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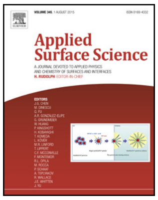

Characterization of corrosion products formed on different surfaces of steel exposed to simulated groundwater solution

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ABSTRACT

The corrosion behavior of a low alloy steel in simulated groundwater was investigated. The upward surface of the steel underwent more serious corrosion than the downward surface. The corrosion products formed on the upward and downward surfaces were characterized by SEM, EDX, and XRD, and the electrochemical properties of bare and rusted samples were analyzed. The difference in the corrosion rates of the different surfaces of the steel could be attributed to the potential difference between the upward and downward surfaces as well as the higher amount of $CaCO_3$ deposits on the downward surface leading to a compact corrosion product.

1. Introduction

Previous studies have shown that exposure conditions can affect corrosion characteristics [1], and corrosion behavior of different surfaces of a specimen can be different even in the same environment [2–16]. Asami et al. [2] analyzed using TEM the difference in rust composition between skyward and earthward surfaces and concluded that the amount of amorphization in the rust on the skyward surface was more than that on the earthward surface. Han et al. [3] observed using in situ SEM that the early-stage corrosion behaviors of skyward and groundward surfaces of carbon steel were different. The initial corrosion products on the groundward surface were mainly filamentous, but such products were sparse on skyward surface after being exposed to air. After studying the protective ability of the rust layer on skyward and groundward surfaces of a structural steel in a simulated marine atmospheric environment, Wang et al. [4] noted that the rust layer on the skyward surface had better protective ability than the groundward surface, which could be attributed to the higher amount of amorphization high-density rust on skyward surface. Li et al. [5] found that the corrosion on the field-ward surface was more severe than that on the skyward surface when a weathering steel was exposed to an environment simulating the Qinghai salt lake atmosphere in China They also found an amorphous phase in the skyward rust and hypothesized that the rougher field-ward rust layer, with more porous and polluted particles, led to more severe corrosion on the latter surface. Liao et al. [12] found that the weight loss of upward specimens was much higher than that of downward specimens in a marine environment: they explained that the invasion of airborne sea salt and raindrop to the surface of downward specimens was hampered. The above research reveals that the corrosion products on skyward and downward surfaces of a specimen had different microstructures and thus provided different protection to the substrates, resulting in different corrosion behavior between the two surfaces of the specimen. Most of this research is limited to atmospheric conditions, and up to now, very little related research in aqueous solution can be found in the literature.

Additionally, scaling is often involved in corrosion processes when the corrosion medium contains scaling elements, such as Ca and Mg. It has been proven that the existence of scaling influences corrosion processes [17,18]. Meanwhile, the deposition of $CaSO_4$ or $CaCO_3$ is affected by the surface condition of the substrate [19–24]. Shekholeslami et al. [19] studied $CaCO_3$ deposition behavior on copper and mild steel and found that the surface chemistry of the material would affect the formation of $CaCO_3$. Liu et al. [22] thought that the effect of surface roughness on the adhesion of fouling was limited and that the adhesion of fouling did not have a simple linear relationship with the surface roughness of the samples. Azimi et al. [24] performed a systematic investigation of the effect of surface energy on scale formation and found that low surface energy substrates have fewer but larger salt crystals deposited on them. Research on $CaCO_3$ deposition behavior on different surfaces of a sample, however, is very limited as well.

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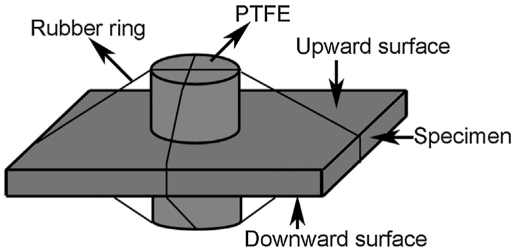

Fig. 1. Schematic diagram of the specimen for immersion testing.

In this paper, the investigation results on the corrosion behavior of different surfaces of a low alloy steel in a solution by immersion tests and electrochemical measurements are introduced. The solution simulated groundwater, which contained scaling elements, such as Ca. The influence of $CaCO_3$ deposition on the corrosion process is explored. The formation mechanism of corrosion products on different surfaces of the steel is discussed.

