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Characterization of CO_2-rich Systems: Phase Behavior and Hydrates

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Abstract

We present results for measurements and observations that quantify the phase behaviour of CO_2-rich systems in support of the current needs for CCS (carbon capture and storage). The systems considered include pure CO_2 and CO_2-rich mixtures with contaminants (totaling 5 mol%), which included N_2, O_2, H_2, C1, C3. The experiments are performed in the rock-flow cell setup, which allows for controlled temperature and pressure under shear (rocking). Videos/images from the in-situ borescope in the cell allows for direct observations of the phase transitiona covering the entire phase space capturing solid, vapor, liquid, vapor-liquid, and supercritical fluid. Results are also reported for tests with water to study the formation and dissociation of hydrates and their impact in the transportation of CO_2.

Keywords

CO2, contaminants, phase transition, transport, hydrates,

Introduction

Carbon capture and storage (CCS) is a major component of the oil and gas industry towards green-house gases abatement. CO_2 can be captured either directly from the atmosphere or at the primary sources of CO_2 emissions. For instance, in oil and gas production, CO_2 is often extracted and subsequently reinjected into deep geological formations. Additionally, during extraction, CO_2 is separated from other hydrocarbon gases like methane and undergoes a drying process. However, it is important to note that the separation and drying processes are inefficient, and small quantities (around 1-5%) of other compounds such as methane, nitrogen, hydrogen, oxygen, etc., can remain with the CO_2-rich stream [1-3].

These compounds remaining in the CO_2-rich stream are known as contaminants and can alter the phase behaviour of CO_2-rich mixtures. Moreover, an incomplete drying process could potentially hinder the transportation of CO_2 through pipelines due to the formation of gas hydrates. Even a small amount of water present in the CO_2 (less than 1%) can contribute to the formation of gas hydrates, posing flow assurance challenges. There is limited data and knowledge on the characteristics of gas hydrates formed from CO_2-rich systems (pure or nearly pure with impurities).

CO_2-rich systems are becoming more prevalent around the world, including the re-injection of CO_2 into the reservoir. CO_2-rich systems pose challenges for flow assurance as CO_2 can readily liquify and form at conditions of higher temperature/lower pressure relative to common natural gas systems. There exists a very limited amount of data on CO_2 with contaminants phase behaviour and for gas hydrate formation on CO_2-rich systems, especially with nearly pure CO_2 and with liquid CO_2. This presentation contributes with data needed to make more informed decisions on the design and operation of CO_2-rich systems.

Methodology

Five mixtures were considered for this study. Table 1 shows the composition of the mixtures, which include pure CO_2 and four mixtures of CO_2 at 95% and contaminants totalling 5%. All gas mixtures were acquired from General Air and the compositions certified to be within 0.1%.

Table 1. CO_2-rich mixtures with contaminants considered.

#	System	Composition (mol%)
G1	CO_2	100
G2	CO_2 + N_2 + C1	95% + 2.5% + 2.5%
G3	CO_2 + N_2 + C1 + O_2	95% + 1.7% + 1.7% + 1.6%
G4	CO_2 + N_2 + C1+O_2 +H_2	95% + 1.25%(x4)
G5	CO_2 + C1 + C3	95% + 2.5% + 2.5%

Experimental Setup

A rock-flow cell (RFC) tool was used to assess the phase behaviour of the different mixtures and the formation of gas hydrates. The RFC is a versatile bench-top tool that allows testing of all flow assurance issues by capturing the thermohydraulic conditions in flowlines. The RFC offers the advantage of coupling solid precipitation with multiphase flow characteristics [4]. The RFC is mainly comprised by a sealed pipe (50.8 mm ID, 1000 mm long) set on a rocking frame, which induces gravity-driven flow in the cell.

