Understanding dense phase CO₂ corrosion problems

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Abstract

Increased carbon emissions from the world’s energy sector have brought carbon capture and storage (CCS) issues to the forefront. Concerns about pipeline materials corrosion, corrosion deposition, elastomers decomposition and hydrate formation play a significant role in pipeline development projects for CCS. Impurities, temperatures, pressures from the source facility (power plant) to the reservoir via on and off-shore pipelines all pose environmental risks and health concerns for operators to consider when planning their operating scenarios: compression and decompression. Therefore it is important to understand the corrosion mechanisms to prevent or mitigate transport fluid challenges. This study focuses on high pressure dense phase CO₂ corrosion problems

The dense phase flow loop facility* at Cranfield is the largest/unique of its kind in the UK, and is capable of running several thousands of hours in flow mode. This development has comprised a number of process equipment, including, high pressure observation window, infrared sensors and monitoring temperature, pressure, and also addition of materials up to 2 inch in diameter and up to 1 m in length for corrosion exposure.

This paper specifically deals with transporting engineering challenges when carbon dioxide occurs in the dense phase (saturated with water) via pipelines and discusses the efforts to put in place proper testing facilities to understand the behavior of the carbon steels (X60, X70 & X100) and elastomers (Buna N, Ethylene Propylene, Neoprene and Fluorocarbon) when exposed to the mixture of CO₂ with SO₂ as impurity (500 ppm) under realistic conditions. For the tests carried out as part of this work, we exposed approximately 30 specimens of different geometry for varying time periods (50h, 200h, 400h, 700h and 1100h) during the course of the 1100 hour test period, using CO₂+SO₂ mixture and the corrosion behavior was investigated via a weight loss method. Surface analyses using ESEM and XRD were applied to understand the morphology and chemical composition of the corroded/deposited sample surface. Initially just after 50h of exposure, very low quantities of corrosion product covered the specimen’s surface, but over time, this was gradually increased to thick uniform product film after an extended period of corrosion (1100 hours). The corrosion product film mainly composed of FeSO₃ trihydrate. This study suggests that the corrosion data obtained to date in this process could be used to provide the short term and long term strategies for CCS solutions.
1. Introduction

One of the measures to reduce climate change is to use carbon capture and storage (CCS) technology. This technology involves the capture of CO₂ from onshore sources, and transportation of CO₂ via pipelines from the source to the sink (under the seabed). In the International Energy Agency (IEA) report published in 2005, it was established that CO₂ pipeline transport is the most economical and efficient way of storing large quantities of CO₂.

Many studies have been conducted regarding transportation of CO₂ through pipelines especially examining factors that determine corrosion rate in realistic pipeline materials under different operating conditions of CO₂ phases. For example, Dugstad et al. (2011) established that no corrosion attack occurs in CO₂ pipelines when the water content is kept below the solubility limit. Choi et al. (2011) conducted a study to understand the effects of water on corrosion behavior of carbon steel under the dense phase CO₂/O₂ mixture. Xiang et al. (2011) conducted a study to investigate the impact of SO₂ content on the corrosion rate of X70 steel. Xiang et al. (2012) established a systematic method of estimating the recommended amount of water for dense phase CO₂ pipeline transport. Xiang et al. (2013) undertook an analysis to study the impact of temperature on the corrosion rate of X70 steel under high pressure CO₂/SO₂/O₂/H₂O ternary composition. Ferelias et al. (2013) carried out a study to examine the effects of changes in CO₂ phase, water and SO₂ on the corrosion behavior of X65 carbon steel in dense CO₂ conditions. Xiang et al. (2013) developed a mechanistic model to determine a uniform corrosion rate and examine the behaviour of corrosion of pipeline steel in dense CO₂/SO₂/O₂/H₂O environments. It is necessary to assess the condition of the CO₂ pipelines in order to protect the environment from negative consequences of catastrophic pipelines failures.

Table 1: Essential factors influencing corrosion behavior in CO₂ pipelines

| Parameter       | Effect on CO₂ pipeline                                                               |
|-----------------|--------------------------------------------------------------------------------------|
| Temperature     | The corrosion rate increases with increasing temperature. FeCO₃ corrosion product film forms when the solubility is exceeded and the product film may fail leading to a high localised corrosion rate. This behaviour is very similar to what has been observed in oil and gas pipelines (Dugstad et al., 2011) |
| Pressure        | Increased CO₂ pressure yields a lower pH. This leads to a higher solubility of corrosion products and more H⁺ ions that corrode the steel. |
| Presence of SO₂ | The presence of SO₂ leads to a reduction in pH and increased H⁺ amounts, thus an increased corrosion rate. |
| Flow regime     | The desired properties of the fluid (CO₂) should be adequately monitored to avoid the phase changes and ensure the maintenance of a single phase flow throughout the pipelines. |
| Flow velocity   | An increase in flow leads to an increase in corrosion rate in the CO₂ pipelines. The large effect of flow is attributed to low pH (Dugstad et al., 2011). |
| Water content   | When water combines with CO₂, it forms carbonic acidic; this is very corrosive to carbon steel. Therefore, CO₂ should always be dehydrated prior to transportation to a water level |
With the vast amount of research conducted, there is still little information regarding the most critical parameters that promote corrosion on CO₂ pipelines. Table 1 depicts the review of the essential factors that affect corrosion in the CO₂ pipeline transport. This study seeks to bridge the gap in corrosion issues regarding CO₂ transport through pipelines, with sulfur oxides present.

