

Effect of H₂S on CO₂ Corrosion of Mild Steel in HPHT Conditions

Yoon-Seok Choi, Fernando Farelas, Luciano Paolinelli, Srdjan Nesic
Institute for Corrosion and Multiphase Technology,
Department of Chemical and Biomolecular Engineering, Ohio University
342 West State Street
Athens, OH 45701
USA

Ahmad Zaki B Abas, Azmi Mohammed Nor, Muhammad Firdaus Suhor
Petronas Research SDN. BHD, Selangor Darul Ehsan, Malaysia

ABSTRACT

The effect of H₂S on the aqueous corrosion behavior of mild steel was evaluated at HPHT conditions (supercritical CO₂ pressure) at a total pressure of 12 MPa and a temperature of 160°C. The corrosion rate of steel samples was determined by electrochemical and weight loss measurements. The surface/cross-sectional morphology and the composition of the corrosion product layers were analyzed by using surface analytical techniques (SEM, EDS, and XRD). Results showed that the corrosion rate decreased with time and no significant difference was observed in the presence of 1000 and 2000 ppm of H₂S at HPHT CO₂ conditions. Surface and cross-sectional analyses revealed that the corrosion process is governed by the formation of FeCO₃ regardless of the presence of H₂S. Furthermore, the corrosion behavior of mild steel in these conditions did not depend significantly on flow velocity.

Key words: Supercritical CO₂, CO₂ corrosion, carbon steel, H₂S, high temperature

INTRODUCTION

The presence of large quantities of CO₂ (from 25% to 89%) in gas fields have imposed increased challenges on the economics of project development and subsequent operations.¹ A major issue in developing those fields is corrosion and materials technology because of aggressive environments (i.e., high CO₂ contents and/or presence of H₂S) with high pressures and high temperatures (HPHT).² Although corrosion resistance alloys (CRAs) have been available as a materials selection option for these severe environments, carbon and low alloy steels are still widely used as tubing materials due to their strength, availability and cost.³⁻⁷

The increment of temperatures and CO₂ pressure in production wells may lead to CO₂ in supercritical state if the temperature and the pressure are over 31.1°C and 7.38 MPa, respectively.⁸ Corrosion issues

in supercritical CO₂ environments relating to carbon capture and storage (CCS), enhanced oil recovery (EOR), and deepwater oil and gas production applications have recently been investigated at relatively low temperatures (< 90°C),⁹⁻¹³ and it has been understood that aqueous corrosion mechanisms in high pressure CO₂ are similar to those in low pressure CO₂ conditions.¹⁴

Regardless of the CO₂ pressure, there has been relatively less research on corrosion at high temperatures, above 100°C.^{15,16} In the temperature range from 90 ~ 250°C, general corrosion rates of carbon steel were shown to decrease with increasing temperature and were strongly dependent on the formation of magnetite (Fe₃O₄) because of the fast kinetics of Fe₃O₄ formation at high temperatures.^{17,18} This indicates that high temperature has a significant effect on the corrosion rate and formation/transformation of the corrosion products. Those effects were also shown in high temperature H₂S corrosion, yet the understanding of the associated corrosion mechanism is very limited.¹⁹⁻²¹

Until now, there are few studies for aqueous corrosion in high temperature supercritical CO₂ environments with H₂S related to the downhole conditions. Thus, the objective of the present study was to identify and quantify the key issues that affect the integrity of carbon steel in high temperature supercritical CO₂ in the presence of small amounts of H₂S.

EXPERIMENTAL PROCEDURE

The test specimens were machined from UNS K03014⁽¹⁾ carbon steel (CS) with two different geometries: cylindrical type with 5 cm² exposed area for electrochemical measurements, and rectangular type with a size of 1.27 cm × 1.27 cm × 0.254 cm for surface analysis. The chemical composition of the CS is shown in Table 1. The specimens were ground sequentially with 250, 400 and 600-grit silicon carbide paper, rinsed with deionized (DI) water, cleaned with isopropyl alcohol in an ultrasonic bath for 60 seconds, and then dried.

