

Exploitation of methane in the hydrate by use of carbon dioxide in the presence of sodium chloride

Li Zunzhao, Guo Xuqiang*, Yang Lanying and Ma Xiaona

State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China

Abstract: The replacement process of CH₄ from CH₄ hydrate formed in NaCl solution by using pressurized CO₂ was investigated with a self-designed device at temperatures of 271.05, 273.15 and 275.05 K and a constant pressure of 3.30 MPa. The mass fraction of the NaCl solution was either 0.5 wt% or 1.0 wt%. The effects of temperature and concentration of NaCl solution on the replacement process were investigated. Experimental results showed that high temperature was favorable to the replacement reaction but high NaCl concentration had a negative effect on the replacement process. Based on the experimental data, kinetic models of CH₄ hydrate decomposition and CO₂ hydrate formation in NaCl solution were established. The calculated activation energies suggested that both CH₄ hydrate decomposition and CO₂ hydrate formation are dominated by diffusion in the hydrate phase.

Key words: CO₂ hydrate, CH₄ hydrate, guest molecule replacement, kinetic model

1 Introduction

CH₄ hydrates are found naturally in regions of permafrost and beneath the sea in outer continental margins. The total amount of methane in CH₄ hydrates worldwide is estimated at 0.9×10^9 - 1.02×10^{10} tons of oil equivalent (Makogon et al, 2007).

There are three methods available for CH₄ hydrate recovery including thermal treatment, depressurization and inhibitor addition (Sloan, 1998). All these methods are aimed at promoting CH₄ hydrate decomposition by external stimulation. There are some shortcomings in using the above methods for CH₄ hydrate exploitation. For example, the problem with the thermal treatment is the heat lost to reservoir rock and water. For the depressurization method, the decomposition processes for CH₄ recovery could lead to weakening the ocean floor (Lee and Holder, 2001). Adding inhibitor into the gas hydrates reservoir would pollute the sea environment.

Another method proposed for gas hydrate exploitation is the injection of CO₂. The idea of exchanging CO₂ for CH₄ in gas hydrates was first advanced by Ohgaki et al (1996). With this method the recovery of natural gas from a gas hydrate is combined with CO₂ sequestration. It offers two advantages: reducing CO₂ emissions into atmosphere and assisting gas hydrate exploitation, thereby helping overcome the economic impediments of CO₂ sequestration and CH₄ hydrate dissociation. Due to the consumption of fossil fuels, the world CO₂ emissions are expected to increase from 24 billion metric tons in 2001 to 39 billion metric tons in 2025 (Goel, 2006).

CO₂ sequestration has become an urgent problem deserving more attention.

The phase equilibrium of the CO₂-CH₄ binary system forming hydrates was investigated by Adisasmito et al (1991) and Ohgaki et al (1996). Experiment results show that the formation pressure of CO₂ hydrate is lower than that of CH₄ hydrate. Seo et al (2001) determined the two-phase equilibria of vapor and hydrate at the three different pressures 20, 26 and 35 bar. They reported that under lower pressure, the empty cavities of the hydrates are preferentially occupied by CO₂ rather than CH₄ and the replacement process may have good selectivity for CO₂. Another mechanism for replacement process is that the exothermic heat of CO₂ hydrate formation might induce the decomposition of CH₄ hydrate. This mechanism based on the fact that the exothermic heat of CO₂ hydrate formation is higher than that required for CH₄ hydrate decomposition.

Several researchers have investigated the replacement process for CH₄ recovery from CH₄ hydrate using pressurized CO₂ on a laboratory scale. Ota et al (2005a) conducted a CO₂ replacement process of CH₄ gas from CH₄ hydrate at a temperature range of 271.05-275.05 K and a pressure of 3.10-3.34 MPa. Jadhawar et al (2005) conducted replacement experiments in porous medium at laboratory scale and the results obtained indicated that the CH₄ recovery rate in porous medium was higher than that in bulk conditions obtained by Hirohama et al (1996).

