

Experimental study on the characteristics of formation and dissociation of CO₂ hydrates in porous media

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Abstract. Geologic carbon sequestration (GCS) has been pursued as a feasible strategy to store the large amount of CO₂ to curb its emission to the atmosphere in an effort to mitigate the greenhouse effects. CO₂ hydrate, which can form when the pressure and temperature satisfy its stability condition, can provide a self-trapping mechanism for an offshore CO₂ geologic storage. For example, direct sequestration of CO₂ in the form of hydrate crystals can be achieved in the storage aquifer under the seafloor. Besides, the formation of CO₂ hydrates in an upper layer of the CO₂ storage zone can potentially provide a secondary caprock. These applications, however, require a thorough understanding of the formation and dissociation of CO₂ hydrates in porous media, which are largely unknown yet. In this manuscript, a laboratory study on the formation and dissociation of CO₂ hydrates in two different environments, a two- (CO₂-water) or three-phase (CO₂-water in glass beads) condition, is presented. Based on the experimental results, it can be anticipated that the pressure and temperature change will be negligible when the formation of CO₂ hydrate is induced for GCS in the actual soil/rock layers. Besides, the formation of CO₂ hydrate in porous media may be faster, compared to the two-phase bulk condition that has been typically used in many laboratory studies, as solid grains help accelerate the hydrate formation by providing nucleus sites of crystals. Further elaborations on the role of solid grains would bring a clear path for the feasible application in the subsea area.

1 Introduction

Carbon dioxide (CO₂) is one of the main greenhouse gases that are believed to contribute to recent climate changes. USA and China are two of the highest CO₂ emitters in the world (more than 45% [1]) due to their significant consumption of fossil fuels, which are the main source of CO₂ emission (65% based on IPCC 2014 [2]). Carbon Capture and Storage (CCS), which represents the sequestration of captured CO₂ to avoid emitting CO₂ to the atmosphere, is one approach that can help address these issues. Geological Carbon Storage (GCS) denotes storing CO₂ in deep geologic formations to achieve the idea of CCS [3,4]. A candidate site for the potential long-term GCS includes depleted oil and gas reservoirs, deep saline aquifers, unmineable coal seams, and basalt formations [5]. One of the most significant concerns about GCS is the leakage of CO₂ after it is injected into such candidate sites, back to the atmosphere, probably because of fractures in overlying layers or tectonic movements [3,6,7].

A gas hydrate-bearing sediment is another suitable site for storing CO₂ for a long time. The gas hydrate is a crystalline solid composed of a gas molecule trapped inside of hosting water molecules. The hydrate-bearing sediments are known to retain a high amount of total gas molecules inside their structure. For example, a tremendous amount of methane exists inside hydrate

crystals in the marine continental margins and permafrost sediments, where the pressure and temperature conditions are suitable for stable CH₄ hydrates. It is estimated that the amount of energy stored as methane hydrates in arctic permafrost is about twice of all fossil fuel reserves on the earth [8,9]. The exchange of those methane gases with CO₂ by injecting it into the sediments is an emerging technology that can not only produce a high amount of energy sources, but also store CO₂ in the form of gas hydrates [10-12]. Aside from the CH₄-CO₂ exchange in the hydrate-bearing sediments, those marine continental margins and permafrost sediments can also provide an excellent space for the geologic CO₂ storage purpose only, without needing any gas exchanging process. Once formed, CO₂ hydrate can function as a stable structure for storing a huge amount of CO₂ [13]. In addition to the direct storage of CO₂ inside hydrate crystals, CO₂ hydrate can also form and act as a second barrier in a GCS site that bears the fracture potential or is tectonically active [14, 15]. The two potential applications of CO₂ geologic storage in the form of gas hydrate are illustrated in Fig. 1. However, a thorough understanding of the characteristics of formation and dissociation of CO₂ hydrates in a porous medium (e.g., rock and soil) is needed to achieve those potential applications. Most of the previous studies related to the CO₂ hydrate formation have been limited to the two-phase (CO₂ and water) bulk

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conditions to date. That is, there are only a few studies that investigated the formation of CO₂ hydrates in the porous medium condition [16-18].

