

Corrosion Inhibition of Carbon Steel in Supercritical CO₂/H₂S Environments

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ABSTRACT

The effect of small amounts of H₂S on the corrosion behavior and corrosion protection of carbon steel was investigated in high pressure CO₂ environments. The experiments were carried out in a 7.5L autoclave with two combinations of CO₂ partial pressure and temperature (12 MPa/80°C and 8 MPa/25°C) with different H₂S concentrations (0, 100 and 200 ppm). The corrosion behavior of specimens was evaluated using electrochemical measurements and surface analytical techniques. It was found that the addition of small amounts of H₂S reduced the corrosion rate of carbon steel in high pressure CO₂ environments. However, the corrosion rate was still higher than the targeted rate (< 0.1 mm/y). Additional protection was required in order to achieve the target. Utilizing 400 ppm of an imidazoline-type corrosion inhibitor reduced the corrosion rate of carbon steel below 0.1 mm/y in a high pressure CO₂ condition with H₂S. Compared to carbon steel, the corrosion resistance of low Cr steels was lower in the corresponding CO₂ conditions with H₂S.

Key words: Supercritical/liquid CO₂, CO₂ corrosion, carbon steel, low Cr alloy steel, corrosion inhibitor

INTRODUCTION

Numerous studies of corrosion issues in high pressure CO₂ environments relating to carbon capture and storage (CCS), enhanced oil recovery (EOR), and deep water oil and gas production applications have recently been published.¹⁻⁵ Aqueous corrosion mechanisms in high pressure CO₂ are similar to those in low pressure CO₂ conditions.⁶ However, the corrosion rate of carbon steel in the presence of high pressure CO₂ without formation of protective corrosion product layers is very high (≥ 20 mm/y) due to the presence of significantly high concentrations of corrosive species, such as H⁺ and H₂CO₃.⁷⁻¹⁴

Controlling corrosion in such cases usually involves use of Corrosion Resistant Alloys (CRAs). Since the use of CRAs is very costly, there is a need to better quantify their performance, as well as that of mild steels, against the risk of corrosion associated with high pressure CO₂ environments. This facilitates identification of production conditions where mild steel may still be used in the construction of pipelines, and related, systems. Furthermore, this has the potential to significantly reduce costs associated with use of CRAs for infrastructure construction.

In previous studies, an attempt was made to control the corrosion of carbon steel in high pressure CO₂ conditions using low Cr alloy steels and corrosion inhibitor (CI).^{15,16} The studies showed that utilizing low Cr alloy steels (1% Cr and 3% Cr) alone was insufficient to decrease the corrosion rate below the targeted value of 0.1 mm/y. Adequate protection was achieved by applying generic “imidazoline+thiosulfate” CI to carbon steel in the high pressure CO₂ environments. Furthermore, the CI performance with carbon steel was better than Cr-containing steels.

It has recently been reported that small amounts of H₂S can be present in high pressure CO₂ streams related to gas field development.^{17,18} Although the effect of H₂S on the aqueous corrosion of carbon steel at low CO₂ partial pressures is well investigated, limited work has been done in high pressure CO₂ environments.¹⁸⁻²⁰ In addition, there is no systematic study on corrosion inhibition in high pressure CO₂ environments with H₂S. Thus, the objective of the present study was to identify and quantify the key issues that affect integrity of carbon steel in high pressure CO₂ in the presence of small amounts of H₂S, and to establish potential corrosion mitigation strategies using low Cr alloy steels and corrosion inhibitors.

EXPERIMENTAL PROCEDURE

The test specimens were machined from UNS K03014 carbon steel (CS), UNS G41300-1Cr steel (1Cr) and UNS G41300-3Cr steel (3Cr) 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 compositions of the studied alloys are shown in Table 1. The specimens were ground sequentially with 250, 400 then 600-grit silicon carbide (SiC) paper, cleaned with isopropyl alcohol in an ultrasonic bath for 60 seconds, and dried. A 1 wt.% NaCl aqueous electrolyte was prepared using deionized (DI) water.