Inside the pressure cell, a borescope camera is placed to observe when, where, how and how much phase transitions occur. The rocking of the cell is controlled with an electric motor. System temperature is controlled by a chiller and monitored by temperature probes (T-type, Omega®, ±0.1 °C). A pressure transducer (PX613, Omega®, ±1%) monitored pressure changes and a LabView® data acquisition system recorded system pressure and temperature. The videos and images recorded are processed with a video editing program.

Experimental Setup

For the phase behaviour experiments, the cell was initially cleaned and then sealed. The cell was purged twice with the gas to remove air. Finally, the cell was pressurized in a quasi-static process while keeping the temperature constant at room temperature (~20 °C).

Before starting the experiment, the angle and velocity of the cell were set. Experiments were following paths under isothermal, isobaric or isochoric conditions. We note that the isochoric conditions, the pressure was varied via the Isco pump, without venting (i.e., no mass addition/removal). It should be noted that all experiments for the phase behaviour were performed under shear (rocking of the cell) simulating the flow behaviour in a flowline. The main data acquired from the tests were the visual observations through the borescope camera to identify the phases. The visual observations were critical to understand the process of phase transitions as simply monitoring temperature and pressure are insufficient to determine the phases and their relative amount in the cell. For the gas hydrates experiments, the difference in the procedure was the initial introduction of water into the cell prior to sealing it.

Results and Discussion

The results obtained to analyse the phase boundaries for the CO_2 and different gases mixtures are presented and discussed through several images taken during each experiment. Videos were recorded with the borescope camera and synchronized with the actual pressure and temperature, but here the discussion will be limited to still images. The goal of these tests was to traverse the phase space covering all possible phases by following constant temperature or constant pressure or varying temperature and pressure paths. A large number of tests were performed and a selected few are shown here as illustration.

The tests shown in Figure 1 for pure CO_2 was done starting from the vapor region and increasing the pressure to the supercritical region and then going to the vapor-liquid line. The returning path was followed the same path in reverse until returning to the original vapor phase. As seen in Figure 1, at 37 °C and 71 bar, the system was in the vapor phase. When the pressure was increased to 74.6 bar, light scattering was initially observed, indicating the phase transition from the vapor to the supercritical phase. At 77 bara and 35 °C, the system was fully under supercritical conditions. The characteristic scattering of light known as critical opalescence was observed in the supercritical phase. This phenomenon appears as a diffuse light blue glow and is caused by fluctuations in the density and refractive index [5]. Once supercritical conditions were reached, the inlet used to inject gas into the cell was closed, that is, the system remained at constant volume and mass after point 3. To achieve the vapor-liquid region from the supercritical phase, the temperature was reduced stepwise, accompanied by a pressure decrease. The image in Figure 1 shows the amount of liquid present in the cell at the conditions of 64.5 bar and 26 °C. The supercritical phase was also noted in the return path.

