

Review

## A Review on Research on Replacement of CH<sub>4</sub> in Natural Gas Hydrates by Use of CO<sub>2</sub>

Jiafei Zhao <sup>1</sup>, Kun Xu <sup>1</sup>, Yongchen Song <sup>1,\*</sup>, Weiguo Liu <sup>1,\*</sup>, Weihaur Lam <sup>1,2</sup>, Yu Liu <sup>1</sup>, Kaihua Xue <sup>1</sup>, Yiming Zhu <sup>1</sup>, Xichong Yu <sup>3</sup> and Qingping Li <sup>3</sup>

<sup>1</sup> Key Laboratory of Ocean Energy Utilization and Energy Conservation of Ministry of Education, Dalian University of Technology, Dalian 116024, China; E-Mails: jfzhao@dlut.edu.cn (J.Z.); tjjxxk@126.com (K.X.); weihaur.lam@gmail.com (W.L.); liuyu@dlut.edu.cn (Y.L.); khxue@dlut.edu.cn (K.X.); ymzhu@dlut.edu.cn (Y.Z.)

<sup>2</sup> Department of Civil Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia

<sup>3</sup> CNOOC Research Center, Beijing 100027, China; E-Mails: yuxch@cnooc.com.cn (X.Y.); liqp@cnooc.com.cn (Q.L.)

\* Authors to whom correspondence should be addressed; E-Mails: songyc@dlut.edu.cn (Y.S.); liuwg@dlut.edu.cn (W.L.); Tel.: +86-411-84706722; Fax: +86-411-84706722.

Received: 28 December 2011; in revised form: 6 February 2012 / Accepted: 8 February 2012 / Published: 22 February 2012

---

**Abstract:** This paper introduces the research advances on replacement of CH<sub>4</sub> in Natural Gas Hydrates (NGHs) by use of CO<sub>2</sub> and discusses the advantages and disadvantages of the method on the natural gas production from such hydrates. Firstly, the feasibility of replacement is proven from the points of view of kinetics and thermodynamics, and confirmed by experiments. Then, the latest progress in CH<sub>4</sub> replacement experiments with gaseous CO<sub>2</sub>, liquid CO<sub>2</sub> and CO<sub>2</sub> emulsion are presented. Moreover, the superiority of CO<sub>2</sub> emulsion for replacement of CH<sub>4</sub> is emphasized. The latest experiment progress on preparation of CO<sub>2</sub> emulsions are introduced. Finally, the advancements in simulation research on replacement is introduced, and the deficiencies of the simulations are pointed. The factors influencing on the replacement with different forms of CO<sub>2</sub> are analyzed and the optimum conditions for the replacement of CH<sub>4</sub> in hydrated with different forms of CO<sub>2</sub> is suggested.

**Keywords:** gas hydrate; replacement; carbon dioxide; feasibility; emulsion; simulation

**Nomenclature:** $t$  = time, s $X_{\text{CH}_4}/X_{\text{CO}_2}$  = ratio of  $\text{CH}_4$  and  $\text{CO}_2$  in the vapor phase $(X_{\text{CH}_4}/X_{\text{CO}_2})_0$  = initial ratio of  $\text{CH}_4$  and  $\text{CO}_2$  in the vapor phase $\alpha$  = fitting parameter related to the a condensation rate of  $\text{CH}_4$  molecules from the vapor phase $n_{\text{CH}_4\text{.H}}$  = remaining amount of  $\text{CH}_4$  in the hydrate phase, mol $n_{\text{CO}_2\text{.H}}$  = amount of  $\text{CO}_2$  in the hydrate phase, mol $f$  = fugacity, MPa $k_{\text{Dec}}$  = overall rate constant of the decomposition, mol/s·m·MPa $k_{\text{Dec.R}}$  = reaction rate constant of decomposition, mol/s·m·MPa $k_{\text{Dec.D}}$  = decomposition rate constant of mass transfer in the hydrate phase, mol/s·m·MPa $k_{\text{Form}}$  = overall rate constant of the formation, mol/s·m·MPa $k_{\text{Form.R}}$  = reaction rate constant of formation, mol/s·m·MPa $k_{\text{Form.D}}$  = formation rate constant of mass transfer in the hydrate phase, mol/s·m·MPa $A$  = surface area between the gas and the hydrate phase,  $\text{m}^2$  $H$  = hydrate phase $G$  = gas phase**1. Introduction**

Natural gas hydrates (NGHs) are non-stoichiometric crystalline compounds formed by natural gas and water molecules under low temperature and high pressure [1]. NGH widely exists below the ocean floor and in permafrost zones [2], and there is a large amount of NGH in Nature [3,4], so it is regarded as a potential future energy resource with great commercial exploitation potential. At present, the main mining methods for natural gas production from hydrates include depressurization, thermal stimulation and addition of inhibitors [5–7]. The methods promote hydrate decomposition to produce natural gas by destroying hydrate's phase equilibrium under initial conditions. However, as various mining methods' technical and economical features are taken into account, it has to be considered that NGH plays an important role in stabilizing the stratum where it exists [8]. During the process of NGH mining by use of the traditional methods, the decomposition of NGH may make the stratum where it exists become unstable and lead to geological disasters such as earthquakes, submarine landslides, *etc.* [9–11]. On the other hand, as the rapid development of human society produces massive discharges of greenhouse gases this has become a big environmental issue which humans have to face, and  $\text{CO}_2$  storage is an effective measure to reduce  $\text{CO}_2$  emissions and reduce the greenhouse effect [12,13].

Based on the two points on the above, Ebinuma [14] and Ohgaki *et al.* [15] suggested a new method for natural gas recovery from hydrates in sediments by use of  $\text{CO}_2$ . As a method which combines  $\text{CO}_2$  long-term storage and NGH mining, this method can not only avoid some traditional mining methods' disadvantages, such as a lack of heat source by depressurization method, the low efficiency of heat by thermal stimulation method, the high cost and damage to the stratum by the inhibitor addition method,

but also provide a way to stabilize the stratum below the ocean floor and store CO<sub>2</sub> for a long time [15,16].

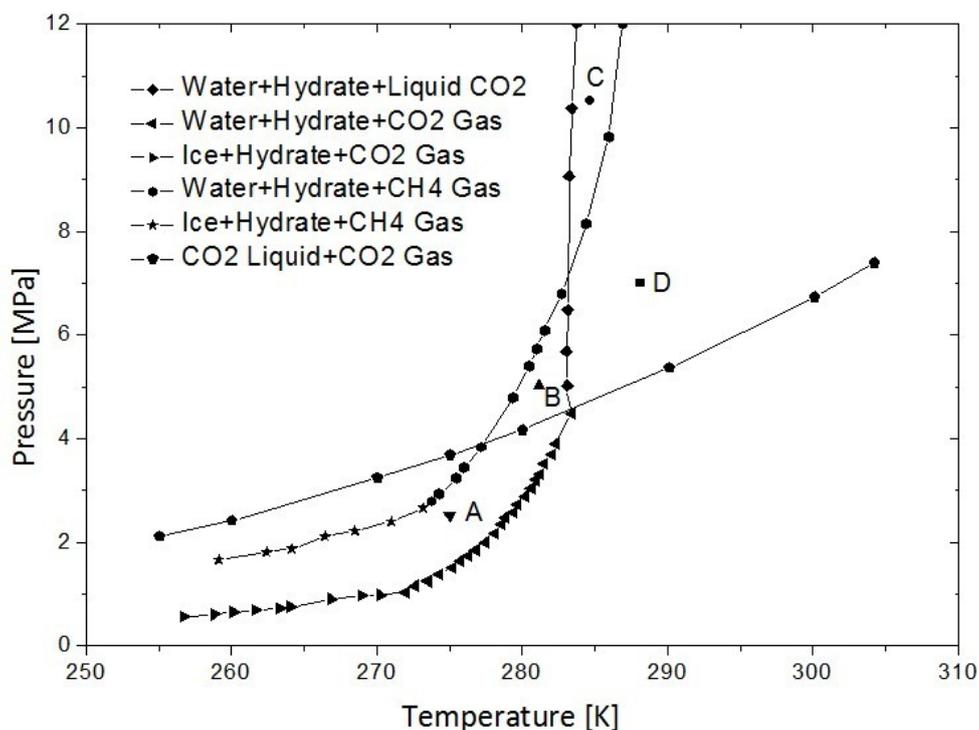
The replacement method by use of CO<sub>2</sub> is regarded as a promising NGH mining method, and has attracted great attention from researchers all over the world, but the slow replacement rate and low replacement efficiency restrict the method's role in commercial applications [2,15]. According to the experimental data reported by Ota *et al.* [17] and Li *et al.* [18,19], during the replacement of CH<sub>4</sub> by use of gaseous CO<sub>2</sub> at temperatures ranging from 271.2 K to 276 K and at an initial pressure of 3.25 MPa, the replacement reaction rate became extremely slow after the early stages (about 10 h), besides, the ratio of CH<sub>4</sub> released from hydrate was no more than 15% within 100 h. If the replacement rate and efficiency cannot be improved, the replacement method should not have any actual practical value.

## 2. Feasibility Study of Replacement Reaction

### 2.1. The Thermodynamic Feasibility of Replacement

Figure 1 is the equilibrium diagram of CH<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>O system drawn based on the data from Sloan *et al.* [20]. In the diagram, areas A and B are above the equilibrium curve of H<sub>2</sub>O-hydrate-CO<sub>2</sub> and below that of H<sub>2</sub>O-hydrate-CH<sub>4</sub>, so in theory, gaseous CH<sub>4</sub> and CO<sub>2</sub> hydrate can coexist in these areas. Thus, it can be concluded that CO<sub>2</sub> hydrate is more stable than CH<sub>4</sub> hydrate under certain condition.

