Experimental study on the formation characteristics of CO$_2$ hydrate in porous media below the freezing point: Influence of particle size and temperature on the formation process and storage capacity

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Abstract

CO$_2$ storage in form of hydrate in stratigraphic sediment has been considered to be one of the effective strategies against global warming and mitigating CO$_2$ emission, which has attracted extensive research interest in the field of greenhouse gas (GHG) reduction and natural gas hydrate exploitation in permafrost regions. How the formation characteristics of CO$_2$ hydrate influences the storage process is a fundamental issue related to the hydrate-based technology of CO$_2$ sequestration and storage in the permafrost regions. In this study, the formation experiments of CO$_2$ hydrate were carried out in porous media below freezing point under the condition of different particle sizes and temperatures. The influence of different factors on the formation rate, conversion rate, and gas storage capacity of CO$_2$ hydrate were studied through experiments. It was indicated that temperature and ice particle size had a significant effect on the formation characteristics of CO$_2$ hydrate in porous media below the freezing point. However, it did not mean that the greater the degree of supercooling was the better the hydrate formation would be. The formation rate and conversion rate of hydrate were relatively higher when the temperature approached to the freezing point. In contrast, the gas storage capacity of CO$_2$ hydrate was higher than that above the freezing point. The average formation rate, conversion rate, and gas storage capacity of CO$_2$ hydrate were obtained under the temperature of 270.15 K, which was $3.68 \times 10^{-4}$ mol h$^{-1}$, 40.47%, and 75.09 L/L, respectively. When the ice particle size was 700 µm under the same particle size of quartz sand, the conversion rate and gas storage capacity of CO$_2$ hydrate was the maximum, reached to 49.69% and 92.19 L/L, respectively. These results provide greater insights into the hydrate-based technology of CO$_2$ sequestration and storage in sediments.
1 INTRODUCTION

With the massive consumption of fossil fuels and the ever-increasing greenhouse effect in the atmosphere, energy and environment issues have become the focus of world attention. CO$_2$ has been considered as a primary greenhouse gas caused by fossil energy consumption for electricity generation, transportation, and heating. The capture and sequestration of CO$_2$ gas is considered to be an effective strategy against the global warming caused by the overall concentration increase of CO$_2$ in atmosphere.$^{1,2}$ It has become a hotspot and common topic for scholars all over the world. In this regard, hydrate-based technology for CO$_2$ sequestration and storage has always been one of the hot spots in the field of gas hydrate application technology. Simultaneously, natural gas hydrate (NGH) is widely distributed in submarine sedimentary belts and terrestrial permafrost regions, and it is considered as a potential clean and efficient new energy source because of its huge reserves.$^{3,4}$ It is considered to be a very promising approach for CO$_2$ gas storage into stratum sediments of naturally occurring gas hydrate reservoirs combined with natural gas hydrate exploitation in permafrost regions.$^{5}$ In addition, the temperature and pressure conditions are very conducive to the storage of CO$_2$ gas in the form of hydrate, as well as natural gas hydrate exploitation in permafrost regions. However, the occurrence conditions of natural gas hydrate was usually in porous media below the freezing point and it had an important influence on the formation characteristics CO$_2$ hydrate.$^{6,5}$ Therefore, understanding and clarifying the effect of the formation mechanism and rules for CO$_2$ hydrate constitutes the fundamental problems in affecting the high-efficiency storage of CO$_2$ in porous media below the freezing point, which has important practical significance for CO$_2$ gas storage in permafrost regions.

