Effect of SO$_2$ concentration as an impurity on carbon steel corrosion under subcritical CO$_2$ environment

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Abstract. Carbon dioxide (CO$_2$) is considered to be easier to transport over moderate distances when turned into supercritical state (dense phase) than at any other state. Because of this reason, the transportation of CO$_2$ during carbon capture and storage requires CO$_2$ to be at its supercritical state. CO$_2$ temperature profile from different regions causes CO$_2$ to deviate between supercritical and subcritical state (gas/liquid phase). In this study the influence of sulphur dioxide (SO$_2$) on the corrosion of carbon steel was evaluated under different SO$_2$ concentrations (0.5, 1.5 and 5%) in combination with subcritical CO$_2$. Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Energy-Dispersive X-ray Spectroscopy (EDS) were used to characterize the CO$_2$ corrosion product layer formed on the carbon steel surface. The weight loss results showed that corrosion rate increased with SO$_2$ concentration with corrosion rate up to 7.45 mm/year while at 0% SO$_2$ the corrosion rate was 0.067 mm/year.

1. Introduction

Carbon capture and storage (CCS) is a recent technology that has been developed to mitigate gradual increase of greenhouse gases by capturing CO$_2$ from the emission point and storing it into geological media [1-9]. During the process of CCS the captured CO$_2$ gas is compressed to the dense phase or supercritical state where temperature and pressure are over 31.1°C and 74.14 bar, respectively, in order to make it easier and less costly to transport [10-11]. According to the CO$_2$ phase diagram calculated by [11], the two-phase or subcritical CO$_2$ phase exists between pressures 7 to 73 bar and temperatures -50°C to 30.978°C. The variation of underground properties increases the likelihood of the subcritical CO$_2$ phase in the pipeline and in the presence of sulfur dioxide (SO$_2$) as one of the emitted CO$_2$ constituents, a corrosive environment can prevail. While most reported work have focused on the supercritical CO$_2$ environment during pipeline transportation, the necessity to understand the subcritical CO$_2$ environment has gained large interest from other researchers. [4] & [12] reported that the present free H$_2$O in the pipeline will react with SO$_2$ to form a corrosive sulfuric acid which will lead to the passivation of the steel pipeline surface. Subcritical CO$_2$ thus presents a new challenge in the CCS operation and the current study was aimed at addressing this challenge by identifying carbon steel corrosion potential under subcritical CO$_2$ in the presence of various SO$_2$ concentrations as an impurity. Weight loss method was used to carry out corrosion experiments through a high pressure reactor. Scanning electron microscope (SEM) and X-Ray Diffraction (XRD) were used to study the morphology of the corroded carbon steel surface.
2. Experimental procedure

2.1. Materials
Carbon steel specimen with the chemical 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 and only 16 × 10 mm 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 [13]. 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 SO₂ 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).](image)

**Table 1. Experimental conditions**

| Sample # | Pressure (bar) | Temperature (°C) | Exposure Time (hours) | CO₂ (%) | SO₂ (%) |
|----------|---------------|------------------|-----------------------|---------|---------|
| 1        | 60            | 25               | 336                   | 100     | 0       |
| 2        | 60            | 25               | 336                   | 99.5    | 0.5     |
| 3        | 60            | 25               | 336                   | 98.5    | 1.5     |
| 4        | 60            | 25               | 336                   | 95      | 5       |
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.

\[
CR = 8.76 \times 10^4 \frac{\Delta m}{\rho \cdot A \cdot t}
\]

where \( CR \) is the corrosion rate, mm/year; \( \Delta m \) is the weight loss of the specimen, g; \( \rho \) is the density of the specimen, g/cm\(^3\); \( A \) is the area of the specimen, cm\(^2\); \( t \) is the immersion time, hour.

3. Results
3.1. Weight loss Results
Figure 1 shows the relationship between corrosion rate of carbon steel and SO\(_2\) concentration at the specified operating conditions. Figure 2 shows that the corrosion rate increased significantly when 0.5% SO\(_2\) was introduced into the system which saw the corrosion rate to be 1.84 mm/year. At this point it is already observed that SO\(_2\) has a huge impact on the corrosion behaviour in comparison to the pure CO\(_2\) scenario. This becomes more evident when the SO\(_2\) concentration is increased to 1.5% further to 5% which gave corrosion rate values of 3.64 mm/year and 7.45 mm/year. A linear trend is observed on the corrosion rate versus SO\(_2\) concentration. The mechanism behind SO\(_2\) increasing corrosion rate so drastically can be explained by the formation of FeSO\(_3\) when SO\(_2\) is added in the supercritical CO\(_2\) as shown in equations (2) & (3):

\[
SO_2 + H_2O \rightarrow SO_3^{2-} + 2H^+
\]

\[
Fe^{2+} + SO_3^{2-} \rightarrow FeSO_3
\]

FeSO\(_3\) is one of the corrosion products that form on the steel surface when SO\(_2\) is added therefore increasing the corrosion rate drastically [12]. On the experiments conducted by [12] at 80 bar, 50°C and 24 hours exposure using a carbon steel specimen, the corrosion rate increased dramatically from 0.38 mm/year to 5.6 mm/year when 1% SO\(_2\) (0.8 bar SO\(_2\) partial pressure) was added. The corrosion behaviour upon SO\(_2\) addition is similar to the one obtained in the current study, the highest corrosion rate obtained by [12] was 5.6 mm/year while in this study is 7.45 mm/year indicating similar trends on SO\(_2\) effect towards corrosion rate.
Figure 2. Relationship between corrosion rate and SO$_2$ concentration under subcritical CO$_2$ environment.

