

## Thermal stability of CO<sub>2</sub> hydrates in porous media with varying grain size in brine solution

AMIRUN NISSA Rehman<sup>1,2,a</sup>, CORNELIUS B. Bavoh<sup>1,2,b</sup>, BHAJAN Lal<sup>1,2,c\*</sup>

<sup>1</sup>Chemical Engineering Department, Universiti Teknologi PETRONAS, Seri Iskandar, 32610 Perak Darul Ridzuan, Malaysia

<sup>2</sup>Research Centre for CO<sub>2</sub> Capture (RCCO<sub>2</sub>C), Universiti Teknologi PETRONAS, Seri Iskandar, 32610, Perak, Malaysia

<sup>a</sup>amirun\_19001666@utp.edu.my, <sup>b</sup>cornelius\_17005250@utp.edu.my, <sup>c</sup>bhajan.lal@utp.edu.my

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**Abstract.** In the present work, the heat transfer behavior of CO<sub>2</sub> hydrate dissociation was studied in three quartz sand particles (QS-1, QS-2 and QS-3) with varying grain sizes. The heat transfer behavior was evaluated by determining the heating rates of the porous media (quartz sand) during the CO<sub>2</sub> hydrate dissociation process in 3.3 wt.% NaCl. The experiment was performed using sandstone hydrate reactor by first forming the CO<sub>2</sub> hydrates at 4 MPa and 274.15 K and then dissociating the hydrates from 274.15 to 277.15 K, respectively. The results indicate that the thermal response of the porous sediment was significantly influenced by the hydrates as well as the porous sediment properties. The heating rate of the porous media increased when the grain size increased. However, the presence of CO<sub>2</sub> hydrates reduced the heat transfer behavior of the porous sediment due to the endothermic nature of hydrate dissociation. The heating behavior of the porous media with hydrates mainly depends on the type and pattern of hydrate formed (pore-filling, load-bearing, and cementation) and the location of the hydrates within the pores of the porous sediment. The pore-filling type of hydrate formation in porous sediments provides high thermal stability for CO<sub>2</sub> hydrate storage due to its less contact with the quartz sand particles. However, the pore-filling hydrate formation type is challenged with low or undesired CO<sub>2</sub> hydrate storage capacity. These findings will provide meaningful insights to select favorable sediment properties/sites for CO<sub>2</sub> storage in the hydrate form in porous sediments.

### Introduction

The stability of CO<sub>2</sub> hydrates in porous media is a great concern for CO<sub>2</sub> sequestration. Unstable hydrates could release CO<sub>2</sub> into the ocean leading to ocean acidification and, in severe cases, could affect the marine ecosystem [1], [2]. Generally, hydrate dissociation exhibits an endothermic nature where heat transfer plays a major role. The thermal stability of carbon dioxide hydrates in sediments is determined by the heat transfer rate [3]. Heat transfer is highly controlled by the thermal conductivity of the porous media arising from the temperature variations within the hydrate stable zone [4], [5]. Therefore, understanding the heating rate of the porous media could fundamentally provide suitable insight into the thermal stability of hydrates in different porous media systems.

In lab-scale analysis, the reactor temperature profiles could be used to evaluate the heating behavior or response of hydrates stability in porous media. Yang et al., [6] investigated the dissociation of carbon dioxide hydrates in porous media using the temperature profiles. They claimed that the hydrate dissociation process is affected by the heating rate. Hence, understanding the heating temperature profiles during CO<sub>2</sub> hydrate dissociation will facilitate selecting proper sites for CO<sub>2</sub> storage. There is limited investigated on the thermal effect of CO<sub>2</sub> hydrate dissociation in sediments. However, most studies in the literature focus on methane production by

thermal simulation or depressurization in porous media [7], [8], [17]–[22], [9]–[16]. According to Zhao et al., [9] during methane production, water saturation and porous media affects the heat transfer. They reported that the high thermal conductivity of the porous media initially promotes hydrate dissociation but later inhibits it. On the contrary, Song et al., [23] claimed that hydrate dissociation is inhibited with increasing thermal conductivity at an early stage but subsequently promotes over time. However, one may expect an initial hydrate inhibition owing to the endothermic nature of hydrate dissociation.

