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A study on the initial corrosion behavior of carbon steel exposed to outdoor wet-dry cyclic condition

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ABSTRACT

The initial corrosion behavior of carbon steel subjected to outdoor wet-dry cyclic exposure and exposure under natural environments have been investigated. The weight loss results indicate a transition from corrosion acceleration to deceleration during the early stage of corrosion of carbon steel under both conditions. The corrosion kinetics under both conditions follow empirical equation $D = At^n$. Outdoor wet-dry cyclic exposure significantly promoted the initiation but the rate of corrosion was about three times as fast. The morphology of corrosion surfaces and cross-section of rust layer have been examined using SEM and the compositions have been analyzed using XRD and EPMA.

1. Introduction

Field exposure experiments for investigating the atmospheric corrosion behavior of metallic materials are time consuming [1–3]. In order to understand the atmospheric corrosion behavior and speed of metallic materials in a relatively short period of time, investigations are often conducted using accelerated indoor testing, including wet-dry cyclic exposure testing [4–9]. Although these indoor accelerated tests present a large number of plausible results [10–12], the correlation between accelerated indoor tests and outdoor field exposure is still unclear. This is attributed to the different number of variables between indoor and outdoor testing conditions. During the indoor testing, environmental parameters such as temperature, humidity, species and concentrations of corrosive media are defined and controlled. In contrast, natural atmospheric corrosion is a complicated process and the environmental condition can be affected simultaneously by many factors, such as temperature, humidity, thickness of aqueous film, dissolution and diffusion of oxygen and contaminants in atmosphere, migration of ions etc. [13,14], coupled with the variation of these parameters with time and location. This may in turn lead to different products formed during the initial corrosion stage, therefore subsequent corrosion kinetics and corrosion rate. This highlights the potential discrepancy between the results obtained from the indoor accelerated testing and the actual field exposure. In order to understand the kinetics and rate of outdoor corrosion, the more representing way is to carry out accelerated outdoor corrosion testing, the essence of which is to prolong the time under the wet condition thereby accelerate the corrosion of metals.

In addition, atmospheric corrosion of metal materials is an electrochemical process under an aqueous film formed on a metal surface. The thickness of an aqueous film increases and decreases alternately due to the daily cyclic change in humidity and temperature of the atmospheric environment [15]. During daytime, the surface of metal is dry under the sun; whilst during night, with the decrease of temperature, the water droplets in atmosphere tend to condense and adsorb on the surface of metal, and form an aqueous film. Besides the rainfall, this dry-wet cycle is equal to 24 h in Shenyang atmosphere. Numerous studies have indicated that corrosion rate of iron and steel can approach maximum when the thickness of the aqueous film is between 1 and 30 μm [16–18]. The corrosion rate increases with the thinning of liquid film and reaches maximum at the transition state from the wet to the dry [19]. Therefore, it is deducted that in theory atmospheric corrosion rate of metals will be accelerated by increasing the frequency of wet-dry cycling.

The present work is to study atmospheric corrosion behavior of carbon steel exposed to outdoor wet-dry cycling and natural environment in Shenyang industrial district thereby revealing the correlation between the two conditions. Shenyang is an important industrial city with a dry climate as is typical in northern China. Its location and environmental parameters have been reported [20]. Such study is useful in terms of selecting construction materials, adopting the appropriate corrosion protection methods and predicting the life of metallic structures under service.

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2. Experimental

2.1. Materials preparation

The material used in this study is carbon steel which composition is shown in Table 1. Specimens of small plates were cur from an A3 sheet of the material. The four parallel samples (three for weight loss measurement and one for rust layer analysis) were cut into the sizes of 100 mm × 50 mm × 5 mm; and 25 mm × 25 mm × 5 mm respectively. The samples for weight loss measurement were ultrasonically cleaned in acetone, dried, weighted and stored in a moisture-free desiccator prior to use. The samples for morphology observation were ground to 2000 grit SiC paper and then polished, degreased by acetone, dehydrated with alcohol and finally dried for 24 h.

