

Corrosion Behavior of Carbon Steel under H₂SO₄ Droplets and Dense Phase CO₂

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ABSTRACT

As carbon capture and storage advances, understanding material degradation in dense phase CO₂ is crucial. Impurities like SO₂, NO₂, O₂, H₂S, and H₂O can generate strong acids that accelerate corrosion. This study examines the corrosion of X65 carbon steel exposed to concentrated sulfuric acid droplets under dense phase CO₂ conditions. Before testing with sulfuric acid, the stability of a water droplet on 316 stainless steel was assessed in a 20 L autoclave equipped with sapphire windows. The water droplet remained stable through CO₂ phase changes. At atmospheric pressure, concentrated sulfuric acid (95 wt. %) showed rapid spreading on 316 stainless steel and X65 carbon steel due to low contact angles. Therefore, a custom X65 steel holder was designed to retain 0.5 mL of acid for corrosion studies. The corrosion test was performed under dense phase CO₂ at 45 °C and 84 bar for five days. Corrosion evolution was monitored via a camera placed near the autoclave window. After exposure, weight loss measurements indicated a corrosion rate of 0.24 mm/year. Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy analysis revealed Fe, S, and O, suggesting iron sulfate (FeSO₄) as the main corrosion product on the X65 steel surface.

Key words: H₂SO₄; Dense Phase CO₂; Carbon Capture; Corrosion, Carbon Steel,

INTRODUCTION

Global warming, driven primarily by the accumulation of CO₂ in the atmosphere, has become a central global concern. To mitigate rising CO₂ levels, strategies such as carbon capture, transport, storage, and transport have been developed.¹ Captured CO₂ streams often contain low concentration impurities, including NO_x, SO_x, H₂S, O₂, and H₂O. The presence of these impurities can lead to the formation of highly corrosive strong acids, such as nitric acid (HNO₃) and sulfuric acid (H₂SO₄), which are highly

corrosive.^{2,3} For example, Svenningsen et al. investigated the effect of H₂O, NO₂, SO₂, O₂, and H₂S impurities on the corrosion behavior of X65 in dense-phase CO₂ at 99 bar and 25 °C. The study showed that chemical reactions among these impurities can generate strong acid droplets, which in turn initiate corrosion of carbon steel.⁴ Dugstad et al. examined the influence of water, O₂, and SO₂ on X65 corrosion in dense-phase CO₂. They found no corrosion was observed in pure CO₂ or in CO₂ with 500 ppm water and O₂, whereas the addition of SO₂ induced corrosion through sulfuric acid formation, evidenced by FeSO₄ formation on the steel surface.⁵ The corrosion behavior of carbon steel in aqueous H₂SO₄ solutions has been extensively investigated and is well documented.⁶ In H₂SO₄ solutions, the formation of FeSO₄ suppresses the corrosion rate, with the extent of suppression depending on the acid concentration and the solubility of FeSO₄.^{6,7} To the best of our knowledge, no studies have reported corrosion in dense-phase CO₂ environments in the presence of H₂SO₄, except for those involving impurities that led to the in situ formation of sulfuric acid droplets.³ In the present study, we investigate the corrosion of X65 under H₂SO₄ (95 wt.%) droplets in dense-phase CO₂ at 84 bar and 45 °C. Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (SEM-EDS) was employed to examine the morphology and elemental composition of the corrosion products. The corrosion rate was determined using the weight loss method.

EXPERIMENTAL PROCEDURE

Materials and Equipment

The experimental setup consisted of a 20 L 316 stainless steel autoclave equipped with sapphire windows for visual observation under high-pressure CO₂ (Figure 1). A light source and a camera were used to capture images of the samples over time. A holder fabricated from X65 steel, with dimensions of 0.3 cm depth and 2.5 cm diameter, was designed to contain sulfuric acid while simultaneously serving as a corrosion sample, as shown in Figure 2.