The hydrate dissociation rate is influenced by the thermal conductivity of the porous media [14]. Li et al., [8] indicated an increase in the dissociation rate with the increase in the thermal conductivity of the porous media. Thus, understanding the thermal conductivity of the porous media could serve as a guideline to select suitable location for CO<sub>2</sub> storage as hydrate with high thermal stability and less gas release. For such applications, a low thermal conductive porous media is highly preferred. However, the thermal conductivity of porous sediments is affected by different sediment properties including grain size, pore size, surface area, and porosity [24]. Hence more studies related to the properties of the porous media are required to facilitate the understanding of the dissociation of hydrates in the porous media. In this regard, evaluating the thermal effect of the dissociation of CO<sub>2</sub> hydrates is required to fully comprehend the thermal stability of CO<sub>2</sub> hydrates in porous sediments.

In this work, the thermal stability behavior of carbon dioxide hydrates in quartz sand was evaluated via a thermal simulation method by estimating the heating rates of the quartz sand and the hydrate systems during the hydrate dissociation process. In addition, the effect quartz sand average pore size, surface area, porosity and grain size on carbon dioxide hydrate dissociation was also studied. This knowledge will enable selecting a proper location with high thermal stability for CO<sub>2</sub> storage as hydrates. The heating rate of carbon dioxide hydrate dissociation was estimated at 4 MPa and 274.15 K in brine system employing quartz sand to simulate the porous media.

## Methodology

### *Materials, Apparatus and Procedure*

CO<sub>2</sub> hydrate dissociation kinetics was studied in 3 different quartz systems (porous media) with varying properties as displayed in Table 2. Quartz sand properties were selected to evaluate the heating rate of the quartz sand on the CO<sub>2</sub> hydrate dissociation kinetics. Pure CO<sub>2</sub> gas with a purity 99.9% was used for all the experimental systems. All the studies were performed in 3.3 wt% NaCl solution as brine to simulate the thermal stability of CO<sub>2</sub> storage as hydrate under real seabed conditions.

Fig. 1 shows the schematic diagram of the complete experimental setup with the internal reactor specifications and sand bed. More details on the apparatus and the experimental procedure followed for carbon dioxide hydrate formation and dissociation in this work using quartz sand can be found in our previous studies [25], [26].

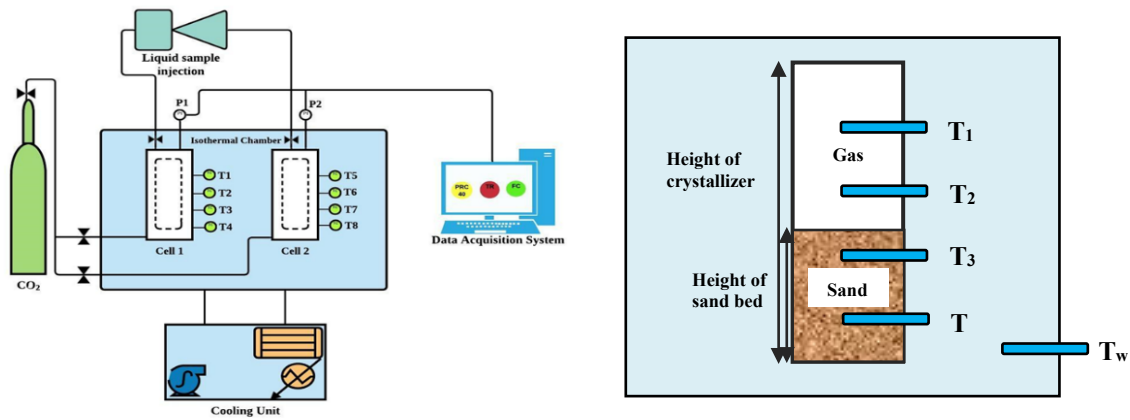


Figure 1. Schematic diagram of the gas hydrate experimental apparatus and internal reactor specification [25].

