Carbon dioxide hydrate kinetics in porous media with and without salts

She Hern Bryan Yang 1, Ponnivalavan Babu 1, Sam Fu Sheng Chua, Praveen Linga ²
Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore

HIGHLIGHTS
• CO₂ hydrate formation and dissociation kinetics in pure and saline water in porous media.
• Slightly lower water conversion to hydrate in presence of salts compared to pure water.
• Dissociation investigated at two different temperature driving forces of 4 K and 10 K.
• Presence of salts did not impact the kinetics of CO₂ hydrate formation in porous media.

ARTICLE INFO
Article history:
Received 23 September 2014
Received in revised form 7 November 2014
Accepted 21 November 2014

Keywords:
Gas hydrates
CO₂ storage
Porous media
Energy recovery
CO₂ sequestration

ABSTRACT
Large amounts of methane (CH₄) exist in the earth in the form of natural gas hydrates, an ice-like substance with guest gas molecules trapped within. One proposed method to recover methane from marine natural gas hydrates is to sequester carbon dioxide (CO₂) as hydrates and produce methane. Fundamental understanding of CO₂ hydrate in marine environments – the formation and dissociation behavior needs to be understood first in order to develop techniques to facilitate the exchange process. In this study, CO₂ hydrate formation and dissociation was studied in Toyoura sand (100–500 μm), pure water, saltwater of 1.5 wt%, 3 wt% and natural seawater at formation pressure of 3.5 MPa and driving force of 1.5 MPa. Slightly lower water conversions to hydrate were observed when comparing pure water to saline water, though initial gas uptake in saline water was higher than that in pure water. Multiple nucleation was observed in pure water systems, possibly explaining a slightly higher rate of gas uptake after extended periods of time. Dissociation behavior was investigated at two different temperature driving forces of 4 K and 10 K. The presence of NaCl might have a slight impact on dissociation kinetics, causing slightly quicker dissociation than in pure water systems at the lower driving force of 4 K. We did not observe evidence of kinetic inhibition during hydrate formation due to the presence of NaCl but as expected, we observed thermodynamic inhibition.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction
Gas hydrates are crystalline non-stoichiometric solid compounds composed of water and gas [1–4]. Under sufficiently high pressure and low temperatures, where water molecules arrange in a rigid cage framework with cavities occupied by a guest gas molecule. Naturally occurring methane gas hydrates were discovered in a Siberian gas field and this resulted in a worldwide search for gas hydrates as a potential energy resource [5–9]. Methane hydrates were discovered to occur not only in permafrost but also along the ocean floors of continental margins and it has been established that gas hydrates in the marine environment outnumber that in the permafrost environment by several orders of magnitude. Despite uncertainties in estimation, the general consensus is that a large amount of methane exists in hydrated form on the earth, possibly twice the total amount of other fossil fuels present. A second consensus is that of the two geological forms in which hydrates are found (continental permafrost and offshore resources), the amount of hydrates offshore greatly exceeds that found on land (permafrost), possibly by two orders of magnitude (100 times).

Conventional and unconventional sources of natural gas are trapped in the earth due to geological factors – an impermeable seal or highly impermeable reservoir rock. However, methane hydrates
are fundamentally different from these other sources of natural gas. The methane molecules in the hydrate are trapped on a molecular level inside cages formed by water molecules bound by van der Waals-London forces [1,6]. The three main proposed methods of recovering methane from natural gas hydrate are thermal stimulation, depressurization and chemical injection [11–21]. Thermal stimulation and depressurization are methods that change the local P–T conditions such that methane hydrate is no longer stable and starts to dissociate while chemical inhibitor injection proposes to introduce substances that lower the stability of the hydrate till it is no longer stable at the natural conditions. Carbon dioxide also forms gas hydrates at suitable temperature and pressure conditions. Though slightly larger than methane, CO₂ also forms sI hydrates [22]. The idea of including CO₂ in the natural gas hydrate production process has been proposed and investigated [23–25]. CO₂ supplied to a hydrate field could assist in recovering the methane and at the same time be sequestered in the natural formation as CO₂ hydrate. In an ideal scenario where the same amount of, if not more, CO₂ is captured in the formation than natural gas produced, energy generation will be carbon neutral. Aside from exploitation of natural gas hydrates, forming CO₂ hydrates in the hydrate stability zones in natural environments is an attractive option for CO₂ sequestration [26–29]. A recent study has investigated the possibility of storing CO₂ in depleted gas reservoirs in North Alberta using various gas injection procedures such as the gas cap mode of gas injection and the spiral tube mode [30].