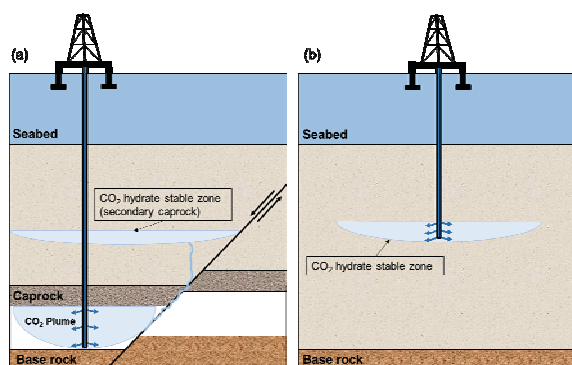


Fig. 1. The potential applications of the CO₂ hydrate for an offshore geological carbon storage.

There are three phases (CO₂+water+solid substrate) in the porous medium condition, while only two phases (CO₂+water) exist in the bulk condition. Due to the different nature of the hydrate formation and dissociation in such two- and three-phase conditions, a comprehensive study of the formation-and-dissociation of CO₂ hydrates in the porous medium condition is important. In this manuscript, the characteristics of CO₂ hydrate formation and dissociation in both bulk (two-phases) and porous medium (three-phases) conditions were examined via experimental studies. Pressure and temperature changes during the formation and dissociation of CO₂ hydrates were monitored, in conjunction with a time-lapse visual observation. The experimental procedure, results, and discussion are provided in the following sections.

2 Materials and Methods

2.1 Experimental Setup

The experimental setup consists of a high-pressure visualization cell (ExtrateX SC350 1/2" cell - capacity of 56 mL), a pressure transducer (Omega) connected to the visualization cell, a high-pressure syringe pump (Teledyne ISCO 260D), a vacuum pump, and a high-purity CO₂ cylinder (99.9%) (Fig. 2).

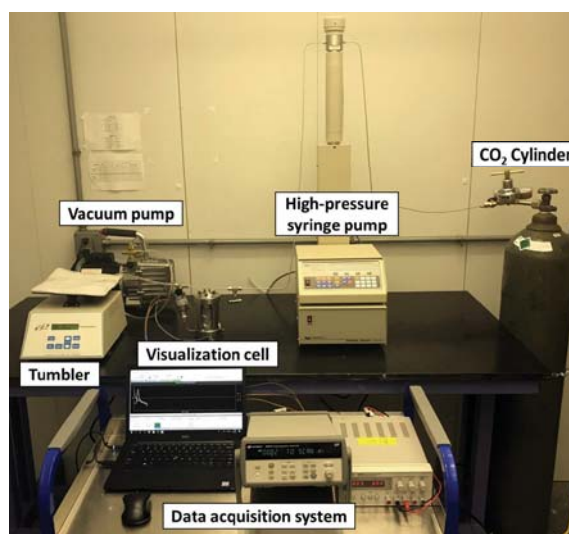
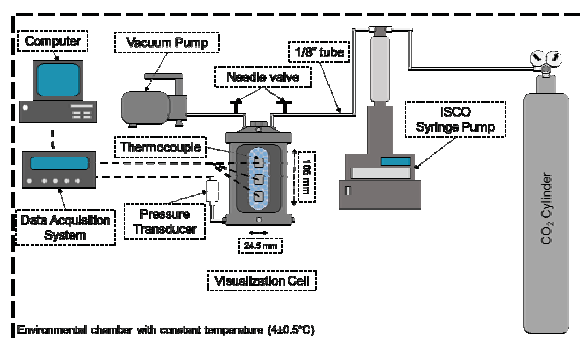


Fig. 2. A schematic view and actual figure of the test setup.

Three thermocouples (type T) were attached to the top, middle, and bottom of the visualization cell to monitor the temperature changes during hydrate formation and dissociation. Two needle valves on the top of the cell were used to control the CO₂ injection and vacuuming processes. The high-pressure syringe pump was connected to the high purity CO₂ cylinder, and a regulator controls the CO₂ pressure between them. The test setup was placed in an environmental chamber (NORLAKE Scientific, USA) in order to keep the entire test setup in the equilibrium temperature (4±0.5°C) before beginning the tests.