The recorded changes in the temperature and pressure were extracted to estimate the heating rate of each temperature probe in the gas phase and the porous media, respectively. Fig. 2 illustrates a typical temperature vs time profile during the hydrate dissociation process in this study. The estimated heating rates were used to investigate the carbon dioxide hydrate dissociation behaviour within the quartz sand bed.

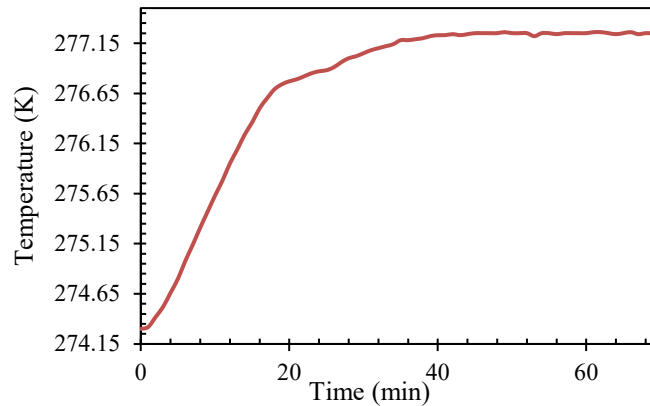


Figure 2. Typical Temperature - time curve of carbon dioxide hydrate dissociation in quartz sand.

### Evaluation Parameters

Since the main objective of this study is to measure the response of the hydrates to the thermal changes, the heating rates of CO<sub>2</sub> hydrate dissociation were used to quantify the heat transfer within the hydrate phase and the gas phase. To understand the correlation between the moles of hydrate formed and the heat transfer, the moles of CO<sub>2</sub> consumed, and the hydrate saturation was determined from the hydrate formation experiments.

CO<sub>2</sub> gas consumed (moles) is estimated using the expression below (Eq. 1)

$$\Delta n_H = \left[ \frac{PV}{zRT} \right]_0 - \left[ \frac{PV}{zRT} \right]_t \quad (1)$$

Hydrate saturation ( $h_s$ ) is evaluated by the following Eq. 2;

$$h_s (\%) = I_s \times 1.1C_{wh} \quad (2)$$

The heating rate (Hr) is calculated from the temperature vs time curve (Fig. 2) for every three minutes for the first one hour of heating (using Eq. 3). The differences in the heating rate within

the temperature profiles were estimated statistically using the analysis of variance (ANOVA) at 95% confidence level [27]. The dissociation rate was determined using Eq. 4.

$$Hr = \left(\frac{\Delta T}{dt}\right)_t \quad (3)$$

$$\left(\frac{d\Delta n_H}{dt}\right)_t = \frac{(\Delta n_H)_{t+\Delta t} - (\Delta n_H)_t}{\Delta t} \quad (4)$$

## Results and Discussion

### *Effect of the Heating Rate on Hydrate Dissociation*

In this work, the effect of the heating rate on carbon dioxide hydrate dissociation was determined in the porous media (quartz sand). The experiments were conducted by first forming the hydrates at 274.15 K and 4 MPa with brine and then heating/dissociating at temperature 277.15 K to evaluate the heating rate of carbon dioxide hydrate dissociation experiment.

Fig. 3 illustrates the temperature profile of the heating curves in the reactor where,  $T_w$  is the water bath temperature and is fixed at 274.15 K, the experimental temperature value. In Fig. 3,  $T_1$ ,  $T_2$  and  $T_3$ ,  $T_4$  represent the temperature profiles in the gas phase and the hydrate phase within the quartz sand, respectively. Here, the water bath temperature ( $T_w$ ) was heated from 274.15 K to 277.15 K initiating the dissociation process to attain equilibrium (Fig. 3). It is seen that the temperature curves in the hydrate phase ( $T_3$  and  $T_4$ ) deviate from  $T_w$  (system temperature) while the gas phase temperature curves ( $T_1$  and  $T_2$ ) go along with the system temperature ( $T_w$ ) profile (Fig. 3). The reason for this deviation is due to  $CO_2$  hydrates formed within the porous sediment (quartz sand). The hydrates delay the heat transfer rate during  $CO_2$  hydrate dissociation because of the endothermic nature of hydrate dissociation [11], [28].

