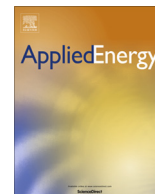




Contents lists available at ScienceDirect

Applied Energy

journal homepage: [www.elsevier.com/locate/apenergy](http://www.elsevier.com/locate/apenergy)

## Carbon dioxide hydrate kinetics in porous media with and without salts<sup>☆</sup>

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### HIGHLIGHTS

- CO<sub>2</sub> 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 CO<sub>2</sub> hydrate formation in porous media.

### ARTICLE INFO

#### Article history:

Received 23 September 2014  
Received in revised form 7 November 2014  
Accepted 21 November 2014  
Available online xxx

#### Keywords:

Gas hydrates  
CO<sub>2</sub> storage  
Porous media  
Energy recovery  
CO<sub>2</sub> sequestration

### ABSTRACT

Large amounts of methane (CH<sub>4</sub>) 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 (CO<sub>2</sub>) as hydrates and produce methane. Fundamental understanding of CO<sub>2</sub> 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, CO<sub>2</sub> 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.

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### 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

<sup>☆</sup> This paper is included in the Special Issue of Energy innovations for a sustainable world edited by Prof. S.k Chou, Prof. Umberto Desideri, Prof. Duu-Jong Lee and Prof. Yan.

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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 [1,6,10]. 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,  $\text{CO}_2$  also forms sl hydrates [22]. The idea of including  $\text{CO}_2$  in the natural gas hydrate production process has been proposed and investigated [23–25].  $\text{CO}_2$  supplied to a hydrate field could assist in recovering the methane and at the same time be sequestered in the natural formation as  $\text{CO}_2$  hydrate. In an ideal scenario where the same amount of, if not more,  $\text{CO}_2$  is captured in the formation than natural gas produced, energy generation will be carbon neutral. Aside from exploitation of natural gas hydrates, forming  $\text{CO}_2$  hydrates in the hydrate stability zones in natural environments is an attractive option for  $\text{CO}_2$  sequestration [26–29]. A recent study has investigated the possibility of storing  $\text{CO}_2$  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  $\text{CH}_4$  hydrate in porous media and pure water [15,38–40]. Mekala et al. [41] studied  $\text{CH}_4$  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  $\text{CH}_4$  hydrates in nature. However, in the context of using  $\text{CO}_2$  replacement as a technique to recover  $\text{CH}_4$  from hydrates, and the possible storage and sequestration of  $\text{CO}_2$  as hydrates, the formation and dissociation of  $\text{CO}_2$  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  $\text{CO}_2$  at various conditions (liquid, gaseous or emulsion with water) into the sample resulting in a mixed hydrate of  $\text{CH}_4$  and  $\text{CO}_2$  as not all  $\text{CH}_4$  in the hydrate phase can be replaced with  $\text{CO}_2$ . This is due not only to the inherent nature of  $\text{CO}_2$  molecules being larger and not able to fit into a significant number of the small cages of the sl hydrate structure [25] but also due to the mass transfer hindrance that arises from the formation of mixed hydrate around the core  $\text{CH}_4$  hydrate [24].  $\text{CO}_2$  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  $\text{CO}_2$  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  $\mu\text{m}$  is used as porous media as it best simulates the porous, unconsolidated structure of marine sediments. As a fundamental study, it was desired to keep  $\text{CO}_2$  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  $\text{CO}_2$  hydrates in the porous media.

## 2. Experimental

### 2.1. Materials

For the porous medium, Toyoura silica sand with an average diameter of 300  $\mu\text{m}$  (diameter varies from 100 to 500  $\mu\text{m}$ ) and pore volume of 0.217  $\text{cm}^3/\text{g}$  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 ( $\text{CO}_2$ ) 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  $\text{cm}^3$ . 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  $\text{cm}^3$  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  $\text{cm}^3/\text{g}$ ). 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

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