Table 1
Chemical compositions of materials used in the present study (wt.%, balance Fe).

	C	Cr	Mn	P	S	Si	Cu	Ni	Mo	Al
CS	0.065	0.05	1.54	0.013	0.001	0.25	0.04	0.04	0.007	0.041

The corrosion experiments were conducted in a 7.5-liter autoclave (UNS N10276) which contained a CS working electrode, a HPHT Ag/AgCl reference electrode, a platinum-coated niobium counter electrode, and a HPHT ZrO₂-based pH electrode. A schematic of the experimental setup is shown in Figure 1. The test solution was a 1 wt.% NaCl aqueous electrolyte prepared using DI water. An impeller was used to stir the solution and to generate flow velocities of about 1 m/s and 1.7 m/s (1000 rpm and 1700 rpm, respectively) during the tests.

The experimental procedure is outlined in Figure 2. Initially, 6 liters of 1 wt.% NaCl solution was placed in the autoclave and purged with a high flow rate of CO₂ for 1 ~ 3 hours in order to remove dissolved O₂. The specimens were then placed in the autoclave while purging with CO₂ to avoid air ingress. After closing the autoclave, additional purging with CO₂ or a mixture of CO₂/10% H₂S was performed for 1 to 2 hours to ensure the removal of O₂ and the saturation of CO₂ or CO₂/H₂S, and then the temperature was increased to the testing temperature. Once the working temperature was reached, the working H₂S partial pressure was achieved by pressurizing with a mixture of CO₂/10% H₂S for the CO₂/H₂S conditions. High pressure was then attained by injecting CO₂ with a booster pump.

⁽¹⁾ UNS numbers are listed in Metals and Alloys in the Unified Numbering System, published by the Society of Automotive Engineers (SAE International) and cosponsored by ASTM International.

Corrosion rate and corrosion potential of specimens were evaluated with time by linear polarization resistance (LPR) measurements. The corrosion rates were also determined from the weight-loss (WL) method at the end of the test. The details of LPR and WL measurements are shown in previous studies.^{22,23} The solution pH was measured at the beginning and end of the experiment by using a commercial HPHT ZrO₂-based pH electrode and the HPHT Ag/AgCl reference electrode. The electrodes were calibrated prior to each test by the procedure supplied by the manufacturer.²⁴ After each test, the morphology and compositions of corrosion products were analyzed with scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD). Table 2 shows the test conditions for the present study.

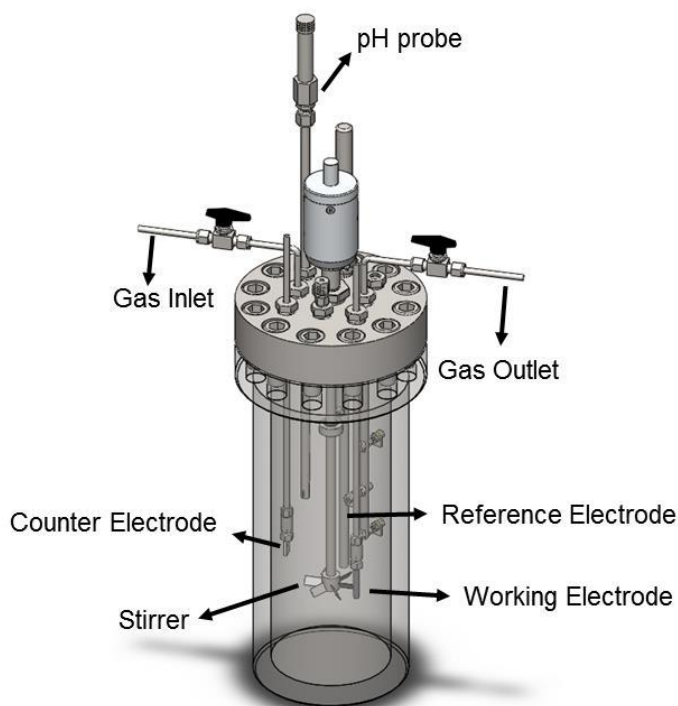


Figure 1: Schematic diagram of the autoclave used for the test under HPHT condition.

