Localized corrosion of carbon steel in a CO_2-saturated oilfield formation water

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ABSTRACT

In this work, corrosion and localized corrosion behavior of X65 pipeline steel were studied in a simulated, CO_2-saturated oilfield formation water by various electrochemical measurement techniques, including electrochemical impedance spectroscopy (EIS), potentiodynamic polarization curves, galvanic current and localized EIS (LEIS). The morphology and composition of the formed corrosion scale were characterized by scanning electron microscopy and energy-dispersive X-ray analysis. A conceptual model was developed to illustrate the occurrence of localized corrosion of the steel under scale. Both galvanic current and LEIS measurements showed that a galvanic effect existed between the bare steel and the scale-covered region. The scale-covered region served as cathode and the bare steel site as the anode. The big cathode vs. small anode geometry accelerated the local corrosion reaction. At an elevated temperature, a compact, crystalline scale was formed on the steel surface, enhancing the galvanic effect. Moreover, the stability of the scale was increased with time, and localized corrosion of the steel under scale experienced mechanistic changes with time.

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1. Introduction

Internal corrosion of pipelines occurs extensively in the petroleum production. The corrosive environment is composed of an oilfield formation or purely condensed water, the dissolved acidic gases, such as carbon dioxide (CO_2), volatile organic acids, and the petroleum hydrocarbons [1]. Being the most commonly used construction materials for pipelines, carbon steels are prone to corrosion in such corrosive environments [2–4]. In particular, localized corrosion, i.e., pitting corrosion and mesa attack, occurs in conjunction with the formation and removal of the corrosion scale in the CO_2-containing formation water [5,6]. The corrosion scale formed consists primarily of $FeCO_3$, which affects the further corrosion of the steel. A number of studies have been conducted to investigate the formation of $FeCO_3$ scale and its effect on corrosion of the steel [7–16]. It was indicated that the CO_2 corrosion of the steel is reduced due to the formation of the scale.

Localized corrosion usually occurs once the protective scale is damaged locally, and constitutes a principal cause resulting in the failure of the carbon steel pipelines. Various factors associated with CO_2 corrosion of pipeline steels have been investigated to establish the correlation with the localized corrosion of the steel. For example, Schmitt [17,18] found that the highest susceptibility to pitting corrosion of pipeline steels occurred at 60–80 °C in the CO_2-containing environment. Gunaltun [19] proposed a model

to predict localized corrosion based on a fluid turbulence factor. Moreover, it was also proposed [6,20] that localized attack could occur when the corrosive conditions are such that a partially protective scale forms. Sun and Nesic [21] proved experimentally that a supersaturation could be used as a good predictor of the probability for localized corrosion. Turnbull et al. [22] assessed the effectiveness of inhibitor in retarding the growth of an active pit using a 'pencil' type of artificial pit. Furthermore, Han and Nesic [23,24] studied the mechanism of localized attack propagation by improving and modifying the 'pencil' type of artificial pit and made it more versatile and realistic. A galvanic mechanism was proposed to explain the localized CO_2 corrosion phenomenon.

While models and theories have been developed to understand and predict CO_2 corrosion and localized corrosion of the steels [6,17,22–27], a direct evidence to support the galvanic effect on the occurrence of localized corrosion is still lacking. In this work, localized corrosion of X65 pipeline steel was studied in a CO_2-saturated oilfield formation water by various conventional electrochemical measurement techniques, including electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves, and, particularly, localized electrochemical impedance spectroscopy (LEIS). Moreover, the galvanic current flowing between a scale-covered steel electrode and a bare steel was recorded to support the LEIS result. The morphology and composition of the formed scale were characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDXA). The parametric effects, including test time, temperature and area ratio of the galvanic couple between the scale-covered and bare steels, on the scale

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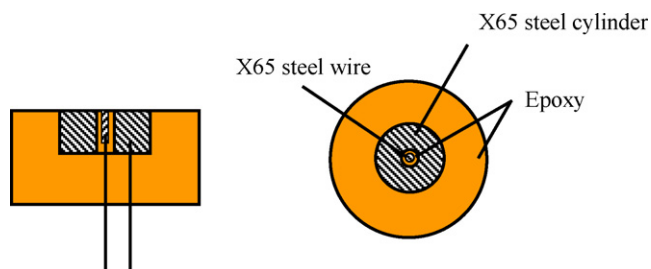
Fig. 1. Schematic diagram of the working electrode for electrochemical measurements.

formation were determined. The localized corrosion process of the steel was analyzed and modeled mechanistically.