**Figure 1.** Diagram of CH<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>O phase equilibrium.



Experimental measurements and theoretical calculations both prove the possibility for CH<sub>4</sub>–CO<sub>2</sub> replacement in the hydrate thermodynamically. Uchida *et al.* [21] used gas chromatography and Raman spectroscopy to analyze several formation and decomposition processes of CH<sub>4</sub>–CO<sub>2</sub> mixed gas hydrates. The experiment and theoretical calculation demonstrated that, when the temperature is below 283 K, the equilibrium pressures of CH<sub>4</sub> hydrate are higher than those of CO<sub>2</sub> hydrate at the same temperature. Anderson *et al.* [22] studied the phase equilibrium conditions of CH<sub>4</sub>–CO<sub>2</sub>–H<sub>2</sub>O system in porous media. Their experimental data supported Uchida's opinion.

Geng *et al.* [23] studied the stabilities of CH<sub>4</sub> hydrate, CO<sub>2</sub> hydrate, and CH<sub>4</sub>–CO<sub>2</sub> mixed hydrate by molecular dynamics (MD) simulations; in these simulations, the temperature ranged from 260 to 280 K and a pressure of 5 MPa was chosen. The simulation results indicate that the CH<sub>4</sub>–CO<sub>2</sub> mixed hydrate is the most stable among the three hydrates discussed, so in theory, after CO<sub>2</sub> is injected into CH<sub>4</sub> hydrate under suitable conditions, CH<sub>4</sub> hydrate will transformed into the more stable CH<sub>4</sub>–CO<sub>2</sub> mixed hydrate, and CH<sub>4</sub> gas is produced at the same time.

Based on chemical thermodynamic basic theory, chemical reactions occur spontaneously if the Gibbs free energy for the reaction is negative. Yezdimer *et al.* [24] analyzed the thermodynamic feasibility of replacing CH<sub>4</sub> gas from the hydrate with CO<sub>2</sub> by MD simulation. Their simulation result showed the residual Gibbs free energy in the mutation process of CH<sub>4</sub> into Ar was negative while that in the mutation process of CO<sub>2</sub> into Ar was positive, this suggested the Gibbs free energy during the CH<sub>4</sub>–CO<sub>2</sub> replacement in the hydrate is negative. Thus, the replacement of CH<sub>4</sub> with CO<sub>2</sub> is thermodynamically feasible.

## 2.2. The Kinetic Feasibility of Replacement

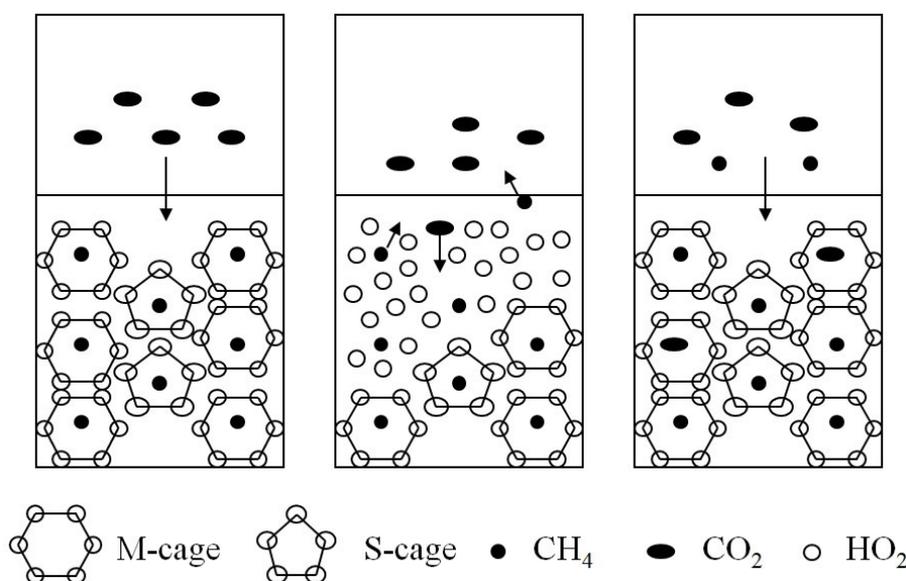
The distribution coefficients of CH<sub>4</sub> and CO<sub>2</sub> between the gas and the hydrate phase were calculated by Ohgaki *et al.* [15]. The results showed that compared with CH<sub>4</sub>, CO<sub>2</sub> tended to distribute in the hydrate phase, so the result preliminarily proved the feasibility of replacement. Uchida [25] was the first researcher to prove that the replacement reaction occurs on the contact surface between CH<sub>4</sub> hydrate and CO<sub>2</sub> gas by use of Raman spectroscopy. Besides, his research group suggested that the replacement rate is very slow and the induction time is up to several days. Uchida *et al.* [21] measured the composition ratio of CH<sub>4</sub> and CO<sub>2</sub> in the vapor phase  $X_{\text{CH}_4}/X_{\text{CO}_2}$  at various times during the formation process of CH<sub>4</sub>–CO<sub>2</sub> mixed gas hydrates, they found that the ratio varied with the formation reaction progressing. The following logarithmic form was used to fit the data:

$$X_{\text{CH}_4} / X_{\text{CO}_2} = (X_{\text{CH}_4} / X_{\text{CO}_2})_0 + \alpha \lg t \quad (1)$$

where  $t$  is the time,  $(X_{\text{CH}_4}/X_{\text{CO}_2})_0$  is the initial composition ratio, and  $\alpha$  is a fitting parameter related to the condensation rate of CH<sub>4</sub> molecules from the vapor phase. From Equation (1), it can be concluded that the ratio of CH<sub>4</sub> in the vapor phase increases with time, this result confirms the conclusion Ohgaki *et al.* drawn [15]. In the experiment, Uchida *et al.* found although the hydrate formation consumed more CO<sub>2</sub> than CH<sub>4</sub> as a whole, more CH<sub>4</sub> was consumed in the early stages. This phenomenon perhaps results from the structure of hydrate and the sizes of CH<sub>4</sub> and CO<sub>2</sub> molecules. On a microscopic scale, crystal structure types of CO<sub>2</sub> hydrate and CH<sub>4</sub> hydrate are both type SI [1,2,26], SI hydrate's unit cell consists of six medium cages (M-cage) and two small cages (S-cage). The CO<sub>2</sub>

molecular dimension is a little larger than the CH<sub>4</sub> molecular dimension, and the molecular size of CO<sub>2</sub> is between that of the M-cage and S-cage of SI hydrate [1,2,27], so CO<sub>2</sub> molecules occupy the M-cages mainly. In the early stages, CH<sub>4</sub> molecules were able to occupy both S-cages and M-cages while CO<sub>2</sub> molecules only occupied M-cages, as a result, more CH<sub>4</sub> gas was consumed. In the later stages, a replacement reaction occurred, and CO<sub>2</sub> molecules occupied the M-cages which held CH<sub>4</sub> molecules, CH<sub>4</sub> gas was released, so the ratio of CH<sub>4</sub> in the vapor phase increased. Uchida *et al.* divided the replacement reaction into two phases: (1) some CH<sub>4</sub> hydrate decomposes and the generated gaseous CH<sub>4</sub> transfers into the vapor phase; (2) CO<sub>2</sub> molecules occupy the M-cages and CH<sub>4</sub> molecules re-occupy the S-cages because of the memory effect. Figure 2 [28] is the schematic diagram redrawn from Ota *et al.* [28], it describes the guest molecule exchange process in the M-cages and the CH<sub>4</sub> re-occupation in the S-cages.

**Figure 2.** Schematic diagram of the guest molecule replacement in the M-cage and the CH<sub>4</sub> re-occupation in the S-cage.



Hirohama *et al.* [29] suggested the driving force for CH<sub>4</sub>–CO<sub>2</sub> replacement in the hydrate seemed to be the fugacity difference between different phases. Ota *et al.* [17,28] built the models for decomposition of CH<sub>4</sub> hydrate and formation of CO<sub>2</sub> hydrate during the replacement process, they assumed the driving force for CH<sub>4</sub>–CO<sub>2</sub> replacement in the hydrate was proportional to the fugacity difference between the gas and the hydrate phase. The model of the CH<sub>4</sub> hydrate decomposition is written as follows:

$$\frac{dn_{\text{CH}_4\text{-H}}}{dt} = -k_{\text{Dec}} A (f_{\text{CH}_4\text{-H}} - f_{\text{CH}_4\text{-G}}) \quad (2)$$

$$\frac{1}{k_{\text{Dec}}} = \frac{1}{k_{\text{Dec.R}}} + \frac{1}{k_{\text{Dec.D}}} \quad (3)$$

where  $n_{\text{CH}_4\text{-H}}$  is the remaining amount of CH<sub>4</sub> in the hydrate phase,  $t$  is the reaction time,  $f$  is the fugacity, and  $k_{\text{Dec}}$  is the overall rate constant of the decomposition.  $k_{\text{Dec}}$  includes  $k_{\text{Dec.R}}$ , which is the

reaction rate constant of decomposition and  $k_{Dec}$ , which is the rate constant of mass transfer in the hydrate phase. In Equation (2),  $A$  is the surface area between the gas and the hydrate phase, and  $H$  and  $G$  refer to the hydrate phase and the gas phase, respectively. The model of  $CO_2$  hydrate formation during the replacement can similarly be written as follows:

$$\frac{dn_{CO_2,H}}{dt} = k_{Form}A(f_{CO_2,G} - f_{CO_2,H}) \quad (4)$$

$$\frac{1}{k_{Form}} = \frac{1}{k_{Form,R}} + \frac{1}{k_{Form,D}} \quad (5)$$

where  $n_{CO_2,H}$  is the amount of  $CO_2$  in the hydrate phase and  $k_{Form}$  is the overall rate constant of the formation,  $k_{Form}$  includes  $k_{Form,R}$  and  $k_{Form,D}$  rate constants.