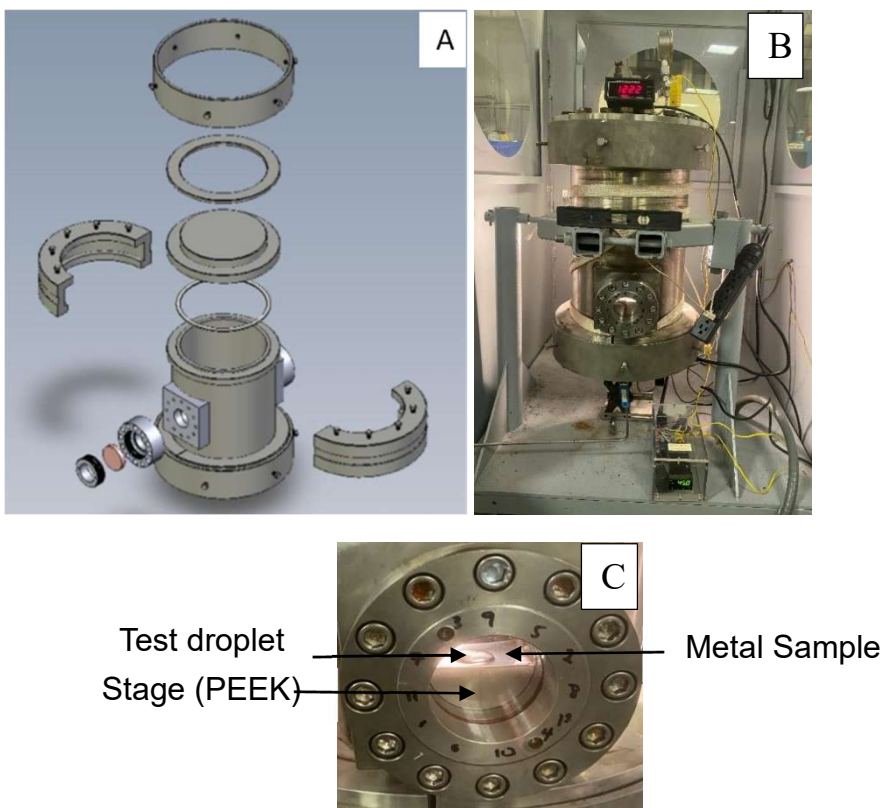


Figure 1. (A) Schematic representation of the 20 L autoclave, (B) photograph of the actual autoclave and (C) metal sample with droplet on the PEEK stage.

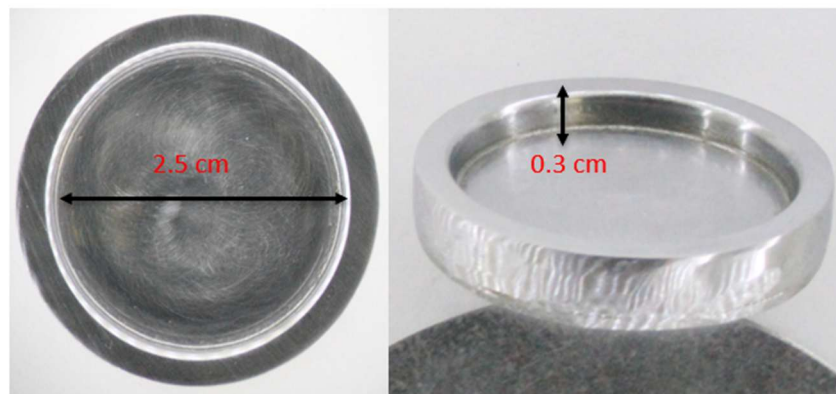


Figure 2. Designed X65 holder to contain sulfuric acid and serve as a corrosion coupon

Tests Procedure

Before conducting corrosion tests of X65 carbon steel in dense CO_2 with sulfuric acid droplets, the stability of a 0.5 mL water droplet on a 316 stainless steel sheet (25 cm^2) was examined during the pressurization step where, CO_2 phase changes from gaseous to liquid. This was achieved by gradually pressurizing the autoclave to 76 bar at room temperature (25°C), holding each step for approximately 30 minutes. Building on these observations, the behavior of sulfuric acid droplets was then studied on 316 stainless steel and X65 samples at atmospheric pressure to establish baseline droplet stability before high-pressure corrosion testing.