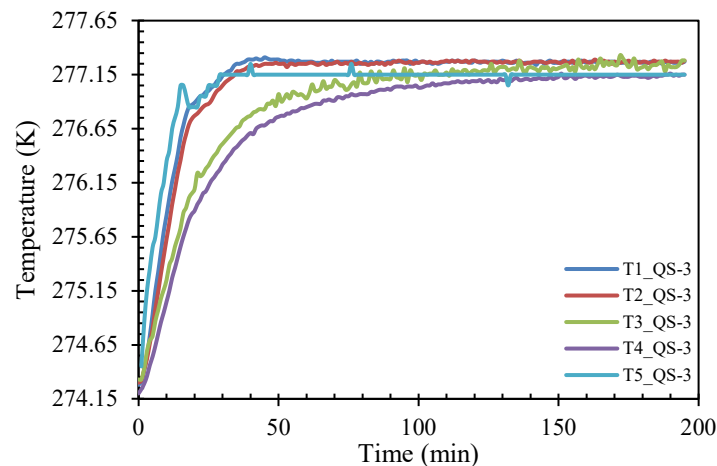


Figure 3. Temperature - time profile of the heating curves in quartz sand.

### *Effect of the Heating rate*

The heating rates of the quartz sand during carbon dioxide hydrate formation and dissociation were calculated to quantify the thermal behavior of the system. The heating rate of the porous media was estimated as a measure to compare the thermal effect in the absence of hydrates. Analysis of variance (ANOVA) was employed to statistically establish the difference in the heating rate of the porous media, respectively. Table 1 represents the calculated heating rates and the obtained P-values from ANOVA analysis in this study.

*Table 1. Heating rate of the porous media with and without CO<sub>2</sub> hydrates.*

Systems	Mean heating rate					P- value	F- value
	T1	T2	T3	T4	Tw		
Systems with CO <sub>2</sub> hydrates							
QS-1	0.026	0.026	0.026	0.026	0.026	0.999	0.003
QS-2	0.039	0.039	0.036	0.032	0.040	0.875	0.304
QS-3	0.042	0.041	0.036	0.035	0.040	0.971	0.130
System without hydrates							
QS-1	0.104	0.104	0.094	0.090	0.129	0.008	3.641
QS-2	0.099	0.098	0.095	0.089	0.117	0.022	2.983

The P-values in Table 1 suggest a statistical difference in the heating rate of the temperature curves in the gas phase (T<sub>1</sub> and T<sub>2</sub>) and the hydrate phase (T<sub>3</sub> and T<sub>4</sub>), as shown earlier in Fig. 3. The difference in the heating rate further confirms that the decrease in the heat transfer rate during the dissociation of CO<sub>2</sub> hydrates is caused by the formed hydrates in the quartz sand. The reduction in the heating rate is due to the absorption of heat by the CO<sub>2</sub> hydrates indicating the endothermic nature of hydrate dissociation [15].

However, the heating rates were similar with acceptable P-values below 0.05 (Table 1), in the absence of hydrates indicating that the response of the porous media towards the thermal behavior is the same. This further suggests that the temperature variation observed for the temperature profiles in the quartz sand/porous media (T<sub>3</sub> and T<sub>4</sub>), is solely due to the presence of hydrates. These findings are in line with the findings of Linga et al., [6] and Li et al., [29] where they claimed that the delay in the heat transfer was due to the hydrates present in the system and the endothermic dissociation behavior of the hydrates. They further confirmed that the magnitude of reduction in the heat transfer depends on the amount of hydrate formed within the porous media.