In recent years, many theoretical and experimental studies have been focused on the formation process of hydrates below freezing point. And macro-structure and micro-structure of porous media had a great influence on the formation and decomposition process of hydrate. Jander et al.$^8$ firstly proposed a model of ice-hydrate conversion. It was showed that the conversion of ice to hydrate started from the formation of a gas hydrate shell on the surface of ice particles, and then gas molecules diffused through the outer gas hydrate shell to achieve further conversion. Staykova et al.$^9$ studied the kinetics of ice powder forming gas hydrates and established a three-stage phenomenological model. Afterward, the three-stage shrinking nucleus model was revised to a two-stage model by Kuhs et al.$^{10}$ which it was considered that there was indistinguishable between the second stage and the third stage. Wang et al.$^{11}$ investigated the formation kinetics of CH$_4$ hydrate by neutron powder diffraction. The results indicated that the reaction proceeded rapidly in the nucleation stage and formed a complete hydrate layer on the face of ice particles. Then the later reaction was controlled by the growth rate of the hydrate layer and the diffusion process of CH$_4$ molecules through the hydrate layer to the unreacted ice core. It was consistent with the diffusion control mechanism of CH$_4$ hydrate formation rate in ice particles. Falenty et al.$^{12}$ found that there was no hydrate shell when the ice particles smaller than 20 µm, which indicated the transformation of micron-sized ice particles did not follow the mechanism described by the shrinking core model. Liu et al.$^{13}$ established a gas-solid reaction model of single-size ice powder forming gas hydrate based on the diffusion theory. And the effective diffusion coefficient of hydrate shell can be obtained by solving the diffusion equation. Vlasov et al.$^{14}$ established a kinetic model for hydrate formation from ice and found that the kinetics of hydrate formation was only limited by the diffusion rate of gas through the gas hydrate layer.

Simultaneously, a number of studies have found that ice was more likely to form hydrate with CH$_4$ gas than water in the formation process of gas hydrate, and there was almost no induction time when ice surface contacts with gas to form hydrates.$^{15}$ Sloan et al.$^{16}$ clarified the molecular mechanism of the nucleation of hydrate crystals on the ice surface and revealed the mechanism of the quasi-liquid layer on the formation of hydrates. Henning et al.$^{17}$ experimentally studied the formation process of CO$_2$ hydrate and found that the reaction between CO$_2$ gas and ice was conducted in the quasi-liquid layer. Shepherd et al.$^{18}$ demonstrated that the quasi-liquid layer played an important role in the nucleation process of hydrate through molecular dynamics simulation. Nagashima et al.$^{19}$ found that the growth rate of hydrate on the surface of ice powder increased with the increase of temperature and it was dominated by the mass transfer process of methane and water molecules. Liu et al.$^{20}$ further found that the reaction rate constant was more sensitive to temperature and the higher temperature could increase the diffusion capacity and promote the reaction when the temperature was close to the freezing point. Hwang et al.$^{21}$ experimentally studied the growth process of CH$_4$ hydrate on ice and
measured the formation rate of hydrate under different pressures. Liu et al. found that lower temperature can promote the formation process and overpressure was the main effect on the formation rate. Rivera et al. investigated the effect of ice particle size and temperature on the formation of propane hydrate in ice powder system. The results indicated that the smaller ice particles have a higher specific surface area and the initial growth rate and total conversion rate of hydrate were higher. This was agreed well with the research results reported by Vlasov et al. Zhao et al. experimentally studied the formation process of xenon hydrate on ice particles used X-ray diffraction. Then the nucleation and growth of hydrate were accurately and directly quantified and the intrinsic reaction rate constant of the xenon hydrate were estimated.

In addition, Wang et al. experimentally studied the effects of particle size and volume ratio of porous media on CH₄ hydrate formation. It was indicated that the ice conversion rates was direct proportion to particle size at different volume ratios of porous media and ice. Meanwhile, Zhang et al. found that, within a certain particle size range, the smaller the particle size of porous medium was, the faster the average formation rate and the greater the gas storage capacity would be. Zhang et al. also investigated the formation characteristics of CO₂ hydrate from frozen quartz sand and found that the formation rate of CO₂ hydrate increased with the increase of the initial pressure of CO₂ when the pressure was lower or higher than the liquefaction pressure. To sum up, many recent studies have focused on the formation characteristics, kinetic process and stability of CO₂ hydrate in porous media. However, the formation process of hydrate was mainly concentrated in porous media with a single spherical surface. Actually, the formation of CO₂ hydrates is a more complex process in porous media below the freezing point and is completely different from the situations above the freezing point. And the occurrence of water and water content imposed an important on the formation characteristics of hydrate in porous media below the freezing point. The reaction process of hydrate formation was affected by multiple factors such as the intrinsic kinetics, heat transfer, mass transfer and so on. Therefore, it is very crucial for understanding and clarifying the influence mechanism and law of different factors in porous media below the freezing point. In this work, the experiments of CO₂ hydrate formation were carried out in porous media below the freezing point under different conditions. The effects of temperature and particle size on the formation rate, conversion rate, and gas storage capacity were accurately quantified through experiments. And the influence mechanism and law of different factors was further clarified. Conducting of the experiments can be helpful not only for fully understanding the quantitative influence of different factors on the formation characteristics of CO₂ hydrate, but also provide an important theoretical basis and reference for sequestration and storage of CO₂ gas into sediments combined with natural gas hydrate exploitation in permafrost region.

