

Effect of Sample Configuration on Autoclave Experiment in Dense Phase CO₂ with Impurities

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ABSTRACT

Corrosion plays an important role in the integrity management of the CO₂ transport pipeline, since carbon steels, the most common material utilized for pipeline construction, are susceptible to corrosion in the presence of impurities, such as water, SO₂, and NO₂. Autoclave tests have been used to examine the corrosion susceptibility and severity in this condition. However, studies have shown a range of corrosion rates in similar experimental conditions, and there are no standard methods for laboratory corrosion testing in dense phase CO₂ with impurities. In this study, the impact of sample configuration, one of the parameters that can affect the results of the corrosion experiment, is investigated. Autoclave experiments were conducted in dense phase CO₂ with O₂, SO₂, NO₂, H₂S, CH₄, and H₂O where the samples were placed either vertically or horizontally. Furthermore, horizontal samples were placed in different locations of the autoclave. The results showed that corrosion was observed on both sides of the vertical samples, while top side of each horizontal sample corroded more compared to the bottom side in some conditions. For horizontal samples, the corrosion rates could increase with the location from top to bottom of the autoclave depending on the combination of impurities.

Key words: CO₂ transport, carbon capture and storage, dense phase CO₂

INTRODUCTION

Corrosion plays an important role in the integrity management of the CO₂ transport pipeline since carbon steels, the most common material utilized for pipeline construction, are susceptible to corrosion in the presence of water.

It is well known that dry CO₂ does not corrode carbon steels, and negligible corrosion occurs at water-unsaturated conditions (below the solubility level) in dense phase CO₂ (liquid and supercritical). However, recent studies have reported that noticeable, and potentially severe, corrosion occurs at water-unsaturated conditions in dense phase CO₂ with the presence of impurities, such as O₂, H₂S, SO₂, NO₂, etc. due to interactions between chemical species that are not properly understood. Therefore, experimental works have been carried out to understand the corrosion risks associated with the dense phase CO₂ system^{1–5}. Carbon steel samples have been used in autoclave setups, but the corrosion rates from different apparatuses could vary even for similar conditions. Morland and Svenningsen pointed out the importance of proper CO₂ injection during experiment⁶. In addition to the injection procedure, the sample configurations, such as sample location in the autoclave, are often omitted in the experimental design, which could cause result variation as well.

The objective of this work is to investigate the impact of sample configuration on its corrosion rate in the dense phase CO₂ environment via exposure experiments and post-exposure surface characterizations with scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and Raman spectroscopy.

EXPERIMENTAL PROCEDURE

API 5L X65 carbon steel was machined into a rectangular type with a size of 3.8 cm × 1.3 cm × 0.3 cm. Prior to exposure, the specimens were grounded sequentially with #180, #400, and #600 grit silicon carbide paper with water flow. They were rinsed with deionized (DI) water, sonicated in an isopropyl alcohol bath for 60 seconds, and dried with lab air.

Corrosion tests were carried out in a high-pressure system, consisting of a 5 L Hastelloy autoclave, impurity injection/analysis system, and CO₂ booster pump. Specimens were placed in the autoclave and the heated autoclave was purged with dry CO₂ for 1 hour to remove any oxygen and humidity. After the autoclave cooled down with continuous dry CO₂ ingress, the dry CO₂ ingress was stopped, and the desired amount of deoxygenated DI water was added to the autoclave prior to adding other impurities. Once the autoclave was sealed, the autoclave temperature was adjusted to the test temperature, 25 °C. Then, the impurity gases were introduced to the autoclave using the gas injection system. The impurities were added from technical grade (ultra-high purity) SO₂, NO₂, H₂S, CH₄, N₂, and O₂ cylinders with a custom-built gas injection system. For NO₂ and CH₄, a mixture with CO₂ was used. For trace quantity of each impurity gas, the required number of moles of gas required in the autoclave was obtained by first injecting the gas into a cylinder of known volume at a known temperature and pressure. The gas was then “pushed” into the autoclave with CO₂. The moles of each impurity required to reach the required concentrations were calculated from the Peng-Robinson equation of state. The impurities were injected into the autoclave separately one by one. The sequence of impurity injection was following the order: H₂O, CH₄, N₂, H₂S, SO₂, O₂, NO₂. High pressure CO₂ sourced from high-purity bottles was added to the autoclave aided with a gas booster pump to achieve the desired working pressure.