2.2. Outdoor wet-dry cyclic test

The outdoor wet-dry cyclic testing was carried out in the Test Station of Atmospheric Corrosion in Shenyang (123°24′ eastern longitude and 41°32′ northern latitude). According to ISO 9223, the categories of time of wetness, chlorides and SO_2 in Shenyang are τ_3, S_0 and P_3, respectively. Therefore, the atmosphere in Shenyang falls into the category C3 to C4 based on the environmental data (time of wetness and chloride ion and SO_2 deposition rates). The specimens were fixed facing south with an angle of 45° to horizontal. Fig. 1 shows the experimental device used in wet-dry cyclic testing. The spray direction was positioned at 45° to samples. The droplets fall on the upward facing of samples by gravity but some migrate to the rear surface of the sample. Spray solution is filtered tap water. The use of filtered tap water is to prevent the sprinkler head from being blocked by impurities. The spray routine is once every 15 min during daytime (6:00 – 18:00), and once every 30 min at night (18:00 – 6:00). Every spray lasted one minute and the amount of spray solution consumed is about 0.5–0.7 L m^{-2} min^{-1}. The test specimens were retrieved from the location for analyses after 10, 30, 60, 90, 120, 150 and 180 days. For gravimetric experiments, corrosion products of the retrieved samples were removed chemically by immersion in a specific solution (500 ml HCl + 500 ml distilled water +3.5 g hexamethylenetetramine) that was vigorously stirred for ~10 min at 25 °C according to ISO 8407. After corrosion products were removed, the specimens were rinsed with distilled water, dried with warm air, and then weighed to determine their mass loss.

2.3. Characterization of rust layers

Rust (the mix of inner rust and outer rust) was scraped from the rust sample surface and was analyzed by X-ray diffraction (XRD) (Rigaku-D/max-2500PC) and fourier transform infrared transmission (FTIR) to determine its phases. The XRD measurements were carried out using a Rigaku-D/max 2000 diffractometer with a Cu $K\alpha$ target under 50 kV, 250 mA and 2θ = 10–85° of range at a scanning speed of 2°min^{-1}. For FTIR measurement, the rust powder was mixed with pure KBr and the mixture was pressed into a transparent circular flake. Nicolet Corporation Model magna-IR 560 infrared spectrophotometer was used to determine the FTIR spectra of the rust powder in the ranges from 400 to 4000 cm^{-1}. The surface morphologies of rust layers were observed at 25 kV using a scanning electron microscopy SEM (XL30FEG). The detail of the methodology has been described previously [20]. The composition of the early-stage corrosion products was analyzed using auger electron spectroscopy (AES) (Escalab 250 made by Thermo Co). For the AES measurements, the incident electron beam energy was set to 3 keV. The elemental distribution on the cross-section of a rust layer was mapped using a Shimadzu Model EPMA-1610 electro probe micro analyzer (EPMA) at 15 kV accelerated voltage.

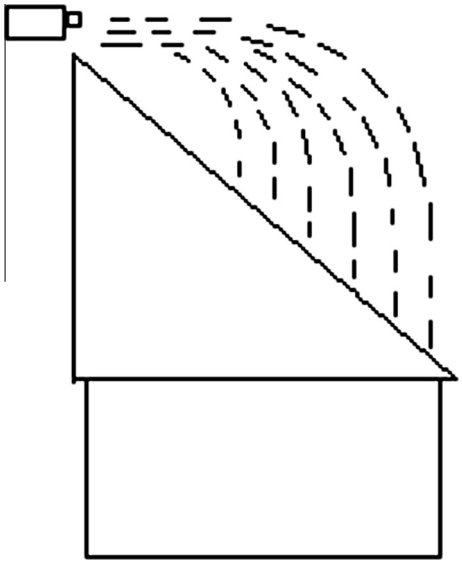

Fig. 1. Schematic illustration of outdoor wet-dry cyclic device.

3. Results

3.1. The initial corrosion kinetics of carbon steel

The initial corrosion kinetics can be determined by measuring the mass loss of carbon steels before and after testing. In order to obtain a clearer view of the corrosion damage, the weight loss obtained for the carbon steel were converted to the thickness reduction (in μm). And the thickness reduction of the samples can be calculated according to the following equation [21]:

$$D = \frac{10000W_t}{\rho A} \quad (1)$$

where W_t is the weight loss (g), ρ is the density (7.86 g/cm^3) of the carbon steel and A is the exposed area (cm^2) of the specimen. Fig. 2 shows the thickness reduction of the carbon steel as a function of exposure time under different testing conditions. It is obvious that the reduction of thickness increases gradually with the increase of exposure time, and the thickness reduces more quickly under wet-dry cyclic condition. For carbon steel, various models have been developed to describe the corrosion kinetics [22,23]. It is widely accepted the corrosion kinetics of carbon steel can be described by empirical equation as follows [24,25]:

Table 1
Chemical composition of tested materials.

Steel type	Chemical composition (mass%)									
	C	S	P	Mn	Si	Cr	Ni	Cu	Al	N
A3	0.04	0.008	0.015	0.18	<0.03	<0.02	<0.05	<0.05	0.023	0.0026