Design overview of high pressure dense phase CO₂ pipeline transport in flow mode.

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Abstract

In open literature, there is little information available with regards to the engineering and technological issues for material corrosion, in relation to high pressure supercritical CO₂ pipeline transport from single point sources, such as the power industry. A typical CO₂ pipeline is designed to operate at high pressure in the dense phase. However, it is evident that although there is considerable experience of testing materials in lower pressure gaseous CO₂ in the oil and gas industry, there is little understanding of the behaviour of pipeline materials when in contact with impure CO₂ captured either from power plants or the oil and gas industry.

In this particular project development, a dynamic dense phase CO₂ corrosion rig has been built (conditions: ~85 bar, 40 °C and up to 5 l/min flow rate) in flow mode, to understand the effect of impurities (SO₂, O₂, H₂, NO₂ & CO) present in captured CO₂ on the pipeline transport materials. This unique facility in the UK was developed via the MATTRANS project funded by the E.ON-EPSRC strategic partnership (EP/G061955/1). The test rig includes different metallic materials (X grade steel: X60, X70 and X100) to assess the corrosion of pipelines, and different geometry components (tubes, plates, charpy and tensile coupons), to assess ageing and decompression behavior of polymeric seals (Neoprene, fluorocarbon, ethylene and Buna N) under water-saturated dense phase CO₂ with different impurity concentrations (0.05 mol % SO₂; 4 mol % O₂; 2 mol % H₂; 0.05 mol % NO₂; 1 mol % CO). The dynamic data generated from this dense phase CO₂ corrosion rig will give vital information with regards to pipeline suitability and lifetimes, when operating with dense CO₂.

Keywords: Pipeline transport, material issues, dense phase CO₂, polymeric seals

1. Introduction

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The capture of CO₂ from power plants is a proposed method to reduce the release of CO₂ to the atmosphere. Particularly, the CO₂ transport system plays a key role in linking the capture and storage of carbon systems. For CO₂ transport systems, the materials challenges lie in establishing the requirements for a system where CO₂ is the major component and not an impurity, as in the oil and gas industry. Whilst a lot of effort has addressed the problem of carbon dioxide corrosion (‘sweet’ corrosion) in pipelines used for oil and gas transport, little work has focused on corrosion associated with CO₂ as major component. The CO₂ pipelines in USA have reported no significant pipeline failures due to internal corrosion. But this mainly depends on water content in the CO₂ in the pipeline. In terms of pipeline design and operations, a dewatering process and water monitoring system is recommended. Dry CO₂ does not cause corrosion in the carbon steel generally used in pipelines under ordinary circumstances. If the CO₂ cannot be dried it can still be transported through corrosion resistant steel that would safely take other contaminants, but this will significantly increase the cost of the pipeline. Open literature indicated that carbon steel is the most attractive alternative for long distance pipelines and that 13% Cr steels can be considered for shorter distance pipelines for CO₂ transport. However, in locations where contact with wet CO₂ is more likely or unavoidable e.g. inlet piping to compressors, coolers and scrubbers, then it becomes economical to select a corrosion resistant alloy (CRA). The CO₂ stream ought preferably to be dry and free of hydrogen sulphide because only very low levels of toxic contaminants such as H₂S would be acceptable, in case of leakage.

CO₂ can cause deterioration and explosive expansion on non-metallic materials (elastomers) which were majorly studied in open literature and specified in the oil and gas industry. Several studies [1] recommended that the currently specified CO₂ (based on oil and gas industry) seal materials need to be tested to ensure their suitability for the CO₂-rich compositions expected from the capture plants. In that context, recently UK academics have been awarded a joint EPSRC-E.ON partnership project which covers materials research for next generation CO₂ transportation (MATTRAN). In the MATTRAN project [2] researchers are testing the several non-metallic seal materials under CO₂ rich compositions, with and without impurities.

1.1 Current experience with CO₂ pipeline transport

At present, the only experience with large scale, long distance CO₂ transport exists in the oil industry, namely in enhanced oil recovery (EOR), where the CO₂ is used to displace oil in the underground reservoirs and thus enhance the oil yields. In the EOR [3] industry, CO₂ pipelines have been used since the early 1970s and at present the CO₂ pipeline network in North America stretches for over 2500 km and its total transport capacity is nearly 50 Mt CO₂ yr⁻¹. The longest pipeline in this network is the 808 km long Cortez pipeline from Cortez in Colorado to Denver City in Texas. Selected existing long-distance pipelines are listed in Table 1.

