

Effect of CO₂ partial pressure and different CO₂ phases on carbon steel corrosion

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Abstract. Carbon capture and storage (CCS) is the recent promising technology aimed at reducing greenhouse gas emission. Like many other developed technologies, CCS is faced with great challenges such as pipeline transportation failure due to corrosion. There are many factors contributing to steel corrosion during the pipeline transportation of carbon dioxide (CO₂). This study focuses on CO₂ partial pressure and different phases of CO₂ as some of the factors contributing to steel corrosion. Carbon steel was used as a testing specimen. High pressure reactor was used in this study to compress CO₂ from low to high pressures ultimately changing the CO₂ from gaseous phase to gas/liquid phase (subcritical) and to dense phase (supercritical). Weight loss method was employed to determine the corrosion rate while scanning electron microscopy (SEM) and X-Ray diffraction (XRD) were used to study the carbon steel morphology and phase analysis. Using low magnification digital camera, the type of corrosion that took place on the carbon steel surface was identified.

1. Introduction

Carbon dioxide (CO₂) corrosion has recently been identified as one of the disastrous concern facing the successful operation of carbon capture and storage (CCS) [1] – [2]. During the process of CCS, CO₂ is transported from the capturing point to the permanent storage sites through a steel pipeline system [3]. CO₂ is first compressed to its supercritical state (74.14 bar and 31.14°C) which makes it denser thus easier to transport over significantly long distances [4]. Many researchers have explained that dry gaseous CO₂ is not corrosive but the presence of moisture in the CO₂ stream leads to significantly severe corrosion threats on the pipeline steel [5]. This is because increasing the CO₂ pressure increases the CO₂ solubility which, in the presence of water, leads to the formation of the corrosive carbonic acid (H₂CO₃) [6]. This behavior has attracted a lot of attention to the CO₂ partial pressure not only as it influences the CO₂ solubility but potentially changes the CO₂ phase from gaseous to supercritical phase. Very little information is known on supercritical CO₂ corrosion as far as steel pipeline transportation is concern.

Many researchers have already published work discussing some of the factors influencing the CO₂ corrosion on steel pipeline. These factors include CO₂ partial pressure, temperature, pH, steel exposure time, impurities, etc [6] – [7]. One of the advantages of supercritical fluids is that they are easy to transport as they exist at higher densities thus lower viscosity. In reference to the CO₂ transportation during the CCS operation, supercritical CO₂ rather than gaseous CO₂ would be the best to optimize the transportation of CO₂ over long distances.



The aim of this study was to investigate the influence of CO₂ partial pressure on the steel pipeline corrosion. A high pressure reactor was used to compress CO₂ from low pressure to high pressure which covers 3 (three) phases of CO₂ thereby shedding a light also on corrosion of steel pipeline under different CO₂ phases. Carbon steel was selected as the testing specimen and was exposed to the varied CO₂ partial pressures. Weight loss method was used to calculate the corrosion rate while the steel surface morphology and phase analysis were carried out by scanning electron microscopy (SEM) and X-Ray diffraction (XRD) respectively.

2. Experimental Procedure

2.1. Materials

Carbon steel specimen with the elemental composition (weight %) of 0.044 C, 0.001 Mo, 0.237 Mn, 0.035 Al, 0.025 P, 0.0007 V, 0.009 S, 0.0001 Nb, 0.01 Si, 0.001 Ti, 0.01 Cu, 0.0002 B, 0.005 Ni, 0.0038 N, 0.01 Cr and Fe balance was cut to 16 × 10 × 5 mm. The surface area measuring 16 mm × 10 mm was exposed to the corrosion media (subcritical CO₂/SO₂ environment) as the tested surface inside the high pressure reactor (shown in Figure 1). The cut samples were grinded to 120 - 1200 grits and polished with the 1 μm using silicone discs. Prior to the experiments, the high pressure reactor was first deoxygenated by purging with N₂ for 24 hours and denitrogenated by purging pure CO₂ into the reactor for 4 hours. Deionized water was added to adjust the H₂O concentration of 1000 ppmv (0.1%) which was well above the H₂O concentration (50 ppmv) needed to enhance the corrosion process inside the steel pipeline [8]. The polished carbon steel samples were rinsed, dried, weighed (precision of 0.0001 g) and stored in a desiccator. CO₂ was charged into the reactor at constant 60 bar and 25°C (subcritical region). Different CO₂ concentrations were added into the subcritical CO₂ (as shown in Table 1), carbon steel samples were then exposed to this environment for a period of 336 hours. The chemical composition of the carbon steel used in this study is shown in table 1 with iron (Fe) being the balance.