The previous work concentrated on the replacement process with methane hydrates formed in pure water. Experiments of methane recovery from methane hydrates formed in NaCl solution have rarely been reported so far. As we all know, the natural gas hydrates stored in the seabed were formed in sea water. Although a salt-removing

*Corresponding author. email: guoxq@cup.edu.cn

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effect exists in the hydrate formation process, some NaCl is still attached to the hydrates and the porous media. So investigation of the kinetic process and the effect of NaCl on the replacement process are necessary for consideration of any future industrial production of methane from methane hydrates using CO₂.

For the first time, we conducted a series of CH₄ replacement experiments of CH₄ hydrate formed in NaCl solution by using pressurized CO₂ at laboratory scale at isothermal conditions (271.05 K, 273.15 K and 275.05 K) under pressures just above the CH₄ hydrate dissociation pressure (3.30 MPa). Based on the experimental data, a kinetic model was developed for CH₄ hydrate decomposition and CO₂ hydrate formation. Our objective was to investigate the effect of different factors on CH₄ replacement from CH₄ hydrates and provide a guide for possible future industrial exploitation of methane hydrates with CO₂ sequestration.

2 Experimental

2.1 Experimental apparatus

Fig. 1 is the schematic diagram of the experimental apparatus which consists of four major sections: an equilibrium cell equipped with a magnetic agitator, a sample supply system, a pressure-temperature measurement system and a composition analyzing system.

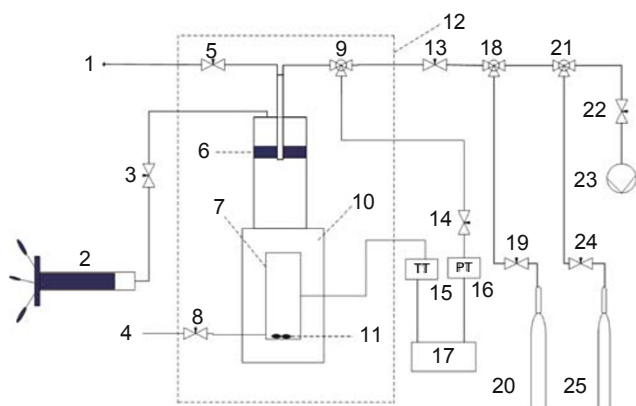


Fig. 1 Schematic diagram of the experimental apparatus

1-sample connection; 2-pressure pump; 3, 5, 8, 9, 13, 14, 17, 18, 19, 21, 22, 24-valve; 4-inlet/outlet for liquid; 6-piston; 7-glass window; 10-equilibrium cell; 11-magnetic stirrer; 12-air bath; 15-temperature sensor; 16-pressure sensor; 17-data acquisition system; 20-CH₄ gas cylinder; 23-vacuum pump; 25-CO₂ gas cylinder

Equilibrium cell The equilibrium cell, with an internal volume of 420 cm³, consists of a visual cell and a blind cell whose volume can be changed by a piston in it using a pressure pump. The pressure of the equilibrium cell can be maintained by changing the volume of the blind cell. The equilibrium cell was made of stainless steel, which allowed a maximum pressure of 20 MPa, and had a pair of glass windows on opposite side for observing gas hydrate and phase behavior. A magnetic stirrer was used to agitate fluids in the cell. Water or solution was fed into the cell by a plunger

pump.

Sample supply system The gas-sample charging system consists of CH₄ and CO₂ gas cylinders and a vacuum pump which was used to evacuate the cell.

Pressure-temperature measurement system The equilibrium pressure was measured by using an online pressure sensor (JYB-KH) with an accuracy of about 0.01MPa. The temperature was controlled by a programmed thermo-controller (CWYF-1) and measured with a temperature sensor (PT 100) with an accuracy of ± 0.1 K.