2.2 Experimental Procedure

In this study, a total of six separate implementations were conducted in the two- and three-phase conditions (three independent tests for each condition). To apply the porous media condition, the visualization cell was filled with 4.76 mm (3/16") diameter of glass beads (Winsted Precision Ball Co.). The resulted porosity was estimated 0.42. Each test includes two stages: (1) formation of CO₂ hydrate and (2) dissociation of CO₂ hydrate.

For the first part of the test (hydrate formation), the visualization cell was filled with deionized water (DI) up to half of the cell volume (two-phase condition) or half of the void volume of the glass bead (three-phase condition). Then, three cycles of CO₂ injection (at ~200 kPa) and vacuum were conducted to ensure that there is no other gas inside of the visualization cell. After that, pressurized CO₂ from the high-pressure syringe pump at 3.79 MPa (550 psi) was injected into the test cell. The injection valve was then closed, and the cell was moved to the top of a tumbling device (Cole-Parmer). A half-tumbling at 60 rpm was applied to the cell to facilitate the formation of CO₂ hydrates by stimulating the mixing of water and CO₂ gas. The pressure and temperature changes were monitored using the pressure transducer and thermocouples during the hydrate formation. After about five hours of mixing, the pressure inside of the cell

was stabilized, and it was assumed that the system reaches an equilibrium. It marked the completion of the hydrate formation stage, and consequently, the system was moved to the next stage of hydrate dissociation. The dissociation of CO₂ hydrates was triggered by moving the test cell into the other environmental chamber where the temperature was set at 14±0.5°C. That is, the temperature was increased by 10°C, causing the pressure-temperature condition to be located outside of the stable region for CO₂ hydrate. Pressure and temperature were again closely monitored during the hydrate dissociation. The visualization cell was also continually captured using time-lapse photography (Canon EOS 80D).

3 Results and Discussion

Three individual tests were conducted in each two- and three-phase condition, separately, to form and dissociate the CO₂ hydrate. An example of the initial test condition (supply of water and CO₂), formed CO₂ hydrate, and CO₂ bubbles/droplets after the CO₂ hydrate is dissociated in the two-phase condition is shown in Fig. 3.

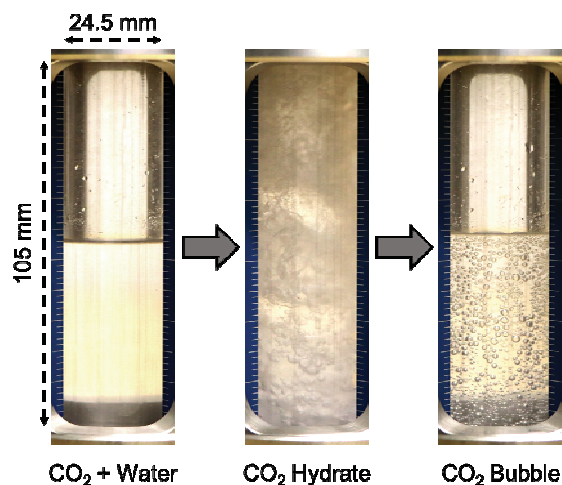


Fig. 3. An example of the initial water+CO₂, after CO₂ hydrate is formed, and CO₂ bubbles/droplets after CO₂ hydrate is dissociated (CO₂ and water only condition).

3.1 Formation of CO₂ Hydrate

Pressure and temperature changes during the hydrate formation in the two- and three-phase conditions are shown in Fig. 4a and 4b, respectively. It was observed that the rate of pressure drop and the time to reach an equilibrium pressure during the formation of CO₂ hydrate were significantly different with and without the presence of the solid substrate.