#### *Effect of the Porous media properties on the Heating rate of CO<sub>2</sub> hydrates*

Heat transfer is a crucial phenomenon in hydrate formation and dissociation which is directly related to the thermal stability of CO<sub>2</sub> hydrates [30]–[32]. Table 2 shows the details of the different quartz sand properties with the results obtained for carbon dioxide hydrate kinetics in this work.

*Table 2. Details of the porous media properties and obtained results for hydrate formation and dissociation.*

Sand Sample	System	Surface area (m <sup>2</sup> /g)	Grain size (mm)	Porosity (%)	Average pore size (nm)	Gas consumed (moles)	Time for 90% CO <sub>2</sub> release (hr)
QS-1	Brine	0.8499	< 0.6	44	9.8721	0.2390	5.23
QS-2	Brine	1.1000	0.6-0.8	38	8.1342	0.3900	1.96
QS-3	Brine	0.6449	0.8-2	42	8.3147	0.2760	2.33

However, when hydrates are present in the porous sediment, the response of the hydrates with respect to the porous sediment is complex in nature and not only depend on the thermal conductivity of the porous sediment [5]. In such instances, any major influence on the heat transfer behavior of the hydrates in the porous media is mainly described based on the exact location of the formed hydrates within the porous sediment. Based on the location, three types of hydrate forming behavior (Fig. 4) could be present, which significantly influences the heat transfer of the hydrates in the porous sediment [33].

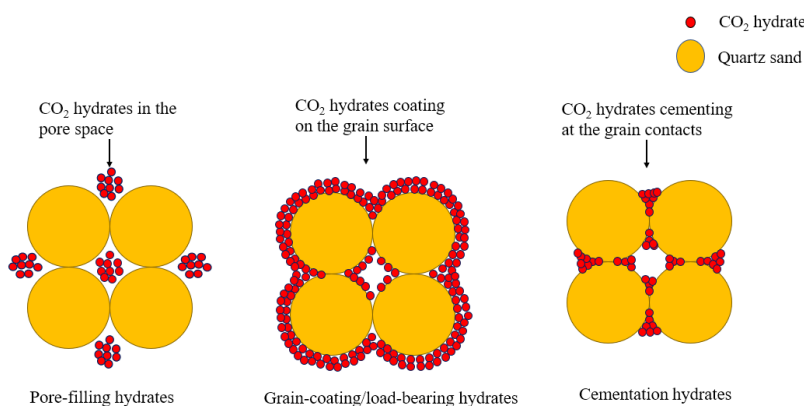


Figure 4. Different types of hydrate forming behavior in porous media.

Carbon dioxide hydrate formation in the porous sediment may occur as pore-filling (formed within the pore space), load-bearing (as particles coating) and cementation [34] type as shown in Fig. 4. For example, in a porous media with the same properties, hydrates formed on the surface of the pores (particles coating/load-bearing) will respond to the heat transfer faster than those formed at the centre of the pore space (pore-filling). It means, hydrate dissociation will be quicker for hydrates formed at the surface of the pores as opposed to the hydrates present within the pore space [33]. This action is because the hydrates formed as load-bearing assumes the same thermal conductivity as the porous media particles due to their direct contact with the surface of the particles. Therefore, CO<sub>2</sub> hydrate thermal stability in this study was further discussed with respect to the porous sediment properties and the hydrate formation behavior. This is necessary to know the heat transfer mechanism of the hydrates with the varying porous sediment properties (Table 2).