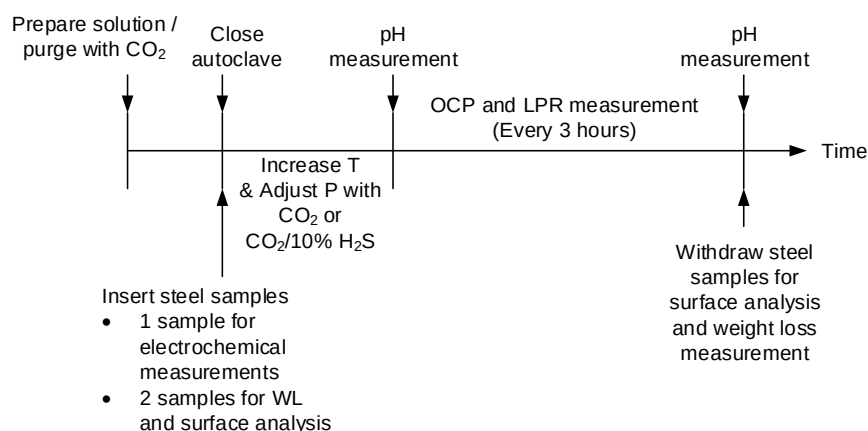


Figure 2: Experimental procedures for evaluating the corrosion behavior in HPHT CO₂ environments with H₂S.

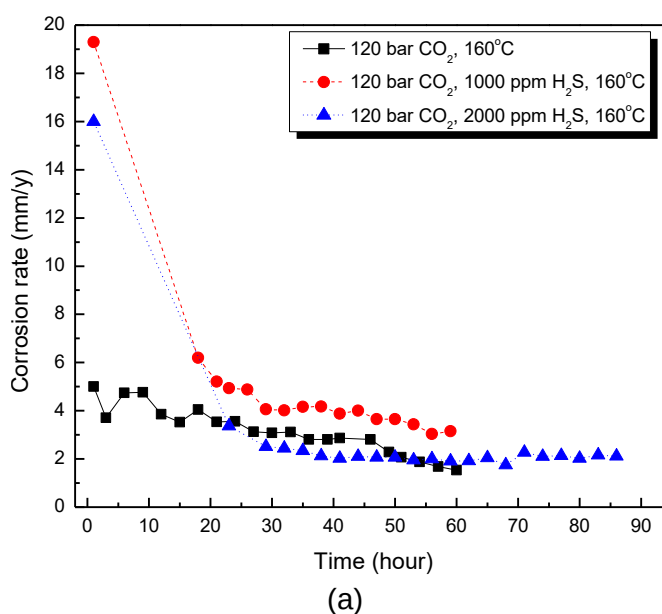
Table 2
Test conditions for corrosion testing

	pCO ₂ (MPa)	H ₂ S (ppm _v)	Temperature (°C)	Rotation speed (rpm)
1	12	0	160	1000
2	12	1000	160	1000
3	12	2000	160	1000
4	12	2000	160	1700

RESULTS AND DISCUSSION

Figure 3 shows LPR and weight loss (WL) corrosion rate data of CS exposed to 1 wt.% NaCl at 12 MPa CO₂ and 160°C with 0, 1000 and 2000 ppm H₂S. The corrosion rate of CS for the CO₂ condition was about 5 mm/y at the beginning of the experiment and then slightly decreased with time, whereas the corrosion rates of CS with H₂S (for both H₂S concentrations) started at much higher values and then decreased to similar values to those of the CO₂ condition after 20 hours. WL corrosion rate shows the same trend as the LPR corrosion rate.

Table 3 lists the solution pH values at the beginning and the end of each test. For all three conditions, the solution pH slightly increased indicating a small change in the bulk water chemistry due to the release of Fe²⁺.