2. Experimental

2.1. Electrode and solution

Specimens used in this work were cut from a sheet of API X65 pipeline steel, with a chemical composition (wt%): C 0.04%, Si 0.2%, Mn 1.5%, P 0.011%, S 0.003%, Mo 0.02% and Fe being the balance. The specimens were machined into cylindrical shape of various diameters, with a working electrode (WE) made from an X65 steel wire embedded in the center of the cylinder, as shown in Fig. 1, where the exposure area of WE was 0.5 mm^2. The cylinder and steel wire were isolated by an epoxy layer which was applied on the wire. The unexposed faces of WE were sealed with an epoxy resin. The working face was ground consequentially up to 1000 grit silicon carbide paper, rinsed with deionized water and degreased in acetone.

The test solution, simulating the formation water extracted from the oilfield, was made up from analytical grade reagents and deionized water. The chemical composition of the solution is shown in Table 1. The pH of the CO_2-saturated formation water solution was about 5.1, and the solution temperatures were controlled using a water bath at 30 °C, 60 °C and 90 °C, respectively.

2.2. Preparation of corrosion scale on the cylindrical steel electrode

The solution was deaerated by purging CO_2 (99.95%) for 4 h before the electrode set shown in Fig. 1 was immersed into the solution. The steel wire electrode was sealed with an epoxy, and only the cylindrical electrode was exposed to the solution for 10 days in the iron carbonate scale formation phase, where ferrous iron ions were from corrosion of steel in the solution. The CO_2 gas-purging was maintained to ensure saturation throughout the test. After formation of the scale on the cylindrical electrode, the epoxy coated on the wire electrode was removed so that the electrode set contained a scale-covered cylindrical electrode with a bare steel wire electrode located at the center. The whole process was performed in the solution to ensure the integrity of the scale formed on the cylinder electrode.

2.3. Conventional electrochemical measurements

Electrochemical measurements were performed on a three-electrode cell, where the bare steel wire and/or scale-covered steel cylinder were alternatively used as working electrodes, a platinum plate as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode, connected to a potentiostat. A steady state of the electrode corrosion was achieved prior to the electrochemical measurement, as indicated by a stable corrosion potential (E_{corr}).

Potentiodynamic polarization curves were measured by scanning the potential from −500 mV (SCE) to +500 mV (SCE) relative to E_{corr} at a sweep rate of 1 mV/s. There was no IR compensation applied due to a high solution conductivity. The polarization curves were measured three times under the individual condition to ensure the reproducibility of the result.

The EIS were measured with a sinusoidal potential excitation of 10 mV in the frequency range from 100 kHz to 1 mHz.

The galvanic current between the scale-covered cylindrical electrode and the bare wire electrode was measured using a zero-resistance ammeter (ZRA).

The electrochemical measurements were performed individually, and there was no necessary sequence between each other.

2.4. LEIS measurements

After the scale formation, a LEIS mapping was performed on the WE through a scanning electrochemical workstation, which was comprised of a scanning control unit, a potentiostat, a lock-in amplifier and a video camera system, as shown in Fig. 2. During the LEIS measurement, a Pt microprobe with a 10 μm tip, set directly above the steel electrode surface, was scanned over a designated area. The scanning took the form of a raster in x–y plane. An AC disturbance signal of 10 mV was applied on the steel electrode which was at E_{corr}. The measuring frequency was fixed at 5 Hz. The distance between the microprobe tip and the electrode surface was about 100 μm. A SCE was used as reference electrode and a platinum plate as counter electrode.

2.5. Surface characterization

The morphology and composition of the scale formed on the steel cylinder electrode surface were characterized by SEM and the coupled EDXA.

3. Results

3.1. Corrosion potential measurements

Fig. 3 shows the time dependence of E_{corr} of the scale-covered cylindrical electrode and the bare wire electrode immersed in the CO_2-saturated simulated formation water at 60 °C for 10 days. It is seen that the E_{corr} of the bare wire electrode shifted negatively from −0.74 V (SCE) to a relatively stable value of −0.75 V (SCE) after 3600 s of immersion in the solution, reflecting an electrode stabilizing process. There was a more positive E_{corr} of the scale-covered cylindrical electrode of about −0.68 V (SCE) than that of the bare steel wire electrode. Apparently, the formation of a layer of scale on the steel surface makes the steel electrode more stable. The difference of E_{corr} between the two electrodes indicates that the scale-covered cylindrical electrode would act as a cathode and the bare steel wire electrode as an anode after coupling to form a galvanic couple.

Table 1
Chemical composition of the formation water extracted from oilfield.

Ions	Na$^+$	Mg^{2+}	Ca^{2+}	Cl$^-$	SO$_4^{2-}$	HCO$_3^-$	Total ionic concentration
Concentration (mg/L)	11,522	288	390	16,718	1152	3050	33,120