All the existing large-scale CO₂ pipelines are designed for dense phase/supercritical conditions, i.e. a CO₂ pressure above 7.38 MPa. The typical operational intervals for temperature and pressure of the CO₂ are 15-30 °C and 10-15 MPa respectively [4]. However, due to the special properties of CO₂ and normal pressure drops in pipeline, it is not easy to maintain the CO₂ within these ranges. CO₂ has to be regularly recompressed along the route. Further, the compressibility and density of CO₂ show strong, nonlinear dependence on the pressure and temperature, which makes it difficult to fully predict the CO₂ flow. At the critical point of CO₂ (7.38 MPa and 31 °C) even a small change in temperature or pressure yields a large change in density (e.g., the density doubles with a change in temperature from 47 to 37 °C at a constant pressure of 9 MPa). In addition to the pipeline operating parameters (i.e., temperature and pressure), the amounts of impurities present in the CO₂ stream also affect its physical properties and can have
considerable impact on pipeline design and operation. The majority of the CO₂ pipelines currently in use for transport of CO₂ are derived from naturally occurring sources. As a result, the composition of the gas stream can be considerably different than in CO₂ streams resulting from CO₂ capture technologies linked with power plants. Table 2 shows examples of gas composition in several existing pipelines transporting CO₂ from both natural and industrial sources.

**Table 1**: Existing long-distance CO₂ pipelines.

<table>
<thead>
<tr>
<th>Pipeline</th>
<th>Location</th>
<th>Operator</th>
<th>Capacity [MtCO₂ yr⁻¹]</th>
<th>Length [km]</th>
<th>Year finished</th>
<th>Origin of CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cortez</td>
<td>USA</td>
<td>Kinder Morgan</td>
<td>19.3</td>
<td>808</td>
<td>1984</td>
<td>Mc Elmo Dome</td>
</tr>
<tr>
<td>Sheep Mountain</td>
<td>USA</td>
<td>BP Amoco</td>
<td>9.5</td>
<td>660</td>
<td>-</td>
<td>Sheep Mountain</td>
</tr>
<tr>
<td>Bravo</td>
<td>USA</td>
<td>BP Amoco</td>
<td>7.3</td>
<td>350</td>
<td>1984</td>
<td>Bravo Dome</td>
</tr>
<tr>
<td>Canyon Reef Carriers</td>
<td>USA</td>
<td>Kinder Morgan</td>
<td>5.2</td>
<td>225</td>
<td>1972</td>
<td>Gasification plants</td>
</tr>
<tr>
<td>Val Verde</td>
<td>USA</td>
<td>Petrosource</td>
<td>2.5</td>
<td>130</td>
<td>1998</td>
<td>Val Verde Gas Plants</td>
</tr>
<tr>
<td>Bati Raman</td>
<td>Turkey</td>
<td>Turkish Petroleum</td>
<td>1.1</td>
<td>90</td>
<td>1983</td>
<td>Dodan Field</td>
</tr>
<tr>
<td>Weyburn</td>
<td>USA &amp; Canada</td>
<td>North Dakota Gasification Co.</td>
<td>5</td>
<td>328</td>
<td>2000</td>
<td>Gasification plant</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>49.9</strong></td>
<td><strong>2591</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2**: CO₂ stream composition in existing pipelines [5]

<table>
<thead>
<tr>
<th></th>
<th>Canyon Reef Carriers</th>
<th>Central Basin Pipeline</th>
<th>Sheep Mountain</th>
<th>Bravo Dome</th>
<th>Cortez Pipeline</th>
<th>Weyburn</th>
<th>Jackson Dome</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>85-98</td>
<td>98.5</td>
<td>96.8-97.4</td>
<td>99.7</td>
<td>95</td>
<td>96</td>
<td>98.7-99.4</td>
</tr>
<tr>
<td>CH₄</td>
<td>2-15</td>
<td>0.2</td>
<td>1.7</td>
<td>-</td>
<td>1-5</td>
<td>0.7</td>
<td>Trace</td>
</tr>
<tr>
<td>N₂</td>
<td>&lt;0.5</td>
<td>1.3</td>
<td>0.6-0.9</td>
<td>0.3</td>
<td>4</td>
<td>&lt;300 ppm</td>
<td>Trace</td>
</tr>
<tr>
<td>H₂S</td>
<td>&lt;200 ppm</td>
<td>&lt;20 ppm wt</td>
<td>-</td>
<td>-</td>
<td>0.002</td>
<td>0.9</td>
<td>Trace</td>
</tr>
<tr>
<td>C₂⁺</td>
<td>-</td>
<td>0.3-0.6</td>
<td>-</td>
<td>Trace</td>
<td>2.3</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>–</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>O₂</td>
<td>-</td>
<td>&lt;10 ppm wt</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;50 ppm wt</td>
<td>-</td>
</tr>
<tr>
<td>NOₓ</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SOₓ</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Trace</td>
<td>-</td>
</tr>
<tr>
<td>Ar</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂O</td>
<td>50 ppm wt</td>
<td>257 ppm wt</td>
<td>129 ppm</td>
<td>257 ppm</td>
<td>20 ppmv</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

wt: weight fraction
2 Experimental methodologies

2.1 Transport flow loop rig

The dynamic high pressure flow loop rig will be used to generate engineering data, test flow measurement devices, and test non-metallic materials degradation in different CO$_2$ contaminant environments. This facility can generate data in gas, liquid and dense phase CO$_2$ test conditions. It comprises a feed compressor, circulation pump, automatic back pressure regulator, viewing cell, temperature conditioning unit and safety interlocks. The total volume of transport flow in the rig is approximately 3 litres and is made from stainless steel 316. Different geometrical specimens and nonmetallic materials, shown in Figure 1, were mounted into the transport flow rig. The test specimens were machined from X60, X70 and X100 plates and the specimens were ground with 600 grit silicon carbide paper. The weight was measured using a balance with a precision of 0.1 mg. After the specimens were mounted, the dense phase CO$_2$ saturated with water is circulated through these specimens for 1000’s of hours. The pressure, temperature and impurities composition were maintained throughout the experiments and the phase behavior changes was observed through view cell. Electrochemical measurements started immediately after the experimental condition was obtained.