Ota *et al.* calculated the fugacity from the model including the van der Waals–Platteeuw theory [20,30] and the Soave–Redlich–Kwong equation of state (SRK-EOS) [31]. The experimental conditions (T, P) were fixed in the SRK-EOS equation to calculate fugacity and the resulting compositions were measured by Raman spectroscopy. The surface area between the gas and the hydrate phase was treated as a constant. The slope of the Arrhenius plot was used to calculate activation energies for  $CH_4$  hydrate decomposition and  $CO_2$  hydrate formation. Ota *et al.* pointed that the rate constant of decomposition seemed to dominate the  $CH_4$  hydrate decomposition, while the mass transfer likely dominated the  $CO_2$  hydrate formation during the replacement process.

According to the experimental data for  $CO_2$  and  $CH_4$  hydrate formation respectively reported by Nagayev *et al.* [32] and Rueff *et al.* [33], the activation energy for  $CO_2$  hydrate formation is 57.98 kJ/mol and that for  $CH_4$  hydrate decomposition is 54.49 KJ/mol. While Ota *et al.* [17] calculated that the activation energy for  $CO_2$  hydrate formation is 73.3 KJ/mol and that for  $CH_4$  hydrate decomposition is 14.5 KJ/mol from these models. The data of Li's experiment [19] shows the activation energies are 68.4 KJ/mol and 28.8 KJ/mol respectively from these models. These differences of activation energy may result from the interaction between formation of  $CO_2$  hydrate and decomposition of  $CH_4$  hydrate during the replacement process. By means of analysis and comparison of the activation energy during the replacement process, it can be concluded the formation of  $CO_2$  hydrate can supply enough heat for the decomposition of  $CH_4$  hydrate, and the extra heat can prevent  $CH_4$  hydrate's self-protection and promote decomposition of  $CH_4$  hydrate further.

### 3. Experiment Study of Replacement Reaction

#### 3.1. Replacement of $CH_4$ Hydrate by Use of Gaseous $CO_2$

Researchers have done the replacement experiment by use of gaseous  $CO_2$  under different conditions [16–19]. The adapted schematic diagram of the experimental apparatus for replacement with gaseous  $CO_2$  is illustrated in Figure 3 [17]. The apparatus mainly consists of a high-pressure cell which has a magnetic agitator inside it for hydrate formation and replacement reaction, a cooling system for keeping the temperature of the cell constant, a data acquisition system for data collection, and a laser Raman spectrometer or a gas chromatograph for gas phase composition analysis. The experimental procedure is as follows: (1) the desired amount of distilled water is firstly introduced into

the cell, When the pressure is controlled at the set value, the magnetic agitator is started to promote the CH<sub>4</sub> hydrate formation; (2) CH<sub>4</sub> hydrate formation is considered to be completed when the experimental measurements remain unchanged. Then the cell is purged by high pressure CO<sub>2</sub> gas, which is confirmed by the laser Raman spectrometer or the gas chromatograph; (3) the replacement reaction starts when the system is controlled at the required pressure and temperature. After the reaction starts, a little gas sample is taken out to be analyzed at required intervals; (4) after a given elapsed time, the hydrate mixtures are decomposed by heating, and the compositions are quantified.

**Figure 3.** Schematic diagram of the experimental apparatus. 1: CO<sub>2</sub> cylinder; 2: Cooler; 3: CO<sub>2</sub> buffer; 4: CH<sub>4</sub> buffer; 5: Cell with cooling jacket; 6: Windows; 7: Stirrer; 8: Pressure reducer; 9: CH<sub>4</sub> cylinder; 10: Thermocouples; 11: Pressure gauge; 12: Back pressure regulator; 13: Laser Raman spectrometer or a gas chromatograph; 14: Tank.

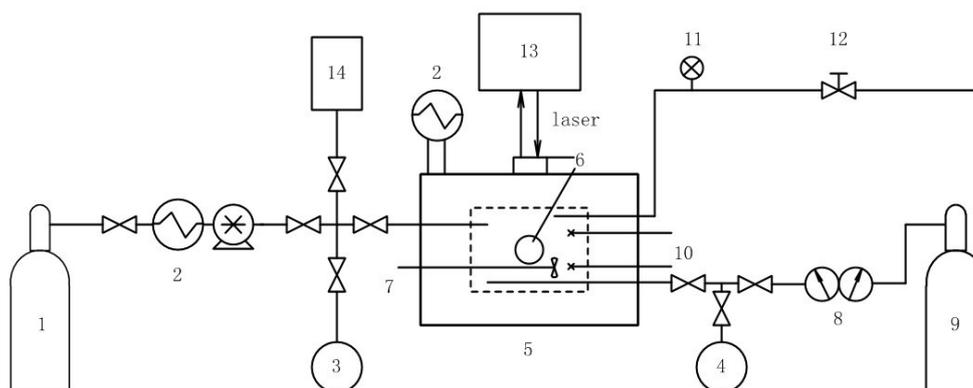


Figure 4 drawn based on the data from Ota *et al.* [17] shows how the amount of the decomposed CH<sub>4</sub> hydrate ( $Q_{\text{CH}_4, \text{Dec}}$ ) and formed CO<sub>2</sub> hydrate ( $Q_{\text{CO}_2, \text{Form}}$ ) changes with time respectively in the experiment.

**Figure 4.** Amount of the decomposed CH<sub>4</sub> hydrate ( $Q_{\text{CH}_4, \text{Dec}}$ ) (a) and the formed CO<sub>2</sub> hydrate ( $Q_{\text{CO}_2, \text{Form}}$ ); (b) against time.

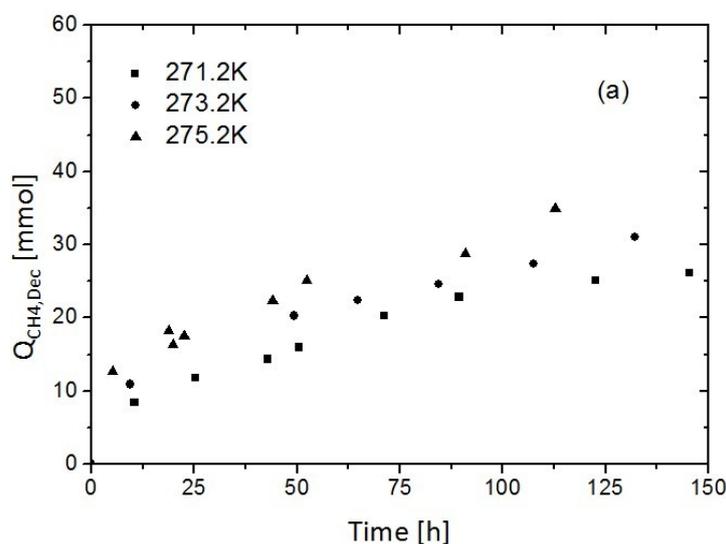
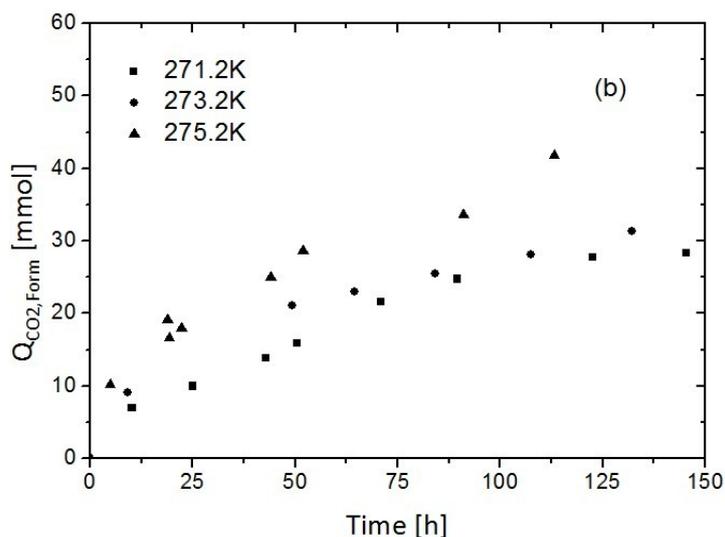


Figure 4. Cont.



Based on the experimental data, we can reach three main conclusions: (1) it promotes CH<sub>4</sub> hydrate decomposition and CO<sub>2</sub> hydrate formation to increase the temperature appropriately at the same pressure; (2) the amount of decomposed CH<sub>4</sub> hydrate is nearly consistent with that of formed CO<sub>2</sub> hydrate. The phenomenon proves the replacement reaction's essence is the process of CO<sub>2</sub> molecules occupying CH<sub>4</sub> molecules' cages; (3) the reaction rate is rapid in the early stages (about 10 h), but it becomes slow after that.

The experimental data reported by Wang *et al.* [16] and Li *et al.* [18,19] show the variation tendency of the decomposed CH<sub>4</sub> hydrate and formed CO<sub>2</sub> hydrate during the replacement process is the same as that of Ota's experiment. In Wang's experiment, after the first 2 h, the rate of CH<sub>4</sub> hydrate decomposition and CO<sub>2</sub> hydrate formation slows, and in Li's experiment, the high replacement rate is sustained for about 10 h, but in their experiments, the amount of CO<sub>2</sub> hydrate formed is much more than that of decomposed CH<sub>4</sub> hydrate. The highest ratio of formed CO<sub>2</sub> hydrate and decomposed CH<sub>4</sub> hydrate can be up to 5.6 and 6.0, respectively. The difference is mainly caused by the free water. In Ota's experiment, there is no free water at the beginning of the replacement reaction, so the amount of decomposed CH<sub>4</sub> hydrate is consistent with that of formed CO<sub>2</sub> hydrate, while in the experiment of Wang and Li, free water exists in the hydrate stratum, and the amount of CO<sub>2</sub> gas dissolved in the free water and formed CO<sub>2</sub> hydrate with the free water is much more than that used for replacing CH<sub>4</sub> from the hydrate. Thus, the factor of the free water in the NGH stratum should be taken into consideration in the actual exploitation of natural gas with CO<sub>2</sub>.