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
1Cr	0.3	0.85	0.91	0.015	0.008	0.29	---	---	---	---
3Cr	0.08	3.43	0.54	0.006	0.003	0.3	0.16	0.06	0.32	---

An ‘imidazoline + thiosulfate’ generic corrosion inhibitor (CI1) and an ‘imidazoline’ generic corrosion inhibitor (CI2) were selected for evaluation under high pCO₂ environments with H₂S. In this instance, ‘imidazoline’ is shorthand for tall oil fatty acid (TOFA) imidazoline-type inhibitor.

The corrosion experiments were conducted in a 7.5-liter autoclave (UNS N10276) with a three-electrode setup, consisting of a working electrode, a high pressure/high temperature Ag/AgCl reference electrode and a platinum coated niobium counter electrode. An impeller was used to stir the solution at a rotation speed of 1000 rpm (corresponding to approximately 1 m/s), stirring was maintained during the test.

Experimental procedure is outlined in Figure 1. Initially, 1 wt.% of NaCl solution was placed in an autoclave and this electrolyte purged with CO₂ for 1 ~ 3 hours in order to remove dissolved O₂. The electrodes and specimens were then placed in the autoclave. After closing the autoclave, temperature was increased to the testing temperature. Once the working temperature was achieved, a mixture of CO₂ and H₂S was injected into the system to achieve the working H₂S partial pressure. High pressure CO₂ was then injected with a booster pump. Corrosion rate and corrosion potential of specimens were evaluated with time by linear polarization resistance (LPR) measurements. The details of LPR measurements are shown in our previous work.¹⁶ After each test, the specimens were removed from the autoclave, rinsed with DI water and isopropyl alcohol, dried with N₂ and stored in a desiccator cabinet in an inert atmosphere until surface analyses could be conducted. For testing with inhibitors, the procedure was the same as shown in Figure 1, except inhibitor was added to the solution before inserting the specimens.

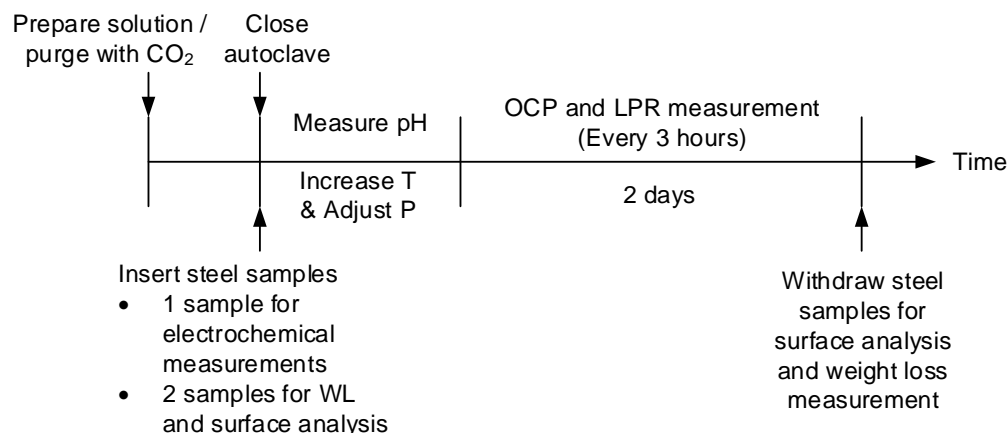


Figure 1: Experimental procedures for evaluating the corrosion behavior of materials in high pCO₂ environments with H₂S.

Table 2 shows the test conditions for the present study. The test conditions were set in order to simulate the inlet and outlet conditions for CO₂ transportation pipeline, where the CO₂ is present in a supercritical state at the ‘inlet’ condition and it exists as a liquid at the ‘outlet’ condition.¹⁷

**Table 2
Test conditions for corrosion testing**

	pCO ₂ (MPa)	H ₂ S (ppm)	Temperature (°C)
Inlet	12	0	80
	12	100	80
	12	200	80
Outlet	8	0	25
	8	100	25
	8	200	25

RESULTS AND DISCUSSION

Experiments at the inlet condition (12 MPa, 80°C)

Figure 2 shows the variations of corrosion rate and corrosion potential with time under different H₂S concentrations. Without H₂S, the corrosion rate is about 90 mm/y at the beginning of the experiment. Note that the corrosion rate decreased after 15 hours because of the change in solution chemistry within the autoclave caused by release of ferrous ion (Fe²⁺) and the formation of protective iron