The transport rig will address the long term materials data (1000’s of hours) including operating cycle conditions, likely damage mechanisms such as pitting, corrosion fatigue, SCC, H$_2$ embrittlement and weld cracking. Figure 1 & 2 shows the mechanism of mounting the corrosion coupons inside the transport rig and its process flow diagram. The corrosion rate was monitored continuously using the LPR technique and weight loss was recorded after the end of the experiments. The corrosion rate for the weight loss method can be calculated by the following equation 1 [6].

\[ \text{Corrosion rate} = \frac{\text{Weight loss}}{\text{Time}} \]
Figure 1 The mounting mechanism of corrosion coupons in transport flow rig.

Corrosion rate (mm/y) = (8.76E4 x weight loss, g)/(area, cm² X density, g/cm³ X time, hours)  \[ (1) \]

Figure 2 Process flow diagram of transport flow rig

2.2 Experimental rig specification

Figure 3 shows the automated transport rig and its components. The specification of the rig components are as follows:

- Transport flow loop rig operates above 80 bar, 35 deg (capable of up to 700 bar, -50 to 150 deg C) in flow mode
- Runs for several hundred hours depends on material corrosion and environment
- Effective measurement and monitoring
  - Continuous monitoring of corrosion by electro chemical noise & linear polarization resistance
  - Offline/online gas composition measurement (infrared, mass spec)
I Incorporating flow meters-venturi, orifice (up to 50mm diameter)

- Rig includes several coupon geometry—plates, tubes, bar, charpy and tensile coupons
- Impurities— H₂O, H₂, H₂S, NOₓ, SO₂ and O₂ etc.
- Materials— X60, X70, X80, X100, 316, duplex steel etc.
- Non-metallic materials degradation—seals, lubricants
  ✓ Buna N, Ethylene Propylene, Neoprene and Fluorocarbon

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2.3 Experimental testing composition

As the future CO₂ transport networks will have to deal with CO₂ from a number of different sources, it is important to identify the likely impurities present in the CO₂ streams from different energy conversion and CO₂ capture technologies. The MATTRAN project attempts to briefly summarise existing knowledge.
of impurities resulting from different technologies. The technologies critically reviewed are: Oxy-fuel combustion, Post-combustion capture and Pre-combustion capture. After careful thought, Cranfield undertaking this work to improve the understanding of the CO₂ pipeline failures and corrosion rates with various CO₂ stream impurities, have outlined the key impurities to be investigated, as shown in Table 3.

Table 3 Component mixtures used for testing materials failure

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Level (%)</th>
<th>Failure mechanism/likely source</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>0.05</td>
<td>Selected to understand the materials behaviour; Realistic composition from Oxy-fuel capture plant.</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.05</td>
<td>Might lead to sulphide corrosion (presence of water); Health and safety issues/challenges.</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.05</td>
<td>Material degradation/ H₂S corrosion cracking; Embrittlement; Composition from pre combustion capture plant</td>
</tr>
<tr>
<td>H₂</td>
<td>2</td>
<td>Embrittlement of the material; Health and safety issues; Hydrogen induced cracking; Pre-combustion capture plants; Cracks from cathodic protection</td>
</tr>
<tr>
<td>O₂</td>
<td>4</td>
<td>No studies available; Issues associated with corrosion mechanisms; From oxy-fuel capture plant;</td>
</tr>
</tbody>
</table>

2.4 Surface characterization
Following the termination of the experiments, the specimens were inspected through microscope for localized attacks. Some of the specimens were analyzed in a scanning electron microscope using a cross-section of the specimen.

2.5 Pipeline risks and mitigation strategies
- CO₂ is not explosive or inflammable like natural gas
- CO₂ is denser than air and might accumulate in depressions (in case of CO₂ leakage)
- High concentrations of CO₂ might have negative impacts on humans (asphyxiation) and ecosystems.
- pipeline rupture.
Pipeline system needs number of safety systems includes:
- Leak/rupture detection- CO₂ leakage can be reduced by decreasing distance between safety valves
- Measurement of T,P and flow-rates by telemetry (provides early detection of potential problems)
- Instrument to detect corrosion or other defects
- Safe de-compression of the pipeline- control closing of block values and/or safety shutdown systems

3 Conclusions
The main aim of this paper was to provide the design overview of a high pressure, dense phase CO₂ transport flow loop rig to understand the pipeline materials. This unique facility looked at design parameters of the pipelines and selected appropriate materials and operating conditions to control corrosion and non-metallic degradation in pipelines carrying dense phase CO₂ from the capture processes. In this context, this paper has critically reviewed the component mixtures to be used for testing the corrosion mechanisms.

References

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