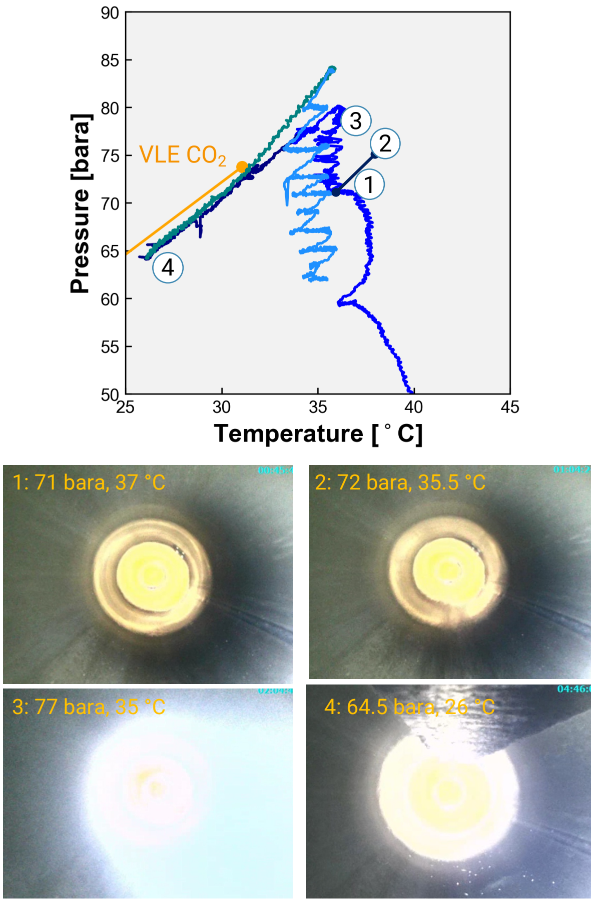

Figure 1. Pure CO_2 starting in the vapor phase, going to supercritical fluid, and then to the vapor-liquid region. The reverse path was followed

returning to the vapor phase. The line colors correspond to the different segments of the experiment.

Figure 2 shows the test done at constant volume for CO_2 + N_2 + C1 + O_2 + H_2 mixture. The test started in the vapor region, and the transition to the supercritical phase was noticed at point 1. For this mixture, the light scattering was observed when the conditions were closer to the supercritical point. Interestingly, as soon as the system passed over the supercritical point, the liquid phase was still observed along with the supercritical behaviour of the material, suggesting some possible metastability for the phase transition. At point 3, shown in the image in Figure 2, a vapor-liquid mixture was observed. The temperature was reduced to 4 °C by what appeared as following a quality line. When the temperature was increased back to the vapor phase, the transition from the vapor-liquid region to the supercritical phase happened at much lower pressure and temperature, as indicated by point 4.

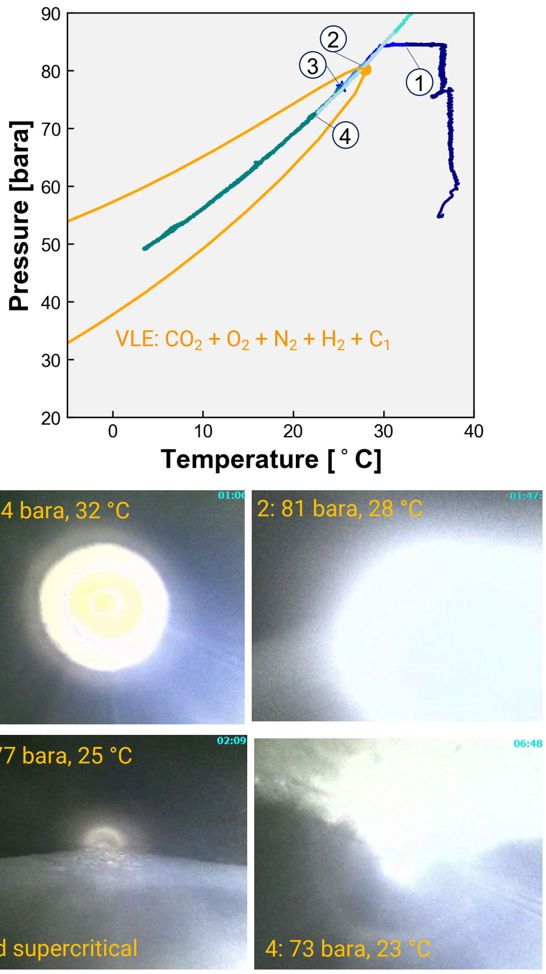

Figure 2. Test for the CO_2 + N_2 + O_2 + H_2 + C1 mixture. The test was done at constant volume from supercritical to vapor-liquid phase and back. A quality line was followed through the middle of the phase envelope. The line colors correspond to the different segments of the experiment.