3.2. Photographic Images on Steel Surface
The type of corrosion attack that took place on the carbon steel surface was identified after corrosion product removal. The green compact scale observed on the samples exposed to subcritical CO$_2$/SO$_2$, i.e. images a) to d) from figure 3, is believed to be iron sulphite hydrate which is in line with the observation made by [8]. Uniform corrosion was observed on the carbon steel sample exposed to pure subcritical CO$_2$ (0% SO$_2$), i.e. image e) from figure 3. This is a similar observation made by [14] after exposing carbon steel to the environment that is almost similar to the one used in this study, i.e. supercritical CO$_2$ (100 bar and 25$^\circ$C) with 1220 ppmv H$_2$O, 0 ppmv SO$_2$ for 336 hours.

The introduction of SO$_2$ into the subcritical CO$_2$ environment appeared to have caused pitting corrosion as pit areas started to be visible when the SO$_2$ concentration in subcritical CO$_2$ was increased from 0 to 0.5% (image f) from figure 3). [14] also observed pit spots on the carbon steel surface when he increased the SO$_2$ concentration from 0 to 344 ppmv in the supercritical CO$_2$ with 1220 ppmv H$_2$O and 336 hours of exposure period. The introduction of SO$_2$ into the subcritical CO$_2$ environment provided the sulphite ions, which are very aggressive to passive metal surfaces generally consisting of chromium and nickel such as, the carbon steel used in this study. [4] also observed pitting corrosion in the presence of sulphate, sulphite and thiosulphate or sulphide.

3.3. Surface Morphology
Figure 4 shows the SEM micrograph of the carbon steel sample exposed to subcritical CO$_2$ with different SO$_2$ concentrations. The SEM image in figure 4 A) shows carbon steel microstructure exposed to pure subcritical CO$_2$ with neither SO$_2$ (0% SO$_2$) nor any impurity present. A slight metallic luster was observed on the steel surface exposed to pure subcritical CO$_2$ (figure 4 a)) which suggested that the corrosion scale did not form on the entire carbon steel surface. This agrees well with the low corrosion rate (0.07 mm/year) obtained from the weight loss results under pure subcritical CO$_2$ with 0% SO$_2$. Furthermore, the introduction of SO$_2$ as an impurity in the subcritical CO$_2$ environment appears to be even more destructive than pure CO$_2$ as far as corrosion is concerned. The SEM images shown in figure 4 b), c) and d) when SO$_2$ concentration was increased to 0.5, 1.5 and 5% respectively also revealed that the increase in SO$_2$ concentration leads to the formation of more corrosion products ultimately destructing carbon steel surface. It can also be observed that corrosion scale on the carbon steel surface becomes more compact with the increase in SO$_2$ concentration with pit area starting to be visible on the surface exposed to 5% SO$_2$. [8] presented SEM images that showed a similar corrosion
behavior but much stronger steel surface deformation as he operated at supercritical (100 bar) rather than subcritical (60 bar) CO$_2$ with SO$_2$ concentrations of 0.2%, 0.7%, 1.4% and 2.0%.

Figure 3. Photographic images (20 cm) of carbon steel surface exposed to subcritical CO$_2$ before corrosion products removal at; a) 0% SO$_2$, b) 0.5% SO$_2$, c) 1.5% SO$_2$, & d) 5% SO$_2$. After corrosion products removal at; e) 0% SO$_2$, f) 0.5% SO$_2$, g) 1.5% SO$_2$, & h) 5% SO$_2$.

FeSO$_3$ (Green layer) Pit spots

Figure 4. SEM images after subcritical CO$_2$ corrosion experiments with; a) 0% SO$_2$, b) 0.5% SO$_2$, c) 1.5% SO$_2$, & d) 5% SO$_2$. 
3.4. Phase Analysis
Figure 5 shows the XRD spectra of the carbon steel samples exposed to subcritical CO$_2$ environment with different SO$_2$ concentrations. Iron sulphite hydrate (FeSO$_3$·3H$_2$O) was detected in all tested SO$_2$ concentrations which confirms the observation made on the photographic images of the carbon steel samples at low magnification before corrosion product removal. The formation of FeSO$_3$·3H$_2$O on the carbon steel surface was due to the presence of SO$_2$ in the subcritical CO$_2$ environment and can be explained by equation (4) [8]:

$$Fe + SO_2 + (x + 1)H_2O \rightarrow FeSO_3 \cdot xH_2O + H_2 \quad (4)$$

The XRD analysis conducted by [4], [8] & [10] under supercritical CO$_2$ with different SO$_2$ concentrations reported FeSO$_3$·3H$_2$O as the major component on the tested steel surfaces. The dominance of FeSO$_3$·3H$_2$O can be explained by the high SO$_2$ solubility at high pressures (supercritical state) leading to greater production of sulphite ions [8].

![XRD spectra](image)

**Figure 5.** Superimposed diffractions of 0.5%, 1.5% and 5% SO$_2$ under subcritical CO$_2$ environment.

4. Conclusion
- An increase in SO$_2$ concentration in subcritical CO$_2$ environment rapidly increases the corrosion rate of carbon steel.
- In the presence of SO$_2$ in the CO$_2$ environment, FeSO$_3$·3H$_2$O was observed to be another significant component as one of the corrosion products under subcritical CO$_2$ environment.
- In the absence of SO$_2$ in the subcritical CO$_2$ environment, FeCO$_3$ appears to be the dominant component on the carbon steel surface.
- The introduction of SO$_2$ in the subcritical CO$_2$ environment gave rise to the pitting corrosion while only uniform corrosion was observed on the carbon steel surface under pure subcritical CO$_2$. 

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