

Influence of High CO₂ Partial Pressure on Top-of-the-Line Corrosion

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ABSTRACT

Top-of-the-line corrosion (TLC) is an important type of material degradation that occurs due to the heat exchange between the pipeline and its surroundings, which results in water condensation on the internal surface of the pipe. This type of corrosion is specific to wet gas pipelines with stratified flow regimes. In this research, the effect of high CO₂ partial pressure (pCO₂) on TLC rate and mechanism was studied. The experiments were conducted in a high-pressure TLC autoclave with pCO₂ ranging from 20 to 100 bar, solution temperatures of 30 and 50 °C, and different water condensation conditions (0.001-0.1 ml/m².s). The experimental conditions covered environments where CO₂ was either gaseous or supercritical. The results revealed that uniform and localized TLC rates increase with water condensation rate and solution temperature. However, as long as CO₂ remained gaseous, pCO₂ showed a negligible influence on both uniform and localized TLC rates. At a high CO₂ content, the formation of a protective FeCO₃ layer decreased the TLC rate, especially at lower water condensation rates. Nevertheless, the risk of localized corrosion at high and medium water condensation rates remained an issue. In the supercritical CO₂ environment (pCO₂ of 100 bar and solution temperature of 50 °C), the difference in temperature between the CO₂ dense phase and the specimens caused water drop out and corrosion. In this environment, the high pCO₂ and low pH of the dropped-out water led to high uniform and localized

corrosion rates. However, under this condition, the difference in corrosion rates of specimens with different cooling rates was negligible due to their similar surface temperature.

Keywords: Sweet corrosion, Top-of-the-line corrosion, Localized Corrosion, Supercritical CO₂

INTRODUCTION

Pipeline corrosion during the transportation of fluids is a well-known problem in the oil and gas industry. The unprocessed fluid extracted from an oil well is typically a complex mixture of oil, solids, gas, and brine (water phase). The presence of water, in which the corrosive gases (CO₂, H₂S) can dissolve and produce weak acids, results in corrosion. In the 1990s, a new mode of corrosion was identified which today is known as top-of-the-line corrosion or TLC. TLC is observed in wet gas transport pipelines at the upper part of the pipe (with a stratified flow regime), where the pipe is not directly in contact with the water phase. TLC of course occurs when the gas contains condensable liquids, e.g., water and some hydrocarbons. The prerequisite for TLC is the heat exchange between the pipeline and its colder surroundings.^{1, 2} This heat exchange leads to the condensation of water or hydrocarbon phases on the cold walls of the pipelines, as a thin film or in droplets. The condensed water phase that contains CO₂, H₂S, and organic acids such as acetic acid can be, at least initially, very corrosive to carbon steel pipelines causing loss of integrity and eventually failure.³⁻⁷

As defined above, TLC is a complicated phenomenon depending on the factors affecting the heat and mass transfer, including temperature gradient across the pipe wall, gas temperature and flow rate, as well as chemistry of the condensed water, such as the acidic gas and organic acid content. Considering sweet corrosion scenarios where the main corrosive species is CO₂, the partial pressure of CO₂ together with the temperature gradient between the gas phase and the pipeline surface are two of the main factors to be studied for the TLC rate estimation. A few parametric studies are available on the effect of these two parameters on TLC.^{4, 8-13} The studies on the effect of temperature (mostly T_g (gas temperature) and T_s (surface temperature)), or the condensation rate (as the one variable directly affected by the temperature) have naturally focused on the formation of protective corrosion product layers (i.e., iron carbonate, FeCO₃) and how it affects the TLC rate and mechanism. The available studies cover a wide range of water condensation rates from 0.001 ml/m².s to 2 ml/m².s⁸ and they also include water/hydrocarbon co-condensation scenarios.^{14, 15}

On the other hand, the range of CO₂ partial pressures that is covered in the literature available to this date usually does not exceed 10 bar.¹³ Considering the inevitable influence of CO₂ partial pressure on the formation of FeCO₃ and the necessity of moving toward systems with higher pressure, especially with the demand for CO₂ storage and capture purposes, it is essential to study TLC under conditions with high CO₂ pressure.

In the current paper, a parametric study is described relating to the influence of temperature and CO₂ partial pressure on TLC of carbon steel with an emphasis on high CO₂ pressure (up to 100 bar), employing weight loss corrosion measurements and surface characterization techniques such as scanning electron microscopy (SEM), Raman spectroscopy, and optical profilometry.