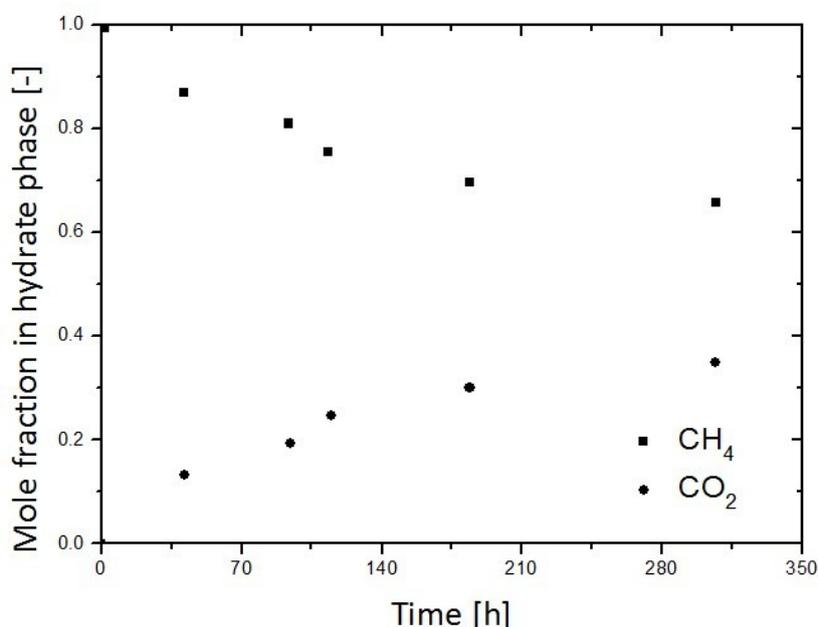
Based on the experimental results reported by different researchers, it is proven feasible to replace CH<sub>4</sub> from the hydrate by use of gaseous CO<sub>2</sub>, but the replacement rate becomes extremely slow after the early stages of reaction, and the replacement efficiency can't satisfy the requirements of commercial production of NGH. Thus more efficient methods of exploiting natural gas from the hydrate with CO<sub>2</sub> should be developed.

### 3.2. Replacement of CH<sub>4</sub> Hydrate by Use of Liquid CO<sub>2</sub>

Ota *et al.* [28] and Zhou *et al.* [34] have done the replacement experiment in the pure hydrate using liquid CO<sub>2</sub>. The initial temperature is 273.2 K and the initial pressure is chosen at 3.25 MPa in their experiments. Compared to the experimental apparatus used for replacement by use of gaseous CO<sub>2</sub>, a liquefying apparatus is added to be used for liquefying CO<sub>2</sub> in this experiment. The procedure is as follows: (1) the desired amount of distilled water and CH<sub>4</sub> gas is first introduced into the cell. When the system is pressurized to the required value, the agitation in the cell is started to promote the CH<sub>4</sub> hydrate formation; (2) when the CH<sub>4</sub> hydrate formation is completed, the cell is purged by high pressure CO<sub>2</sub>. Then the system is pressurized to the required value by keeping introducing CO<sub>2</sub>; (3) when the temperature of the system is controlled at the required value, saturated liquid CO<sub>2</sub> is then introduced into the cell to replace CH<sub>4</sub> from the hydrate; (4) the replacement process is observed and analyzed with *in situ* Raman spectroscopy. After a given amount of time, the CO<sub>2</sub> remaining in the cell is released and the remaining hydrate mixture is resolved and analyzed.

Figure 5 drawn according to the data from Ota *et al.* [28] shows the time profile of the mole fractions of CH<sub>4</sub> and CO<sub>2</sub> in the hydrate phase in experiment. It can be seen the mole fraction of CH<sub>4</sub> hydrate decomposition is consistent with that of CO<sub>2</sub> hydrate formation, the phenomenon confirms the feasibility of replacement of CH<sub>4</sub> in the hydrate by use of liquid CO<sub>2</sub>, and proves the replacement reaction's essence is the process of CO<sub>2</sub> molecules occupying CH<sub>4</sub> molecules' cages further.

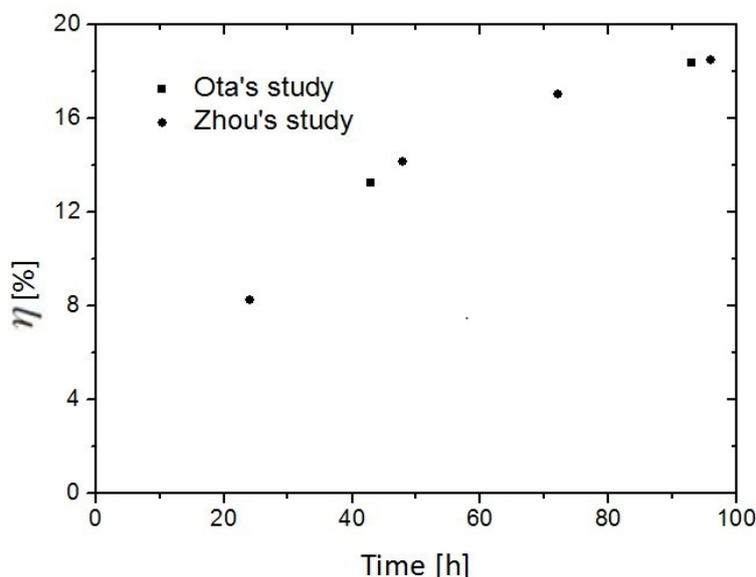
**Figure 5.** Mole fraction of CH<sub>4</sub> and CO<sub>2</sub> in the hydrate phase as a function of time.



Zhou *et al.* [34] studied the replacement of CH<sub>4</sub> in the hydrate by use of liquid CO<sub>2</sub> under the same conditions as in Ota's experiment [28]. Figure 6 redrawn from Zhou *et al.* [34] shows the CH<sub>4</sub> ratios replaced from the hydrate of the two experiments, from the figure we can see that the results are equivalent approximately in less than 100 h. Li *et al.* [35] changed the experimental conditions in the replacement reaction by use of liquid CO<sub>2</sub>, the initial temperature and pressure were 282.2 K and 6 MPa respectively, and the experiment was conducted in porous sediment. His research showed

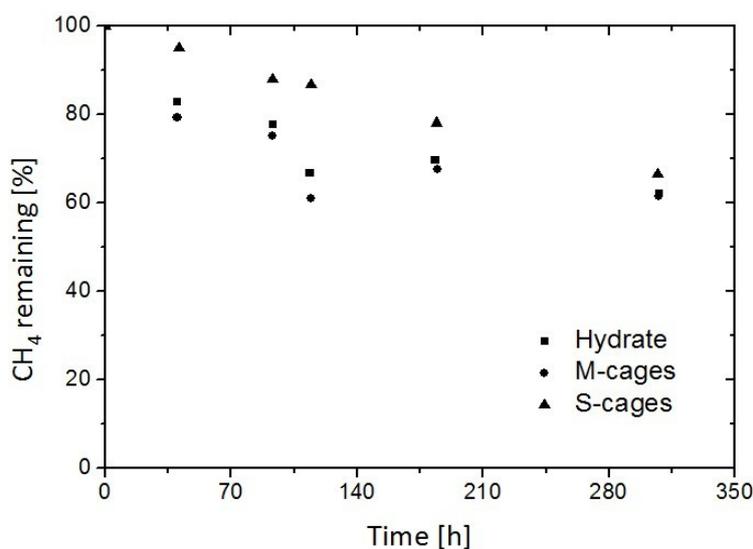
the recovery ratio of CH<sub>4</sub> can reach approximately 45% after 288 h, while in Ota's experiment, the recovery ratio is about 37% after 307 h and the recovery ratio is 18.6% after 96 h in Zhou's experiment.

**Figure 6.** CH<sub>4</sub> ratios replaced from the hydrate of the two different experiments.



Ota *et al.* [28] observed the guest molecules' transformation in the different cages and hydrate during the replacement process with Raman spectroscopy. Figure 7 redrawn from Ota *et al.* [28] shows the CH<sub>4</sub> remaining in each cage and hydrate with time.

**Figure 7.** Time evolution of CH<sub>4</sub> in the M-cages, S-cages and hydrate.



It can be seen that the CH<sub>4</sub> remaining in both the M-cages and S-cages decreased with time, however, the decay in the S-cages is much slower than that in the M-cages, and the ratio of CH<sub>4</sub> in the M-cages is practically consistent with that of CH<sub>4</sub> in the hydrate, which proves the replacement reaction mainly proceeds in the M-cages.

Researchers have applied experimental methods to prove the feasibility of replacing CH<sub>4</sub> from the hydrate with liquid CO<sub>2</sub>. Compared with the replacement experiments with gaseous CO<sub>2</sub>, the replacement rate, efficiency and reaction time in the experiments with liquid CO<sub>2</sub> are all improved, this shows that liquid CO<sub>2</sub> is more suitable for the replacement than gaseous CO<sub>2</sub>.