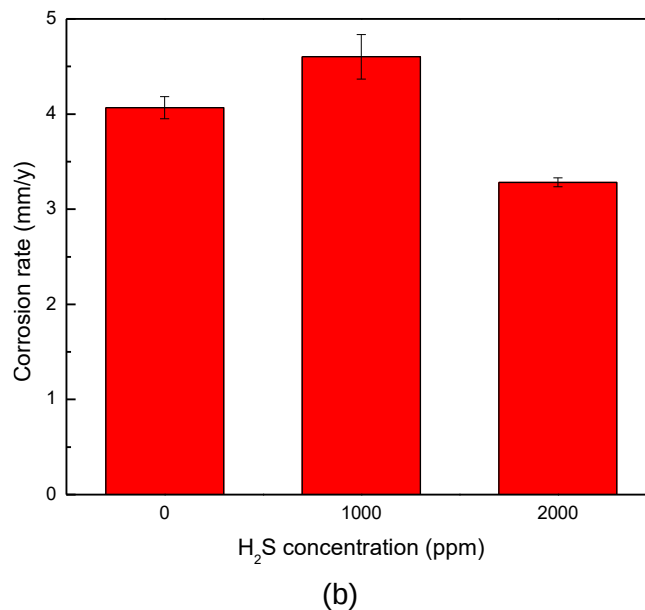


Figure 3: Comparison of corrosion rate with different H₂S concentrations at 12 MPa CO₂ and 160°C: (a) LPR corrosion rate, (b) WL corrosion rate.

Table 3
Measured initial and final solution pH at 12 MPa CO₂ and 160°C.

	Initial pH	Final pH
0 ppm H ₂ S	4.3	4.8
1000 ppm H ₂ S	4.2	4.7
2000 ppm H ₂ S	4.4	4.8

Figure 4 shows the surface morphology and chemical analysis of the corroded sample after 60 hours of exposure to the CO₂ condition. A uniform corrosion product was found covering the exposed surface. EDS analysis shows that the corrosion product mainly consists of iron, carbon, and oxygen.

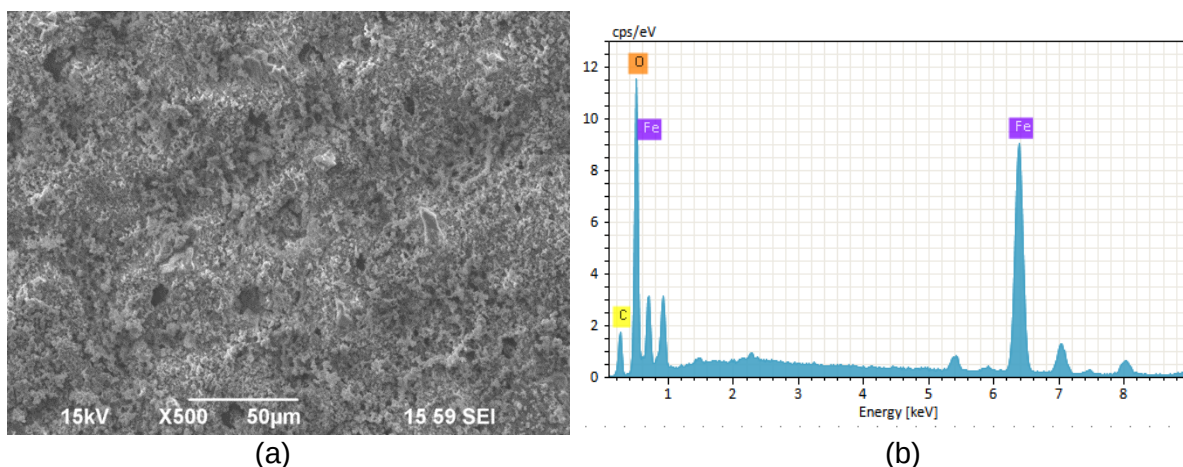


Figure 4: SEM surface view (a) and EDS analysis (b) of the corrosion product formed at 12 MPa and 160°C.