Finally, the corrosion of X65 in the presence of sulfuric acid under dense phase CO_2 was investigated at 84 bar and 45°C . For both high-pressure tests, the polyether ether ketone (PEEK) sample holder was first positioned on the inner edge of the sapphire window, and the corrosion samples were placed on the holder with 0.5 mL of sulfuric acid applied to each coupon. Oxygen was then removed by purging the autoclave with CO_2 until the concentration dropped below 5 ppb, measured using an Orbisphere oxygen sensor. After oxygen removal, the autoclave was pressurized to 84 bar at a constant temperature of 45°C , allowing CO_2 to transition directly from the gas to the supercritical state without passing through the liquid phase. The CO_2 source used in the experiment contained 25 ppm of water. A camera was positioned in front of one of the sapphire windows to capture photos over time, while a light source was placed on the other side of the autoclave, behind the opposite window, to provide illumination for clearer imaging. The test was conducted over a period of five days. At the end of this period, the autoclave was slowly depressurized, and the X65 sample was retrieved for further analysis, including SEM-EDS and weight loss measurements.

RESULTS

Figure 3 demonstrates the stability of a water droplet placed on 316 SS sample under varying pressures in a 20 L autoclave. As shown, the droplet remains stable on the 316 SS sample as the pressure increases from 1 bar to the target pressure of 76.4 bar. The water droplet stayed stable and was not destroyed during pressurization.

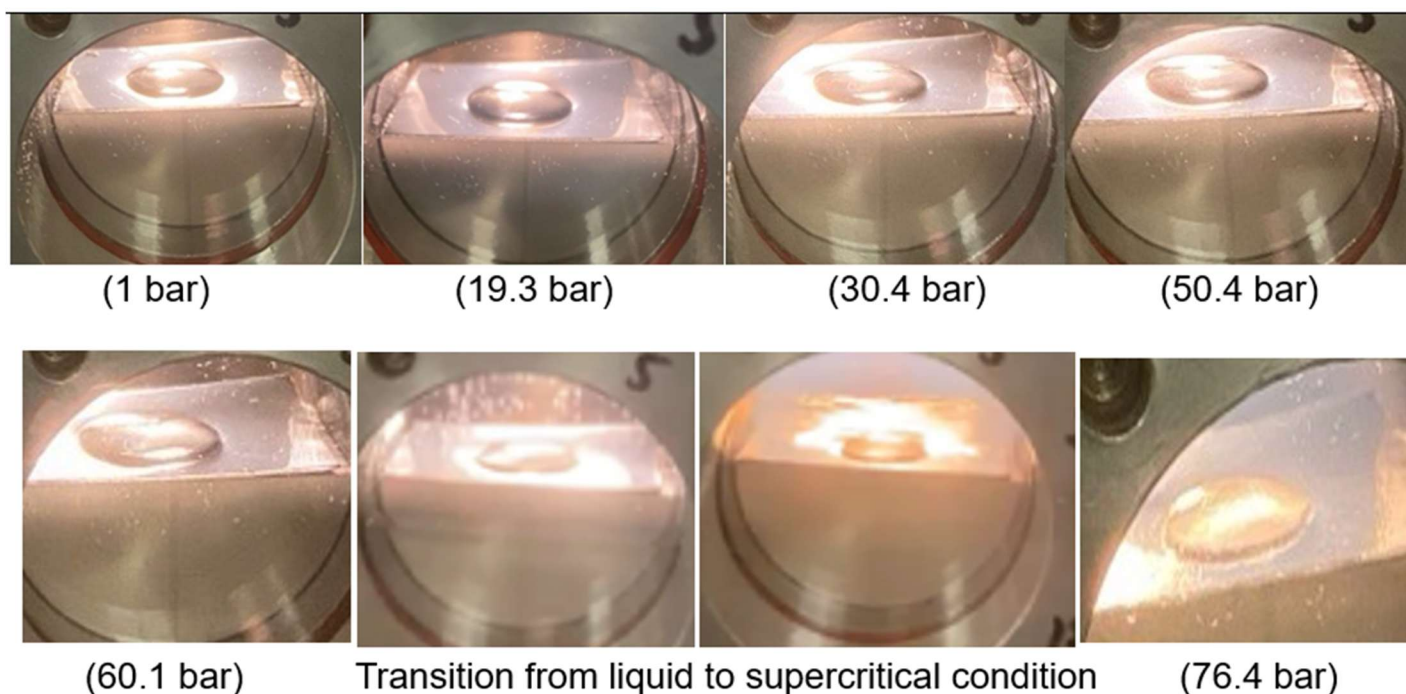


Figure 3. Stability of a water droplet under varying pressures in a 20 L autoclave.