In order to track the impurity concentration during the test, the concentration of impurities was measured with a gas detector tube by taking a small volume sample of the mixture from the autoclave daily. The measurement error is +/- 10%. Impurities were not replenished during the test.

Table 1 shows the test matrix for the present study. Four corrosion tests were performed with 2 different sample configurations as shown in Figure 1. Tests 1 and 2 were conducted with in total two vertical positioned X65 specimens (Figure 1a) whereas Tests 3 and 4 were performed with in total six horizontal positioned X65 specimens at different locations in the autoclave (Figure 1b).

The water solubility limit at the testing pressure and temperature is above 3000 ppm in the dense phase CO₂⁷. In order to make sure all impurities distributed homogeneously inside the experimental chamber instead of phasing out in the undissolved water, water contents were controlled to be lower than 3000 ppm in this work (200 ppm and 1000 ppm). The ppm unit used in the present study represents mole basis concentration.

Table 1
Test matrix for the corrosion test

Test No.	T (°C)	P(bar)	CO ₂	O ₂ (ppm)	H ₂ S (ppm)	SO ₂ (ppm)	NO ₂ (ppm)	CH ₄ (ppm)	H ₂ O (ppm)	N ₂ (ppm)	Period (day)
1	25	100	Bal	100	100	100	100	100	200	500	2
2	25	100	Bal	100	100	100	100	100	1000	500	2
3	25	100	Bal	100	100	100	100	100	200	500	2
4	25	100	Bal	100	100	100	0	100	1000	500	2

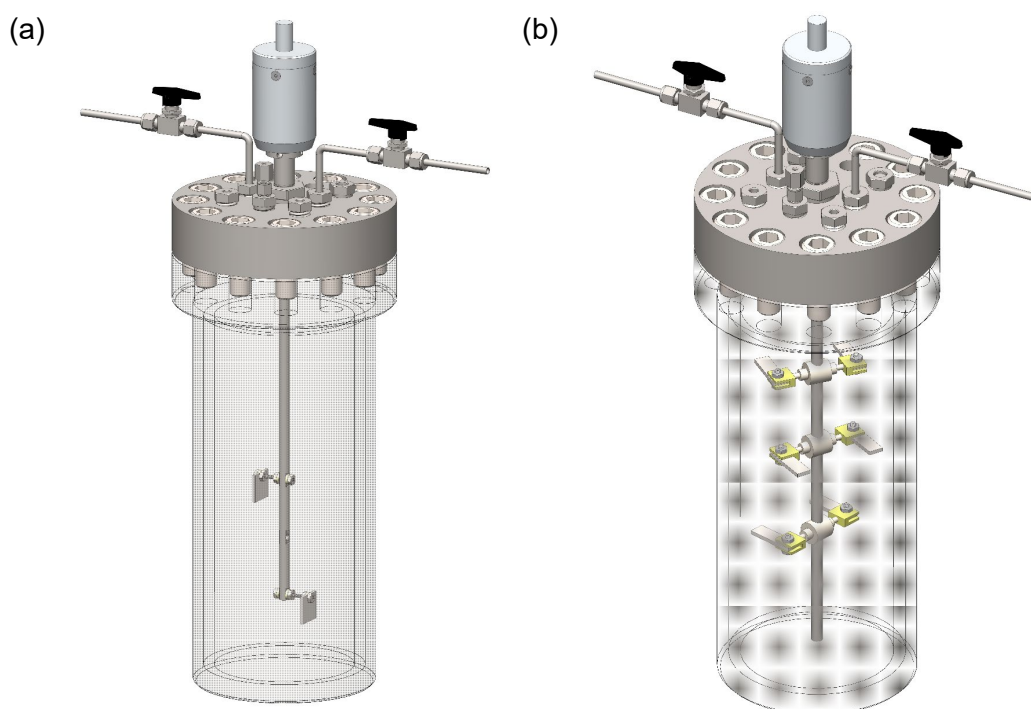


Figure 1: Schematic of sample layouts in the 5L autoclave: (a) two-sample vertical arrangement, (b) six-sample horizontal arrangement. Samples were arranged to not overlap with each other.