Figure 3 shows results for a test with CO_2 + N_2 + C1 mixture and 10% water done under static conditions (no rocking). The test started in the liquid phase at 150 bara and 16 °C. The temperature was gradually reduced up to 4 °C. The formation of hydrates was observed at about 7.7 °C, as seen in image A in Figure 3. For this case, the formation of hydrates was observed through light shadow reflection. The growth of hydrates was faster in the first 3 hours of the test. Images B and C in Figure 3 show the morphology of the hydrates formed after 1.5 and 14 h, respectively. It is seen that hydrates are porous and have “veins” that allow for the transport of water through the porous structure. Once the apparent hydrate volume appeared unchanged, the temperature was gradually increased until full dissociation. The complete dissociation of the hydrates under static conditions was observed at about 4 °C higher than the hydrate equilibrium boundary, which may be due to the lack of shear/mixing in the system.

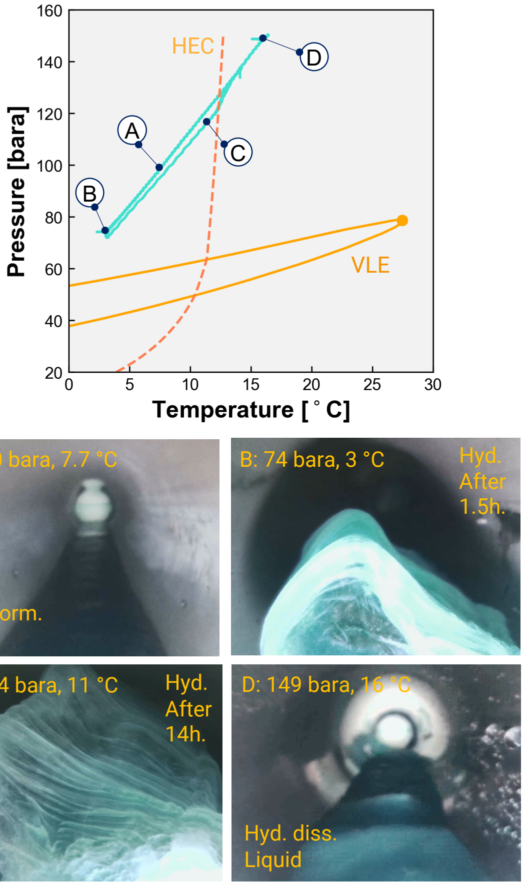

Figure 3. Test with CO_2 + N_2 + C1 mixture and 10% water for gas hydrate formation under static conditions. The line colors correspond to the different segments of the experiment.

Figure 4 shows the P-T trace for the test with the CO_2 + N_2 + C1 + O_2 + H_2 mixture with 10% water done following the formation of hydrates in the vapor, vapor-liquid, and liquid phases. Hydrates formed at 4 °C in all the phases. However, the hydrate morphology obtained from the vapor phase (image A in Figure 4) was quite different from those obtained from the vapor-liquid and liquid phases (images B and C in Figure 4). The latter ones appear more rigid and are formed as big chunks. Moreover, two remarkable observations were extracted from these data. First, the large apparent hydrate volume for only 10% WC almost filled the entire cross-section of the cell. Second, the region hydrate formation in the vapor-liquid phase happened out of the vapor-liquid area predicted by PVTsim®. Therefore, as noticed for the experiments of this system conducted without water, the predicted VLE data do not match with the measured data in the vapor-liquid region.