Figure 1. High pressure reactors (bolted and OC reactors).

Table 1. Experimental conditions

Sample #	Pressure (bar)	Temp. (°C)	Time (days)	H ₂ O (ppm)	CO ₂ (Phase)
1	1	25	336	1000	Gas
2	50	25	336	1000	Subcritical
3	60	25	336	1000	Subcritical
4	70	25	336	1000	Subcritical
5	95	25	336	1000	Supercritical

2.2. Steel Surface Characterization

A 5 mega pixel (auto focus) Lumia 520 digital camera was used to take photographic images of the carbon steel specimen at low magnification. After the experiments, the samples were removed from the reactor and weighed again for the weight loss calculations using the weight loss given in equation (1). The steel surface morphology analysis was carried out using JEOL JSM-7600F Field Emission Scanning Electron Microscopy (SEM) and the phase analysis was carried out using EMPYREAN PANalytical X-Ray Diffraction (XRD). After characterization the samples were washed with a concentrated hydrochloric acid and acetone to remove the corrosion products on the steel surface in order to identify the type of corrosion that occurred.

$$CR = 8.76 \times 10^4 \frac{\Delta m}{\rho \cdot A \cdot t} \quad (1)$$

where CR is the corrosion rate, mm/year; Δm is the weight loss of the specimen, g; ρ is the density of the specimen, g/cm³; A is the area of the specimen, cm²; t is the immersion time, hour.

3. Results

3.1. Weight loss Results

The first data point, i.e. corrosion rate; pressure = 0.000 mm/year; 1 bar, is in good agreement with the fact that dry gaseous CO₂ is not corrosive. The prepared carbon steel in this instance was pressured with CO₂ at 1 bar for a period of 336 hours at 25°C and no change of mass was observed implying no corrosion took place on the carbon steel surface. Figure 2 again shows a gradual increase in corrosion rate as CO₂ partial pressure increased to 50 bar, a region where CO₂ is in a subcritical phase (gas/liquid) with corrosion rate increasing from 0-0.0533 mm/year. Reference [4] also published a study showing a corrosion rate of approximately 0.3 mm/year at a CO₂ pressure of 60 bar exposed for 24 hours. This study shows a rather similar finding as the corrosion rate was found to be 0.1419 mm/year under similar experimental conditions (CO₂ partial pressure of 60 bar). The corrosion rate increased further to 0.5604 mm/year at the CO₂ partial pressure of 70 bar. The highest corrosion rate of 0.7806 mm/year was obtained at supercritical CO₂, i.e. 95 bar, concluding that an increase in CO₂ pressure increases the corrosion rate of carbon steel. According to [4], [7] and [9], the possible explanation for this behavior is that liquid or dense CO₂ interacts differently from gaseous CO₂. An increase in CO₂ pressure increases the concentration of H₂CO₃ which accelerates the cathodic reaction and ultimately enhancing the corrosion rate. The corrosiveness in aqueous phases coexisting with sub and supercritical CO₂ is a major driving force behind the trend observed when increasing the CO₂

partial pressure [7]. Furthermore, [7] explained that density of CO₂ at supercritical state can increase up to 0.4 to 0.5 g/cm³ which makes the CO₂ solubility to be much higher than that at lower pressures.

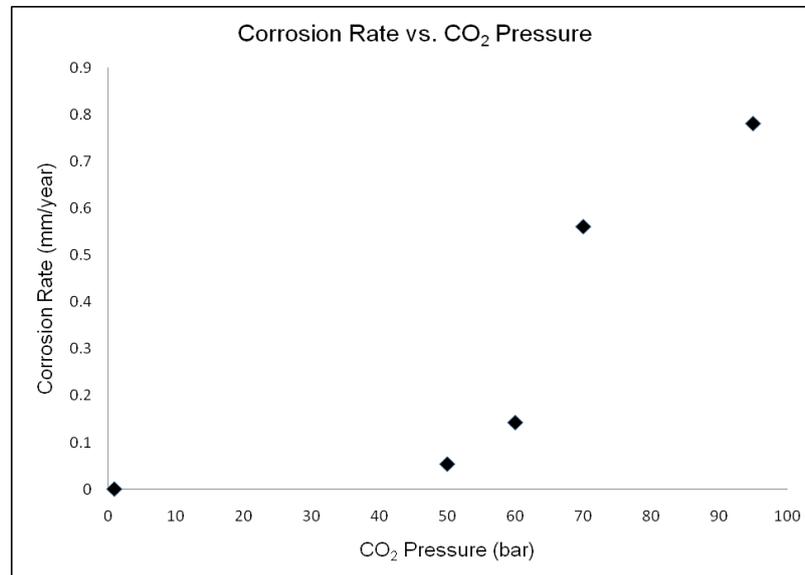


Figure 2. Relationship between corrosion rate and CO₂ partial pressure.