Figure 4 shows the behavior of sulfuric acid (95 wt.%) droplets on (a) 316 SS and (b) X65 carbon steel under ambient conditions. As observed, the droplets spread on both surfaces and are unstable. This instability is attributed to the low contact angle and surface tension of the acid, caused by the immediate onset of the corrosion process when the droplets contact the samples.^{1,2} The droplet remained more stable on 316 SS than on X65. On X65, gas bubbles formed immediately upon contact, indicating the rapid onset of corrosion. The X65 sample experienced a mass loss of 2.7 mg during the 2 hours of exposure to acid at atmospheric pressure.

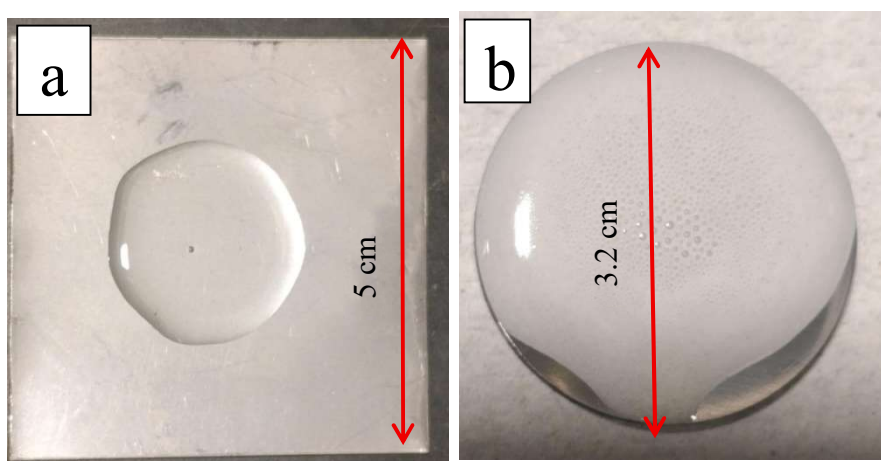


Figure 4. Sulfuric acid droplet behavior on (a) 316 SS, (b) X65 carbon steel.

To investigate the behavior of X65 in the presence of sulfuric acid under dense phase CO_2 , a sample holder made of X65 was designed as shown in Figure 2. This sample holder was filed with 0.5 ml of H_2SO_4 (95 wt.%) and put in 20L autoclave equipped with sapphire windows. The autoclave was pressurized with CO_2 to 84 bar at constant temperature of 45°C . The progress of corrosion over the course of 5 days was monitored using a camera place in the front of the sapphire window as shown in Figure 5. Although capturing very high-quality images was challenging, changes in light reflection at the

edges of the sample holder could indicate corrosion progress, as the surface became less shiny with the formation of corrosion products. The yellow/orange color observed on the stage is attributed to the reaction of sulfuric acid with PEEK, the stage material, which is known to react severely with sulfuric acid.