A fundamental understanding of hydrate formation and dissociation in the marine environment where the hydrates form in porous media and saline water is needed. It is already well established that NaCl is a thermodynamic inhibitor to hydrate formation and that in porous media of size smaller than 30 nm, significant changes in the hydrate phase equilibrium was observed [31,32]. The effect of particle size, pore size distribution, pore volume, porosity, permeability on hydrate phase equilibria has been investigated by several groups for different porous media [31,33–37]. Other studies have also studied formation and dissociation of CH₄ hydrate in porous media and pure water [15,38–40]. Mekala et al. [41] studied CH₄ hydrates in porous media (silica sand) and seawater, and reported that natural seawater showed signs of kinetic inhibition in porous media.

We note that most literature so far has focused on investigating CH₄ hydrates in nature. However, in the context of using CO₂ replacement as a technique to recover CH₄ from hydrates, and the possible storage and sequestration of CO₂ as hydrates, the formation and dissociation of CO₂ hydrates in marine environments need to be simulated. Several groups have directly investigated the replacement process in a laboratory setting [24,25,42–49]. These experiments involved the formation of methane hydrate samples in porous media and followed by injecting CO₂ at various conditions (liquid, gaseous or emulsion with water) into the sample resulting in a mixed hydrate of CH₄ and CO₂ as not all CH₄ in the hydrate phase can be replaced with CO₂. This is due not only to the inherent nature of CO₂ molecules being larger and not able to fit into a significant number of the small cages of the sI hydrate structure [25] but also due to the mass transfer hindrance that arises from the formation of mixed hydrate around the core CH₄ hydrate [24]. CO₂ can also form hydrates with free water present in the porous medium, posing additional hindrances to full recovery.

The objective of the present study is to understand the kinetics of hydrate formation and dissociation of CO₂ hydrates in various water/aqueous systems (pure water, 1.5 wt% NaCl, 3.0 wt% NaCl and seawater) in porous media. Toyoura sand with a particle size of 100–500 μm is used as porous media as it best simulates the porous, un consolidated structure of marine sediments. As a fundamental study, it was desired to keep CO₂ in the gas phase throughout the experiment and hence the experiments were carried out at a pressure of 3.5 MPa. Thermal stimulation at two driving forces were employed to study the dissociation characteristics of CO₂ hydrates in the porous media.

2. Experimental

2.1. Materials

For the porous medium, Toyoura silica sand with an average diameter of 300 μm (diameter varies from 100 to 500 μm) and pore volume of 0.217 cm³/g was used. We have employed this sand in our previous works on methane hydrates in porous media [40,41,50]. Deionized and distilled water was used as the pure water for hydrate formation. For the experiments involving laboratory made salt solution, pure NaCl salt was mixed with deionized water in proportion to produce 3.0 wt% and 1.5 wt% saltwater. The natural seawater (3.03 wt% salinity) used in this work was obtained from Pulau Tekong in Singapore, similar to that used in our previous works [40,41]. Carbon dioxide (CO₂) gas was supplied by Soxal Private Limited, Singapore.

2.2. Apparatus

Fig. 1 presents the schematic diagram of the crystallizer, a cylindrical shaped stainless steel 316 pressure vessel of 10.2 cm inner diameter, 15 cm inner height giving a volume of 1240 cm³. Five Omega copper–constantan T-type thermocouples were used to monitor the temperature at various points in the reactor and the layout is also presented in Fig. 1. Fig. 2 presents the overall experimental setup. The crystallizer (CR) and a 1000 cm³ gas reservoir (R) are immersed in a water bath coupled with an external refrigerator (ER) for temperature control. Each pressure vessel is connected to a Rosemount smart pressure transmitter and a Wika analog gauge. One additional Omega thermocouple is placed in the water bath to monitor water bath temperature. A control valve coupled with a PID controller was equipped between the crystallizer and the gas reservoir, which helps to maintain constant pressure during hydrate decomposition. All temperature and pressure data are acquired using the data acquisition system (National Instruments) and LabVIEW (National Instruments) via a computer to consolidate data and communicate with the control valves for the experiment.

