

## **Pitfalls and Artefacts in Corrosion Experiments With Dense Phase CO<sub>2</sub>**

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### **ABSTRACT**

There was a large variation of the reported corrosion rates for the condition when the water is fully dissolved in the dense phase CO<sub>2</sub>. Some laboratories measured insignificant corrosion rates while other laboratories reported corrosion rates as high as 3 mm/y.

To better understand the corrosion of carbon steel in a CO<sub>2</sub> transport system, it is important to be able to explain the large spread in reported corrosion rates. Is there naturally a large variation of corrosion rates in this type of systems, or can it be explained by for example differences in the experimental approach?

Several experiments were performed with dense phase CO<sub>2</sub> and water at 25 °C and 40 °C and it was clearly shown that certain experimental approaches could result in overestimation of corrosion rates. It was shown that as long as water is fully dissolved in the CO<sub>2</sub> phase, up to the saturation limit, the corrosion rates in dense phase CO<sub>2</sub> is very low, around 0.001 mm/y.

**Keywords:** CO<sub>2</sub> corrosion, CCUS, free water phase, dissolved water, experimental artefacts, dissolution time

### **INTRODUCTION**

CO<sub>2</sub> can cause corrosion of carbon steel under certain conditions, and it is therefore a key element in the integrity management of CO<sub>2</sub> transport pipelines to have good understanding of the corrosion processes.

From a corrosion perspective it is important to distinguish between the two principally different situations when water is present as a separate phase and when the water is fully dissolved in the CO<sub>2</sub> phase. The corrosion mechanism is most likely the same, but the rates will be significantly different since the amount of water differs by many orders of magnitude. The presence of liquid water is a key factor to drive the corrosion reactions and will result in high corrosion rates, especially if the water phase is large compared to the steel surface.<sup>1,2</sup> Water can probably be a limiting reactant by itself, for

example in thin water surface films. Thin water films will force rapid saturation and precipitation of corrosion products that reduces or prevents further corrosion.

### **Corrosion when water is present as a separate phase**

It is well known that CO<sub>2</sub> transport pipelines must be operated in a manner that prevents liquid water to be present. However, accidental water ingress may still occur due to equipment malfunction, carry-over from the compression stage, or other types of operational errors.

### **Corrosion in CO<sub>2</sub> with dissolved water**

During normal operation, the transported CO<sub>2</sub> should only contain a small amount of water, at a level where it will be fully dissolved in the CO<sub>2</sub> phase. For several years the understanding has been that exposure to CO<sub>2</sub> with fully dissolved water leads to very low corrosion rates for carbon steel.<sup>3-11</sup> These low rates (much less than 0.010 mm/y) are usually acceptable for the pipeline operators. However, corrosion rates in the range of 0.5 to 3 mm/y have been reported for conditions where the water nominally should be fully dissolved in the CO<sub>2</sub> phase.<sup>12-15</sup> A summary of published corrosion rates for conditions where the water should be fully dissolved in the CO<sub>2</sub> phase is listed in Table 1. Hua et al.<sup>16</sup> reported that the corrosion rate was about 0.1 mm/y with 8.0 MPa CO<sub>2</sub> and 35 °C when the water content was 3400 ppmv, at the solubility limit. Furthermore, the localised corrosion penetration rate was reported to be as high as 0.9 mm/y. Even when the water content was reduced to 700 ppmv the penetration rate was as high as 0.2 mm/y. Similar pitting corrosion was also reported by Sim et al.<sup>17</sup> although the general corrosion was 0.03 mm/y for a large range of water contents (from 244 to 3670 ppmv water at 8.0 MPa and 40 °C). These relatively high corrosion rates are in contrast with the work of Morland et al. who reported negligible corrosion rates (~0.001 mm/y) as long as the water was fully dissolved in the CO<sub>2</sub> phase.<sup>18</sup> Even if many of these experiments were carried out in different manners, there are conflicting results for conditions where the water is dissolved in the CO<sub>2</sub> phase.