Analyzing system for gas composition For a mixed hydrate system, the composition of the gas-phase in equilibrium at a given temperature and pressure was measured directly by a gas chromatograph (HP6890). As the amount of water in the gas phase is negligibly small in the present experimental conditions, the gas-phase composition was only analyzed for CO₂ and CH₄. The composition was determined by comparing the peak area ratio of the unknown sample with that of a known standard sample of similar concentration.

Materials CH₄ and CO₂ gases used in this study were purchased from AP Beifen Gases Industry Co., Ltd, Beijing, China, with a certified purity of 99.99 vol%. NaCl was purchased from Beijing Shuanghuan Chemical Reagent Factory, China, with a certified purity 99.5 wt%. Distilled water was produced with a water distillation apparatus (SZ-93, Shanghai Yarong Biochemistry Instrument Factory, China).

2.2 Experimental procedures

Formation of CH₄ hydrates NaCl solution (0.5 wt% or 1.0 wt%) was added into the equilibrium cell at 273.2 K. CH₄ gas was introduced into the cell from the CH₄ cylinder. The cell was then pressurized up to 8.0 MPa, which is much higher than the three-phase equilibrium pressure of CH₄ hydrate at the operating temperature which was listed in Table 2. Agitation in the cell was started to promote the CH₄ hydrate forming. The gas phase pressure (8.0 MPa) was kept constant during the CH₄ hydrate formation.

Replacement of CH₄ from CH₄ hydrate using pressurized CO₂ First, the piston in the blind cell was moved to its bottom to make the volume of the equilibrium cell minimum. The temperature of the air bath was set to 267.8 K, at which CH₄ hydrate is very stable (Stern et al, 2001). Then in order to purge the cell by CO₂ gas, the CH₄ gas in the cell was released gradually to 1.60 MPa which was slightly higher than the equilibrium pressure of CH₄ hydrate at 267.8 K. Second, CO₂ gas was introduced into the cell gradually to 3.00 MPa which was slightly lower than the saturation pressure of CO₂ at 267.8 K and at the same time the volume of the blind cell was expanded to the maximum value (200 mL) by moving the piston to the top of the blind cell. The above two steps were repeated for three times to make sure that only a little CH₄ gas (less than 0.075 mol%) remained in the gas phase. The temperature of the cell was gradually raised to the desired operating value (Table 1) and the pressure was also increased to the desired value (Table 1) by driving the piston in the blind cell. A small amount of gas phase was sampled with an injector for analysis of the initial composition of the gas phase by gas chromatography. The time for temperature

rising was usually less than 60 minutes. The gas phase was sampled and analyzed as a function of time. Finally, after 100-150 hours passed, the hydrate mixture was decomposed by increasing the cell's temperature to 298.15 K and the gas composition was analyzed.

Table 1 lists the experimental conditions. The total amount (n_{Total}^{end}) of the gas mixture in the gas phase was determined with PT equation of state (Patel and Teja, 1982) by using the experimental temperature, and the gas phase volume and the gas composition were measured after the CH₄ and CO₂ hydrates mixture was decomposed. The initial amount ($n_{CH_4, H}^i$) of CH₄ trapped in the CH₄ hydrate phase was determined by Eq. 1. The initial amount ($n_{CH_4, H}^i$) of CO₂ and the total amount (n_{Total}^i) of the gas mixture were also calculated with PT equation of state by using the experimental temperature, the gas phase volume and the gas composition

which were measured at the beginning of the replacement reaction. The results showed that not all the H₂O molecules can react with CH₄ molecules to form CH₄ hydrate and the average gas storage of CH₄ hydrate is about 45.2 Sm³ of methane per m³ of pure hydrate.

$$n_{CH_4, H}^i = n_{Total}^{end} \times n_{CH_4} \% \quad (1)$$

$$n_{CO_2, G}^i = n_{Total}^i \times n_{CO_2} \% \quad (2)$$

Where, $n_{CH_4} \%$ and $n_{CO_2} \%$ mean the mole fraction of CH₄ and CO₂, respectively. The volume of gas phase at the beginning of the replacement reaction, which was used to calculate the n_{Total} in Eq. 2, was calculated from the volume of equilibrium cell, the dilatation of structure I hydrate, and the initial volume of the liquid solution or water.