EXPERIMENTAL PROCEDURE

TLC setup and testing procedure

A 20 L autoclave made of alloy C-276 (UNS N10276), designed to simulate TLC scenarios, was used to conduct the experiments. The TLC experiments were performed at three different water condensation rates named as “High-water condensation rate (HWCR)”, “Low-water condensation rate (LWCR)”, and “(in) Gas phase” condition. Figure 1 depicts the specimen configuration within the autoclave along with simulation-derived water condensation rate values for the experimental conditions of this study. Six X65 steel¹⁶ specimens were placed in the TLC corrosion specimen holder which was then screwed to the

autoclave lid. This holder is in contact with a coiled tubing chiller system inside the lid that cools down the sample holder and the specimens. The chiller system is run by using a chilled glycol solution that is circulated in the system from an external source. This external source is equipped with a pump and a temperature control/monitoring system. In this study, the water condensation rate on each specimen was controlled by adjusting the temperature difference between the gas phase and the surface of the specimen. At a fixed condition, the higher the temperature difference, the higher the water condensation rate would be. As shown in Figure 1, the specimens that are directly flush mounted to the holder are under high(er) water condensation rate condition (HWCR) as they are directly in contact with the chiller system and therefore have a greater temperature difference with the gas phase. The specimens that are placed in the PEEK holders are at low(er) water condensation rate condition (LWCR) as they are separated from the chiller system with a layer of PEEK with low thermal conductivity and therefore are at a higher temperature and have a smaller temperature difference with the gas phase. The specimens that are separated from the chiller system with a stud (as shown in Figure 1) are named (in) Gas phase specimens and have the lowest water condensation rate. In all cases, the actual value of WCR is always quite low ($<0.1 \text{ mL/m}^2/\text{s}$). The “HWCR”, “LWCR” and “Gas Phase” are used for ease of comprehension.

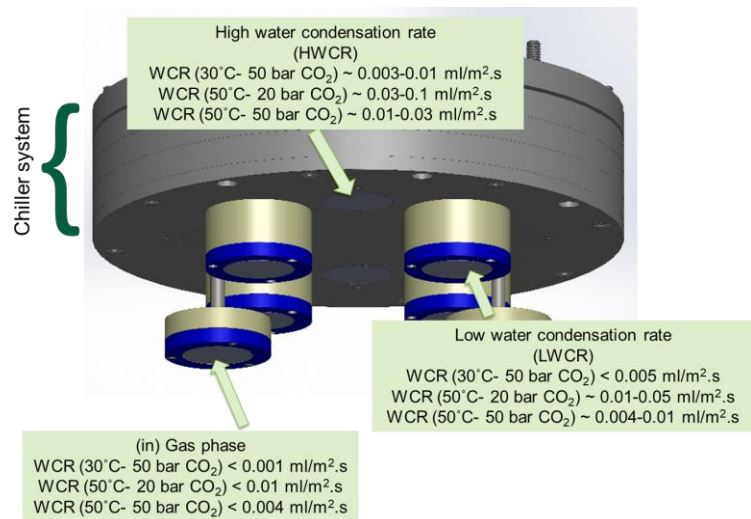


Figure 1: The internal autoclave lid TLC specimen setup.

Table 1
Experimental conditions for the TLC experiments

Test ID	Solution temperature (°C)	CO ₂ partial pressure (bar)	Duration (days)
1-1	30	50	2
1-2	30	50	7
1-3	30	50	21
2	50	20	21
3	50	50	21
4 (Supercritical CO ₂)	50	100	21

The experimental conditions of this study are outlined in Table 1. The first three experiments (1-1 to 1-3) were performed to determine the optimal testing duration, in terms of detection of localized corrosion. The duration of the next three experiments was selected based on the results of these first three experiments.

It should be noted that under the conditions of experiment 4, CO₂ will turn into a supercritical phase. Therefore, water condensation does not occur as it only occurs in a gas/liquid system. Instead, a similar phenomenon known as water drop-out happens. The solubility of water in CO₂ depends not only on its

pressure but also on the temperature.¹⁷ The change in temperature of the CO₂ dense phase, as it approaches the chilled sample holder, causes a change in its water solubility and therefore water drop-out. Similar to the condensed water, this water is corrosive to the steel specimen due to the presence of dissolved CO₂. Accordingly, the names of specimens for experiment 4 are changed to HWDR, LWDR, and Dense Phase.

The following experimental procedure was pursued. Before each experiment, the autoclave body was cleaned with isopropanol and deionized (DI) water, followed by wiping with a paper towel. 12 liters of DI water was then poured into the autoclave and sparged with CO₂ for at least 12 hours for deoxygenation. The temperature of the solution was simultaneously increased to the target temperature. Six weight loss specimens of X65 steel (two for HWCR, two for LWCR, and two for Gas phase conditions) were sequentially polished up to 600 grit using SiC abrasive papers. After polishing, the specimens were ultrasonically cleaned with isopropanol and air dried, and the initial mass of each specimen was measured using a balance of 0.1 mg precision. After the desired solution temperature was reached, the system was opened, and the specimens were placed in the top lid. As mentioned earlier, the autoclave lid is equipped with an internal cooling system connected to an external source. The temperature of the glycol solution in the external source was accordingly set to have a temperature difference of 10 °C between the HWCR specimens and the gas phase. After closing the autoclave, any remaining oxygen in the brine, headspace, and lines was purged with CO₂. An oxygen sensor was connected to the pressure release valve and the oxygen concentration for all the tests did not exceed 5 ppb. After checking the oxygen concentration, the autoclave was pressurized to the target CO₂ pressure and then heated to the desired temperature. The temperature of the gas, the solution, and the HWCR steel specimens were monitored during the experiment.