For atmospheric conditions, corrosion may occur even if *liquid* water is not present. It is often referred to 60 - 80% relative humidity (RH) as a starting point for corrosion in air.<sup>19</sup> The reason is that the thickness of the adsorbed water film (some monolayers) on the metal surface increases with increasing humidity, and at about 60% RH the surface water film exceeds a critical thickness where its properties approaches those of a bulk water phase in which corrosion may take place.<sup>20,21</sup> The conditions in a system with liquid or supercritical CO<sub>2</sub> are naturally very different from atmospheric conditions, especially since the amount of CO<sub>2</sub> is several orders of magnitude higher. However, it is not unlikely that the same principles with surface absorption of water do apply. If so, there is probably an equilibrium between the water content in the CO<sub>2</sub> phase and the thickness of the absorbed water film. At a certain critical thickness (water content in the CO<sub>2</sub> phase) the surface film will achieve “bulk water” properties, after which it can absorb CO<sub>2</sub> and form carbonic acid, which again may lead to corrosion. Hua et al.<sup>22</sup> observed an increase in general corrosion between 1300 to 1800 ppmv, which equals about 40 to 54% of the water solubility limit in CO<sub>2</sub>.

Since water is essential for the corrosion process, it is crucial to maintain good control of water throughout the experiments' duration, in particular for experiments near the solubility limit. The water solubility in CO<sub>2</sub> is strongly affected by temperature and pressure, particularly when the CO<sub>2</sub> changes from gaseous to liquid or supercritical state, as shown in Figure 1. Thus, the process of adding water to the CO<sub>2</sub> phase and subsequent pressurisation and depressurization procedures may affect corrosion in many ways. A series of experiments was therefore carried out to systematically study these effects.

There are no recognized standards for corrosion testing in dense phase CO<sub>2</sub>, and many different approaches are used. The large discrepancy between experiments seemingly conducted at the same conditions needs to be explained. Is there a naturally large spread in the corrosion rates under these conditions, or are they related to the way the experiments are carried out? For example, the experimental setup, operational procedure or control of water are factors that in principle could affect the results.

**Table 1**  
*Reported corrosion rates for carbon steel exposed to CO<sub>2</sub> with dissolved water.*

| Pressure (MPa) | Temp. (°C) | Dissolved H <sub>2</sub> O (ppmv) | Exposure time (days) | Flow/mixing | Corrosion rate (mm/y) | Reference |
|----------------|------------|-----------------------------------|----------------------|-------------|-----------------------|-----------|
| 6.3            | 22         | 610                               | 42                   | No          | No                    | 6         |
| 7.6            | 40         | 244                               | 0.3                  | No          | 1.2                   | 12        |
| 7.6            | 40         | 2440                              | 0.3                  | No          | 2.3                   | 12        |
| 7.6            | 40         | 4880                              | 0.3                  | No          | 2.5                   | 12        |
| 7.9            | 31         | 100                               | 0.3                  | No          | 1.1                   | 14        |
| 7.9            | 31         | 1000                              | 0.3                  | No          | 2.5                   | 14        |
| 8.0            | 50         | Sat*                              | 1                    | No          | 0.4                   | 13        |
| 8.0            | 40         | 244-3670                          | 7                    | No          | 0.4 - 0.6             | 17        |
| 8.0            | 35         | 300                               | 2                    | No          | 0.003                 | 22        |
| 8.0            | 35         | 700                               | 2                    | No          | 0.005                 | 22        |
| 8.0            | 35         | 1200                              | 2                    | No          | 0.01                  | 22        |
| 8.0            | 35         | 1770                              | 2                    | No          | 0.03                  | 22        |
| 8.0            | 35         | 3500                              | 2                    | No          | 0.1                   | 22        |
| 8.2            | 35         | Sat*                              | 5                    | Yes         | 0.026                 | 23        |
| 8.2            | 35         | Sat*                              | 5                    | Yes         | 0.032                 | 23        |
| 10             | 25         | 1220                              | 18                   | Yes         | <0.01                 | 24        |
| 10             | 20         | 1220                              | 30                   | No          | No                    | 25        |
| 10             | 25         | 488                               | 14                   | Yes         | No                    | 26        |
| 10             | 8-25       | 100-2500                          | 30                   | Yes         | 0.001                 | 18        |
| 10             | 35         | 2500                              | 14                   | Yes         | No                    | 18        |
| 13             | 40         | 4880                              | 0.3                  | No          | 3.5                   | 12        |
| 15             | 80         | Sat*                              | 28                   | No          | 0.1                   | 27        |