2 | EXPERIMENTAL SECTION

2.1 | Materials

CO₂ (99.99% purity) applied in this study was supplied by Lanzhou Lanheng Special Gas Co., Ltd., China. N₂ (99.9% purity) used in the experiment was supplied by Chongqing Zhaoyang Gas Co., Ltd., China. Quartz sand (99.0% purity) was provided by Tianjin Liyuan., Ltd., China. Distilled water produced in the laboratory and was used to prepare ice powder in the experiment.

2.2 | Apparatus

A schematic diagram of the experimental apparatus used in this work is as shown in Figure 1. The experimental apparatus consist of a high-pressure vessel, a thermostatic alcohol bath, a vacuum pump, a CO₂ gas cylinder and a data acquisition system. The high-pressure vessel is the main part of the system, which is made of 316 L stainless steel with volume of 300 ml. The maximum operating pressure attain to 20 MPa of the high-pressure vessel. Two temperature sensors, with the accuracy of ±0.1 K, are installed in the reactor to measure the temperature of the gaseous phase and sediment of porous media during the experiment. A pressure sensor, with the accuracy of 0.05%, is installed and employed to measure the pressure of the reactor. And the measuring range is 0–10 MPa. The temperature of the reaction system was controlled and adjusted by the thermostatic alcohol bath, which the working temperature ranges from 253 K to 373 K. CO₂ gas cylinder are employed for CO₂ gas injection in the experiment. Data acquisition was performed using an Agilent 34970A data acquisition instrument supplied by Agilent Technology Co., Ltd. And the data logger is used to record the temperature and pressure every 10 s during the experiment.

2.3 | Experimental procedure

The experiments for CO₂ hydrate formation were performed in porous media in the batch mode under the condition of constant volume using the following procedure. Before the experiment, ice powder with the required particle was prepared. Firstly, 200 g distilled water was frozen
through freezer and ice was crushed to ice powder under the protection of liquid nitrogen. Then the samples of different particle diameter were sieved with a standard sieve under the protection of liquid nitrogen. Subsequently, the quartz sand with the particle size of 700 µm was employed for CO₂ hydrate formation in porous media. The experimental conditions for formation process of CO₂ hydrate as shown in Table 1.

After that, the high-pressure vessel was rinsed with distilled water three times and dried with a dryer. Then nitrogen was loaded into the high-pressure vessel for the airtightness test. And after the airtightness test, the quartz sand and ice powder were mixed in the low-temperature chamber, and then the samples were put into the high-pressure vessel cooled beforehand. The high-pressure vessel was sealed and immersed in the constant temperature bath with the temperature below the freezing point to prevent the ice from melting. The high-pressure vessel was vacuumed by a vacuum pump to remove the residual air in the system. In the experiment, the total mass and the ratio of quartz sand and ice powder were 80 g and 4:1 in each group, respectively. Set the temperature of the constant temperature alcohol bath to experimental temperature and the reaction system started to cool until the temperature and pressure was in a stable state in the high-pressure vessel. Subsequently, CO₂ gas was slowly injected into the high-pressure vessel until it attained to the predetermined value. The temperature and pressure were monitored by the data acquisition system during the formation process of CO₂ hydrate and the data logger recorded and logged into the computer every 10 s. Finally, the pressure change was negligible in the high-pressure vessel at least 3 h, it was considered that the formation process of CO₂ hydrate was completed. As a consequence, the consumed amount of CO₂ gas can be calculated according to the experimental data in the experiment.