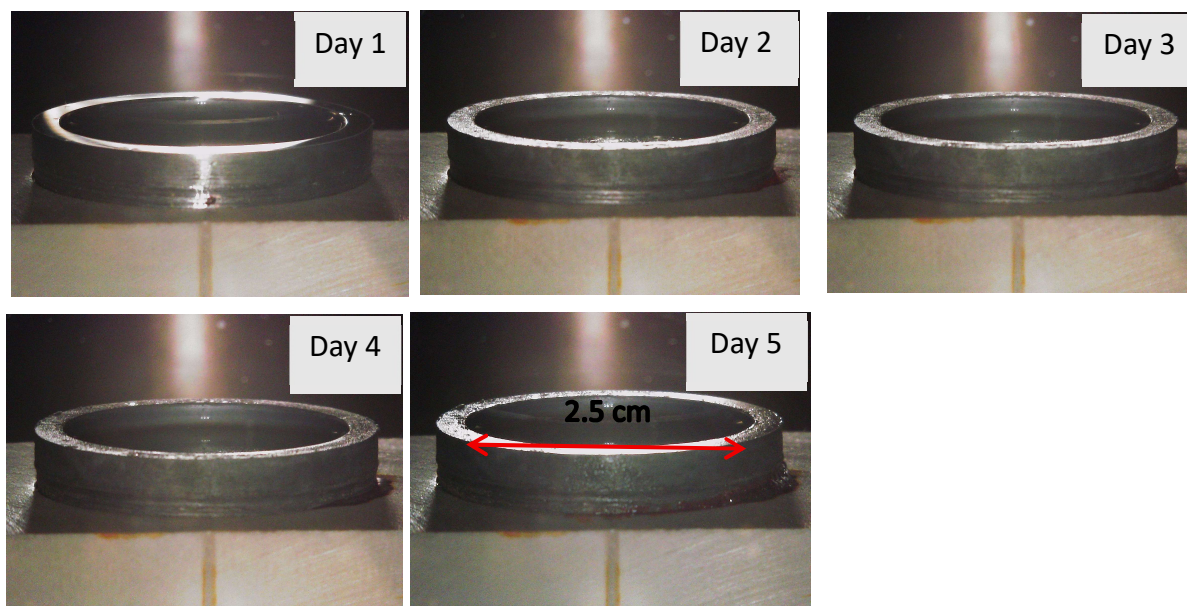


Figure 5. Corrosion evolution of X65 over the course of 5 days exposure to H_2SO_4 (95 wt.%) in dense phase CO_2 at 84 bars, at 45 °C.

At the end of the 5-day test, the X65 sample was retrieved, and post-corrosion analyses, including SEM-EDS and weight-loss measurements were performed. Figure 6 depicts the images of X65 sample at the end of the tests. Corrosion was observed both on the surface where H_2SO_4 was filled and along the edge of the sample.



Figure 6. X65 sample at the end of 5 days exposure to H_2SO_4 (95 wt.%) in dense phase CO_2 .

Figure 7 shows the SEM images and EDS analysis of X65 samples after 5 days exposure to H_2SO_4 (95 wt.%) in dense phase CO_2 at 84 bars and 45°C. Fe, S, and O were identified in the corrosion products by EDS, suggesting that iron sulfate (FeSO_4) is likely the main corrosion product formed on the X65 surface. After removing the corrosion products with Clarke's solution, the weight loss was measured, revealing an 18.8 mg mass loss over the 5-day exposure to H_2SO_4 (95 wt.%). This corresponds to a corrosion rate of 0.24 mm/year.

The corrosion resistance of carbon steel in sulfuric acid is controlled by the stability of the protective FeSO_4 layer, which depends on its solubility and the acid concentration. The lowest corrosion rate has been reported at around 70 wt.% H_2SO_4 .^{6,7} At concentrations above 70%, further increases in acid concentration enhance both the solubility of FeSO_4 and the corrosion rate of carbon steel. However, in the 90–100 wt.% range, increasing the acid concentration again decreases FeSO_4 solubility and reduces the corrosion rate.^{6,7} Dilution of sulfuric acid accelerates carbon steel corrosion by dissolving the protective FeSO_4 layer. This effect is particularly critical when sulfuric acid forms through impurity reactions in dense phase CO_2 , where water uptake can dilute the acid, destabilize the FeSO_4 layer, and intensify corrosion.

As mentioned above, the CO_2 used in the present experiment contained approximately 25 ppm of water. Given the strongly hygroscopic nature of sulfuric acid, this water could be absorbed into the acid droplets present on the sample surface. However, the measured low corrosion rate after 5 days of exposure suggests that such a limited amount of water was insufficient to significantly dilute the sulfuric acid droplets. Consequently, the acid concentration likely remained high, preventing any substantial acceleration of the corrosion process. This observation indicates that under the tested dense phase CO_2 environment, trace amounts of dissolved water at the level of 25 ppm do not provide enough capacity to alter the local chemistry at the droplet-metal interface to a degree that would enhance corrosion.