\*Water added in excess to ensure that the CO<sub>2</sub> phase was fully saturated with water.

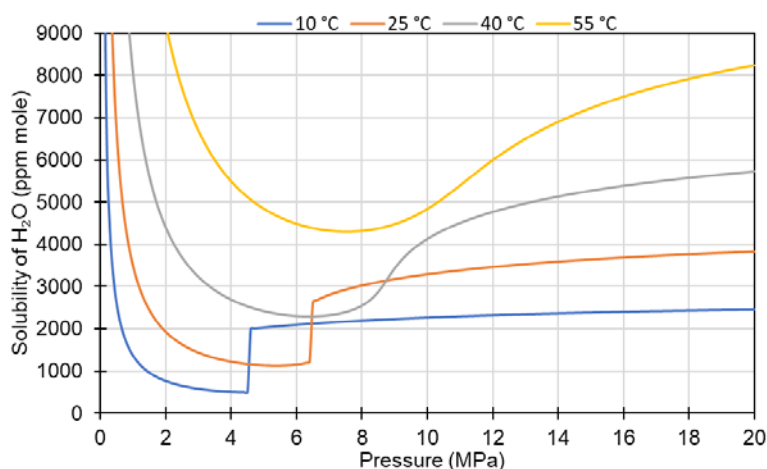


**Figure 1:** Water solubility in CO<sub>2</sub> as a function of pressure and temperature, calculated with a thermodynamic model.<sup>28,29</sup>

## EXPERIMENTAL PROCEDURE

The experiments were performed in a transparent autoclave and observations of artefacts were recorded by still pictures or videos. The autoclave consists of a steel body (SS316), soda lime glass (1 cm thick, CO<sub>2</sub> exposed), and 7 cm thick poly carbonate plates as pressure support, see Figure 2A.

A tray of polyether ether ketone (PEEK) was placed inside the autoclave to keep track of the water and to act as coupon holder when carbon steel (S355MC grade) was present, see Figure 2B and C. A booster pump was used to feed the system with pure (99.999%) CO<sub>2</sub> at a high pressure. A liquid pressure regulator was used to provide a constant pressure of about 10 MPa. Liquid water (osmotic water) was injected with a precision syringe pump either before or after pressurization with CO<sub>2</sub> (variation between experiments). The autoclave was located inside an air heated cabinet.

The carbon steel corrosion coupons were ground with P1000 grit paper and then cleaned with first acetone and then isopropanol in ultrasonic bath before mounting inside the autoclave. Depressurization was one of the parameters that were studied, and several different approaches were used. Normally, the moist CO<sub>2</sub> was diluted with dry CO<sub>2</sub> to a water content of about 50 ppmv before depressurization was started. However, in some experiments the CO<sub>2</sub> was water saturated when the depressurization started, and the speed of depressurization was varied. The exposed steel coupons were rinsed in isopropanol to remove any traces of water before they were dried.

