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Experimental Investigation of Formation of Carbon Dioxide Hydrates during Injection into Cold Water Zones

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Abstract

The growing concern on carbon dioxide (CO₂) emission is gaining attention and makes it imperative to remove the emitted CO₂ somewhere away from the habitat. Injecting carbon dioxide (CO₂) into subsea water zones with temperatures below CO₂'s hydrate-forming point has recently been proposed as a method to store CO₂ in solid hydrate form. However, there are concerns that CO₂ hydrates may form during the injection process, potentially reducing well injectivity. This study explored CO₂ injection into sandstone cores under simulated subsea temperatures of 2°C and 3°C. The subsea scenario is simulated using circulating cooler with continuously flowing water around the insulated core holder. The high pressure confined situation is maintained using Nitrogen gas. The experiments revealed that at 2°C, CO₂ flowing at a Darcy velocity of 0.033 cm/s starts forming hydrates in the sandstone core at approximately 3.06 MPa (450 psi), which is significantly higher than the minimum required pressure of 1.5 MPa (220 psi) for hydrate formation under static conditions. This results in a pressure ratio of $450/220 = 2.05$. Similarly, at 3°C, CO₂ flowing at a Darcy velocity of 0.045 cm/s begins forming hydrates in the sandstone core at around 3.67 MPa (540 psi), also much higher than the minimum required pressure of 1.87 MPa (275 psi) under static conditions, with a pressure ratio of $540/275 = 1.96$. The reason for this discrepancy, where the required pressure for hydrate formation under dynamic conditions is nearly double that of static conditions, remains unclear. It is speculated that the shear rate effect of flowing fluids may slow down hydrate crystal growth or break up hydrate films, delaying the formation of bulk CO₂ hydrates. Previous studies on gas hydrate formation have not considered the dynamic conditions where the effect of moving gas significantly impacts hydrate formation. This research aims to address that research gap by applying real laboratory-scale experiments. However, further investigations are necessary to gain a comprehensive understanding of the process.

Introduction

Most Carbon Capture, Utilization, and Storage (CCUS) processes involve injecting carbon dioxide (CO_2) into depleted oil and gas reservoirs, offering high volumetric efficiency due to the reservoirs' permeability but posing risks of CO_2 leakage through wellbores in its supercritical state. However, studies suggest lower leakage risks in subsea geological storage where CO_2 exists in liquid form. Projects like Sleipnir in the Norwegian Sea (1996) and Hokkaido (2016) have explored CO_2 injection into sub-seabed water zones. Recently, injecting CO_2 into low-temperature subsea water zones to form solid hydrates has been proposed, though the feasibility of hydrate formation during injection remains unclear. Gas hydrates are crystalline solids formed under high-pressure and low-temperature conditions, with their formation kinetics extensively studied in static conditions. Models by Englezos et al. (1987) and others describe hydrate formation as driven by factors like fugacity, chemical potential, and temperature differences. However, these studies largely neglect dynamic conditions, where gas movement impacts hydrate formation. Addressing this gap, this work investigates CO_2 hydrate formation in sandstone cores at 2°C and 3°C under dynamic conditions, revealing that the required pressure for hydrate formation is approximately double that of static conditions. Further research is needed to fully understand hydrate formation dynamics and its implications for CCUS.

Experimental Procedure

Figure 1 depicts the experimental setup for investigating dynamic hydrate formation in porous media. It includes a temperature-controlled, insulated core holder for a sandstone core (2" diameter, 22" length), fluid accumulators for continuous injection, a backpressure regulator for sealing, a gas meter for flow rate monitoring, and a gas chromatograph for composition analysis.

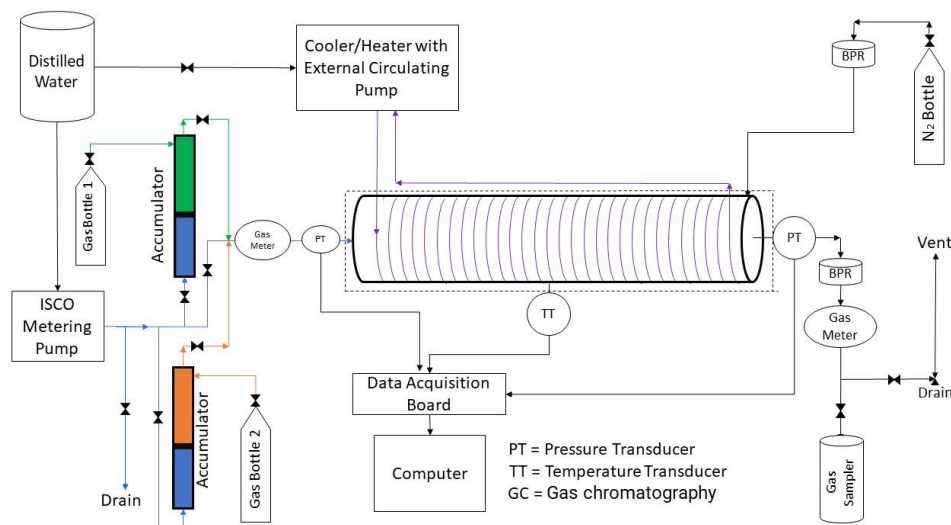


Figure 1: Schematic of experimental setup for investigating dynamic hydrate formation in porous media

First, dry weight and dimensions of the core sample the sample was measured, then it is vacuumed in distilled water to 0.01 MPa absolute pressure. Later, the wet weight was measured and porosity is determined based on weight change. The wet core is placed inside the core holder, confining pressure is applied, and distilled water is injected to determine permeability using Darcy's law. The the core temperature is lowered with the cooler, the backpressure regulator (BPR) is set to the desired outlet

pressure, and finally CO₂ is injected into the core holder while monitoring inlet and outlet pressures. Finally, the pressure drop is analyzed across the core to assess CO₂ hydrate formation.