3.2. CO₂ Phase Effect

To investigate the effect of CO₂ phase on corrosion behaviour, pure CO₂ was charged at three (3) phases, i.e. gas, gas/liquid (subcritical) and liquid (supercritical) phase. In order to achieve the above phases, the relationship between pressure and temperature in reference to the CO₂ physical properties were considered. The literature done in this study states that CO₂ at the pressure of 73.82 bar (and above) and temperature of 31.1°C is no longer in the gas phase but dense phase and behaves as a liquid meaning it possesses the properties of liquids. Below 73.82 bar and 31.1°C CO₂ falls within the region called subcritical where it possesses both gas and liquid properties referred to in this study as gas/liquid phase. At pressures between 1 to 50 bar and temperatures below 25°C CO₂ is in a gas phase. Taking note of these CO₂ properties, it was then pressurized to 1 (dry gas), 60 (subcritical) and 95 bar (supercritical) into the reactor to investigate the effect of CO₂ phase. Figure 3 shows the data obtained at all three CO₂ phases.

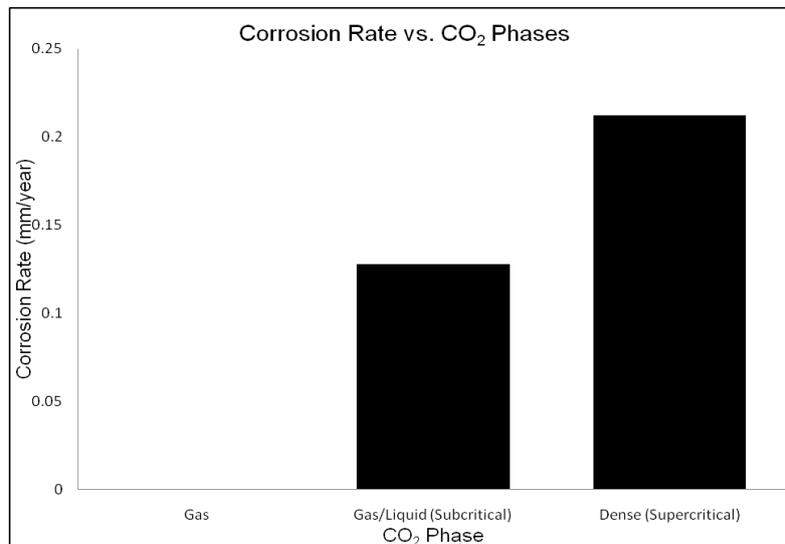


Figure 3. Relationship between corrosion rate and pure CO₂ phases.

Dry gaseous CO₂ resulted into almost no corrosion (0.0002 mm/year) which is in good agreement with literature. This indicates that dry pure CO₂ has very little negative influence towards corrosion of the steel pipe. Figure 3 shows a much higher corrosion rate of 0.1276 mm/year when CO₂ is at subcritical region indicating that as CO₂ changes from gaseous to liquid phase corrosion rate increases. Furthermore, corrosion rate increases even much higher when CO₂ is completely in the dense phase (supercritical state) with a corrosion rate of 0.2138 mm/year. This behavior is attributed to the CO₂ solubility changes at different conditions which then either accelerates or decreases the reaction to form corrosion products (mainly FeCO₃).