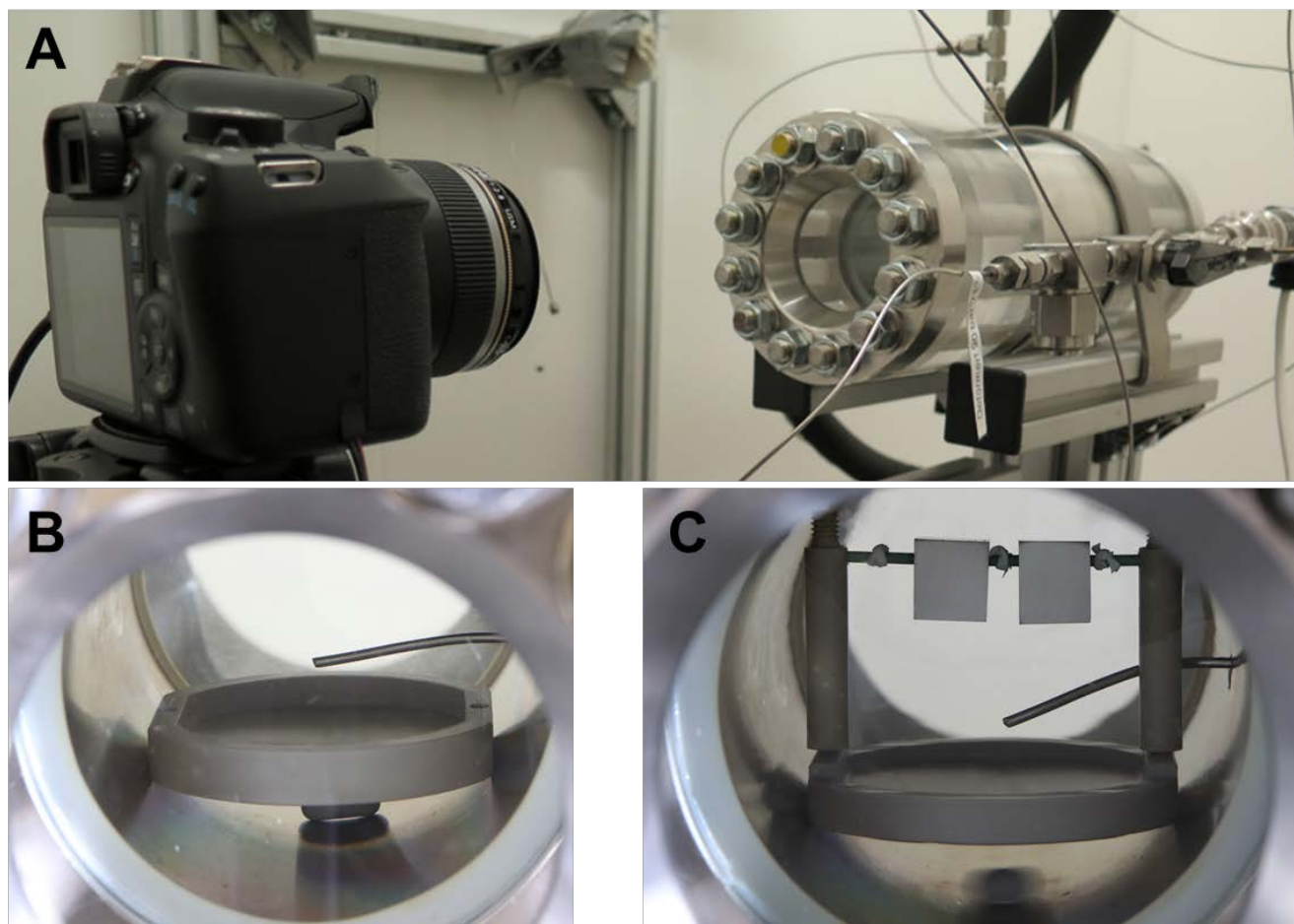


Figure 2: Transparent autoclave with camera (A), water tray (B) and coupon holder with water tray (C).

The rate of liquid water dissolution was studied in the first three experiments (Table 2). The dissolution was observed at 25 and 40 °C, at stagnant conditions without corrosion coupons (Exp-01, Exp-02), and with mechanical convection and carbon steel present (Exp-03). The amount of injected water was approximately 0.3 g, which equals about 2500 ppmv (69 %RH) at 25 °C and 3200 ppmv (76 %RH) at 40 °C. The time to dry-up was acquired from pictures taken at 5 minutes intervals. The injected amount of water was verified by analysing the water content of the CO<sub>2</sub> during the depressurization.

