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Effect of H_2S on the CO_2 corrosion of carbon steel in acidic solutions

Yoon-Seok Choi[a,*], Srdjan Nesic[a], Shiun Ling[b]

[a] *Institute for Corrosion and Multiphase Technology, Department of Chemical and Biomolecular Engineering, Ohio University, 342 West State Street, Athens, OH 45701, USA*
[b] *ExxonMobil Research and Engineering Company, 1545 Route 22 East, Annandale, NJ 08801, USA*

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ABSTRACT

The objective of this study is to evaluate the effect of low-level hydrogen sulfide (H_2S) on carbon dioxide (CO_2) corrosion of carbon steel in acidic solutions, and to investigate the mechanism of iron sulfide scale formation in CO_2/H_2S environments. Corrosion tests were conducted using 1018 carbon steel in 1 wt.% NaCl solution (25 °C) at pH of 3 and 4, and under atmospheric pressure. The test solution was saturated with flowing gases that change with increasing time from CO_2 (stage 1) to CO_2/100 ppm H_2S (stage 2) and back to CO_2 (stage 3). Corrosion rate and behavior were investigated using linear polarization resistance (LPR) technique. Electrochemical impedance spectroscopy (EIS) and potentiodynamic tests were performed at the end of each stage. The morphology and compositions of surface corrosion products were analyzed using scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). The results showed that the addition of 100 ppm H_2S to CO_2 induced rapid reduction in the corrosion rate at both pHs 3 and 4. This H_2S inhibition effect is attributed to the formation of thin FeS film (tarnish) on the steel surface that suppressed the anodic dissolution reaction. The study results suggested that the precipitation of iron sulfide as well as iron carbonate film is possible in the acidic solutions due to the local supersaturation in regions immediately above the steel surface, and these films provide corrosion protection in the acidic solutions.

1. Introduction

The number of sour ($CO_2 + H_2S$ containing) oil and gas fields being produced worldwide is increasing, as sweet (CO_2 containing) fields are being depleted, and higher oil prices made it possible for profitable development of sour oil and gas fields. A concern in the production and transportation sour oil and gas is the corrosion caused by the acid gases CO_2 and H_2S. Even though corrosion resistant alloys (CRA) has long been available as a material selection option that mitigates CO_2 and H_2S corrosion, carbon steel is in general more cost-effective for oil and gas facilities and hence, is the most widely used material option [1]. The internal corrosion of carbon steel pipeline in the presence of CO_2 and H_2S was firstly recognized in the 1940s and has been investigated for over 60 years [2].

Several studies have shown that the presence of H_2S could either cause an acceleration or an inhibition of the corrosion of carbon steel, depending on the partial pressure of H_2S. It was reported from early studies that at H_2S concentrations below 690 Pa, a protective iron sulfide film formed. At H_2S concentrations greater than 690 Pa, a non-protective film formed [3–5]. More recently, Ma et al. claimed that H_2S provides a strong inhibition under certain special conditions that have lower H_2S concentration ($\leq$0.04 mmol dm^{-3}), pH value of 3–5, and longer immersion time ($\geq$2 h) [6]. Abelev et al. also reported that 5 ppm of H_2S concentration have an inhibiting effect on corrosion in the presence of CO_2 [7]. Even though there is no absolute criterion for the H_2S concentration that provides inhibition, it has been suggested that the inhibition effect is related to the formation of iron sulfide with different crystal structures, such as amorphous ferrous sulfide, mackinawite, cubic ferrous sulfide, smythite, greigite, pyrrhotite, troilite, and pyrite [8–12].

However, there is no clear understanding of the nature of the surface layer formed in CO_2/H_2S environments as well as their protective properties in acidic solutions when the concentration of H_2S is too low to cause a concern of the surface layer cracking or blistering. The objective of this study is to evaluate the effect of very low-level H_2S on CO_2 corrosion of carbon steel in acidic solutions, and to investigate the mechanism of the iron sulfide layer formation in CO_2/H_2S environments.

2. Experimental

The specimens were made of carbon steel (AISI C1018) that has a chemical composition of 0.21% C, 0.05% Mn, 0.09% P, 0.05% S, 0.38% Si and balance Fe. The specimen shape was of a cylindrical geometry, 1.3 cm in diameter and 1.3 cm in height, and would have its

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* Corresponding author. Tel.: +1 740 593 9944.
E-mail address: choiy@ohio.edu (Y.-S. Choi).

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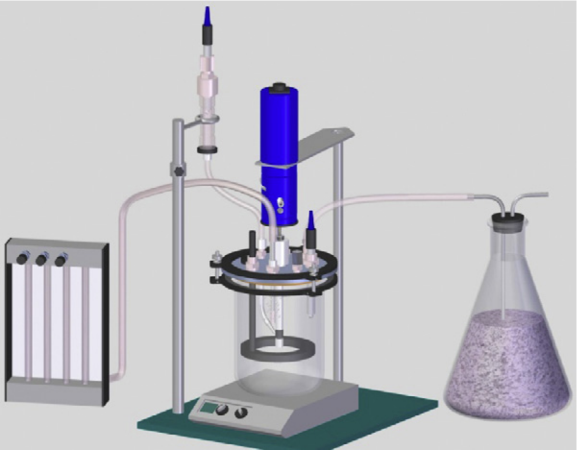

Fig. 1. Schematics of the test apparatus.

outer surface exposed to solution during testing. The specimen surface was grounded to a 600 grit finish using silicon carbide paper, then cleaned with isopropyl alcohol in an ultrasonic bath and dried.