Post-processing methodology

After the experiments, according to ASTM Standard G1-03,¹⁸ the corrosion products on the corroded specimens were removed using Clarke solution. Specimens were then rinsed with DI water and isopropanol and subsequently air dried. The corrosion rate was calculated using the difference between the initial and the final weight of each specimen before and after the cleaning process. The following equation was used:

$$CR = 87600\Delta m/\rho At \quad (1)$$

where CR is the corrosion rate in mm/y, Δm is the mass difference in grams, ρ is the density of carbon steel (7.874 g/cm³), A is the exposed area in cm², and t is time in hours.

After the corrosion tests (and before Clarke solution cleaning), the surfaces of the specimens were examined using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), Raman spectroscopy, and optical profilometry.

Apart from the corrosion rate obtained from the weight loss measurements, the maximum penetration rate for each specimen was determined from the optical profilometry data using determined maximum penetration depth and a simple proportion calculation.

RESULTS

The effect of test duration

In the first part of this research, the effect of test duration on uniform TLC rate and the occurrence of localized corrosion at three different water condensation conditions was investigated. These series of experiments were done at a solution temperature of 30 °C and pCO₂ of 50 bar; experimental durations of 2, 7, and 21 days were selected.

Figure 2 depicts the results for TLC rate as a function of test duration for HWCR, LWCR, and Gas phase specimens. Firstly, as shown in this figure, regardless of the test duration, the uniform TLC rate (calculated based on weight loss measurements) increases with the water condensation rate. This trend can be explained by the possible formation of protective corrosion product layers.¹⁹ At a high water condensation rate, such as the condition of HWCR specimen, the refreshment of condensed water droplets on the specimen dilutes the existing water film and limits or decreases the saturation value with regard to FeCO_3 ($S_{\text{FeCO}_3} = [\text{Fe}^{2+}][\text{CO}_3^{2-}]/K_{\text{sp,FeCO}_3}$). This disrupts the formation of a protective FeCO_3 layer or leads to the dissolution of any formed layer. However, in LWCR and Gas phase conditions, the refreshment of condensed water on the surface of the specimen is slower due to the lower condensation rates and longer droplet retention time,⁸ therefore, the FeCO_3 layer can form and decrease the corrosion rate.

Regarding the test duration, according to Figure 2, it seems that the rate of uniform TLC decreases with time, and this is independent of the water condensation rate.

To understand the effect of time and condensation rate on the formation of corrosion product layers and the occurrence of localized corrosion, the specimen surfaces after the 2-day, 7-day, and 21-day experiments were further characterized.

Figure 3 shows the SEM images of surfaces of the specimens after 2 days of the experiment. The images in this figure were taken at two different magnifications, providing a representative view of the entire surface at a lower magnification (50x) and the detailed morphology of the corrosion products at a higher magnification (2000x). As was hypothesized earlier, the surface of the specimen at HWCR condition is only partially covered by the corrosion products (possibly FeCO_3). This is obvious by looking at the high magnification image where the crystals of corrosion products are seen on top of a corroded matrix. On the other hand, the surfaces of the specimens in LWCR and Gas phase conditions are entirely covered by a dense, and hence protective, layer of corrosion product. The composition of the corrosion product layers on the three specimens was investigated by EDS (the results are not shown here). The EDS results are not conclusive and cannot be used to identify phases, however, due to the presence of Fe, O, and C they suggest that the corrosion product is most probably FeCO_3 .

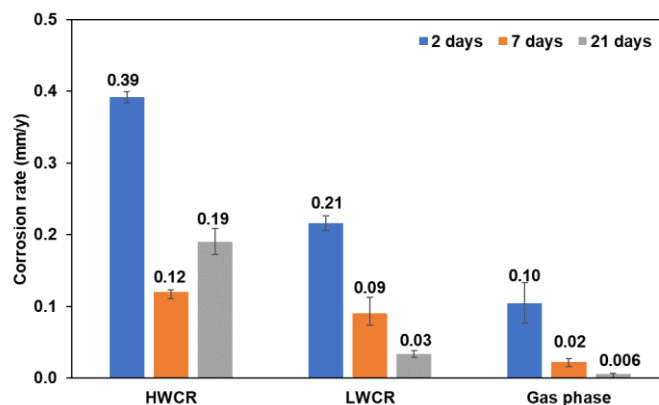


Figure 2: Results of corrosion rate after TLC experiment under different water condensation rates at T_{sol} of 30 °C with $p\text{CO}_2$ of 50 bar for 2, 7, and 21 days (the error bars show max and min).

The occurrence of localized corrosion during TLC is one of the most important subjects from both industrial and research standpoints. Therefore, after removing the corrosion product layers, the surfaces of the three specimens were characterized by optical profilometry to investigate the presence of such corrosion features. The results are shown in Figure 4. According to this figure, no sign of localized corrosion on any of the specimens was observed after 2 days of experiment. The results of SEM, EDS, and optical profilometry of the specimens after the 7-day experiment were identical to those after the 2-