3.3. Steel Surface Morphology

The SEM analysis carried out on all carbon steel corroded surfaces before and after corrosion experiments are shown in figure 4. In an attempt to clearly identify the corrosion impact on the carbon steel surface, a blank carbon steel specimen (prior to corrosion experiment) was first analyzed then used as a reference basis. The blank carbon steel specimen is shown in figure 4 a) and no corrosion scale is observed. Scratches from sample preparation are however observed on the blank carbon steel surface. SEM image b) from figure 4 shows a carbon steel surface that is clear off any corrosion scale and also almost similar to the blank carbon steel SEM image. This makes a good agreement with the results obtained from weight loss (0 mm/year at 1 bar CO₂) in this study, i.e. gaseous CO₂ is not corrosive. As the CO₂ partial pressure is increased (from 1 to 50, 60, 70 and 95 bar) massive corrosion scale is observed on the carbon steel surface. The corrosion scale on SEM images c), d), e) and f) also shows the impact of increasing CO₂ partial pressure as it (corrosion scale) appears to be more compact and greater with an increase in CO₂ partial pressure. The observations from the CO₂ partial pressure behavior also concludes that CO₂ partial pressure increase change the CO₂ solubility which results in an accelerated formation of FeCO₃ on the carbon steel surface.

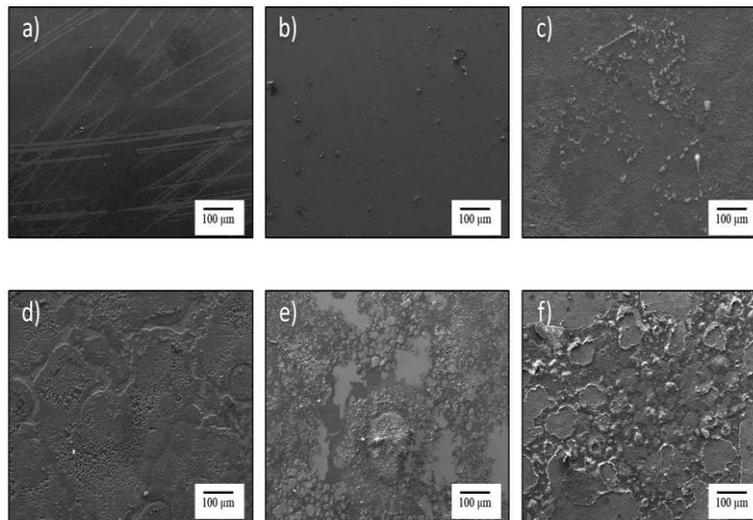


Figure 4. SEM images after corrosion experiments with CO₂ partial pressures: a) Blank sample, b) 1 bar, c) 50 bar, d) 60 bar, e) 70 bar & f) 95 bar.

Figure 5 shows photographic images of carbon steel specimen before and after corrosion experiments under various CO₂ environments. In order to identify the type of corrosion attack on the carbon steel surface, corrosion scale was removed from all carbon steel specimen. Localized corrosion attack is observed on the carbon steel surface when exposed to pure CO₂ under various partial pressures while pitting corrosion attack occurs in the presence of impurities under various CO₂ partial pressures [2].

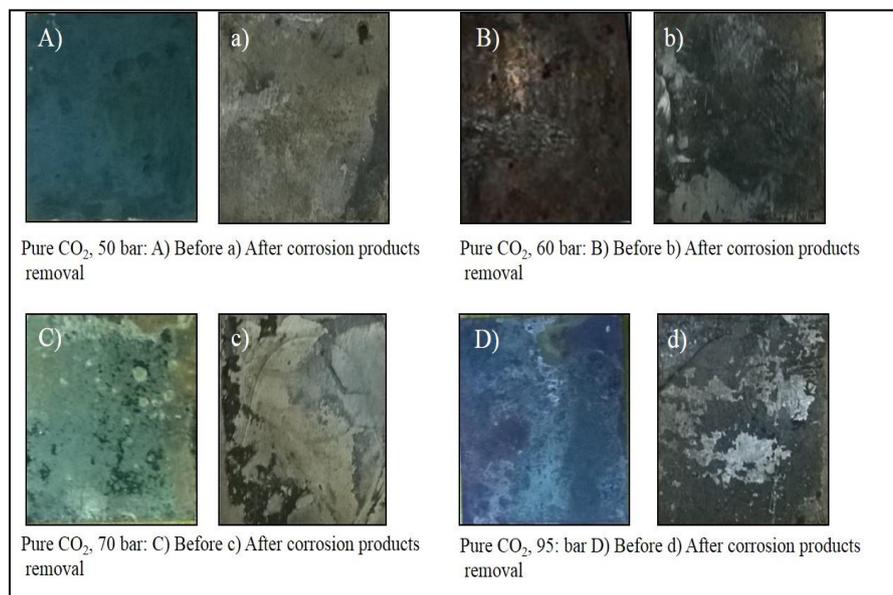


Figure 5. Photographic images of carbon steel specimen before and after corrosion.