### 3.3. Replacement of CH<sub>4</sub> Hydrate by Use of CO<sub>2</sub> Emulsion

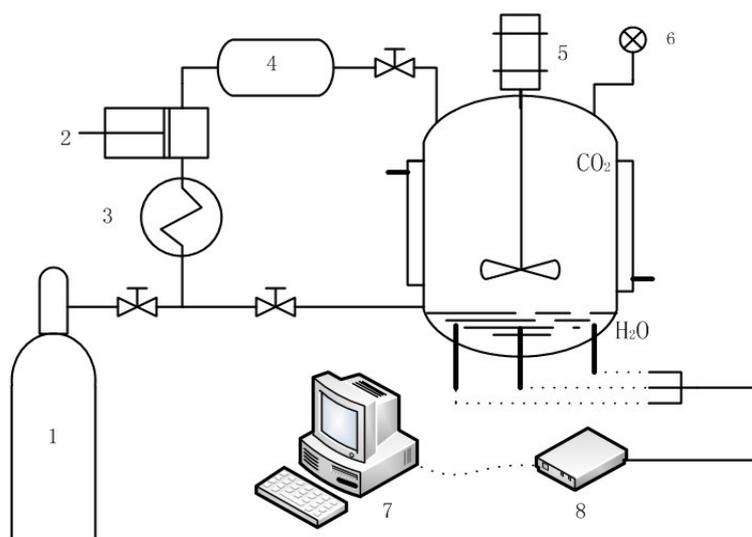
Researchers have paid attention to finding out the reason why the replacement rate becomes slow after the early stages of reaction. According to an experimental study, Yoon *et al.* [36] pointed that in the early stages, the contact area between CO<sub>2</sub> molecules and CH<sub>4</sub> hydrate is large, so the reaction rate is fast. As the reaction progresses, the crust layer of CH<sub>4</sub> hydrate is covered with CO<sub>2</sub> hydrate, the CO<sub>2</sub> hydrate layer provides a shielding effect, hinders the CH<sub>4</sub> hydrate decomposition, and leads to the rate's decrease and the reaction finally ceases.

In order to improve the replacement reaction rate, McGrail *et al.* [37] put forward the method of enhanced gas hydrate recovery (EGHR). The key of the method is to prepare an emulsion in which water is the continuous phase and CO<sub>2</sub> is the dispersed phase, and the emulsion is substituted for gaseous and liquid CO<sub>2</sub> to replace CH<sub>4</sub> gas from the hydrate. In McGrail's opinion, this method combines the advantages of controlled multiphase flow, heat, and mass transport processes in hydrate-bearing porous media, makes full use of the physical and thermodynamic properties of mixtures in the H<sub>2</sub>O-CO<sub>2</sub> system, thus it can increase the contact area between CO<sub>2</sub> molecules and CH<sub>4</sub> hydrate and enhance the replacement reaction. White *et al.* [38] used numerical simulations to analyze the replacement process of CH<sub>4</sub> from the hydrate stratum by use gaseous CO<sub>2</sub>, liquid CO<sub>2</sub> and CO<sub>2</sub> emulsion, and his simulation results show the replacement rate with CO<sub>2</sub> emulsion is the highest among the three methods.

Replacement by CO<sub>2</sub> emulsion is regarded as the best one among the three replacement methods by use of CO<sub>2</sub>, but the technique for preparing CO<sub>2</sub> emulsions is still immature. DhanuKa *et al.* [39] used a new kind of emulsifier, TMN-6 (octa(ethylene glycol)-2,6,8-trimethyl-4-nonyl ether), for CO<sub>2</sub> emulsion preparation. According to DhanuKa's experiment, at a temperature below 318 K, the stability of the emulsion increases with pressure and the mass ratio of CO<sub>2</sub> in the emulsion, in some cases the stable time of the emulsion with 90% CO<sub>2</sub> in the emulsion can exceed 24 h.

A schematic illustration of the experimental apparatus for the CO<sub>2</sub> emulsion formation redrawn from Zhou *et al.* [34] is shown in Figure 8. The apparatus mainly includes a CO<sub>2</sub> liquefier used for liquefying CO<sub>2</sub>, a high-pressure cell for emulsion formation, a cooling system for controlling temperature and a high-speed magnetic agitator for promoting the CO<sub>2</sub> emulsion formation. The emulsion was prepared as follows: (1) known amounts of water and TMN-6 are placed into the high-pressure cell; (2) CO<sub>2</sub> gas is introduced into the cell to pressurize the system, after the pressure in the cell achieves the required value, liquid CO<sub>2</sub> is injected into the cell, and the temperature is controlled to the required value by running the cooling system; (3) the magnetic agitator is started to promote the CO<sub>2</sub> emulsion formation.

**Figure 8.** Experimental apparatus for CO<sub>2</sub> emulsion formation. 1: CO<sub>2</sub> cylinder; 2: plunger pump; 3: CO<sub>2</sub> liquefier; 4: liquid distributing cell; 5: high-pressure cell; 6: pressure gauge; 7: PC; 8: data collector.



Zhou *et al.* [34] used the prepared CO<sub>2</sub> emulsion to replace CH<sub>4</sub> in the hydrate in porous media. The procedures and apparatus of the experiment are similar to the experiment by use of liquid CO<sub>2</sub>, the only difference is that CO<sub>2</sub> emulsion is substituted for liquid CO<sub>2</sub>. Zhou did three groups of replacement experiments using CO<sub>2</sub> emulsion, the experimental initial pressure and temperature were the same, 90:10, 70:30, and 50:50 (W<sub>CO<sub>2</sub></sub>:W<sub>H<sub>2</sub>O</sub>) CO<sub>2</sub>-in-water (C/W) emulsions were used to replace CH<sub>4</sub> from its hydrate. The CH<sub>4</sub> ratios replaced from the hydrate of the three groups of experiments by use of CO<sub>2</sub> emulsion and one group of experiment by use of liquid CO<sub>2</sub> at set intervals are calculated and shown in Figure 9 redrawn from Zhou *et al.* [34].

**Figure 9.** CH<sub>4</sub> ratios replaced from the hydrate with different forms of CO<sub>2</sub>.

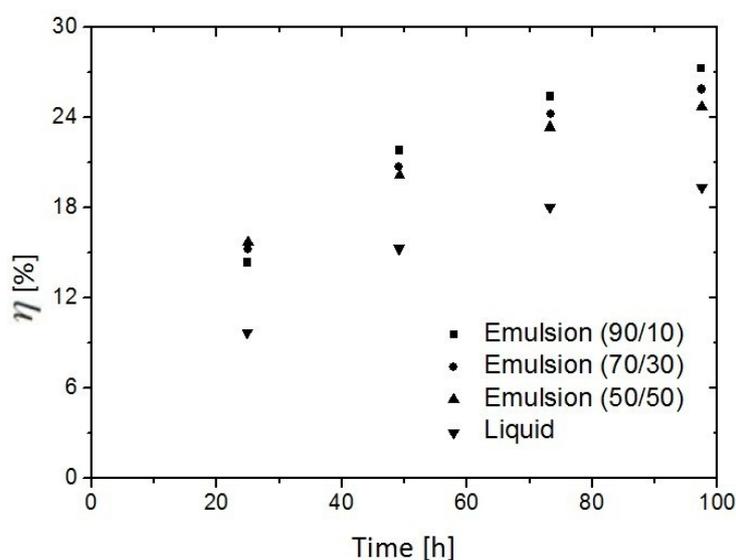
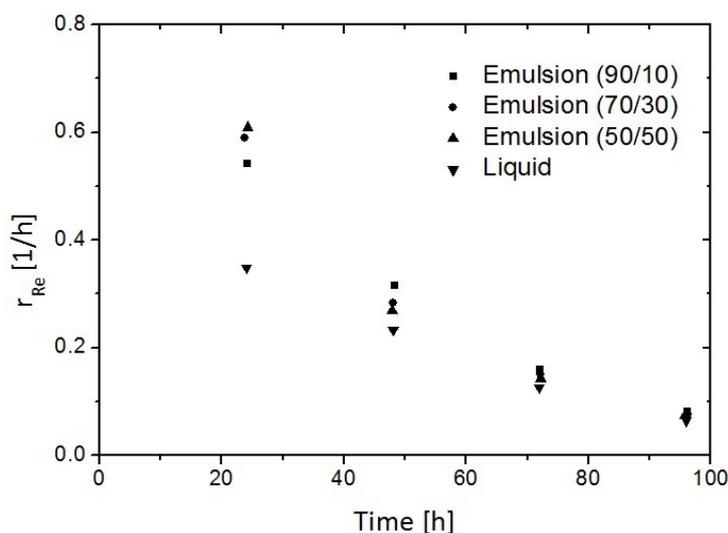


Figure 10 redrawn from Zhou *et al.* [34] shows the replacement rates of CH<sub>4</sub> versus time in different experiments. From the figures we can see that the replacement ratios of CH<sub>4</sub> with the above

emulsions are higher than that with liquid CO<sub>2</sub>, the former are about the latter 1.5 times, and the replacement efficiency increases with the mass ratio of liquid CO<sub>2</sub> in the emulsion increasing. In addition, the replacement rate with emulsions reaches 5–7 times of the rate with liquid CO<sub>2</sub>. Thus, it can be concluded that CO<sub>2</sub> emulsion is more efficient than liquid CO<sub>2</sub> in replacing CH<sub>4</sub> from the hydrate.

**Figure 10.** Replacement rates of CH<sub>4</sub> with different forms of CO<sub>2</sub>.



In addition, in order to prove the superiority of CO<sub>2</sub> emulsion in replacing CH<sub>4</sub> from the hydrate, Zhou *et al.* [40] compared the replacement ratio of CH<sub>4</sub> by use of CO<sub>2</sub> emulsion and gaseous CO<sub>2</sub>. Zhou did three groups of contrast experiments under different conditions. The different molar quantities of CH<sub>4</sub> gas replaced by gaseous CO<sub>2</sub> and CO<sub>2</sub> emulsion is shown in Figure 11 which is drawn based on the data from Zhou *et al.* [40].

**Figure 11.** Amount of the replaced CH<sub>4</sub> gas by use of gaseous CO<sub>2</sub> and CO<sub>2</sub> emulsion against time.