### 2.4 Theoretical calculations

#### 2.4.1 Gas consumption

The experiments were carried out in porous media under the condition of constant volume and the temperature and

| Exp. No. | Quartz sand particle size (µm) | Ice particle size (µm) | \(T_f\) (K) | \(P_i\) (MPa) | \(P_e\) (MPa) | \(\text{CO}_2\) gas consumption (mol) |
|----------|-------------------------------|------------------------|-------------|--------------|--------------|----------------------------------|
| 1        | 700                           | 500                    | 268.15      | 3.03         | 2.79         | 0.0278                           |
| 2        | 700                           | 500                    | 270.15      | 3.01         | 2.56         | 0.0588                           |
| 3        | 700                           | 500                    | 272.15      | 3.00         | 2.57         | 0.0554                           |
| 4        | 700                           | 250                    | 270.15      | 2.98         | 2.46         | 0.0712                           |
| 5        | 700                           | 700                    | 270.15      | 2.98         | 2.42         | 0.0768                           |
pressure changes were recorded by the data acquisition system. Therefore, the total amount and the consumed amount were calculated according to the experimental data. During the experiment, the cumulative amount of consumed CO₂ gas was the difference from the initial time to a given time \( t \) and it can be calculated as follows:

\[
\Delta n = n_t - n_0 = \frac{P_0 V_0}{Z_0 R T_0} - \frac{P_c V_c}{Z_c R T_c}
\]

(1)

Where \( P_c \) represents the pressure in the high-pressure vessel at time \( t \), MPa; \( P_0 \) represents the initial pressure in the high-pressure vessel, MPa; \( T_0 \) represents the temperature of the gas in the high-pressure vessel, K; \( T_c \) represents the temperature of the gas in the reactor at time \( t \), K; \( V_0 \) represents the initial volume of the CO₂ gas in the high-pressure vessel, ml; \( V_c \) represents the volume of the CO₂ gas in the high-pressure vessel at time \( t \), ml; \( Z_0 \) represents the compression factor of the gas when the pressure is \( P_0 \), and \( Z_c \) represents the compression factor of the gas when the pressure is \( P_c \), which are calculated by the PR equation iteratively.²⁹ \( R \) represents the ideal gas constant, \( R = 8.314 \text{ J/(mol K)} \).

Simultaneously, the equation is used to obtain the initial gas volume \( V_0 \) in the high-pressure vessel and it can be described as follows:

\[
V_0 = V_1 - V_s - V_i
\]

(2)

Where \( V_1 \) represents the volume of the reactor, \( V_1 = 300 \text{ ml} \); \( V_s \) represents the volume of quartz sand in the mixture, ml. \( V_i \) represents the volume of ice in the mixture, ml. The density of quartz sand used in the experiment is quoted as 2.660 g/cm³. The density of ice is quoted as 0.917 g/cm³ in the experiment.

2.4.2 | Formation rate of CO₂ hydrate

During the experiment, the average formation rate of CO₂ hydrate was calculated through the gas consumption of CO₂ gas at different instants of time. In this work, the formation rate of CO₂ hydrate was calculated every 5 min³⁰:

\[
\left( \frac{\Delta n}{\Delta t} \right)_t = \frac{n_{t+\Delta t} - n_t}{\Delta t}, \Delta t = 5 \text{ min}
\]

(3)

Subsequently, the formation rate of CO₂ hydrate can be obtained through formation experiment of CO₂ hydrate in porous media per 30 min.

2.4.3 | Conversion rate of ice to hydrate

During the experiment, the conversion rate is defined \( C \) and employed to describe the conversion degree of ice to hydrate in porous media. And it can be calculated as follows³¹:

\[
C = \frac{n \times 6.15 \times 18}{m_i} \times 100\%
\]

(4)

Where \( n \) represents the amount of consumed CO₂ gas in the experiment, mol. The hydrate number (the ratio of the amount of CO₂ to water in the hydrate) is 6.15 in this work.²¹ And \( m_i \) represents the total mass of ice in porous media, g.

2.4.4 | Gas storage capacity of CO₂ hydrate

The gas storage capacity of CO₂ hydrate was defined as the volume of CO₂ gas stored in the form of hydrate per unit volume under a certain condition. It was employed to describe the gas storage capacity of porous media below the freezing point. So the gas storage capacity can be calculated as follows³²:

\[
S_W = \frac{V_{G0}}{V_i} = \frac{(m_G/M_G) \times 22.4}{V_i}
\]

(5)

Here, \( V_{G0} \) represents the volume of CO₂ gas stored in porous media in the form of hydrate during the experiment. \( m_G \) represents the mass of CO₂ gas consumed in the experiment. And \( M_G \) represents the molar mass CO₂ gas.