3. Experimental procedure

3.1. Hydrate formation

3.1.1. Silica sand bed preparation

A bed height of 5 cm was employed and accordingly 645.16 g of silica sand was used. In order to completely saturate the silica sand bed, 140 ml of water was used. The volume of water required for complete saturation of the bed was calculated based on the interstitial void space of the sand bed (0.217 cm³/g). The bed was set up by uniformly layering sand and water in five to seven stages avoiding the formation of any air pockets. This procedure has been adapted from our previous works [51,52]. For other runs investigating the effect of salinity, salt solution of 1.5 wt% NaCl, 3 wt% NaCl or actual seawater were used in place of pure water to saturate the sand bed.

3.1.2. Hydrate formation procedure

The crystallizer was placed inside the water bath and the thermocouples, the gas supply and vent lines were connected. The water bath temperature is then set to the desired temperature of
hydrate equilibrium pressure, by careful venting. After depressurization, the temperature was allowed to stabilize at the experimental temperature, and then thermal stimulation was performed by increasing the water bath temperature to dissociate the formed hydrates. Decomposition was studied for two different incremental temperature rise from the formation temperature ($\Delta T = 4$ and 10 K). The temperature of the crystallizer was increased at a rate of 0.1–0.2 K/min. When the temperature crosses the equilibrium phase boundary conditions, the hydrate would start to decompose, resulting in a rise in the crystallizer pressure. The PID controller and a control valve maintains pressure in the crystallizer at 2.2 MPa by automatically opening and releasing gas into the gas reservoir. The temperature and pressure profiles in both the crystallizer and reservoir were recorded every 20 s.

The pressure recorded during dissociation also accounts for gas expansion during the thermal stimulation step. It has been shown by Babu et al. [52] that this expansion needs to be accounted in dissociation studies involving the presence of gas cap (overlying gas phase). This is done by carrying out control experiments involving heating under similar conditions but without the presence of hydrates. The actual dissociation pressure of hydrate in porous media is then adjusted by the pressure increase obtained during the control experiment.

The crystallizer is then depressurized with CO$_2$ by pressurizing to 500 kPa and depressurizing three times to flush the air present in the system. After which, the temperature of the reactor is allowed to settle back to the desired temperature. When the temperature of the reactor was steady at the desired level, the reactor was then pressurized to the desired pressure of 3.5 MPa with CO$_2$. CO$_2$ is a gas. When steady experimental temperature and pressure was attained, pressure and temperature data were recorded every 20 s. Hydrate nucleation is characterized by a sudden spike in bed temperatures followed by a period of increased gas uptake, represented by a higher rate of pressure drop in the reactor. The formation is said to be complete when there is no further gas uptake and the pressure drop is very small (~1–2 kPa/h).

### 3.2. Hydrate decomposition procedure

The crystallizer is first depressurized to 2.2 MPa after the end of formation experiment, corresponding to about 10% above the

### 4. Calculation

#### 4.1. Formation data

The experimental pressure and temperature data were used to calculate the CO$_2$ gas consumed at any time during the experiment. This is calculated based on below:

\[
(D\n_{H})_{t} = V_{CR} \left( \frac{P}{2RT} \right) \left( 1 - \frac{P}{2RT} \right)
\]

where $D_{H}$ is the amount of CO$_2$ gas consumed in moles, $z$ is the compressibility factor (calculated by Pitzer's correlations [53]), $V_{CR}$ is the volume of the crystallizer, $P$ and $T$ are the pressure and temperature of the crystallizer at any time.

Eq. (2) shows how the number of moles of water consumed was calculated.

**Conversion of water to hydrates, $C_{WH}$ (%)**

\[
C_{WH} = \frac{(D\n_{H})_{t}}{n_{H,0}} \times \text{hydration number} \times 100
\]

where $D_{H}$ is the number of moles of gas consumed at the end of the hydrate formation experiment can be determined from Eq. (1) and $n_{H,0}$ is the number of moles of water present in the reactor. The hydration number is the number of water molecules required to enclathrate one guest gas molecule. A hydration number of 6.28 was used for the present study [22].