Uniform corrosion rate of carbon steel was measured by weight loss (WL) method at the end of 48 hours exposure. After surface analysis, the samples were cleaned by using Clarke's solution per ASTM⁽¹⁾ G1⁸. The samples were then rinsed in DI water and isopropanol, dried, and weighed to 0.1 mg. The average corrosion rate during the test period was calculated by the following equation:

⁽¹⁾ ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959.

$$\text{Corrosion rate (mm/year)} = \frac{8.76 \times 10^4 \times \text{weight loss (g)}}{\text{area (cm}^2\text{)} \times \text{density (g/cm}^3\text{)} \times \text{time (hour)}}$$

After each test, corrosion product layers were analyzed using a variety of surface analytical tools, including SEM, EDS, and Raman microscopy, to characterize corrosion product morphology and composition.

RESULTS AND DISCUSSION

Vertical Samples

Two vertical X65 specimens were exposed to dense phase CO₂ (100 bar and 25°C) in Test 1 (with 200 ppm water and 100 ppm of O₂, H₂S, SO₂, NO₂, and CH₄) and Test 2 (with 1000 ppm water and 100 ppm of O₂, H₂S, SO₂, NO₂, and CH₄). The samples were placed vertically in these tests. The photos of specimens after exposure and after cleaning are illustrated in Figure 2. The post exposure samples (Figure 2, before cleaning) were covered with dark corrosion products. Localized corrosion was not observed on any of the samples after removing the corrosion products. The corrosion rate of the Test 1 upper sample was 0.08 mm/year, and the lower one was 0.28 mm/year. The corrosion rate of the Test 2 upper sample was 0.06 mm/year, and the lower sample corrosion rate was 0.07 mm/year.

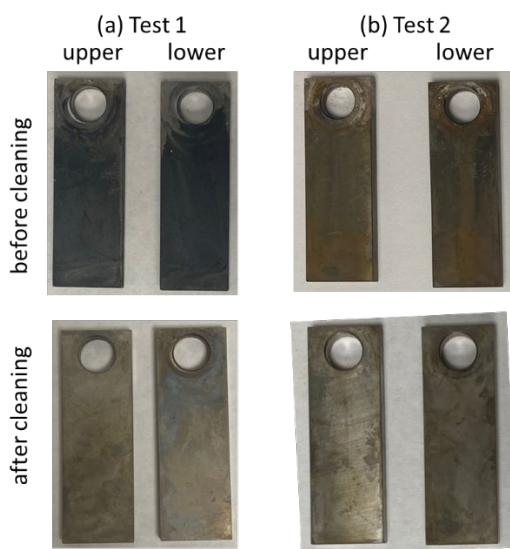


Figure 2: Photos of (a) Test 1 and (b) Test 2 vertical samples before and after cleaning. “Upper” and “lower” are the locations where the samples were in the autoclave.

The surface morphology and corrosion products were examined with SEM and EDS. One characteristic area of each test is shown in Figure 3. Test 1 sample in Figure 3a featured nodule-like bright spots, a thick corrosion product layer, and a thin corrosion product layer. These were analyzed by using EDS, and they were all enriched with C, S, O, and Fe. Test 2 sample in Figure 3b had less corrosion product accumulation than Test 1 sample, since the polishing lines were still visible (Figure 3b, 500x magnification), not covered by corrosion products. Elemental analysis showed that both the nodule-like spots and the surface corrosion product layer were composed of Fe, S, O, and C, likely FeSO₄ and FeCO₃.