Results

A sandstone core (24.5% porosity, 116 mD permeability) was tested at 2–3°C with CO₂ injection rates of 20–60 ml/min under confining pressure twice the injection pressure. At 2°C, CO₂ hydrate formation requires a minimum pressure of 1.5 MPa (220 psi) (Sloan and Koh, 2008). During testing, the core holder was cooled to 2°C, and CO₂ was injected at varying outlet pressure settings. At 40 ml/min, consistent inlet and outlet pressures indicated no hydrate formation, as all injected gas passed through unobstructed. If hydrates form, inlet pressure should rise while outlet pressure stabilizes, reflecting restricted flow. **Figure 3** indicates a slight increase in pressure drop across the core, indicating the initiation of hydrate formation at 450 psi. The continuation of this hydrate formation is presented here which shows the inlet pressure is increasing continuously whereas the outlet pressure remains nearly the same. This increasing pressure drop across the core indicates the formation of hydrates.

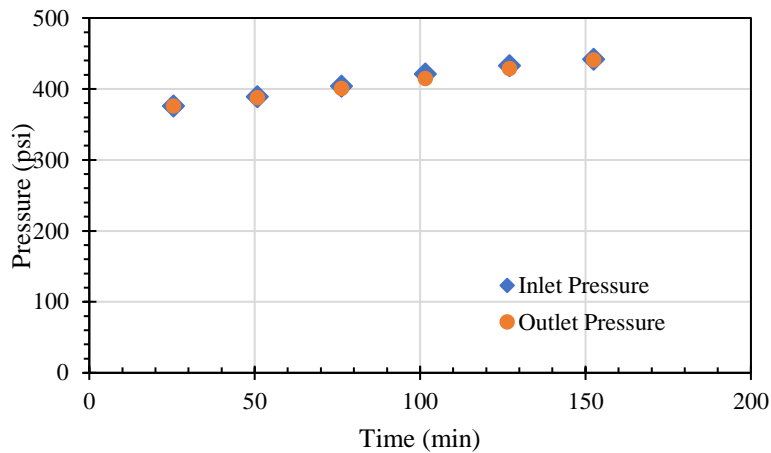


Figure 2: Observed pressures during CO₂ injection at 20 ml/min and 2°C in core holder (when no hydrate formed)

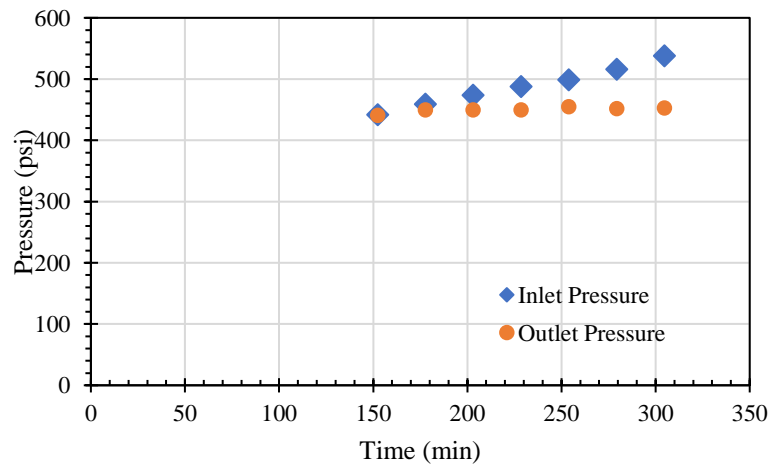


Figure 3: Observed pressures during CO₂ injection at 20 ml/min, 2°C in core holder (when hydrate formed)

Similar results have been generated for an operating temperature of 3 °C where minimum pressure required for CO₂ to form hydrate at this temperature is about 1.87 MPa (275 psi) (Sloan and Koh, 2008). But the hydrate formation in this condition is ensured when outlet pressure was increasing initially but later on it started to remain constant around 540 psi even though the inlet pressure was increasing continuously. The trend demonstrates increasing pressure differential with time which basically indicates that a reasonable portion of hydrates are formed across the core.

Discussion

The experimental data obtained from this study shows that, at 2°C and 3°C temperature, flowing CO₂ at 40 ml/min (Darcy velocity 0.033 cm/s) begins to form hydrate in porous media at about 450 psi and 540 psi, which is much higher than the minimum required pressure 220 psi and 275 psi for CO₂ to form hydrate in static condition. Roughly the required minimum pressure for CO₂ to form hydrates in dynamic conditions is about double the required hydrate forming pressure in static conditions. The higher minimum pressure required in dynamic conditions may be due to two factors. First, hydrate formation, a crystallization process, is hindered by fluid shear, which slows crystal growth and disrupts film development (Englezos et al., 1987; Kashchiev and Firoozabadi, 2002; Mohebbi et al., 2014). Second, non-equilibrium temperatures contribute, as CO₂ entering at room temperature may not fully cool to match the core holder's temperature. Additionally, the study does not account for CO₂ dissolution during and after injection, highlighting areas for future research.

Conclusions

Analysis of experimental results may yield the following conclusions:

1. At 2°C, hydrates formed at ~450 psi with a Darcy velocity of 0.033 cm/s, over twice the static pressure of 220 psi (ratio: 2.05).
2. At 3°C, hydrates formed at ~540 psi with a Darcy velocity of 0.033 cm/s, nearly double the static pressure of 275 psi (ratio: 1.96).
3. The elevated pressures in dynamic conditions may result from fluid shear hindering hydrate growth or breaking films and experimental limitations, such as insufficient CO₂ cooling inside the core holder. Further research is needed to clarify these findings.

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