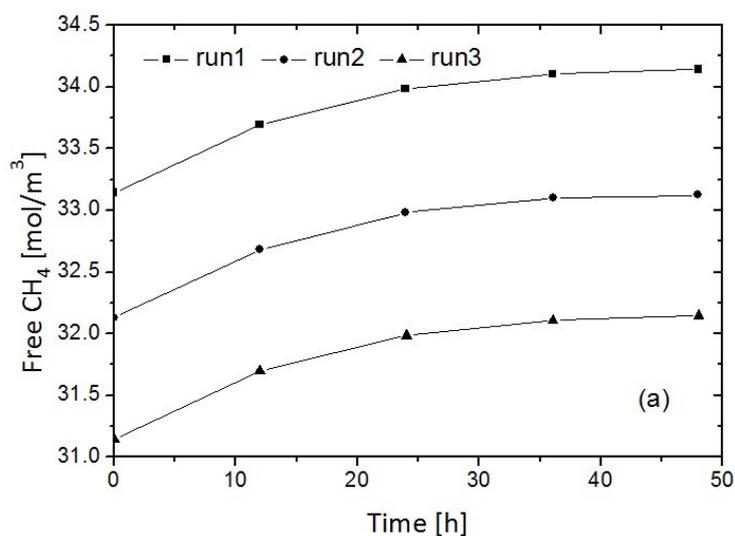
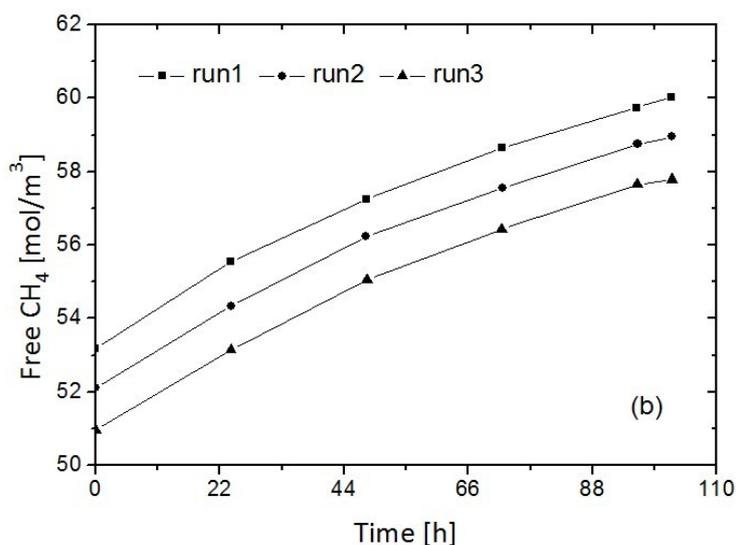


Figure 11. Cont.



The graph (a) shows the molar quantity of free CH<sub>4</sub> gas in the replacement process with gaseous CO<sub>2</sub> and the graph (b) shows that in the replacement process with CO<sub>2</sub> emulsion. From the figure, we can reach two conclusions: (1) CO<sub>2</sub> emulsion is more effective than gaseous CO<sub>2</sub> in replacing CH<sub>4</sub> (2) the replacement rate with gaseous CO<sub>2</sub> becomes slow after reaction for 10 h, and the reaction stops in about 50 h, the rate with CO<sub>2</sub> emulsion is higher, and the reaction time can last over 100 h. Zhou pointed out that the result may due to the higher reaction temperature and the better conductivity and diffusibility of the CO<sub>2</sub> emulsion. The heat given by emulsion promotes CH<sub>4</sub> hydrate decomposition and increases the replacement rate, the better diffusibility of the CO<sub>2</sub> emulsion leads to larger reaction area between CO<sub>2</sub> molecules and CH<sub>4</sub> hydrate, thus the reaction time extends.

Zhang *et al.* [41] pointed that the kinetics of CH<sub>4</sub> replacement by CO<sub>2</sub> emulsion, the varieties and contents of emulsifier, the ratio of water and liquid CO<sub>2</sub>, the influence on replacement rate of dispersed phase in the emulsion have to be further researched. In the actual exploitation, the existence of porous media, the statistical circumstances of CH<sub>4</sub> hydrate presence in the stratum and the pumping of CO<sub>2</sub> emulsion need to be considered.

Compared with gaseous CO<sub>2</sub> and liquid CO<sub>2</sub>, CO<sub>2</sub> emulsion is proved to be more efficient in replacing CH<sub>4</sub> from the hydrate by experimental methods, but the preparation technique of CO<sub>2</sub> emulsion is still immature, and the experimental research on the replacement with CO<sub>2</sub> emulsion is scarce, so the influencing factors of reaction are not quite clear. Thus, the technique of CO<sub>2</sub> emulsion preparation and the optimum conditions for replacement with CO<sub>2</sub> emulsion should be studied further in the future work.

#### 4. Advances in Simulation Research on Replacement

The Phase Field Theory (PFT) has been proved to be one of the most effective methods to model solidification in binary, ternary and multi-component melts over the past decade. PFT is applied to describe complex solidification morphologies, including thermal and solutal dendrites and eutectic/peritectic fronts [42]. The technique of Magnetic Resonance Imaging (MRI) is supposed to be a useful tool to visualize the process of hydrate formation and decomposition [43]. Baldwin *et al.* [44]

and Ersland *et al.* [45] used MRI to observe CH<sub>4</sub> hydrate formation and spontaneous conversion of CH<sub>4</sub> to CO<sub>2</sub> hydrate in porous media, and confirmed the feasibility of visualizing the replacement process by use of MRI. In order to investigate the micro-mechanism of replacement, researchers combine the PFT and the observation approach of MRI, and build corresponding models to simulate the replacement process.

Kvamme *et al.* [42,43] applied MRI to observe the replacement process by use of liquid CO<sub>2</sub> and developed a corresponding model based on PFT. The model was used for describing the nucleation of hydrate in aqueous solution and the transformation of CH<sub>4</sub> hydrate to CO<sub>2</sub> hydrate. According to their reported results, the PFT-based model is more accurate than the classical nucleation theory in describing the nucleation process of hydrate. The theory simulations of Kvamme's model indicate that the reformation kinetic rate is directly proportional to the kinetic rate characteristic for CO<sub>2</sub> transport through an aqueous solution. The conclusion agrees with Yoon's suggestion [36], but in Kvamme's model, the effects of many other factors are ignored, and the model doesn't give a good explanation of the replacement mechanism, so multiscale simulations are required for describing the replacement mechanism further.

Tegze *et al.* [46] built a multiscale model based on PFT to calculate the nucleation and growth rates of CO<sub>2</sub> hydrate in aqueous solutions in which the parameters of the model were deduced from experiment and molecular dynamics simulation. In the paper, in order to determine the thickness of the CO<sub>2</sub>-hydrate-aqueous-solution interface, Tegze *et al.* performed molecular dynamics simulations taking realistic interaction potentials. The interface thickness from the MD simulations and the experimental interfacial free energy were used to fix the model parameters of multiscale model based on the PFT. Tegze *et al.* applied phase field calculations to determine the rate of the homogeneous nucleation and the velocity of the growth of CO<sub>2</sub> hydrate in the aqueous solutions. The simulation result shows a homogeneous nucleation can be ruled out as a possible mechanism for initiating a hydrate formation, and the most probable obstruction factor of hydrate growth seems to be kinetic barriers caused by complex molecular motions.

In order to investigate the replacement microscopic mechanism further, Tegze *et al.* [47] built a multiscale model combining the phase field approach and the purely diffusive model, the model was used to describe the CH<sub>4</sub> replacement process with liquid CO<sub>2</sub> under conditions characteristic of underwater hydrate reservoirs. Data from experiments and atomistic simulations was used to fix the modes' parameters, while the diffusion coefficient of CO<sub>2</sub> in the hydrate phase was a set value, which was adjustable. The simulation result shows the replacement rates predicted by both the PFT and purely diffusive models are consistent with experimental results from MRI measurements. The agreement between the predicted and experimental rates supports the assumption that the hydrate conversion process is controlled by solid state diffusion. The PFT simulations indicate that hydrate conversion starts with the formation of a mixed SI hydrate and the simple purely diffusive model is proved to be useful to estimate transition kinetics with confidence, so it is concluded that multiscale simulation is a convenient tool to describe the replacement process microscopically. Besides, Tegze *et al.* pointed out that in further work, dedicated atomistic simulations should be added to the multiscale model to identify the micro-mechanism for the solid state transformation and to extend the model to the conversion of natural gas hydrates.

Multiscale simulation combining PFT and molecular dynamics provides a theoretical research method for analyzing the replacement microscopic mechanism, but current research on simulation of replacement focuses on the replacement with liquid CO<sub>2</sub>, the combination of simulations and advanced micro detection techniques are few, and the comparison between simulation results and experimental data is lacking, so in future work, researchers should pay attention to combining simulations and advanced detection techniques, develop simulations based on PFT and molecular dynamics, study the interfacial effect in the porous media and the effect of CO<sub>2</sub> emulsion during the replacement process further, and build models which are suitable for explaining the replacement with CO<sub>2</sub> emulsions.

## 5. Research on Factors Influencing the Replacement Reaction

Although the replacement method is regarded as a promising NGH exploitation method, the low replacement rate and efficiency are important obstacles to its application in commercial production. In order to improve the replacement rate and efficiency, researchers have utilized experimental and simulative methods to search for the optimal conditions for replacing CH<sub>4</sub> from the hydrate with CO<sub>2</sub>.

The effects of the initial temperature and pressure during the replacement by use of gaseous CO<sub>2</sub> have been studied with experimental methods [9,16–19,48,49]. According to the experimental data reported by the literature, higher initial temperature and pressure are both beneficial to improve the replacement rate and efficiency. Graph (a) in Figure 4 shows the effect of the initial temperature on the replacement efficiency with CO<sub>2</sub> gas, and Zhou's [48] experimental data show the ratio of released CH<sub>4</sub> gas from the hydrate increases from 20.0% to 44.9% with the initial pressure of CO<sub>2</sub> gas ranging from 3.97 MPa to 4.84 MPa. Wang *et al.* [16] and Qi *et al.* [49] found the effect of temperature is more obvious than that of pressure. In addition, Li *et al.* [18] studied the effect of sodium dodecyl sulfate (SDS) on the replacement reaction, and the results show that SDS is beneficial to improving the replacement rate. Adding SDS may become a method for enhancing the replacement reaction, but the feasibility has to be studied further.