Similarly, the conversion of carbon dioxide to hydrates is an important parameter since CO$_2$ storage or sequestration would require such as estimate for process design and scale up. The conversion of carbon dioxide to hydrates is given by:

**Conversion of CO$_2$ to hydrates, $C_{CH}$ (%)**

\[
C_{CH} = \frac{(D\n_{H})_{t}}{[n_{\text{start}} - n_{eq}]} \times 100
\]

where $D_{H}$ is the number of moles of gas consumed at the end of the hydrate formation experiment can be determined from Eq. (1), $n_{\text{start}}$ is the number of moles of CO$_2$ in the gas phase at the start of the experiment, $n_{eq}$ is the number of moles of CO$_2$ in the reactor at equilibrium ($P$ and $T$) that will remain in the gas phase of reactor, $n_{end}$ is the number of moles of CO$_2$ in the gas phase at the end of
the experiment. It is noted that $n_{eq}$ should be accounted in the denominator since that quantity will never participate in hydrate formation due to thermodynamic limit which would otherwise under estimate the CO$_2$ conversion to hydrates significantly.

The rate of hydrate formation can be computed by forward differentiation method through the following Eq. (4):

$$\frac{d\Delta n_{H}}{dt} = \frac{(\Delta n_{H})_{t + \Delta t} - (\Delta n_{H})_{t}}{\Delta t}, \Delta t = 5 \text{ min}$$

(4)

The average gas uptakes was computed for every 0.5 h and reported.

4.2. Decomposition data

Number of moles of gas recovered at a given time $t$ is calculated using Eq. (5):

$$\left(\Delta n_{H}\right)_{t} = V_R \left(\frac{P}{2RT}\right)_{t} - V_R \left(\frac{P}{2RT}\right)_0$$

where $\Delta n_H$ is the amount of CO$_2$ gas consumed in moles, $z$ is the compressibility factor (calculated by Pitzer’s correlations), $V_R$ is the volume of the reservoir, $P$ and $T$ are the pressure and temperature of the reservoir at any time.

The normalized gas recovery curves are calculated using Eq. (6):

$$\text{Normalized gas recovery} = \frac{(\Delta n_{H})_t}{(\Delta n_{H})_{t_{end}}}$$

(6)

where $(\Delta n_{H})_t$ is the number of moles of gas released at a given time $t$ during the hydrate dissociation experiment. $(\Delta n_{H})_{t_{end}}$ is the number of moles of gas recovered at the end of the hydrate dissociation experiment.

5. Results and analysis

All formation experimental studies of CO$_2$ hydrate were conducted in Toyoura sand (100–500 μm) with an initial pressure of 3.5 MPa in pure water, 1.5 wt% NaCl solution, 3.0 wt% NaCl solution and seawater. In order to maintain an initial pressure driving force of 1.5 MPa, experimental temperature was varied for pure water, seawater and different concentrations of NaCl solution as shown in Table 1.
5.1. Hydrate formation analysis

5.1.1. Pure water hydrate formation

Fig. 3 shows the gas uptake and the temperature profile for experiment P1, representative of all formation experiments conducted in pure water. Initially, CO₂ dissolves in the water dispersed in the sand bed. The time interval between the start of formation experiment and hydrate nucleation is known as the induction time (IT). Hydrate formation is marked by an initial nucleation event which is random in terms of its location within the bed. As hydrate formation is an exothermic process, the nucleation event shows up as a spike in temperature in the hydrate bed. Typically, the first nucleation is the largest in magnitude, giving rise to the largest spike in temperature among all subsequent nucleation events. Fig. 3A shows that the first nucleation event within the first 2 h from the start of the formation experiment. Fig. 3B shows the close-up of the nucleation event. We can clearly observe the initial dissolution phase of CO₂ into the sand bed. However, upon nucleation...
ation (~t = 1.18 h), gas uptake increases significantly, indicating the formation of hydrates within the crystallizer.

5.1.2. Hydrate formation in NaCl solution

Fig. 4 shows the corresponding gas uptake – temperature profiles for hydrate formations carried out in 3.0 wt% NaCl solution. We observed similar induction behavior and a relatively large temperature spike indicating initial nucleation. Gas uptake profiles are largely similar to that in pure water (see Fig. 3), where the initial rate is greatest on nucleation and decreases as formation progresses. However, one difference of note is that there were significantly fewer nucleation events post-first nucleation and this was observed for all 4 experimental runs. In formation experiments with NaCl solution, we clearly observe the initial nucleation, but did not observe multi-nucleation behavior as seen in the experiments with pure water. Similar behavior was observed for 1.5 wt% NaCl and seawater experiments and the gas uptake and temperature profiles are shown in Figs. S1 and S2 (given in supporting information). We did indeed observe that the presence of salts in the water has suppressed nucleation activity significantly. This is consistent with conclusions in the literature as it has been shown that the salts disrupt the regular lattice structure of gas hydrates and thus their presence could reduce the incidence of nucleation.