Table 1 Experimental conditions

T, K	P, MPa	Mass of NaCl solution, g	Molality of NaCl, wt%	$n_{CH_4, H}^i$, mol	$n_{CH_2, G}^i$, mol	$n_{CH_2, G}^i/n_{CH_4, H}^i$
271.05	3.30	140.0	1.0	0.2989	0.4840	2.866
273.15	3.30	140.0	1.0	0.2963	0.5061	1.708
275.05	3.30	140.0	1.0	0.2371	0.4878	2.057
275.05	3.30	140.0	0.5	0.2982	0.4933	1.654

Table 2 shows the equilibrium pressures of CH₄ hydrate and CO₂ hydrate at different conditions which were

calculated with the Chen-Guo hydrate model(Chen and Guo, 1998).

Table 2 Equilibrium pressures of methane hydrate and CO₂ hydrate at different conditions

T, K	P, MPa	Molality of solute, wt%	Equilibrium pressure of CH ₄ hydrate, MPa	Equilibrium pressure of CO ₂ hydrate, MPa
271.05	3.30	1.0	2.38	1.02
273.15	3.30	1.0	2.70	1.30
275.05	3.30	1.0	3.27	1.68
275.05	3.30	0.5	3.18	1.57

During the replacement process, the moles of each components in the gas phase and in the hydrate phase were calculated with the following equations.

$$n_{CH_4, G} = n_{Total, G} \times n_{CH_4} \% \quad (3)$$

$$n_{CO_2, G} = n_{Total, G} \times n_{CO_2} \% \quad (4)$$

$$n_{CH_4, H} = n_{CH_4, H}^i - n_{CH_4, G} \quad (5)$$

$$n_{CO_2, H} = n_{CO_2, G}^i - n_{CO_2, G} \quad (6)$$

Where $n_{Total, G}$ refers the total moles of CH₄ and CO₂ in gas phase. While $n_{CH_4, H}$ and $n_{CO_2, H}$ mean the moles of CH₄ and CO₂ respectively trapped in the hydrate phase.

3 Results and discussion

Fig. 2 and Fig. 3 show the relationship of CH₄ amount ($n_{CH_4, G}$) from CH₄ hydrate decomposition, and CO₂ amount ($n_{CO_2, H}$) trapped in CO₂ hydrates, with time, respectively, at different temperatures. The amount of CH₄ recovered from CH₄ hydrate and that of CO₂ formed to CO₂ hydrate increased with time. The effect of temperature on the replacement efficiency is significant. Increasing the temperature can enhance the replacement rate.

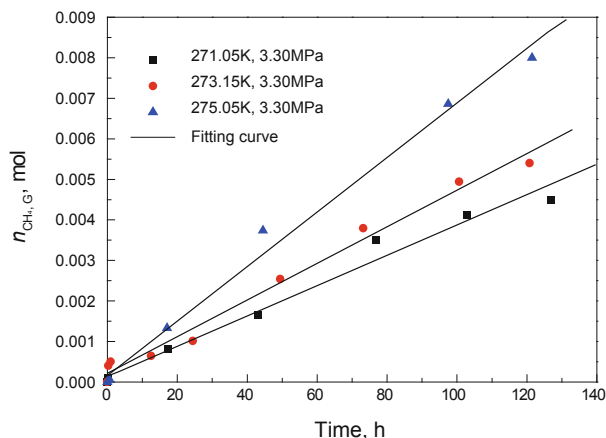


Fig. 2 Relationship of the CH₄ amount ($n_{CH_4,G}$) from CH₄ hydrate decomposition with time at different temperatures

