in integrated circuit. It is found that these devices or metal parts corrode at a higher rate than in other conditions. Recently, according to some researchers, the existence of homogeneous electric field has been found to have a huge influence on the structure and growth of crystals [15–16]. Lu et al. investigated the effect of electric field on the phase transitions of ferroelectric thin film [17]. Zhao et al. studied the solidification of metal under electric field, and concluded that the presence of the electric field alters the electro-migration of metal ions, as well as the size of metal crystal particles [18]. For these reasons, it is believed that the DC electric field, as another critical factor, affects the formation and crystallization of the corrosion products mentioned above, which further influences the protective ability of the layers and the subsequent corrosion process. Unfortunately, studies on the effect of the DC electric field on the corrosion of steels have rarely been reported before. Given that, it is of great significance to explore effects of the DC electric field on the corrosion process of steel.

The aim of this study was to clarify the effect of the DC electric field on the initial corrosion of steel and which aspects do the DC electric field influence the corrosion process of steel. For the better implementation of our work, a self-manufactured chamber was established to simulate the industrial atmospheric corrosion in solution containing $SO_4^{2-}$ under a DC electric field environment. The weight loss tests and electrochemical measurements were performed. Additionally, the characterization of the corrosion products was carried out using different and complementary techniques: X-ray diffraction (XRD) and scanning electron microscopy (SEM).

## 2. Experimental details

### 2.1. Material and solution preparation

The steel was cut into Ø45 mm round sheets with a thickness of 2 mm. The chemical composition of the tested steel is listed in Table 1. Then both their surfaces were polished with SiC paper down to 1200 grit, washed with double-distilled water, ultrasonically cleaned in ethanol, and dried in air. After that, as Fig. 1 shows, the specimens were sealed with epoxy resin and embedded into the bottom of the ring-shaped PMMA holder, so that a space was obtained in which a volume of 10 ml of media solution could be loaded.
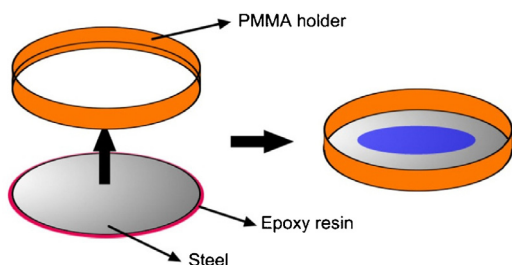


**Fig. 1.** Diagram of substrate specimen.

In order to simulate the industrial environment, 50.0 mmol/l $FeSO_4$ aqueous solutions were prepared. What is more, as it is a little hard for steel to release $Fe^{2+}$ ions, in order to yield more $Fe^{2+}$ ions and facilitate rusting more easily at a high rate, solution containing $Fe^{2+}$ ions was used. The solution was prepared with analytical grade reagents and double-distilled water. To avoid generating precipitation, it is better to use the solution immediately after preparation. Afterwards, the substrate specimens were filled with the prepared solution and then placed on the electrode plates with and without a DC electric field.

### 2.2. Establishment of the system of simulated atmospheric corrosion under the DC electric field

A self-designed chamber system (made of PMMA) was established to provide a stable temperature and relative humidity (RH), as well as to generate a series of different high voltages. As Fig. 2 shows, in the inner space of the chamber, a heating cushion with a controllable heating system was placed at the bottom of the whole chamber to maintain a steady temperature of $28 \pm 2\,^{\circ}C$. In addition, a trough was placed above the cushion, in which glycerine and water were mixed at a ratio of 3:1 to control the relative humidity at around $60\% \pm 1$, with a small addition of cupric sulfate ($CuSO_4$) to avoid mildewing. A dry and wet bulb thermometer was also put inside to determine the temperature and relative humidity. Two rectangular boards (Board A and Board B) were set up at the upper part of the system. One was prepared for fixing of the electrode plates, with a distance between the two plates of 50 mm, and the other was used for placing the contrastive samples, around which there was no DC electric field. Another vital part was the system for generating different DC electric field intensities, for the sake of which a self-designed electrical system was built at the upper exterior of the chamber. A high voltage power supply (DC) was employed to generate the stable high voltage (20 kV), and with the help of the electrical system, different levels of voltage, 20 kV, 10 kV and 5 kV, could be distributed to the three pairs of electrode plates respectively. Correspondingly, a series of DC electric field intensities 400 kV/m, 200 kV/m and 100 kV/m, were obtained respectively. It should be noted that the setting of the DC electric field intensity in this studies is according to the determination of practical electric field intensity around high voltage transmission lines. Table 2 shows the location of the specimens and the use of corresponding solution. Complementarily, taking into account the practical DC electric field environment in which the metals are located, the electrode plates fixed on Board A were connected to the earth-wire through the electrical wire.

### 2.3. Experimental process

After the temperature and humidity in the chamber were controlled in a stable condition, as Table 2 shows, the substrate samples were placed onto the surface of the electrode plate, and each pair of electrodes was loaded with three parallel substrates, which were filled with $FeSO_4$ solution. Another board was set up without fixing the electrode plate, onto which some contrastive specimens could be placed. During the passage of the exposure time, some water could evaporate from the solution, so it is necessary to add some supplementary water to the specimens to avoid disturbance arising from the change of the ion concentration. It should be noted that the high voltage may be dangerous, so it is necessary to provide a warning sign to ensure that electric shocks are avoided. After one week exposure, the specimens were removed from the chamber and the remaining solution was poured away. Additionally, the surfaces of the specimens were cleaned with distilled water and ethanol to avoid accumulation of salt on the surface, and then dried in an oven at $50\,^{\circ}C$ for 24 h. After the pretreatment of the specimens, the