5.1.3. Conversion comparison at 90 h

In order to have a meaningful comparison between experiments involving water and different salt solutions, the first 90 h of each experiment were used as a basis for comparison. The first 90 h of a hydrate formation experiment includes the initial nucleation phenomena followed by a period of gas uptake where meaningful observations between pure water and saline water can be made. It is noted that all the experiments reached a steady state by 90 h. Beyond the period of 90 h, the rate of hydrate formation for all runs are close to zero and thus are not of significant interest to the discussion.

Fig. 5 shows the average rate of hydrate growth during the initial 5 h as well as between 50 and 60 h after the induction period for all studies. Noting once again that initial pressure driving force for all experiments were similar at 1.5 MPa, we observed that initial rate of hydrate formation in salt water systems were slightly greater than that in pure water systems. However, beyond the initial 2 h, the rates of hydrate formation for all systems have fallen significantly except that of pure water system. Beyond the initial time period, the rate of hydrate formation of that in pure water systems progresses at a rate faster than that in NaCl solution, as can be observed from Fig. 5B. This can possibly be attributed to the numerous multiple nucleation events observed for pure water systems, contributing to an increased rate of hydrate formation that sustains longer than that in salt water systems. Fig. 6 shows the temperature profile of a thermocouple T3 located within the sand bed at 3.25 cm from the gas–sand interface for a set of experiments representative of the different due to the release of excess gas during hydrate dissociation used. We clearly observed multiple nucleation phenomena for the pure water experiment while nucleation activity is suppressed in systems with NaCl or seawater. Also,
it can be postulated that the greater initial hydrate formation in salt water systems could have resulted in the reduction of potential pathways for CO₂ gas to penetrate into the sand bed and hence slowing down hydrate growth than in pure water systems. Similarly, a temperature profile of thermocouple T₁ located at 0.5 cm within the sand bed from the sand–gas interface for experiments conducted with pure water, different NaCl solution concentration and seawater is shown in Fig. S3 (given in supporting information).

Fig. 7 shows the gas uptake until nucleation and the final gas uptake with average and standard deviation for all the formation experiments performed. It appears that pure water systems did show slightly higher water conversion than systems that had salts present. The conversion of CO₂ to hydrates for all the experiments are tabulated in Table 1 and can be seen that about 59.3 (±5.8)%, 49.6 (±2.5)%, 49.1 (±5.1)%, and 51.35 (±8.4)% conversion is achieved for pure water, 1.5 wt% NaCl, 3.0 wt% NaCl solutions and seawater tested in this study.

Putting our results for hydrate formation into perspective, we can conclude that we did not observe significant kinetic inhibition in the presence of salts in CO₂ hydrate formation in porous media—this is in line with well documented literature on salts being thermodynamic inhibitors and not kinetic inhibitors for hydrate forma-
hydration formation in porous media and natural seawater. Hydrate formation needs to be investigated typically occupying mostly the large cages is able to occupy significantly recovery occurred in three stages system with the hydrate. This also transport hindrance within the experiments were at 4.2 MPa and 6.2 MPa, which are much higher – while both form sI structure hydrates, difference in cage occupation due to molecular size difference has already been mentioned study and observed that CO2 hydrate formation in porous media did not show signs of kinetic inhibition. The dissociation of CO2 hydrates is an endothermic process and that is why we observe that the temperature profiles within the sand bed do not mirror that of the gas phase. In fact, since heat transfer in solid and liquid media is faster than that in gas phase, where there is no chemical change taking place in the sand bed, we would expect the sand bed temperature to mirror that of the water bath temperature more closely than that of the gas phase. We observe that the temperature T4 increased the fastest among all thermocouples in the sand bed. This suggests that there were very few hydrates present around that location. With reference to Fig. 1, T4 is located deep within the sand bed and given that overall water conversion for Experiment P1 was 49%, it is reasonable to postulate that very little or no hydrate formation at such depths in the sand bed, possibly due to CO2 transport hindrance within the experiment time scale. Temperature profiles T2 to T4 rise initially then level off for a period of almost 40 min around 278.3 K. This is due to endothermic hydrate dissociation, which causes temperature rise to temporarily slow down as heat introduced from the water bath goes to the latent heat of dissociation of CO2 hydrate. This also reveals that the measured phase equilibrium temperature between gaseous CO2, liquid water and hydrates in porous media at 2.2 MPa and 278.3 K.