3.4. Phase Analysis

Figure 6 shows the overlaid XRD spectra of the carbon steel specimen under various CO₂ partial pressures. Only iron (Fe) was detected on the carbon steel surface exposed to 1 bar (gaseous CO₂) indicating no formation of corrosion scale. This, again, shows a good agreement with the weight loss and SEM results discussed earlier in this study, i.e. gaseous CO₂ is not corrosive. A solid compact iron

carbonate (FeCO_3) was detected as a major component on the carbon steel surface as CO_2 partial pressure was further increased. Wet iron oxide ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) also made an appearance on the carbon steel surface which normally occurs in the presence of oxygen (O_2) within the CO_2 environment. Recalling that in this study the high pressure reactors were deoxygenated prior to the experiments, the oxidation of iron can only be explained by exposure of the carbon steel specimen to air during sample preparation prior to SEM and/or XRD analysis. A very important observation made from the XRD spectra in figure 6 is the fact that Fe was not detected almost at all under 95 bar CO_2 (supercritical phase). This implies that the entire surface of carbon steel was filled with corrosion scale implying that the further increase of CO_2 partial pressure to 95 bar increased the CO_2 solubility which resulted to more formation of mainly FeCO_3 according to the overall equation (2) shown below:

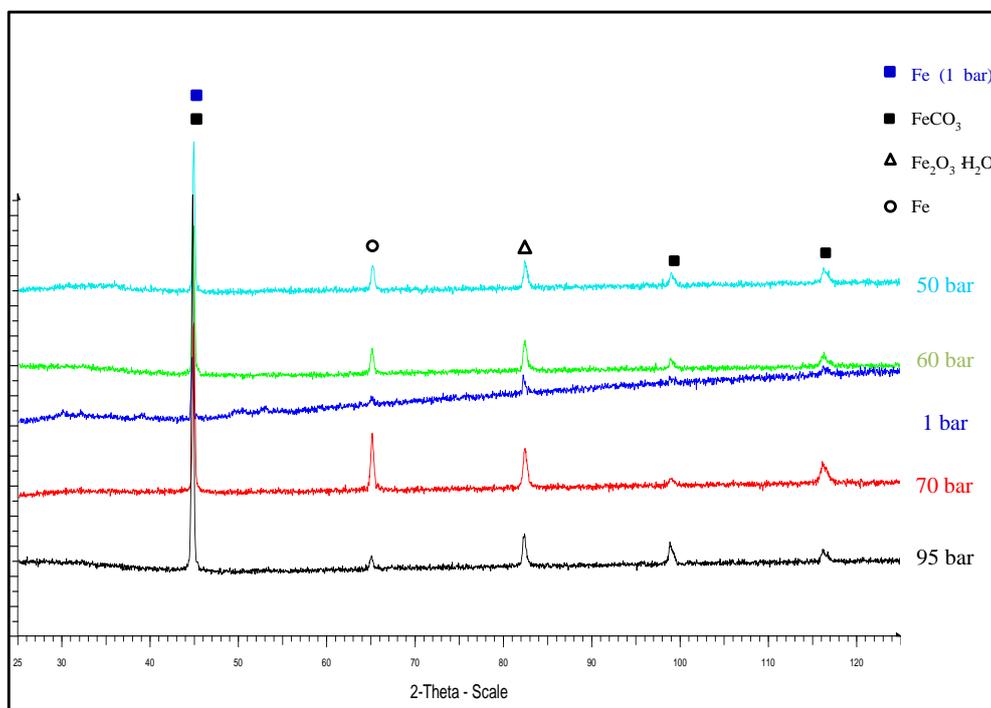


Figure 6. XRD spectra of carbon steel specimen corroded with different CO_2 partial pressures: a) 1 bar, b) 50 bar, c) 60 bar, d) 70 bar & e) 95 bar.

4. Conclusion

Based on the results obtained and discussed on this study, the following conclusions were drawn:

- An increase in CO_2 partial pressure increases the carbon steel corrosion rate.
- Gaseous CO_2 showed no corrosion on the carbon steel while significant corrosion was observed under subcritical CO_2 with the highest corrosion being occurring under supercritical CO_2 .
- Localized corrosion attack was observed on the carbon steel surface when exposed to pure CO_2 under various partial pressures.
- Iron carbonate (FeCO_3) was the dominant component on the corrosion scale formation on the carbon steel surface.

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