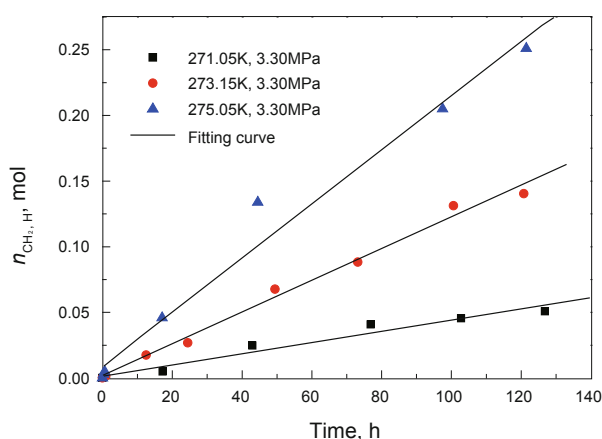


Fig. 3 Relationship of the CO₂ amount ($n_{CO_2,H}$) trapped in CO₂ hydrate with time

Fig. 4 and Fig. 5 show the effect of NaCl concentration on the replacement process. It can be seen that NaCl concentration did not influence the replacement rate nearly as much as the temperature did. And that at the same temperature, the lower the NaCl concentration, the higher the replacement rate, indicating that NaCl concentration is an influencing factor for the replacement process.

Fig. 4 and Fig. 5 also show that the CH₄ released from CH₄ hydrate decomposition by replacement with CO₂ is not equal to the amount of CO₂ trapped in the hydrate phase, the former is larger than the later. Table 1 shows that the gas storage of CH₄ hydrate did not reach the ideal storage (150-180 Sm³ of methane per m³ of pure hydrate) (Hao et al, 2008) and some absorbed water existed in the CH₄ hydrate phase. One reason for the difference in CH₄ and CO₂ amounts might be that some CO₂ molecules formed hydrate with the absorbed water in the CH₄ hydrate phase or dissolved in the water phase. Another reason might be that the CH₄ molecules engaged in the small cages are more stable (Ota et al, 2005b) than those in the large cages at low CH₄ gas storage, hence the CO₂ can replace the most of CH₄ trapped in the large cages of methane hydrate and only a small part of CH₄ in the small cages. The

above two reasons may result in the difference between the CH₄ amount from CH₄ hydrate decomposition and the CO₂ amount trapped in the hydrate phase.

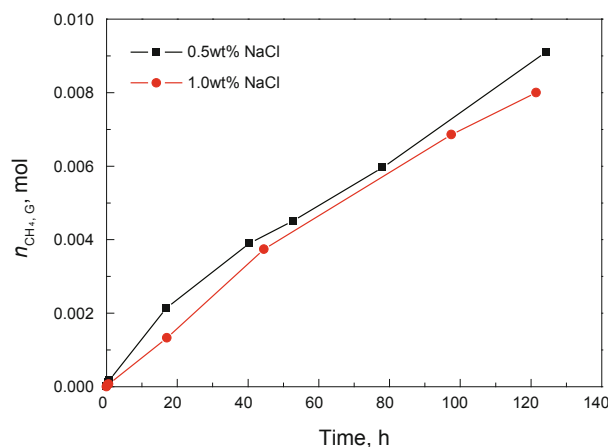


Fig. 4 Relationship of the CH₄ amount ($n_{CH_4,G}$) from CH₄ hydrate decomposition with time at different NaCl concentrations at 275.05K and 3.30 MPa

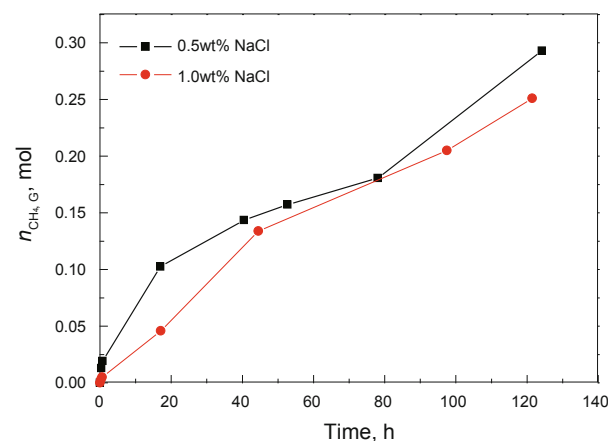


Fig. 5 Relationship of the CO₂ amount ($n_{CH_2,H}$) trapped in CO₂ hydrate with time at different NaCl concentrations at 275.05 K and 3.30 MPa