3 | RESULTS AND DISCUSSION

3.1 | The formation process of hydrate in porous media below the freezing point

The formation process of CO₂ hydrate was carried out in porous media with different particle size of ice powder at different temperature (Exp. 1–5 in Table 1). Figure 2 shows the evolutions of pressure and temperature of CO₂ hydrate formation in porous media below freezing point when the particle size of ice powder was 500 µm and the initial pressure was 3.01 MPa under the condition of 270.15 K (Exp. 2 in Table 1). It was defined the highest point of inflation pressure as the zero point in the experiment. In order to eliminate the influence of hydrate formation on the research results, the aeration rate was fast...
as soon as possible. Clearly seen from Figure 2, the highest point of temperature in the solid phase is still below the freezing point. This indicates that ice has not melted in porous media during the experiment. In addition, seen from Figure 2, the formation process of \( \text{CO}_2 \) hydrate can be divided into two stages. At the beginning of the experiment, the pressure dropped faster in the high-pressure vessel. It indicates that hydrates were formed rapidly in porous media. \( \text{CO}_2 \) gas could diffuse quickly in the mixture of quartz sand and ice powder. In this case, \( \text{CO}_2 \) hydrate would be quickly forming on the surface of ice when the pressure had reached the phase equilibrium condition of \( \text{CO}_2 \) hydrate formation. As a result, the hydrate layer grew gradually and the continuous diffusion process was hindered by the hydrate shell formed on the ice surface. So the formation rate of \( \text{CO}_2 \) hydrate slowed down and the formation of hydrate process shifted to the second stage. Meanwhile, the temperature of the gas phase and the solid phase were always descending in the first 5 h. This is because the cooling process of the gas and solid phases was delayed by the reaction heat released by \( \text{CO}_2 \) hydrates formation. It was agreed well with the research results reported by Liu et al.\textsuperscript{33}

Simultaneously, Figures 3 and 4 show the evolutions of pressure and temperature of \( \text{CO}_2 \) hydrate formation in porous media below the freezing point when the particle
size of ice powder was 500 µm at the same initial pressure under the condition of 268.15 K and 272.15 K (Exp. 1 and 3 in Table 1). The phenomena displayed in Figures 2 and 3 are similar and consistent with the shrinking nucleus model proposed by Kush et al.10 Seen from Figure 3, the formation process of CO2 hydrate can be divided into two stages. At the beginning of the reaction, the formation rate of hydrate is relatively fast. As the reaction proceeds, the formation rate gradually slows down. As showed in Figure 4, the formation process of CO2 hydrate is different from that showed in Figure 2. It can be viewed as the rapid reaction stages in the first 10 h of formation process during the experiment. The drop rate of pressure was fast and then slowed down with the hydration continuing. Simultaneously, the pressure dropped suddenly faster when the hydration reaction proceeded among 60–80 h in the experiment. However, the pressure gradually tends to be stable after 80 h during the formation process of hydrate. This is because the formation process of CO2 hydrate is still conformed to the shrinking nucleus model in the first 60 h of the experiment.9–11 The second stage of rapid formation for CO2 hydrate occurred on the surface of ice powder and hydrate quickly formed with molten water in porous media during the experiment. This can be verified from the temperature changes of the gas and solid phases about 75 h in Figure 4. Clearly seen in Figure 4, the temperature of the gas phase and the solid phase rose briefly during the experiment. Since the reaction heat was absorbed by the process of melting ice, the rising temperature peak only approached the melting point of ice and then it disappeared quickly. The phenomena have been reported by Wang et al. in their researches when the formation process of hydrate was conducted in porous media close to the freezing point.11 Furthermore, it is consistent with the theory about superheated ice.3,16,19,34 Just as Moudrakovski et al.34 reported, it would be helpful to the formation process of hydrate at higher temperature when the temperature was below freezing point. This further demonstrates that, the temperature has a significant influence on the formation characteristics of hydrate in porous media below the freezing point in the experiment.