Table 2 summarizes the results of the dissociation experiments. Table 2 shows the CO2 recovery curve for experiment P4 carried out 2.2 MPa and ΔT of 10 K. Time zero correspond to the start of CO2 release from the hydrate. The CO2 recovery occurred in three stages for all dissociation experiments. For each stage, the gas release rate was calculated by fitting a straight line and presented along with the R2 values in Table 2. The gas release rate was faster in the first stage compared to second and third stage for all experiments. The time interval for each stage varied with respect to driving force (ΔT of 4 or 10 K) and solution (pure water, sea water, 1.5 and 3.0 wt% 

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Salt concentration (wt%)</th>
<th>Pressure (MPa)</th>
<th>ΔT (K)</th>
<th>Temperature (K)</th>
<th>Rate of CO2 release (mol/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Stage 1 [R2]</td>
</tr>
<tr>
<td>P1</td>
<td>0.0</td>
<td>2.2</td>
<td>4</td>
<td>281.2</td>
<td>0.5099 [0.9927]</td>
</tr>
<tr>
<td>P2</td>
<td>0.0</td>
<td>2.2</td>
<td>4</td>
<td>281.2</td>
<td>0.2581 [0.9898]</td>
</tr>
<tr>
<td>P3</td>
<td>0.0</td>
<td>2.2</td>
<td>10</td>
<td>287.2</td>
<td>1.3138 [0.9963]</td>
</tr>
<tr>
<td>P4</td>
<td>0.0</td>
<td>2.2</td>
<td>10</td>
<td>287.2</td>
<td>1.0968 [0.9932]</td>
</tr>
<tr>
<td>A1</td>
<td>1.5</td>
<td>2.2</td>
<td>4</td>
<td>280.5</td>
<td>0.4927 [0.9930]</td>
</tr>
<tr>
<td>A2</td>
<td>1.5</td>
<td>2.2</td>
<td>4</td>
<td>280.5</td>
<td>0.5611 [0.9931]</td>
</tr>
<tr>
<td>A3</td>
<td>1.5</td>
<td>2.2</td>
<td>10</td>
<td>286.5</td>
<td>1.1480 [0.9973]</td>
</tr>
<tr>
<td>A4</td>
<td>1.5</td>
<td>2.2</td>
<td>10</td>
<td>286.5</td>
<td>1.1042 [0.9960]</td>
</tr>
<tr>
<td>B1</td>
<td>3.0</td>
<td>2.2</td>
<td>4</td>
<td>279.7</td>
<td>0.4844 [0.9921]</td>
</tr>
<tr>
<td>B2</td>
<td>3.0</td>
<td>2.2</td>
<td>4</td>
<td>279.7</td>
<td>0.5382 [0.9956]</td>
</tr>
<tr>
<td>B3</td>
<td>3.0</td>
<td>2.2</td>
<td>10</td>
<td>283.8</td>
<td>1.0639 [0.9958]</td>
</tr>
<tr>
<td>B4</td>
<td>3.0</td>
<td>2.2</td>
<td>10</td>
<td>283.8</td>
<td>0.9654 [0.9884]</td>
</tr>
<tr>
<td>S1</td>
<td>Seawater</td>
<td>2.2</td>
<td>4</td>
<td>279.7</td>
<td>0.5126 [0.9878]</td>
</tr>
<tr>
<td>S2</td>
<td>Seawater</td>
<td>2.2</td>
<td>4</td>
<td>279.7</td>
<td>0.4734 [0.9914]</td>
</tr>
</tbody>
</table>

5.2. Dissociation analysis

5.2.1. P–T profile

For interpretation of color in Fig. 8, the reader is referred to the web version of this article.
NaCl solution). For the case of experiment P4, the first stage occurred till 20 min and second stage till 40 min and it took 1.4 h for complete recovery of CO2. A three stage gas release curve for experiment B2 with 3.0 wt% NaCl solution at 2.2 MPa and \( T_D \) of 4 K is shown in Fig. S4 (given in supporting information). For \( T_D \) of 4 K experiments, the first stage lasted for 30 min and also gas release rate was slower. It took 2.5 h for the gas release curve to reach steady state.