4 Development of kinetic model

In order to further study the replacement process, the hydrate decomposition and formation models suggested by Bishnoi and Natarajan (1996) were applied to correlate the obtained experimental data. The models were also used for describing the CH₄ replacement process in a pure water system by Ota et al (2005a). In this work, the driving force for the CH₄-CO₂ replacement process was assumed to be proportional to the fugacity difference between the gas phase and the hydrate phase. The model for CH₄ hydrate decomposition is given as follows:

$$\frac{dn_{CH_4,H}}{dt} = -k_{Dec} A (f_{CH_4,H} - f_{CH_4,G}) \tag{7}$$

$$\frac{1}{k_{Dec}} = \frac{1}{k_{Dec,R}} + \frac{1}{k_{Dec,D}} \tag{8}$$

Because the CH_4 amount increased in the gas phase was equal to that of CH_4 hydrate decomposition, Eq. 7 can be expressed as the following form:

$$\frac{dn_{\text{CH}_4,\text{H}}}{dt} = -\frac{dn_{\text{CH}_4,\text{G}}}{dt} = -k_{\text{Dec}}A(f_{\text{CH}_4,\text{H}} - f_{\text{CH}_4,\text{G}}) \quad (9)$$

Where t is the reaction time (s), f is the fugacity (MPa), k_{Dec} is the overall rate constant of the CH_4 hydrate decomposition ($\text{mol}^{-1}\text{m}^{-2}\text{MPa}^{-1}$), A is the surface areas (m^2) between the gas phase and the hydrate phase, which can be calculated from the diameter of the equilibrium cell. k_{Dec} consists of $k_{\text{Dec,R}}$ and $k_{\text{Dec,D}}$. The former ($k_{\text{Dec,R}}$) is the rate constant of CH_4 hydrate decomposition reaction and the latter ($k_{\text{Dec,D}}$) is the rate constant of mass transfer of CH_4 in the hydrate phase.

The model for CO_2 hydrate formation during the replacement was similarly given by:

$$\frac{dn_{\text{CO}_2,\text{H}}}{dt} = k_{\text{Form}}A(f_{\text{CO}_2,\text{G}} - f_{\text{CO}_2,\text{H}}) \quad (10)$$

$$\frac{1}{k_{\text{Form}}} = \frac{1}{k_{\text{Form,D}}} + \frac{1}{k_{\text{Form,R}}} \quad (11)$$

Where k_{Form} is the overall rate constant of the CO_2 hydrate formation ($\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{MPa}^{-1}$), which also consists of two rate constants.

In these models, $f_{\text{CH}_4,\text{G}}$ and $f_{\text{CO}_2,\text{G}}$ are calculated with PT equation of state (Patel and Teja, 1982) for a certain elapsed time using the experimental temperature, pressure and gas composition of the gas phase. The fugacity in the hydrate phase ($f_{\text{CH}_4,\text{H}}$ and $f_{\text{CO}_2,\text{H}}$) was calculated with the Chen-Guo hydrate model (Chen and Guo, 1998) using the experimental conditions. The k_{Dec} and k_{Form} were determined by minimizing the sum of squares of differences between the experimental values and those calculated from the proposed models. The calculated results and deviations are listed in Table 3.