2. Methodology

Several steel materials were exposed to the mixture of CO₂ and SO₂ and the following test conditions were maintained:

- Temperature—35 °C
- Pressure—95 bar
- SO₂ concentration—500 ppm
- Exposure time—up to 1100 h
- Specimen coupons—pipe and plates for different X grade steels
- Elastomers—Buna, Neoprene, fluorocarbon etc.

After exposure, a weight loss corrosion method was employed to determine the corrosion rate on steel samples and analytical measurements like SEM and XRD were applied to study the effects of various parameters as well as the morphology and chemical composition of the surface of the exposed sample. More detailed specification of this facility was given in author’s earlier publication (Patchigolla and Oakey, 2013).

3. Results and Discussion

Figure 1 shows the procedure to achieve the dense phase conditions (~95 bar and 35 °C) from simple atmospheric conditions. In this paper the saturation data for water in dense phase under the testing conditions were taken from the literature. The addition of water to dense phase CO₂ leads to the formation of two phases (main CO₂ dense phase and a condensed water phase). In this study, we maintained water saturation to create a thin surface film on the coupons to drive the corrosion mechanisms. The corrosion rate measurement was studied in the dynamic flow loop facility developed at Cranfield and more details were given in author’s earlier publication (Patchigolla and Oakey, 2013). Following the termination of the tests, the coupons were inspected visually for localized attacks. No pits or any sign of localized corrosion were found. No cross-section of the coupons has been examined in this paper.
Figure 1: Transport rig characteristics, in particular—the charging procedure.

Figure 2: Exposed coupons for varying time periods (50h, 200h, 400h, 700h and 1100h) during the course of 1100h test period.

Figure 2 shows the photographs of the coupons straight after the exposure, showing increasing corrosion with exposure time and the following remarks may be made:

- In general the coupons surface had a blackish appearance on the surface of exposed coupon
- Surfaces were covered with thin corrosion film indicating that it was partly removed by the fluid flow and settled in the filter ends.
Figure 3 SEM and XRD analysis of corroded samples of X100 steel: free surface sample after the exposure.

Figure 3 presents the surface morphologies of the corroded samples of X100 steel observed using SEM. For this study with presence of SO$_2$, a thin film of corrosion product was formed, and mushroom structures were observed on the surface product film. The XRD scanning suggested that the deposit on the surface was likely to be iron sulphite tri-hydrate (FeSO$_3$·3H$_2$O). A relatively high content of iron was also detected, suggesting that a large percentage of iron was not yet corroded at the sample surface.

Table 2: Corrosion rates of carbon steel in dense phase CO$_2$/SO$_2$ phase under flow conditions.

| Environment                  | Material   | Metal loss, micron |
|------------------------------|------------|--------------------|
|                              |            | 400 h | 1100 h |
| CO$_2$ + SO$_2$ + H$_2$O     | X70 Tube   | 1.00705 | 4.16730 |
| Temperature—35 °C            | X100 Tube  | 2.34497 | 5.98901 |
| Pressure—95 bar              | X60 Plate  | 2.16986 | 9.74082 |
| Mass flow rate-50 g/min      | X70 Plate  | 1.53175 | 2.99996 |
| SO$_2$-500 ppm               | X100 Plate | 2.40751 | 6.84080 |
| H$_2$O-3300ppm               |            |        |       |
The general corrosion rate of X-grade steels under dense phase flow conditions is about 10 micron metal loss (Table 2). Under the wet dense phase conditions, the condensed water film formed upon the steel surface is very thin; the mass transport might be the controlling factor. The iron carbonate grains might induce a good protective ability. These factors can be attributed to lower corrosion rate and limited growth of corrosion product.

4. Conclusions

Based on the research outcome of the present paper, a number of conclusions can be drawn as follows:

- CCS is gaining significant interest—once captures, CO₂ needs to be transported to storage sites and this is done mainly through pipelines in “dense phase”.
- Significant corrosion has occurred under this dense phase conditions in the presence of SO₂ and H₂O by 1100 h of exposure
- And the dominant species appears to be iron sulphite tri-hydrate for the steel materials studied
- More work is needed to understand the corrosion mechanisms in this regime.

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