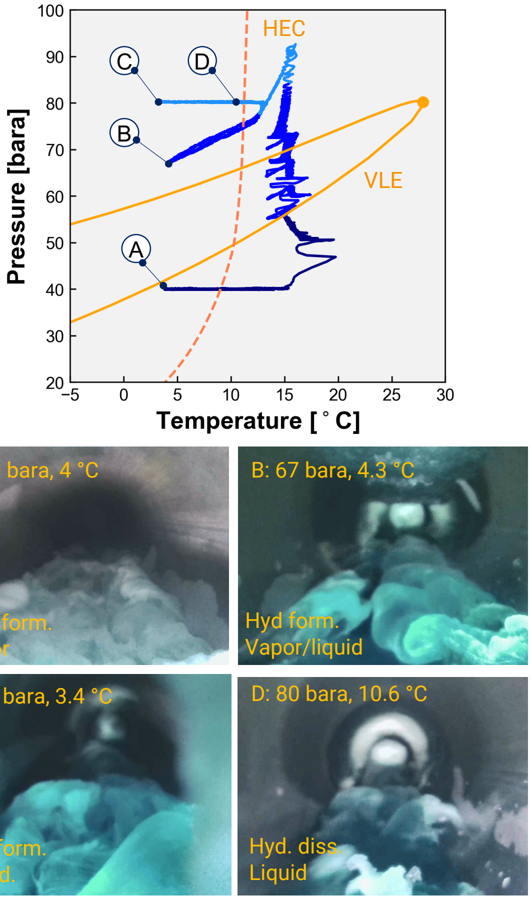

Figure 4. Test with $CO_2 + N_2 + C1 + O_2 + H_2$ mixture and 10% water for hydrate formation. The line colors correspond to the different segments of the experiment.

The selected results presented here will be further elaborated in the presentation, which will show the dynamics of the tests and other results involving phase transition and hydrate formation and dissociation. Overall, this study allows for insight into a number of important observations for CO_2-rich systems in terms of phase behaviour and transitions under shear and the formation of hydrates with the different phases of CO_2. The study was made possible by the unique experimental setup (rock-flow cell) developed in our lab, which brings visual characterization under controlled temperature and pressure, and set shear equivalent to pipe flow.

Conclusions (Arial 12, bold)

From all the tests performed considering all the CO_2-rich mixtures, the main learnings are:

- For pure CO_2, crossing of the VLE line requires complete phase transition, that is, all vapor condenses to liquid or all liquids boils to vapor. The system will remain on the VLE line until full phase conversion is completed, that is, the system P and T will follow the VLE line. It is unclear that flow simulators properly account for the phase transition, which must be carefully checked.
- For CO_2 with contaminants, the amount of vapor and liquid are determined by the quality lines depending on the P and T of the system. Like for pure CO_2, the P and T will follow a quality line inside the VLE envelope.
- Isobaric cooling/heating or isothermal compression/expansion can only be done when the fluid is a single phase, that is, vapor, liquid, or supercritical.
- The measurements suggest good agreement of the dew curve for the VLE envelope for the mixtures. However, significant deviations were seen for the bubble curve, which were typically at higher pressure, for a given temperature, than those predicted by PVTsim®.
- The collection of experiments performed show that the actual phase transition under dynamic and sheared condition does not happen exactly at the P and T defined by the thermodynamic equilibrium boundary. More often, phase metastability may occur, and as such, the VLE boundary should be treated as a band, defined and limited by the heat transfer in the system.
- The characteristic scattering of light in the supercritical region was clearly observed, with very intense light scattering near the critical point. It should be noted that the free water appears to change the phase behaviour of supercritical fluids, as qualitatively, the supercritical fluid did not show as intense light scattering.

From all the tests performed to form hydrates with the CO_2-rich mixtures, the main learnings are:

- Water is not dispersed by CO_2 vapor or liquid, but isolated water droplets can remain attached to the wall in liquid CO_2.
- Hydrates formed from vapor CO_2 quickly deposits on the bottom of the pipe.
- A hydrate film initially forms between the water and liquid CO_2-rich interface. As water leaks out through the film, the hydrate growth appears to expand and swell into the CO_2-rich liquid, forming a solid network with apparent volume many times the original volume of water. This suggests that hydrate blockages may be easily formed even with low water content.
- Hydrates formed from liquid CO_2-rich appears to be very porous.
- In most instances, hydrates formed from CO_2-rich liquid only needed less than about 1 °C subcooling to form hydrates, whereas the

subcooling to form hydrate from vapor, required more than 3 °C.

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Responsibility Notice

The authors are the only responsible for the paper content.

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