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Characterization of the effect of hydrogen sulfide on the corrosion of X80 pipeline steel in saline solution

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ABSTRACT

The corrosion products and electrochemical corrosion behavior of X80 pipeline steel in saline solution with saturated H_2S at 50 °C were evaluated. The results showed that mackinawite and cubic FeS were the primary and secondary crystalline phases observed and that a series of changes in the size, shape, thickness, and chemical composition occurred as the immersion stages developed. Electrochemical results showed that the sulfide film hindered pitting and enhanced the corrosion resistance definitely. Zero-resistance ammeter measurements showed that the sulfide film repaired itself when local failure occurred.

1. Introduction

High-strength low-alloyed (HSLA) pipeline steel, such as X80 steel, is widely used to meet increasing global energy demands because of its favorable mechanical properties, high transportation efficiency, and relatively low cost [1,2]. However, serious internal and external corrosion problems develop in transmission pipes in the presence of corrosive environments, such as those exposed to carbonate/bicarbonate (CO_3^{2-}/HCO_3^-) [3,4], carbon dioxide (CO_2) [5,6], hydrogen sulfide (H_2S) [7–27] and chloride ion (Cl^-) [28,29]. Internal H_2S corrosion, which can result in sulfide stress corrosion cracking (SSCC) [9,13] or hydrogen induced cracking (HIC) [9,13,30], is one of the most serious corrosion types. In addition, H_2S corrosion leads to sharp reductions in Charpy-absorbed energy and tensile strength [27]. Although several characteristics of H_2S corrosion have been investigated [11], the mechanism of this corrosion type remains controversial and ambiguous.

Corrosion and the sequential reactions between iron and an electrolyte involve complex interactions of physical, chemical, and biological factors. Corrosion films rich in iron sulfide can be formed when steel is immersed into a medium with H_2S [19,25,26]. The composition, crystal structure, and micromorphologies of sulfide films depend highly on their immersion time, temperature, partial pressure, and medium [19,25,26]. The main corrosion products, which may contain mackinawite, cubic FeS, pyrrhotite, troilite, pyrite, and other mixed minerals, are sensitive to severe test environments [19,25,26]. Phase transition may occur at the initial immersion stages [19,22]. The effects of sulfide films on the corrosion behavior of steel have attracted much attention. Huang found that the polarization resistance of a simulated heat-affected zone of A516 steel in H_2S increased during the first hours of immersion and then decreased with further increases in immersion time [9]. Bai studied the electrochemical behavior of X52 in H_2S and found that the charge transfer resistance (R_{ct}) fluctuated during immersion for 15 h and then increased with further increases in immersion time [26]. At the same time, Zhang found that localized corrosion of steel under scale easily occurs because of the galvanic effect whenever the $FeCO_3$ scale is damaged in CO_2-saturated formation water [6]. It is intriguing that what would happen when the sulfide film was damaged due to the flow fluid hydrodynamic force or other reasons. The galvanic effect between the sulfide-film-covered steel and fresh steel should also be examined.

In the present study, corrosion products of steel in National Association of Corrosion Engineers A (NACE A) solution with saturated H_2S at 50 °C were identified by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and transmission electron microscopy (TEM). The effects of corrosion product films on the corrosion behavior of the steel were evaluated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The galvanic effect between fresh and corrosion product film-covered steel electrodes

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was further studied by zero-resistance ammeter (ZRA) measurements.

2. Material and methods

2.1. Materials and solutions

Composition of the X80 pipeline steel used in this study was (wt.%): C 0.046, Si 0.305, Mn 1.76, P 0.007, S 0.001, Al 0.058, Nb 0.079, V 0.008, Ni 0.225, Cr 0.023, Mo 0.226, B 0.00025, Ti 0.015, Ca 0.001, Cu 0.215, and Fe balanced. The microstructure of the steel mainly contained polygonal ferrite (PF) and martensite/austenite (M/A) components as secondary phases (Fig. 1a–c). Indexed selected-area-diffraction (SAED) patterns of zones 1 and 2 of Fig. 1c are shown in Fig. 1d, e. Fig. 1d shows the $[\bar{1}01]$ plane of ferrite; the patterns observed indicate that the bright zones in Fig. 1c are ferrite. Fig. 1e shows the $[10\bar{1}]$ plane of martensite and the $[1\,\bar{1}\,\bar{1}]$ plane of austenite; the patterns obtained indicate that zone 2 comprises M/A constituents.

The specimens used for immersion and electrochemical tests were rectangular electrodes; about 1 cm^2 of the electrode was exposed to the solution. Prior to immersion measurements, the specimens were ground using an 800 grit emery paper, cleaned sequentially with acetone, alcohol, and distilled water, and mounted in silica gel. The test solution used in this study was NACE A solution, which contains 5 wt.% NaCl and 0.5 wt.% CH_3COOH with saturated H_2S at pH 2.8. The temperature was maintained at 50 °C during tests. Prior to the test, the solution was purged with N_2 for 2 h, and H_2S flow was maintained during the test duration.