*Table 2*  
*Summary of experimental conditions.*

| ID     | Temp. (°C) | Pressure (MPa) | H <sub>2</sub> O added (g) | H <sub>2</sub> O content (ppmv) | Remark                                                                                            |
|--------|------------|----------------|----------------------------|---------------------------------|---------------------------------------------------------------------------------------------------|
| Exp-01 | 25         | 9.8            | 0.27                       | 2500                            | Dissolution without corrosion coupons                                                             |
| Exp-02 | 40         | 10.3           | 0.27                       | 3200                            | Dissolution without corrosion coupons                                                             |
| Exp-03 | 40         | 10.2           | 0.27                       | 3200                            | Dissolution with CS and stirring, 500 rpm.                                                        |
| Exp-04 | 40         | 10             | 0.27                       | 3200                            | Water injection at 0.1 MPa with CS. Rapid depressurization with water-saturated CO <sub>2</sub> . |
| Exp-05 | 25         | 0.1            | 1.46                       |                                 | Water splashing/CO <sub>2</sub> loading only                                                      |
| Exp-06 | 40         | 10.2           | 0.74                       | 9000*                           | Gentle water injection and depressurisation with corrosion coupons.                               |
| Exp-07 |            |                |                            |                                 | Temperature drop as a function of depress. rate.                                                  |

\*The CO<sub>2</sub> phase was saturated with 4200 ppmv of water, the excess water was present as a separate liquid phase.

The effect of pressurization and depressurisation was studied in the last three experiments (Table 2). Exp.04 focused on the effect of rapid depressurisation, while Exp-05 studied the effect of rapid pressurisation when liquid water present. Experiment, Exp-06, tested long term corrosion in water-saturated CO<sub>2</sub> with a gentle depressurisation at the end. Exp-07 studied the temperature drop that occurred for depressurisation of large volume. The fast depressurisation time for 30 L autoclave (started at 7.8 MPa and 4 °C) was 19 minutes and for 0.3 L autoclave (started at 11.3 MPa and 41 °C) the time was 4 minutes. While the slow depressurisation of 0.3 L autoclave (started at 9.8 MPa and 22 °C) lasted about 308 minutes.

## RESULTS

### Water dissolution

The results of the water dissolution experiments are summarised in Table 3, and a series of pictures from Exp-01 are shown in Figure 3. SEM pictures of the corrosion coupons from Exp-03 are shown in Figure 4. The time to dissolve a few droplets of water in 0.3 litre dense phase CO<sub>2</sub> was from 13 to 36 hours. Although based on a limited number of tests, the results indicate that the dissolution rates increase with increasing temperature and with convection.

*Table 3*  
*Summary of water dissolution experiments.*

| ID      | Temp. (°C) | Press. (MPa) | Convection (rpm) | Dry-up time (h) | Carbon steel coupons |
|---------|------------|--------------|------------------|-----------------|----------------------|
| Exp-01  | 25         | 9.8          | Stagnant         | 36.2            | No                   |
| Exp-02  | 40         | 10.3         | Stagnant         | 15.8            | No                   |
| Exp-03* | 40         | 10.2         | 500              | 12.8            | Yes                  |

The water injection was always observed as a number of individual droplets that emerged from the tip of the 1/16" injection tube. When a droplet had reached a certain size, it fell down and a new droplet would start to form. High interfacial tension between water, CO<sub>2</sub>, and PEEK was clearly observed as the water, droplets bounced several times on the PEEK tray before settling (Exp01 through Exp-03). Individual droplets did sometimes merge into one larger droplet on the tray, sometimes they remained as several smaller droplets.

The corrosion coupons from Exp-03 were practically not corroded. The mass loss rate was less than 0.002 mm/y and just a few scattered spots of corrosion products could be observed by SEM investigation (Figure 4), which is in full agreement with previous results.<sup>18</sup>