The corrosion tests were carried out in a 2 L glass cell which contained a rotating cylinder working electrode, a reference electrode consisted of a glass capillary probe connected to a saturated Ag/AgCl electrode, and a platinum wire counter electrode. The schematic of this experimental setup is shown in Fig. 1. All the tests were conducted in 1 wt.% NaCl solutions at room temperature and atmospheric pressure. Gas mass-flow controllers were used to control the flow rates of CO_2 and H_2S to the test cell, as well as to obtain the desired H_2S concentration. These gases were mixed by flowing through a mixer before injecting into the test cell. Before specimen was inserted into the solution, the solution was purged with CO_2 for 2 h in order to deoxygenate, then with pH adjusted to the desired value by adding a deoxygenated HCl solution or $NaHCO_3$ solution as appropriate.

Table 1 shows the test conditions, and Fig. 2 shows the experimental procedures. This test procedure was designed to investigate the effect of H_2S on the corrosion of carbon steel in CO_2 environments; the environment was changed from CO_2 (stage 1) to CO_2/100 ppm H_2S (stage 2) and then back to CO_2 (stage 3). During experiment, instantaneous corrosion rates were monitored with linear polarization resistance (LPR) measurements made at regular time intervals. Using the polarization resistance (R_p) obtained from LPR measurements, the corrosion current density (j_{corr}) was calculated using Eq. (1) [13], and the resulting j_{corr} yields the corrosion rate using Eq. (2) [14]:

$$j_{corr} = \frac{B}{R_p} = \frac{\beta_a \times \beta_c}{2.3 \times R_p \times (\beta_a + \beta_c)} \qquad (1)$$

$$\text{corrosion rate (mm/year)} = \frac{0.00327 \times j_{corr}\,(\mu A/cm^2) \times EW}{\text{density}\,(g/cm^3)} \qquad (2)$$

Table 1
Test conditions.

Parameter	Description
Material	C1018 carbon steel
Rotation speed	1000 rpm
Solution	Deionized water with 1 wt.% NaCl
Temperature	25 °C
Total pressure	0.1 MPa
CO_2 partial pressure	0.097 MPa
H_2S concentration	100 ppm (0.01 kPa)
pH	3, 4

where β_a is the anodic Tafel constant, β_c is the cathodic Tafel constant, 0.00327 is a constant factor used for dimension and time conversion factor, and EW is the equivalent weight in grams. In the present study, different B values were applied to each stage. For CO_2 environments (stages 1 and 3), 0.026 V was used as B value, whereas 0.013 V was used for CO_2/H_2S environment (stage 2).

The experimental procedures shown in Fig. 2 were to have electrochemical impedance spectroscopy (EIS) measurements and potentiodynamic scan performed at the end of each stage. There was, however, the concern that the potentiodynamic scan may cause irreversible alterations to the sample surface (especially the anodic scan) which could render the subsequent testing questionable. Consequently, the actual study consisted of three separate tests; each had only one potentiodynamic scan performed at the very end of the test. In other words, each of these tests had started from the very beginning shown in Fig. 2, and had run to the end of stages 1, 2 and 3, respectively, when a potentiodynamic scan was performed that concluded the respective test.

LPR measurements were performed in a range of ±10 mV with respect to the corrosion potential, and a scan rate of 0.166 mV/s. EIS measurements were conducted in the frequency range from 10 kHz and 10 mHz, with an AC signal amplitude of 10 mV (rms) at the corrosion potential. The potentiodynamic scans were carried out after the completion of the EIS measurements, and was conducted in the following manner. The scan was first conducted in the cathodic direction from the open-circuit potential (OCP) to −1.2 V vs. sat. Ag/AgCl, with a scan rate of 0.166 mV/s. The OCP was then allowed to return to its previous value, which would occur within about 20 min. Then the scan was conducted in the anodic direction from OCP to −0.4 V vs. sat. Ag/AgCl, with a scan rate of 0.166 mV/s.

After the experiment, the specimen was used for additional ex situ analyses. The morphology and compositions of corrosion products from each stage were analyzed with scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS).

3. Results

3.1. Effect of H_2S addition/removal in CO_2 environment at pH 4

The results of OCP and LPR measurements at pH 4 are summarized in Fig. 3. At the transition from stage 1 to stage 2, when 100 ppm H_2S was added into the CO_2 environment, the OCP increased and the corrosion rate decreased immediately. This phenomenon is probably related to the formation of protective iron sulfide film on the steel surface. At the end of stage 3, at which point H_2S was completely removed from the CO_2 environment, the OCP and the corrosion rate returned their previous levels in stage 1, which suggest the dissolution of the iron sulfide film and re-exposure of the bare steel surface to the environment.

Fig. 4 shows the Nyquist plots measured at the end of each stage. All impedance spectra showed a depressed capacitive loop at high frequencies indicating a double-layer capacitance, as well as an inductive loop at low frequencies. Depressed semi-circles are not uncommon for iron dissolution in acidic media and it had been suggested in the literature that this behavior might be related to a heterogeneous surface roughness and the nonuniform distribution of current density on the surface [15,16]. In addition, no mass transfer controlled impedance was observed under these conditions. However, it was not a pure charge transfer controlled process either because the inductive loop at low frequencies [17] indicated that the iron dissolution mechanism might occur in two or more steps involving an adsorbed intermediate [18,19]. As Fig. 4 shows, the diameter of the semi-circle increased with the addition of H_2S indicating a decreased corrosion rate, which suggests