2.2. Immersion and electrochemical measurements

A three-electrode electrochemical cell system was employed with X80 steel as the working electrode, a platinum plate as the counter electrode, and a saturated calomel electrode (SCE) of +0.241 V_{SHE} as the reference electrode. The potential used in this study was relative to SCE. EIS measurements were performed with 10 mV amplitude and frequencies ranging from 10^5 to 10^{-2} Hz after immersion of the specimens for a certain period of time. Potentiodynamic polarization scans were conducted at a sweep rate of 0.5 mV/s.

2.3. Corrosion product characterization

The morphologies and composition of corrosion product films formed on the steel surface after immersion for a certain period of time were characterized by a JSM-6480LA SEM coupled with an EDS. Crystal structures were characterized by DX-2700 XRD with a scanning step of 0.5°/min and EM-002B TEM.

2.4. Galvanic current

Galvanic currents between the corrosion products-covered and fresh steel electrodes were measured using a ZRA, and the distance between the two electrodes was maintained at 5 cm. The area ratio between the corrosion product-covered and fresh steel electrodes was maintained 50:1 to obtain a relatively high anodic current and achieve more apparent results.

3. Results

3.1. Corrosion products characterization

Previous studies have shown that the corrosion products and their effects on corrosion resistance depend highly on the applied temperature. The real temperature of some oil and gas pipelines is below 100 °C, although some investigations have also been performed at high-temperature conditions [19]. Many investigations on H_2S corrosion used a fixed temperature of around 50 °C. For example, Fragiel studied the electrochemical behavior of microalloyed steel in a H_2S environment at 55 °C [10]. Lucio-Garcia studied the H_2S corrosion resistance of C–Mn pipeline steel with three different microstructures using electrochemical techniques in 3 wt.% NaCl solution at 50 °C [15]. Bai studied the corrosion products of carbon steel in an aqueous H_2S environment at 50 °C [19,26]. Some studies were also performed at temperatures lower (e.g., room temperature [23]) or higher (e.g., 90 °C [19]) than 50 °C. We note here that the effects of temperature are not the key point in the present study. Over the last few years, we performed several studies on H_2S corrosion that were put forward by oil or gas pipelines factories. Based on our practical experience, temperatures are generally fixed at 50–60 °C. Thus, the temperature was fixed at 50 °C in the present study.

3.1.1. Corrosion products morphologies

3.1.1.1. Surface morphologies. Fig. 2 shows the representative SEM micrographs of the corrosion products formed on the steel surface at different immersion stages in NACE A solution with saturated H_2S at 50 °C. Corresponding EDS results are shown in Table 1. The corrosion products were rich in Fe and S, so the corrosion product film could be called a sulfide film. The corrosion products underwent rapid nucleation and growth processes as shown in Fig. 2. The surface of steel was covered with a layer of uniformly distributed sulfide film, and scratches disappeared after immersion for 0.5 h (Fig. 2a), indicating drastic reactions between Fe and H_2S at the first immersion stage. Moreover, changes in the shape, size, and composition of the corrosion products were observed. The concentration of S gradually increased during immersion, contrary to the gradual decrease in the concentration of C.

Corrosion products were of the nanoscale level at the initial immersion stage from 0.5 h to 4 h (Fig. 2a, b). The shape of the products was difficult to visualize because of their nanoscale size. The shape changed to nanoscale bulk, and some microcracks were observed on the surface of the products after immersion for 8 h (Fig. 2c, d). The SEM micrograph after immersion for 16 h seems dry land (Fig. 2e). The sulfide film surface after immersion for 24 h could be divided into three different parts denoted as A, B, and C (Fig. 2f). The micrograph in part A was similar to that at 16 h. Two new corrosion products of B and C were generated on the surface of A. The size of B presented polygonal block with size of approximately dozens of microns. However, product C presented a slice-layer shape with a dentate margin (Fig. 2g). The polygonal block-shaped corrosion products grew larger than 200 μm as immersion continued for 96 h (Fig. 2h). In addition, the slice-layer-shaped corrosion products changed to chip-shaped and clavate (Fig. 2i).

The thickness of the dissolved steel and sulfide film at different immersion stages is shown in Fig. 3. The former is much thicker than the latter at the initial immersion stage. However, the thickness of the sulfide film remarkably increased after immersion for 24 h and gradually exceeded that of the steel after immersion for 72 h.

Table 1
Corresponding EDS results (at.%) of the corrosion films in Fig. 2.

Time (h)	0.5	4	8	16	24	96
Fe	67.82	67.16	49.91	47.17	49.19	46.32
S	0.86	2.53	27.41	31.79	45.23	51.78
C	28.94	28.30	22.15	19.52	4.03	0.96
Si	1.07	0.79	0.28	1.04	0.68	0.41
Mn	1.30	1.22	0.25	0.48	0.87	0.53