5.2.2. Comparison with different temperature driving force

Due to differing amounts of gas hydrate formed in each run, the absolute amounts of gas recovered in each decomposition experiment will vary. Hence, all decomposition data are normalized with respect to the final amount of gas recovered for meaningful comparison of data. Fig. 10 compares the normalized gas recovery curves for decomposition of hydrates formed in 1.5 wt% NaCl at \( \Delta T = 4 \) K and 10 K. Gas recovery for \( \Delta T = 10 \) K is much faster than \( \Delta T = 4 \) K and this falls within expectations since a greater temperature gradients gives a greater heat flux and thus more energy provided per unit time for the latent heat of dissociation of CO2 hydrates. Similar faster gas recovery was observed for \( \Delta T = 10 \) K than \( \Delta T = 4 \) K for experiments conducted with pure water and 3.0 wt% NaCl solution.

5.2.3. Comparison between pure and salt water

The time taken to obtain 90% gas recovery (t90) was calculated and given in Table 2. We observed that for all runs at the higher temperature driving force of 10 K, gas recovery is quick as the heat transfer is much faster. Fig. 11 clearly shows the difference in the time duration required to recover 90% of CO2 gas at 4 K driving force is much longer in pure water systems than in systems with NaCl. However, it is noted that the water conversions obtained from salt water runs (A1, A2, B1 & B2) ranges from 29.3% to 34.8%, while experiments P1 and P2 conducted with water had 44.1% and 42.5% water conversion respectively. The higher levels of hydrate present could be the main reason why gas recovery was slower as compared to that in salt water. On the other hand, t90 for gas recovery for experiments conducted at \( \Delta T (10) \) in water, 1.5 wt% NaCl and 3.0 wt% NaCl were 63.5, 53.5 and 47.5 min respectively. The difference between the water and salt experiments of t90 for gas recovery is not that significant compared to that observed for the \( \Delta T (4) \) K experiments. It is noted that the average water conversions for the respective formation experiments for water, 1.5 wt% NaCl and 3.0 wt% NaCl that were subjected to \( \Delta T (10) \) were 36.6 (±4.1)%, 31.9% and 33.2 (±1.1) % respectively. A future study can further this by performing dissociation experiments at even lower temperature driving forces as larger temperature driving forces reduce the overall time taken for dissociation.

5.2.4. Comparison of equilibrium conditions

As mentioned in the previous sections, it is possible to determine the equilibrium temperature corresponding to the phase equilibrium pressure between gaseous CO2, water (pure or saline) and CO2 hydrate in porous media. Fig. S5 (given in supporting information) shows the average of the equilibrium temperature deduced from each experiment for water or saline solutions conducted at an experimental pressure of 2.2 MPa. We observe, as expected, that the presence of NaCl does inhibit the thermodynamic stability of CO2 hydrate as equilibrium temperature decreases with increasing NaCl content.

6. Conclusion

CO2 hydrate formation and dissociation was studied in conditions of Toyoura sand (100–500 \( \mu \)m), pure water, saltwater of 1.5 wt%, 3 wt% and natural seawater. Slightly lower conversions were observed when comparing pure water to saline water formation. It was observed that CO2 hydrate formation in salt water had a higher initial rate (for the first 2 h) than that in pure water but formation rates in pure water after the initial period were higher than that in saltwater. We did not observe significant kinetic inhibition to the formation of CO2 hydrates in the presence of salts. Dissociation behavior was also investigated at two different temperature driving forces. A three stage CO2 release was observed for all experiments. Higher temperature driving forces resulted in faster dissociation rates. For a temperature driving force of 4 K, we observed a difference in dissociation rate in systems with pure water as compared to systems with NaCl.
Acknowledgements

The authors thank the Ministry of Education’s AcRF Tier 1 (R-279-000-386-112) and National University of Singapore (R-279-000-420-750) for the financial support.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apenergy.2014.011.052.

References