Ota *et al.* [50] investigated the effects of pressure and fugacity on the CH<sub>4</sub>–CO<sub>2</sub> replacement in CH<sub>4</sub> hydrate using quantitative analysis with *in-situ* laser Raman spectroscopy. It was found that the CH<sub>4</sub>–CO<sub>2</sub> replacement at the boundary of liquid and hydrate phase (273.2 K and above 3.60 MPa) proceeds faster than that at the boundary of gaseous and hydrate phase (273.2 K and 3.26 MPa). The result shows the liquid CO<sub>2</sub> is more effective in replacing CH<sub>4</sub> from the hydrate than gaseous CO<sub>2</sub>. Zhou *et al.* reached the same conclusion with experimental method [40]. Ota *et al.* also found that in the replacement process by use of liquid CO<sub>2</sub>, pressure dependence was hardly observed under the conditions studied (3.60–6.00 MPa), but according to the experimental data reported by Xiong *et al.* [35], the recovery ratio of CH<sub>4</sub> can reach approximately 45% after 288 h, which is higher than the results from obtained by Ota *et al.* [28], as in Ota's experiment, the recovery ratio is about 37% after 307 h. The initial conditions in Xiong's experiment are 282.2 K and 6.00 MPa, so through comparison of the two experiments, it can be concluded the initial temperature has an important influence on the replacement efficiency by use of liquid CO<sub>2</sub>, and a higher initial temperature favors of improved replacement efficiency.

White *et al.* [38] applied a simulation method to simulate the replacement process with gaseous CO<sub>2</sub>, liquid CO<sub>2</sub> and CO<sub>2</sub> emulsion, respectively, and proved the superiority of CO<sub>2</sub> emulsion.

Zhou *et al.* [34,40] used experimental methods to compare the replacement rate and efficiency using different forms of CO<sub>2</sub>, and the experimental results are shown in Figures 9–11. From the figures, it can be concluded that the replacement rate and efficiency with CO<sub>2</sub> emulsion are both higher than that with gaseous CO<sub>2</sub> and liquid CO<sub>2</sub>. Furthermore, Zhou *et al.* proved that the higher quality fraction of CO<sub>2</sub> in water results in the higher replacement efficiency, and Dhanuka *et al.* [39] pointed the varieties and contents of emulsifier have an important influence on the stability of CO<sub>2</sub> emulsions and suggested that a higher pressure and quality fraction of CO<sub>2</sub> in water can improve the stability of CO<sub>2</sub> emulsions. To sum up, CO<sub>2</sub> emulsion with higher quality fraction of CO<sub>2</sub> and opportune emulsifier should be selected for the replacement reaction, and the initial pressure should be appropriately high. Literature about replacing CH<sub>4</sub> from the hydrate with CO<sub>2</sub> are few at present, and the micro-mechanism of the replacement process with CO<sub>2</sub> emulsion is still an issue, so the factors influencing preparation of CO<sub>2</sub> emulsions should be studied in the future. In addition, in the actual exploitation, the influences of porous media, statistics circumstance of CH<sub>4</sub> hydrate in the stratum should be also taken into account.

## 6. Conclusions

This paper introduces the research advances on replacement of CH<sub>4</sub> from NGHs by use of CO<sub>2</sub> at home and abroad, proves the feasibility of replacement from the points of view of kinetics and thermodynamics, summarizes the progress of experiments and replacement simulations, and analyzes the factors influencing the replacement with different forms of CO<sub>2</sub>. The following conclusions are drawn according to this paper:

(1) The feasibility of replacing CH<sub>4</sub> from the hydrate by use of CO<sub>2</sub> has been proven from the points of view of kinetics and thermodynamics, and experiments on replacement confirm the conclusions. Besides, by means of experimental observation, the replacement reaction mainly occurs in the hydrate phase and its essence is the process of CO<sub>2</sub> molecules occupying CH<sub>4</sub> molecules' cages, so the replacement method is beneficial to stabilize the NGH stratum during natural gas recovery.

(2) Replacement of CH<sub>4</sub> from the hydrate by combining the techniques of CO<sub>2</sub> liquefaction and CO<sub>2</sub> emulsification are new methods considered to be able to enhance the replacement reaction. According to the experiments on replacement with different forms of CO<sub>2</sub>, it is concluded that the replacement reaction with CO<sub>2</sub> emulsion has faster reaction rates, higher replacement efficiencies and longer reaction times compared to that with gaseous and liquid CO<sub>2</sub>, so the replacement method with CO<sub>2</sub> emulsion is considered as a new approach for commercial production of CH<sub>4</sub> from the hydrates.

(3) The multiscale simulation combined the PFT and molecular dynamics provides a theoretical research method for analyzing the replacement microscopic mechanism. The simulation results prove the superiority of CO<sub>2</sub> emulsion in replacement and indicate the diffusivity of CO<sub>2</sub> in the hydrate phase is the key to the replacement efficiency, but the research on simulation of replacement is still in its infancy, and the descriptions of the micro-mechanism of replacement are still immature, so the simulation of replacement should be studied further, and multiscale models for replacement, especially for replacement with CO<sub>2</sub> emulsion, should be built in the future work.

(4) The factors influencing the replacement reaction with different forms of CO<sub>2</sub> are discussed. The factors mainly include the phases of CO<sub>2</sub>, the initial pressure and temperature, and the effect of additives. The ultimate purpose of the analysis of different factors is to find the optimal conditions for

enhancing the diffusivity of CO<sub>2</sub> in the hydrate reservoir and improve the replacement efficiency and rate. Besides, in actual exploitation, the sizes of the porous media, the distribution of NGH in the actual stratum, and the manners of CO<sub>2</sub> injection to the NGH reservoir should be also taken into account.

### Acknowledgment

This study has been supported by State Key Development Program for Basic Research of China (Grant No. 2009CB219507), Major National S&T Program of China (Grant No. 2011ZX05026-004-07) and Natural Science Foundation of China (Grant No. 51006017 and No. 50736001).

### References

1. Fan, S.S. *Storage and Transportation Technologies of Natural Gas Hydrate*, 1st ed.; Chemical Industry Press: Beijing, China, 2005; pp. 1–2.
2. Chen, G.J.; Sun, C.Y.; Ma, Q.L. *Science and Technology of Gas Hydrate*, 1st ed.; Chemical Industry Press: Beijing, China, 2007; pp.1–4.
3. Luo, S.S.; Liu, H.J.; Sun, Y. Advancement on natural gas production from hydrate in deep-sea sediments with CO<sub>2</sub>. *China Resour. Compr. Util.* **2008**, *26*, 19–23.
4. Milkov, A.V.; Sassen, R. Economic geology of offshore gas hydrate accumulations and provinces. *Mar. Pet. Geol.* **2002**, *19*, 1–11.
5. Tsimpanogiannis, I.N.; Lichtner, P.C. Parametric study of methane hydrate dissociation in oceanic sediments driven by thermal stimulation. *J. Pet. Sci. Eng.* **2007**, *56*, 165–175.
6. Ji, C.; Ahmadi, G.; Smith, D.H. Natural gas production from hydrate decomposition by depressurization. *Chem. Eng. Sci.* **2001**, *56*, 5801–5814.
7. Gayet, P.; Dicharry, C.; Marion, G.; Graciaa, A.; Lachaise, J.; Nesterov, A. Experimental determination of methane hydrate dissociation curve up to 55 MPa by using a small amount of surfactant as hydrate promoter. *Chem. Eng. Sci.* **2005**, *60*, 5751–5758.
8. Zhou, X.T.; Fan, S.S.; Liang, D.Q. Advancement in research on replacement of CH<sub>4</sub> from hydrate with CO<sub>2</sub>. *Chem. Ind. Eng. Process* **2006**, *25*, 524–527.
9. Maslin, M.; Mikkelsen, N.; Vilela, C.; Haq, B. Sea-level and gas hydrate-controlled catastrophic sediment failures of the Amazon Fan. *Geology* **1998**, *26*, 1107–1110.
10. Zhao, X.M. A new advance of gas hydrate research. *Mar. Geol. Quat. Geol.* **1999**, *19*, 39–46.
11. Xu, W.S.; Yu, X.H.; Liu, N.N.; Liu, W.L. The development perspective and environmental problems of natural gas hydrate. *Nat. Gas Geosci.* **2005**, *16*, 680–683.
12. Cui, Z.D.; Liu, D.A.; Zeng, R.S.; Tian, T. Geological Sequestration of CO<sub>2</sub> and China's Sustainable Development. *China Popul. Resour. Environ.* **2010**, *20*, 9–13.
13. Kuang, G.S. Global warming and carbon dioxide mitigate. *Modern Chem. Ind.* **2007**, *27*, 1–12.
14. Ebinuma, T. Method for dumping and disposing of carbon dioxide gas and apparatus therefore. U.S. Patent 5,261,490, 16 November 1993.
15. Ohgaki, K.; Takano, K.; Sangawa, H.; Matsubara, T.; Nakano, S. Methane exploitation by carbon dioxide from gas hydrates-phase equilibria for CO<sub>2</sub>-CH<sub>4</sub> mixed hydrate system. *J. Chem. Eng. Jpn.* **1996**, *29*, 478–483.