#### *Effect of porosity and particle size*

Fig. 5a illustrates the thermal response of the three different quartz sand particles (QS1- <0.6mm, QS2- 0.6-0.8mm, and QS3- 0.8-2mm). The thermal conductivity of the porous media particles increases with the particle size [35]–[37]. The heat transfer in the larger particles was 36% faster than the smaller particle sizes. In comparison, the moderate particle size conducts heat about 25% faster compared to the smaller particles (Fig. 5). This finding agrees with the results of Li et al., [29], where they reported that smaller particles respond slowly to heat transfer. This response indicates that the heat transfer behavior for any porous media is constant for specific particle sizes, but dependant on the hydrate formation mechanism/behavior and the petrophysical properties within that particular particle size. Also, the porosity of the porous media correlated with the heating rates showing that high porosity transfers the heat slowly due to the large void spaces between the particles, thus agreeing with the findings of Ahn and Jung [24].

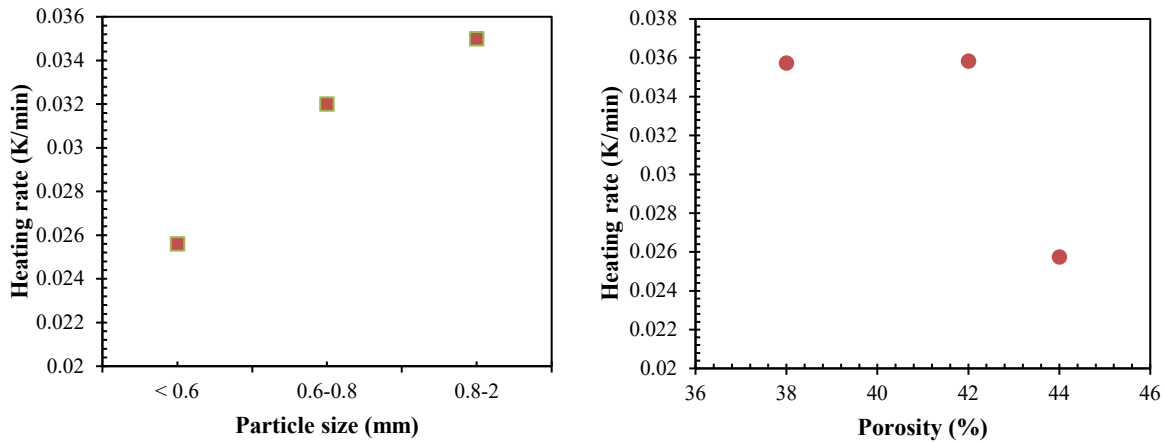


Figure 5. Effect of particle size and porosity on the heating rate of the quartz sand.

#### Effect of CO<sub>2</sub> Uptake and Hydrate Saturation

To know the thermal response of the carbon dioxide hydrates in the porous sediment, the measured heating rates were related to the amount of hydrate formed and the hydrate saturation in the porous media systems (Figure. 6). The heat absorption rate of the carbon dioxide hydrates formed are not consistent with the heating rates of the porous media particle sizes, as shown in Figure 5, especially for the QS-3 system. This is due to the heat transfer effect or variation in the quartz sand properties arising from the location at which the carbon dioxide hydrates formed within the quartz sand. The system with the largest porosity (QS-1) exhibited the slowest heating rate though it had the least hydrate uptake and saturation. However, it took the maximum time (5.23 hr) to achieve 90% of the carbon dioxide hydrate dissociation amongst the studied sand systems (Table 2). This is because QS-1 likely exhibits a pore filling hydrate formation mechanism owing to its large porosity. Which results in a slow heat transfer from the particle's surface to the hydrate crystals mainly due to the loose contact between the hydrates and the particle surface. This further implies that porous sediments with high porosity and pore-filling hydrate behavior are more suitable to store carbon dioxide hydrates with high thermal stability. However, such sediments might face challenges of high carbon dioxide storage capacity.