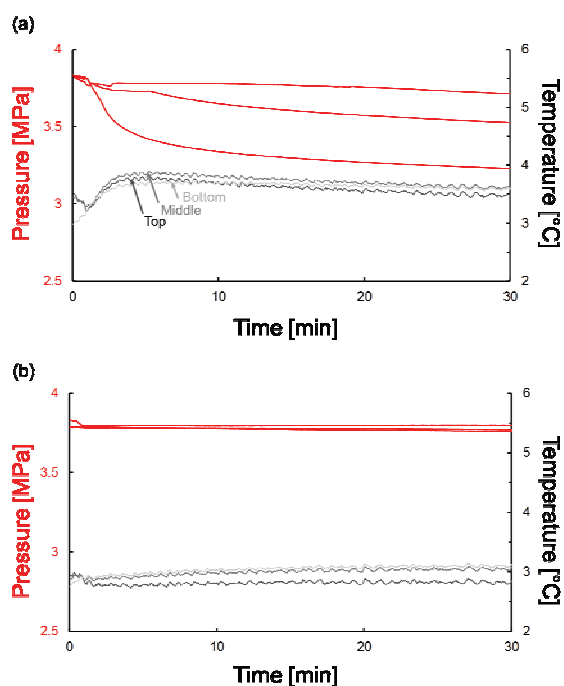


Fig. 4. Pressure and temperature changes during the formation of CO₂ hydrate: (a) in the two-phase, and (b) three-phase condition. Note: the measurement data only for the first 30 minutes is shown here.

The pressure drop during the hydrate formation was much higher in the two-phase (bulk) condition compared to the three-phase (porous medium) condition, as shown in the lower equilibrium pressure (average value was 3.15 MPa (456 psi) vs. 3.73 MPa (540 psi); Table 1). The initial contact between CO₂ and water before initiating the physical agitation (i.e., tumbling) is much greater in the two-phase condition. It implies that the CO₂ gas can easily enter the water cages and form the hydrate crystals during the gentle mixing, leading to the larger consumption of CO₂ and thus a bigger pressure drop. Besides, a larger amount of CO₂ and water was supplied into the test cell in the two-phase condition, meaning that more CO₂ can dissolve in the water phase. In this regard, a bigger pressure drop in the two-phase condition is as expected.

On the other hand, a relatively long time was taken before reaching the equilibrium pressure in the two-phase condition, which implies that the formation of CO₂ hydrate may be faster in the three-phase condition. The presence of solid particles is known to cause two opposite effects. The beneficial aspect is that porous media enhance the contact area between CO₂ and water and serve as the nucleus sites of crystallization during the hydrate formation. The negative aspect is that porous media lead to the emergence of capillary action in the pore space, which decreases the activity of water and consequently slows down the formation of gas hydrate [19-21]. The nominal diameter of glass beads used in this study is 4.76 mm, so the effective pore size lies between 1.03 mm and 1.38 mm (0.43 and 0.58 of the radii for the hexagonal packing [22]). With this range, it

is hard to anticipate that the capillary surface tension would substantially decrease the activity of water. Based on those logics, the presence of solid particles seemed to help accelerate the formation of CO₂ hydrates by providing nucleus sites of hydrate crystals at the CO₂-water-solid interfaces.

The temperature changes during the hydrate formation also showed a meaningful difference between the two- and three-phase conditions (Fig. 4). The formation of CO₂ hydrate is an exothermic process, which implies that the system temperature might increase during the hydrate formation. In the two-phase condition, the temperature increase was clearly captured in the first 10 minutes of gentle tumbling. Besides, the moment when the rate of temperature rise rapidly decreased was observed to coincide with the moment when the rate of pressure drop diminished significantly (i.e., at around 5-10 minutes after the gentle mixing is initiated; Fig. 4a). Thus, it can be conjectured that a significant portion of reactions associated with the hydrate formation would intensely occur in the first 10 minutes.

An insignificant temperature change in the three-phase condition supports the observation made based on the pressure drop that a limited amount of CO₂ hydrate was formed in the porous medium. Nonetheless, the temperature change captured in the very early period (< 5 minutes) supports the point that the rate of hydrate formation might be enhanced due to the presence of the solid substrate, as reported in the literature [23,24], resulting from numerous hydrate nucleation sites.