16. Wang, J.B.; Guo, X.Q.; Chen, G.J.; Li, Z.Z.; Yang, L.Y. Experimental research on methane recovery from natural gas hydrate by carbon dioxide replacement. *J. Chem. Eng. Chin. Univ.* **2007**, *21*, 715–719.
17. Ota, M.; Abe, Y.; Watanabe, M.; Smith, R.L.; Inomata, H. Methane recovery from methane hydrate using pressurized CO<sub>2</sub>. *Fluid Phase Equilib.* **2005**, *228*, 553–559.
18. Li, Z.Z.; Guo, X.Q.; Wang, J.B.; Yang, L.Y. Experiment studies on CH<sub>4</sub> recovery from hydrate using CO<sub>2</sub> in different systems. *Natu. Gas Ind.* **2008**, *28*, 129–132.
19. Li, Z.Z.; Guo, X.Q.; Chen, G.J.; Wang, J.B.; Yang, L.Y.; Wang, T. Experimental and kinetic studies on methane replacement from methane hydrate formed in SDS system by using pressurized CO<sub>2</sub>. *J. Chem. Ind. Eng. (China)* **2007**, *58*, 1197–1203.
20. Sloan, E.D.; Koh, C.A. Estimation Techniques for Phase Equilibria of Natural Gas Hydrates. In *Clathrate Hydrates of Natural Gases*, 3rd ed.; Heinemann, H., Speight, J.C., Eds.; Taylor & Francis Group, LLC: New York, NY, USA, 2008; Chapter 6, pp. 320–523.
21. Uchida, T.; Ikeda, I.Y.; Takeya, S.; Kamata, Y.; Ohmura, R.; Nagao, J.; Zatsepina, O.Y.; Buffett, B.A. Kinetics and stability of CH<sub>4</sub>-CO<sub>2</sub> mixed gas hydrates during formation and long-term storage. *ChemPhysChem* **2005**, *6*, 646–654.
22. Anderson, R.; Llamedo, M.; Tohidi, B.; Burgass, R.W. Experimental measurement of methane and carbon dioxide clathrate hydrate equilibria in mesoporous silica. *J. Phys. Chem. B* **2003**, *107*, 3507–3514.
23. Geng, C.Y.; Wen, H.; Zhou, H. Molecular simulation of the potential of methane reoccupation during the replacement of methane hydrate by CO<sub>2</sub>. *J. Phys. Chem. A* **2009**, *113*, 5463–5469.
24. Yezdimer, E.M.; Cummings, P.T.; Chialvo, A.A. Determination of the gibbs free energy of gas replacement in SI clathrate hydrates by molecular simulation. *J. Phys. Chem. A* **2002**, *106*, 7982–7987.
25. Uchida, T.; Takeya, S.; Ebinuma, T. Replacing Methane with CO<sub>2</sub> in Clathrate Hydrate: Observation Using Raman Spectroscopy. In *Proceedings of the 5th International Conference on Greenhouse Gas Control Technologies*, Cairns, Australia, 13–16 September 2000.
26. Yang, G.; Qi, Y.X.; Zhang, H.; Tang, C.W. Advancement in experimental research on replacement of CH<sub>4</sub> from hydrate with CO<sub>2</sub>. *Cryo. Supercond.* **2010**, *38*, 70–75.
27. Fan, Y.; Liu, D.P.; Xie, Y.M.; Zhong, D.L.; Xiao, Y. Feasibility Analysis on Replacement of CH<sub>4</sub> from Hydrate Sediment by CO<sub>2</sub>. *Nat. Gas Geosci.* **2007**, *18*, 317–320.
28. Ota, M.; Morohashi, K.; Abe, Y.; Watanabe, M.; Smith, R.L.; Inomata, H. Replacement of CH<sub>4</sub> in the Hydrate by Use of Liquid CO<sub>2</sub>. *Energy Convers. Manag.* **2005**, *46*, 1680–1691.
29. Hirohama, S.; Shimoyama, Y.; Wakabayashi, A.; Tatsuta, S.; Nishida, N. Conversion of CH<sub>4</sub>-hydrate to CO<sub>2</sub>-hydrate in liquid CO<sub>2</sub>. *J. Chem. Eng. Jpn.* **1996**, *29*, 1014–1020.
30. van der Waals, J.H.; Platteeuw, J.C. Clathrate solutions. *Adv. Chem. Phys.* **1959**, *2*, 1–57.
31. Soave, G. Equilibrium constants from a modified Redlich-Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27*, 1197–1203.
32. Nagayev, V.B.; Gritsenko, A.I.; Murin, V.I. CO<sub>2</sub> Hydrates and CO<sub>2</sub> Sequestration. In *Proceedings of the All Union Conference on Calorimetry and Chemical Thermodynamics*, Iyonovo, Russia, 25–27 September 1979.

33. Rueff, R.M.; Sloan, E.D.; Yesavage, V.F. Heat-capacity and heat of dissociation of methane hydrates. *AIChE J.* **1988**, *34*, 1468–1476.
34. Zhou, X.T.; Fan, S.S.; Liang, D.Q.; Du, J.W. Replacement of methane from quartz sand-bearing hydrate with carbon dioxide-in-water emulsion. *Energy Fuels* **2008**, *22*, 1759–1764.
35. Xiong, L.J.; Li, X.S.; Zeng, Z.Y.; Li, G.; Chen, Z.Y.; Zhang, Y.; Li, Q.P. Experimental Investigation into Replacement of CH<sub>4</sub> in Hydrate in Porous Sediment with Liquid CO<sub>2</sub> injection. In *Proceedings of the 7th International Conference on Gas Hydrates (ICGH)*, Edinburgh, UK, 17–21 July 2011.
36. Yoon, J.H.; Kawamura, T.; Yamamoto, Y.; Komai, T. Transformation of methane hydrate to carbon dioxide hydrate: *in situ* Raman spectroscopic observations. *J. Phys. Chem. A* **2004**, *108*, 5057–5059.
37. McGrail, B.P.; Zhu, T.; Hunter, R.B.; White, M.D.; Patil, S.L.; Kulkarni, A.S. A New Method for Enhanced Production of Gas Hydrate with CO<sub>2</sub>. In *Proceedings of the AAPG Hedberg Conference on Gas Hydrates: Energy Resource Potential and Associated Geologic Hazards*, Vancouver, Canada, 12–16 September 2004.
38. White, M.; McGrail, P. Designing a Pilot-Scale Experiment for the production of natural gas hydrates and sequestration of CO<sub>2</sub> in class 1 hydrate accumulations. *Energy Procedia* **2009**, *1*, 3099–3106.
39. Dhanuka, V.V.; Dickson, J.L.; Ryoo, W.; Johnston, K.P. High internal phase CO<sub>2</sub>-in-water emulsions stabilized with a branched nonionic hydrocarbon surfactant. *J. Colloid Interface Sci.* **2006**, *298*, 406–418.
40. Zhou, X.T.; Fan, S.S.; Liang, D.Q.; Du, J.W. Determination of appropriate condition on replacing methane from hydrate with carbon dioxide. *Energy Convers. Manag.* **2008**, *49*, 2124–2129.
41. Zhang, W.; Wang, Z.; Li, W.Q.; Li, W.Y.; He, D.W. Research progress in the enhanced replacing methane out of gas hydrate by carbon dioxide emulsion. *Nat. Gas Chem. Eng.* **2009**, *34*, 59–63.
42. Kvamme, B.; Graue, A.; Aspenes, E.; Kuznetsova, T.; Gránásky, L.; Tóth, G.; Pusztai, T.; Tegze, G. Kinetics of solid hydrate formation by carbon dioxide Phase field theory of hydrate nucleation and magnetic resonance imaging. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2327–2334.
43. Kvamme, B.; Graue, A.; Buanes, T.; Kuznetsova, T.; Ersland, G. Storage of CO<sub>2</sub> in natural gas hydrate reservoirs and the effect of hydrate as an extra sealing in cold aquifers. *Int. J. Greenh. Gas Control* **2007**, *1*, 236–246.
44. Baldwin, B.A.; Stevens, J.; Howard, J.J.; Graue, A.; Kvamme, B.; Aspenes, E.; Ersland, G.; Husebø, J.; Zornes, D.R. Using magnetic resonance imaging to monitor CH<sub>4</sub> hydrate formation and spontaneous conversion of CH<sub>4</sub> to CO<sub>2</sub> hydrate in porous media. *Magn. Reson. Imaging* **2009**, *27*, 720–726.
45. Ersland, G.; Husebø, J.; Graue, A.; Baldwin, B.A.; Howard, J.; Stevens, J. Measuring gas hydrate formation and exchange with CO<sub>2</sub> in Bentheim sandstone using MRI tomography. *Chem. Eng. J.* **2010**, *158*, 25–31.
46. Tegze, G.; Pusztai, T.; Tóth, G.; Gránásky, L.; Svandal, A.; Buanes, T.; Kuznetsova, T.; Kvamme, B. Multiscale approach to CO<sub>2</sub> hydrate formation in aqueous solution: Phase field theory and molecular dynamics. Nucleation and growth. *J. Chem. Phys.* **2006**, *124*, 234710:1–234710:12.

47. Tegze, G.; Gránásy, L.; Kvamme, B. Phase field modeling of CH<sub>4</sub> hydrate conversion into CO<sub>2</sub> hydrate in the presence of liquid CO<sub>2</sub>. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3014–3111.
48. Zhou, W.; Fan, S.S.; Liang, D.Q.; Li, D.L.; Tang, C.P.; Tian, G.L. Influence of pressure to replacement of CH<sub>4</sub> in the hydrate by use of CO<sub>2</sub>. *J. Wuhan Univ. Technol. (Transp. Sci. Eng.)* **2008**, *32*, 547–550.
49. Qi, Y.X.; Zhang, H.; Zhao, S.X.; Ji, L.M. Experimental Research of Thermal Effects on Replacement of Methane Hydrates with Carbon Dioxide. In *Proceedings of the 7th International Conference on Gas Hydrates (ICGH)*, Edinburgh, UK, 17–21 July 2011.
50. Ota, M.; Saito, T.; Aida, T.; Watanabe, M.; Sato, Y.; Smith, R.L.; Inomata, H. Macro and microscopic CH<sub>4</sub>-CO<sub>2</sub> replacement in CH<sub>4</sub> hydrate under pressurized CO<sub>2</sub>. *AIChE J.* **2007**, *53*, 2715–2721.

© 2012 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).