Table 3 Calculation values of k_{Dec} and k_{Form} at different temperatures and 3.30 MPa

T, K	$k_{\text{Dec}} \times 10^5, \text{mol}\cdot\text{MPa}^{-1}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$	$k_{\text{Form}} \times 10^5, \text{mol}\cdot\text{MPa}^{-1}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
271.05	0.30±0.02	4.50±0.41
273.15	0.35±0.03	15.10±0.70
275.05	0.42±0.04	32.86±2.91

Fig. 6 shows the relationship of $\ln k_{\text{Dec}}$ and $\ln k_{\text{Form}}$ with temperature. The activation energies for CH_4 hydrate decomposition and CO_2 hydrate formation were calculated from the slope of the Arrhenius plot shown in Fig. 6. The measured activation energies for CH_4 hydrate decomposition and CO_2 hydrate formation were 52.01 kJ/mol and 308.20 kJ/mol, respectively.

In this work, the activation energy of CH_4 hydrate decomposition was calculated to be 52.01 kJ/mol. Ota et al (2005a) investigated the kinetics of methane recovery from

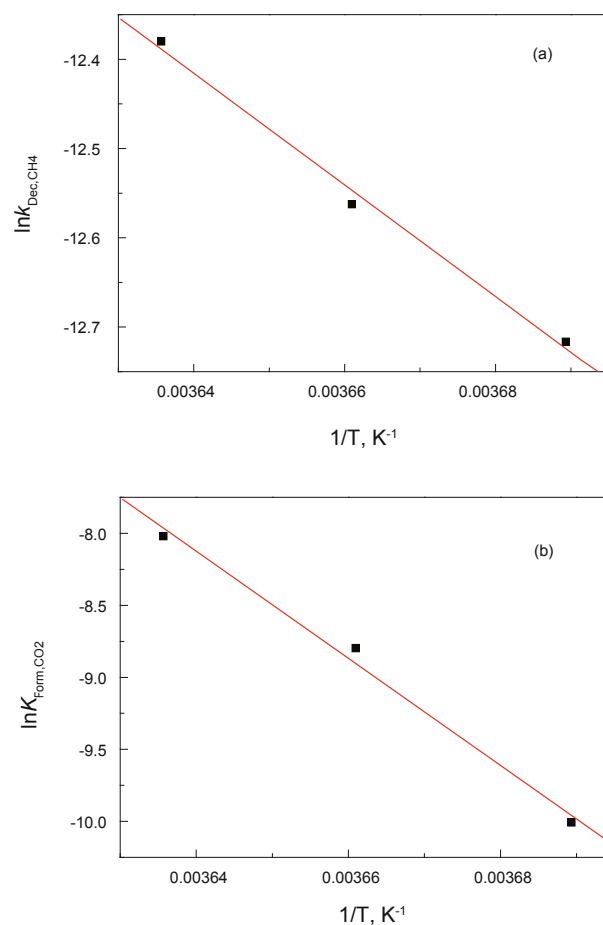


Fig. 6 Temperature dependence of the rate constants (k_{Dec} and k_{Form}) at 3.30 MPa

methane hydrate formed in pure water system by use of CO_2 and obtained the activation energy for the CH_4 hydrate decomposition as 14.5 kJ/mol. Li et al (2007) conducted the replacement process of methane from methane hydrate formed in sodium dodecyl sulfate (SDS) system and obtained an activation energy for the CH_4 hydrate decomposition as 28.8 kJ/mol. The reason for great difference between the activation energies of CH_4 hydrate decomposition reported by the above two group researchers and that obtained in this study might be that the mass transfer of CH_4 gas in hydrate phase formed in NaCl system was more difficult than that in pure water system or SDS system. As mentioned above, the absorbed water existed in CH_4 hydrate formed in NaCl system, making it difficult for CO_2 diffusion in the hydrate phase. The activation energy for molecular diffusion in the solid phase has been reported often, for instance, the activation energy for H_2O molecular diffusion in ice was 70 kJ/mol (Livingston et al, 1997). In addition, Wang et al (2002) measured the kinetics of CH_4 hydrate formation from neutron diffraction and reported that the activation energy for CH_4 diffusion in the hydrate phase was 61.5 kJ/mol. From the above results, $k_{\text{Dec,D}}$ in Eq.8 seem to be the controlling factor in the CH_4 - CO_2 replacement process.