3.2 Dissociation of CO₂ Hydrate

As explained earlier, the temperature increase was applied to the test cell to induce the dissociation of previously formed CO₂ hydrate. That is, the system temperature was moved outside of the CO₂ hydrate stability region. The hydrate dissociation is an endothermic process, which results in the temperature decrease and pressure increase. The pressure inside of the test cell is expected to increase during the dissociation of CO₂ hydrate due to the following two reasons: (1) release of the trapped CO₂ gas from the water cages of the hydrate structure, and (2) pressure increase because of the temperature rise of the system. Pressure and temperature changes during the hydrate dissociation in the two- and three-phase conditions are shown in Fig. 5a and 5b, respectively. And Table 1 summarizes the equilibrium pressure after the formation and dissociation of CO₂ hydrate, and the time for the complete melting of CO₂ hydrate for the two- and three-phase conditions.

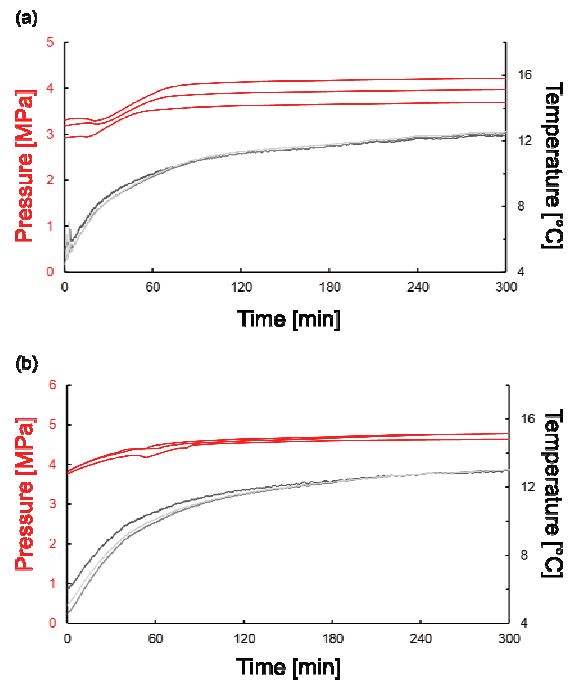


Fig. 5. Pressure and temperature changes during the dissociation of CO₂ hydrate: (a) two-phase, and (b) three-phase condition.

Table 1. The equilibrium pressure after the formation and dissociation of CO₂ hydrate, and the melting time of CO₂ hydrate in the two- and three-phase conditions.

Test condition	Hydrate formation pressure [MPa]	Hydrate dissociation pressure [MPa]	*Melting time [min]
2-phase	3.17	3.98	60
(Bulk)	2.92	3.71	71
	3.35	4.23	70
Average	3.15	3.97	67
3-phase	3.71	4.85	71
(Porous medium)	3.75	4.82	80
	3.72	4.62	82
Average	3.73	4.76	77.7

* Calculated as the time to reach the equilibrium pressure

It is worth to note that the rate of pressure change during the dissociation of CO₂ hydrate was quite different between those two conditions (Fig. 5). In the two-phase condition, the pressure barely changed for about the first 20 minutes while temperature kept increasing (Fig. 5a). After that, the pressure began to increase quasi-linearly until the equilibrium pressure was reached. On the other hand, both the pressure and temperature continued to increase steadily from the beginning of the hydrate dissociation until an equilibrium pressure was reached in the three-phase condition (Fig. 5b). Small pressure fluctuations were also observed at around 50-70 minutes before the equilibrium pressure was reached. These

fluctuations may be associated with the transition from the hydrate stable region to the outside of it (more detailed discussion is provided in Section 3.3).

The final equilibrium pressure at the end of the hydrate dissociation was higher in the three-phase (porous medium) condition (average 3.97 MPa vs. 4.76 MPa; Table 1). Note that the initial pressure at the beginning of the hydrate dissociation was higher in the three-phase condition as a result of the smaller pressure drop during the hydrate formation. Nevertheless, the magnitude of the pressure buildup was greater in the three-phase condition ($\Delta P \approx 1$ MPa from 3.73 to 4.76 MPa in the three-phase vs. $\Delta P \approx 0.8$ MPa from 3.15 to 3.97 MPa in the two-phase). It may be attributable to the contact angle change in the porous medium associated with the temperature increase. More in-depth analysis is needed to elucidate the effect of contact angle and capillary pressure on the pressure buildup during the hydrate dissociation in the porous medium.