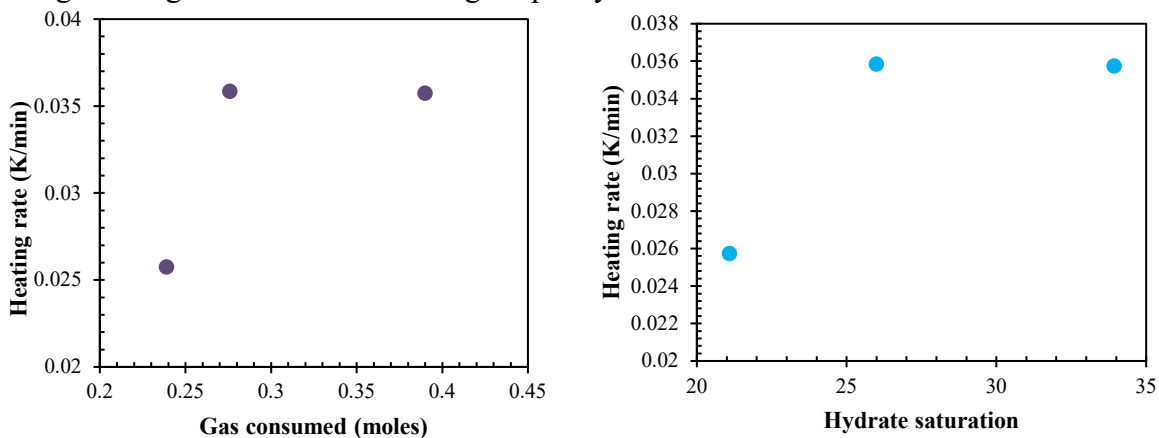


Figure 6. Effect of gas consumption and hydrate saturation on the heating rate.

On the contrary, the system with the lowermost and moderate porosity (QS-2 and QS-3), showed high heating rates and formed more hydrates with high gas uptake and hydrate saturation compared to the QS-1 system, respectively. However, the time elapsed to obtain 90% hydrate dissociation in these systems was 124 -166% faster than the QS-1 system (Table 2). The fast

dissociation time could be because both the systems QS-2 and QS3 have larger particle sizes and low porosity resulting in a higher rate of heat transfer between the porous media particles and the hydrates [37]. In the QS-2 system, more hydrates formed, and the dissociation time was less than QS-3 though they have relatively similar heating rates within the hydrate zone (Table 2 and Figure 7). Based on the effect of particle size, one may expect QS-3 (0.8-2 mm) to dissociate the hydrate faster than QS-2 (0.6-0.8 mm). This unusual dissociation trend between QS-2 and QS-3 is related to the heat transfer responses of the type of carbon dioxide hydrate formed within the pores and the location of the hydrate formed in the porous media. In QS-2, where the amount of hydrate formed is much higher (Table 2), it is most likely that the CO<sub>2</sub> hydrate formed within the pores are compact and acts as load bearing framework to the sand particles. This mechanism provides a direct contact of the hydrate to the particles with an enhanced surface area for fast heat conduction from the particles to the hydrates, leading to a faster hydrate dissociation. On the other hand, the hydrate formed in QS-3 is relatively less and probably have much less contact with the particles compared to QS-2. Thus, the hydrate exists in pores, causing a slow response of the hydrate to the heat from the porous media particles. This response suggests that the type of hydrate forming behavior and the location of the hydrate within the porous media are critical phenomenon to consider for the successful storage of carbon dioxide as hydrate in porous sediment.

### Conclusion

Herein, the heating rates of CO<sub>2</sub> hydrate dissociation in three quartz sand particles were evaluated to study the response of hydrates to heat transfer during carbon dioxide storage in quartz sand. The endothermic nature of hydrates controls their dissociation behavior in the porous sediment. Hydrate dissociation in porous media is highly controlled by the heat transfer between the porous sediment particles and the hydrates formed within the pores of the porous media. Porous media particles with high hydrate storage capacity most likely dissociate faster due to the high heating rate of the hydrates originating from the close contact of the hydrates formed within the pore network of the porous media. The type of hydrate forming behavior (pore-filling, load-bearing, cementation) influenced the thermal stability of carbon dioxide hydrates significantly. This mechanism suggests that smaller particle size is highly preferable to achieve optimum carbon dioxide hydrates thermal stability in porous media.

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