The activation energy for CO_2 hydrate formation was determined to be 308.20 kJ/mol in this work, which was

larger than that for CH₄ hydrate decomposition (52.01kJ/mol). Ota et al (2005a) obtained the activation energy for CO₂ hydrate formation as 73.3kJ/mol and concluded that the CO₂ diffusion in hydrate controlled the process of replacement. The activation energy for CO₂ hydrate formation obtained in this study was very much larger than the value measured by Ota et al (2005a). We suggested that the CO₂ hydrate formation may involve the following processes: As lots of absorbed water surrounded the CH₄ hydrates, CO₂ had to dissolve in the water phase and some CO₂ contact with the CH₄ hydrates to replace CH₄ from CH₄ hydrate. This process may need more reaction energy. So the diffusion for CO₂ in hydrate ($k_{\text{From, D}}$) in Eq.11 seems to be the controlling factor in the replacement process.

5 Conclusion

The replacement of CH₄ from CH₄ hydrate formed in NaCl solution by using pressurized CO₂ was investigated. It was found that the amount of CH₄ released from CH₄ hydrate and that of CO₂ trapped in the hydrate increased with time. The higher the temperature, the more rapid the replacement reaction. The experimental data showed that NaCl has a negative effect on the replacement process. Kinetic models for CH₄ hydrate decomposition and CO₂ hydrate formation were developed by hypothesizing that the fugacity difference between the gas phase and the hydrate phase was the driving force for the CH₄-CO₂ replacement process. The experimental data and activation energies indicated that both CH₄ hydrate decomposition and the CO₂ hydrate formation were dominated by diffusion in the hydrate phase.

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Nomenclatures

A	Surface area between gas phase and hydrate phase, m ²
$f_{\text{CH}_4, \text{H}}$	Fugacity of CH ₄ in hydrate phase, MPa
$f_{\text{CH}_4, \text{G}}$	Fugacity of CH ₄ in gas phase, MPa
$f_{\text{CO}_2, \text{G}}$	Fugacity of CO ₂ in gas phase, MPa
$f_{\text{CO}_2, \text{H}}$	Fugacity of CO ₂ in hydrate phase, MPa
k_{Dec}	Overall rate constant of the decomposition, mol·s ⁻¹ ·m ⁻² ·MPa ⁻¹
$k_{\text{Dec, D}}$	Rate constant of mass transfer of CH ₄ in hydrate phase, mol·s ⁻¹ ·m ⁻² ·MPa ⁻¹
$k_{\text{Dec, R}}$	Rate constant of decomposition reaction of CH ₄ in hydrate phase, mol·s ⁻¹ ·m ⁻² ·MPa ⁻¹
k_{Form}	Overall rate constant of formation, mol·s ⁻¹ ·m ⁻² ·MPa ⁻¹
$k_{\text{Form, R}}$	Rate constant of formation of CO ₂ in hydrate phase, mol·s ⁻¹ ·m ⁻² ·MPa ⁻¹

$n_{\text{CH}_4, \text{H}}^i$	Initial amount of CH ₄ trapped in hydrate phase, mol
$n_{\text{CO}_2, \text{G}}^i$	Initial amount of CO ₂ in gas phase, mol
$n_{\text{CH}_4, \text{H}}$	Mole fraction of CH ₄ in gas phase
$n_{\text{CO}_2, \text{H}}$	Mole fraction of CO ₂ in gas phase
$n_{\text{CO}_2, \text{G}}$	Total amount of CH ₄ and CO ₂ in gas phase, mol
T	Temperature, K
$time$	Reaction time, hour

Superscripts

i	Initial stage of the reaction
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Subscripts

D	Diffusion of molecule
Dec	Decomposition reaction
Form	Formation reaction
G	Gas phase
H	Hydrate phase
R	Reaction

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