Besides, the average melting time of CO₂ hydrate during its dissociation was longer in the three-phase (porous medium) condition (Table 1). It may be due to the aspect that the CO₂ hydrate formed on the solid grains and in the limited pore space, which might delay the liberation of trapped CO₂ gases, and thus, cause a longer time to melt completely. Or, slower heat transfer in the porous medium may have caused the longer time for CO₂ hydrate to dissociate completely, compared to the bulk condition (note that the thermal conductivity is 0.17 W/m/K and 0.5 W/m/K for glass beads and CO₂ hydrate, respectively). Interestingly, in conclusion, CO₂ hydrate was formed faster and melted slower in the three-phase (porous medium) condition, compared to the two-phase (bulk) condition.

3.3 Analysis of Pressure-Temperature Path

Fig. 6 provides a graphical illustration of the pressure-temperature change paths during the formation and dissociation of CO₂ hydrate.

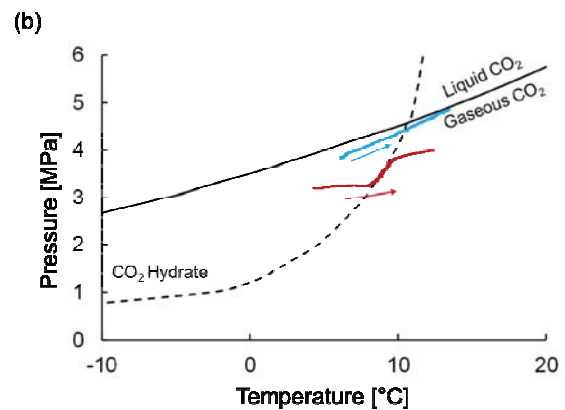
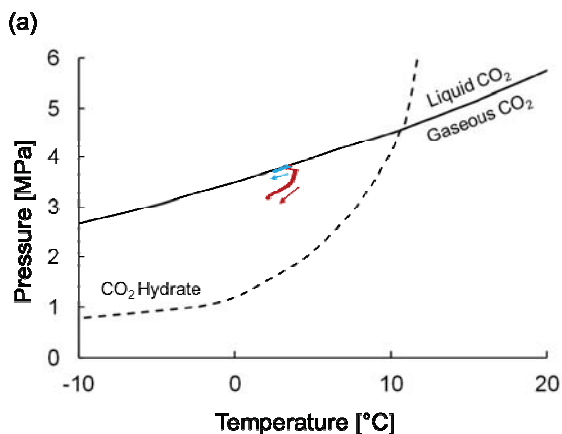


Fig. 6. Paths of the pressure and temperature changes during (a) hydrate formation, and (b) hydrate dissociation in both two- (red) and three-phase (blue) conditions.

The pressure drop during the formation of CO₂ hydrate was greater in the two-phase condition (Fig. 6a), being consistent with Section 3.1. The pressure-temperature paths confirm that the system is within the region of hydrate stability after the equilibrium pressure is reached.

The pressure-temperature path during the dissociation of CO₂ hydrate was markedly different between the two- and three-phase conditions, as shown in Fig. 6b. During the hydrate dissociation in the two-phase condition, the pressure maintained almost constant while the temperature continued to increase toward the boundary of the region of CO₂ hydrate stability. Then, once the pressure-temperature path encountered the hydrate stability boundary, the pressure-temperature path moved along the hydrate stability boundary while the phase change was occurring from the hydrate-water-gaseous CO₂ to the water-gaseous CO₂ system. The path finally deviated from the hydrate boundary as the phase change was being completed, and entered the outside of CO₂ hydrate region. This path of pressure-temperature changes is consistent with the previous study results by Yang et al. (2019) on the hydrate dissociation [25]. In contrast, the pressure-temperature path in the three-phase condition moved nearly parallel to the liquid-gaseous CO₂ boundary line during the entire duration of CO₂ dissociation. The small fluctuation of the pressure-temperature path was observed when the path went across the hydrate stability boundary, but it did not move along the hydrate boundary during the phase change, unlike the two-phase condition. The small pressure fluctuation during the hydrate dissociation shown in Fig. 5b is also associated with the transition of the system from the hydrate stable region to its outside (Fig. 6b). It needs more in-depth analysis to identify why the pressure-temperature path shows a clear difference with and without the presence of a solid substrate.