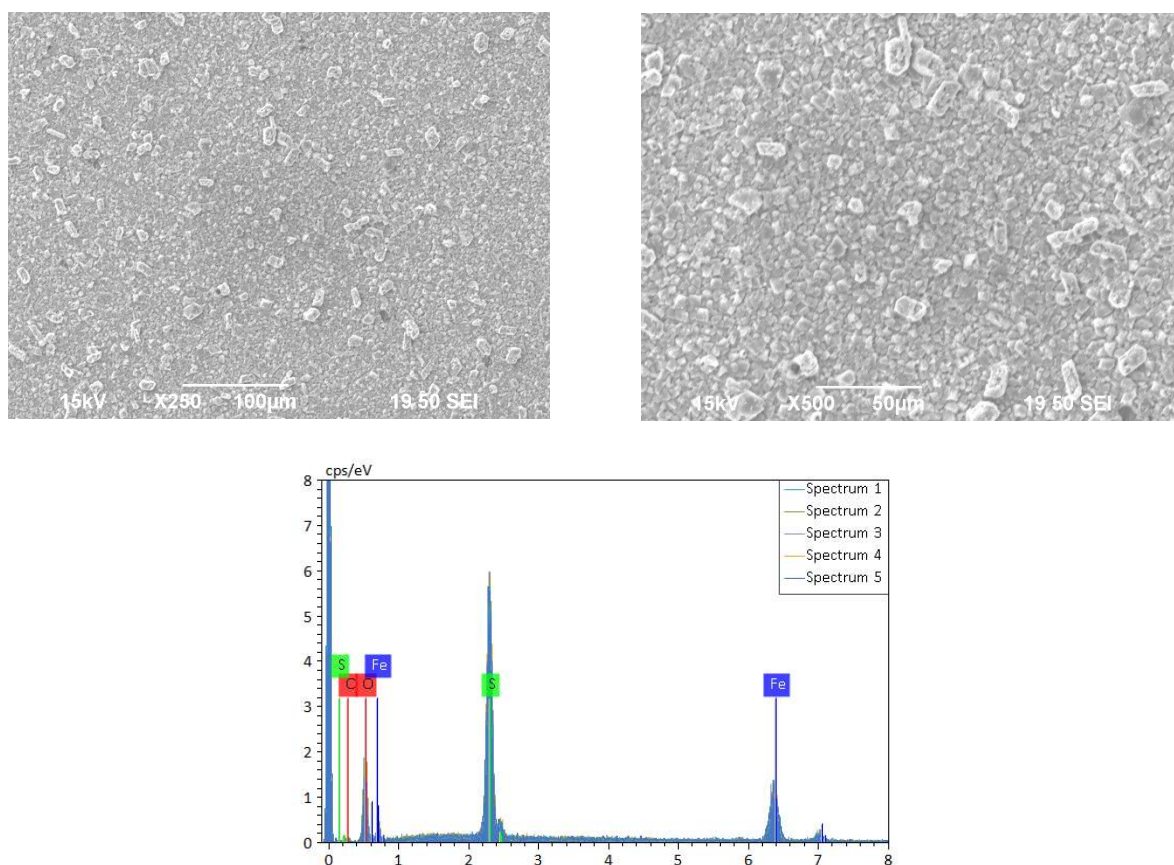


Figure 7. SEM images and EDS analysis of X65 sample after 5 days exposure to H_2SO_4 (95 wt.%) in dense phase CO_2 at 84 bars and 45 °C

CONCLUSIONS

- Water droplets on 316 SS remained stable across CO_2 phase transitions (gas $\rightarrow$ liquid $\rightarrow$ supercritical).

- H₂SO₄ (95 wt.%) droplets were unstable on both 316 SS and X65 at atmospheric pressure, requiring a custom X65 sample holder for testing.
- Under dense phase CO₂ (84 bar, 45 °C), exposure of X65 to 0.5 mL of H₂SO₄ (95 wt.%) for five days produced iron sulfate as the primary corrosion product, with a corrosion rate of 0.24 mm/y.
- The CO₂ stream contained ~25 ppm water, which may have been absorbed into H₂SO₄ due to its hygroscopic nature; however, this trace level was insufficient to dilute the acid or enhance corrosion.

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