2. Experimental

2.1. Immersion tests

A low alloy steel was used here, and its chemical composition (wt.%) is 0.16 C, 0.29 Si, 1.39 Mn, 0.019 P, 0.017 S, and balance Fe. The size of the specimen was 50 mm × 25 mm × 3 mm. The specimen surface was ground with silicon carbide (SiC) paper progressively up to 150 grit. To be able to measure the corrosion rate of different surfaces of a sample, a special sample design was used here, as shown in Fig. 1. The specimen was clamped by two cylinders made of polytetrafluoroethene (PTFE) and bundled by a low sulfur rubber ring ($S \le 0.02\%$). The cylinders were 12.7 mm in both diameter and height, and the cylinders contained grooves with dimensions of 1.6 mm × 1.6 mm to avoid slippage of the rubber ring. In this case, the shielded area under the cylinders was protected from corrosion. The specimens were placed at the bottom of a glass bottle, which contained 5 L of solution. The testing solution was made from analytical reagents and deionized water with a chemical composition (mg/L) of 1027.0 Na^+, 16.1 K^+, 1.9 F^-, 138.0 CO_3^{2-}, 30.2 NO_3^-, 206.0 Ca^{2+}, 51.2 Mg^{2+}, 1155.0 Cl^-, 0.057 Br^-, and 1074.0 So_4^{2-}. The pH value of the solution was adjusted by H_2SO_4 to 7.2. The surface of the specimen facing the bottom of the glass bottle was defined as downward and the other surface was defined as upward. The immersion tests were performed for five days, 30 days, and 365 days at room temperature under open-air conditions, and the solution was renewed once a week.

2.2. Surface observation and analysis

After each immersion experiment, the samples were washed with acetone, rinsed with deionized water, and dried. The morphologies of corrosion products on the upward and downward surfaces were observed by a Zeiss Evo 18 scanning electron microscope (SEM), and the compositions of the corrosion products were analyzed by energy dispersive X-ray diffraction (EDX) as well as by D/MAX - RB X-ray diffraction (XRD).

To remove the corrosion products, the specimen was pickled in 10% hydrochloric acid (HCl) inhibited with 10 g/L hexamethylenetetramine (urotropine), rinsed subsequently in deionized water and acetone, and dried. After the corrosion product was removed, the height difference between the shielded area and the unshielded area on the sample surface was measured by a Dektak 150 Surface Profiler, and then the corrosion rate on different surfaces of the sample was calculated.

2.3. Polarization curve measurement

Polarization curves were measured using a CS350 electrochemical workstation. The electrochemical cell consisted of three electrodes: a working electrode (WE, including a bare sample and a rusted sample), a reference electrode (RE, Ag/AgCl), and a counter electrode (CE, platinum sheet). All of the electrochemical test specimens were enclosed with epoxy resin, leaving a working area of 1.0 cm^2. The rusted sample was the steel with corrosion products after a 365-day immersion test. The exposed surfaces of the rusted upward and downward samples were facing upward and downward, respectively, during the immersion test. Prior to the potentiodynamic polarization curve measurement, the samples were immersed in 500 mL of solution for 1 h to stabilize. The polarization potential was swept from −0.6 V to 1.0 V vs. open circuit potential (OCP) at a scan rate of 0.5 mV/s. All of the potentials reported here were measured with respect to the value of Ag/AgCl.

2.4. OCP measurement

The OCP was measured using the above three-electrode system. Here the upward and downward samples were the exposed surfaces of the bare steel facing upward and downward, respectively, as shown in Fig. 2. The measurements were carried out in two different solutions: the simulated groundwater solution, and a NaCl solution in which the NaCl concentration was the same as that in the simulated solution.

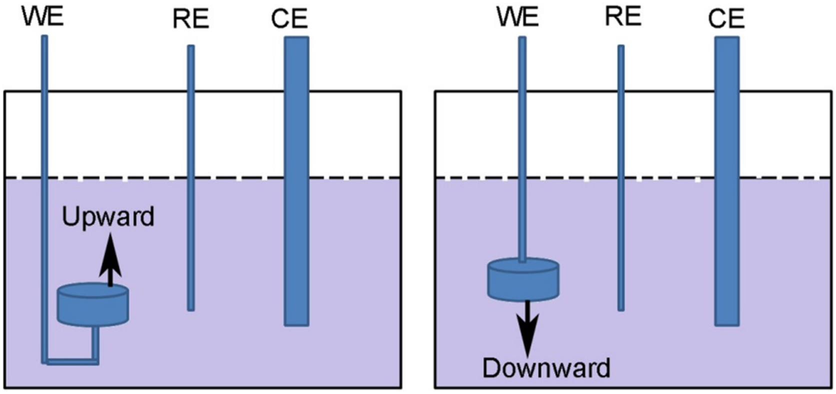

Fig. 2. Schematic diagrams of OCP measurements.