3.4 Implications to GCS

The suggested applications of CO₂ hydrate for GCS are two-fold: (1) direct carbon storage in the target geologic layer, or (2) formation of a second barrier in the upper geologic layer as leaked CO₂ is used to form the CO₂ hydrate. In either case, CO₂ will be in the gaseous (or liquid) state considering the temperature and pressure conditions suitable for the stable CO₂ hydrate. Based on the experimental observations during the CO₂ hydrate formation in the porous medium of this study, it can be anticipated that the pressure and temperature change will be negligible when the formation of CO₂ hydrate is induced for the purpose of geologic carbon storage in the actual soil/rock layers. Besides, the formation of CO₂ hydrate for the GCS purpose may be faster, compared to the two-phase bulk condition that has been more scrutinized in previous laboratory studies. Once formed, CO₂ hydrate may remain more stable in the porous medium, compared to the bulk condition, given that a longer time was required for its dissociation under the same temperature rise. The pore occupancy of CO₂ is anticipated much higher when CO₂ is injected pressure-driven for the purpose of permanent storage, compared to the case when a portion of CO₂ leaks and migrates to an upper soil/rock layer. In this regard, a follow-up study about the impact of different CO₂ saturations in the porous medium and different pore sizes on the kinetics of CO₂ hydrate formation and dissociation is needed to set a better strategy for utilizing CO₂ hydrate.

4 Conclusions

In this study, the characteristics of CO₂ hydrate formation and dissociation in both two-phase (bulk) and three-phase (porous medium) conditions were examined via experimental studies. Salient observations are summarized as follows:

The pressure drop during the hydrate formation was much higher in the two-phase condition compared to the three-phase condition. And the presence of solid particles appears to help accelerate the formation of CO₂ hydrates by providing nucleus sites of hydrate crystals at the CO₂-water-solid interfaces. The temperature change captured in the very early period also supports this point.

The magnitude of the pressure buildup during the dissociation of CO₂ hydrate was greater in the three-phase condition. It needs more analysis to elucidate which factors might contribute to such higher pressure buildup. The average melting time of CO₂ hydrate was longer in the three-phase condition. It may be due to the aspect that slower heat transfer of solid particles may have caused the longer time for CO₂ hydrate to dissociate completely, or the pore structure may have delayed the liberation of trapped CO₂ gases.

In the two-phase condition, the pressure-temperature path moved along the hydrate stability boundary for a noticeable duration while the phase change was occurring from the hydrate-water-gaseous CO₂ to the

water-gaseous CO₂ system. This path of pressure-temperature changes is consistent with the previous study results. In contrast, the pressure-temperature path in the three-phase condition moved in parallel to the liquid-gaseous CO₂ boundary line during the entire duration of CO₂ dissociation. It needs more in-depth analysis to identify why the pressure-temperature path shows a clear difference with and without the presence of a solid substrate.

The suggested applications of CO₂ hydrate for GCS are two-fold: (1) direct carbon storage in the target geologic layer, or (2) formation of a second barrier in the upper geologic layer as leaked CO₂ is used to form the CO₂ hydrate. It can be anticipated that the pressure and temperature change will be negligible when the formation of CO₂ hydrate is induced for the purpose of GCS in the actual soil/rock layers. Besides, the formation of CO₂ hydrate may be faster, compared to the two-phase bulk condition that has been more scrutinized in the previous laboratory study. A follow-up study about the impact of different CO₂ saturations in the porous medium and different pore sizes on the kinetics of CO₂ hydrate formation and dissociation is needed to set a better strategy for utilizing CO₂ hydrate.

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