3.2 Effects of temperature and ice powder particle size on the formation process of hydrate

Table 1 shows the pressure changes of CO2 hydrate formation in porous media below the freezing point under different temperature conditions (Exp. 1–3 in Table 1). The experiments were carried out in the porous media with the ice particle size of 500 µm at different temperature when the initial pressure was fixed at 3.0 MPa. During the experiments, the pressure drops were 0.23 MPa, 0.45 MPa, and 0.43 MPa, when the temperatures were 268.15 K, 270.15 K, and 272.15 K, respectively. The results indicated that, there was little difference on the final pressure when the experimental temperatures were 272.15 K and 270.15 K. By contrast, the pressure drop was much smaller than others when the temperature was 268.15 K. As a result from the experiment, there was an abnormal phenomenon that the degree of subcooling was the largest when the temperature was 268.15 K, but the pressure drop was the smallest. The result further indicated that, it did not mean that the higher the degree of supercooling corresponded to the faster the formation rate of hydrate in
porous media below the freezing point. The results agreed well with researches from Kawamura et al. These results showed that, the initial formation rate was fast and the final consumption of CO$_2$ gas was relatively high when the temperature ranged from 268.15 K to 272.15 K in porous media below the freezing point. However, when the initial temperature ranged from 263.15 K to 268.15 K, the hydration reaction was slower at the beginning and the final consumption of CO$_2$ gas was less to some extent. Previous studies have shown that, the lower the experimental temperature was, the greater the degree of supercooling. Actually, the formation process is quite different in porous media below the freezing point.

In addition, it can be seen from Figures 2–4, the pressure drop was the slowest in the initial stage of the experiment when the temperature was 268.5 K (Exp. 1 in Table 1). This was because the formation rate of hydrate was not only related to the degree of supercooling, but also was related to “the quasi-liquid layer” (QLL) on the surface of ice particle. Studies have shown that CO$_2$ gas is difficult to dissolve in solid ice and “the quasi-liquid layer” plays an important role in the nucleation process of hydrate on the ice surface. Meanwhile, there may also be a quasi-liquid layer between the hydrate layer and the unreacted surface of the ice particles. According to the thermodynamic theory, it can be predicted that the thickness of the QLL increased with the power law approach the melting temperature. Additionally, many research works have been done by scholars to measure the relationship between the thickness of the QLL and the temperature through experiments, which indicated that the thickness of “the quasi-liquid layer” on the ice surface increased as the temperature approached the freezing point. Therefore, it is considered to be the lower the temperature and the greater the degree of supercooling was, the thinner the QLL would be. And the thickness of “the quasi-liquid layer” was thinnest when the temperature was at 268.5 K in the experiments. It is not conducive to the nucleation and growth process of CO$_2$ hydrate in porous media. Thus, the formation rate of hydrate was not only depending on the degree of supercooling, but also related to the thickness of the QLL on the ice surface. The degree of subcooling and the thickness of the QLL were determined by the experimental temperature at the same time. In this case, the lower the experimental temperature was, the greater the degree of subcooling and the thinner the QLL would be. According to the experimental results, it is most conducive to the formation process of CO$_2$ hydrate when the temperature is approaching the freezing point under the temperature range of 268.15 K–272.15 K.

Figure 5 shows the pressure changes of CO$_2$ hydrate formation in porous media below the freezing point under different particle size of ice powder (Exp. 2, 4 and 5 in Table 1). The experiments were carried out in the porous media at the same temperature and pressure conditions. Clearly seen from Figure 5, the pressure trend are basically same in the three cases and the pressure decreased rapidly in the early stage of the three experiments. Furthermore, by contrast, the pressure drop was the largest in the porous media with the ice powder of 250 µm in the early stage of the experiment. This was because it had larger specific surface area in the porous media with the smaller ice particle size in the experiments. So the formation rate of hydrate was the fastest in the early stage of the experiment. As shown in Figure 5, compared with ice particle size of 250 µm, the final pressure drop was larger in porous media with ice particle size of 700 µm. In the initial stage of the reaction, hydrates are rapidly formed along the ice surface, at this time the ice powder particle size changes little. When the ice particles are wrapped by the hydrate shell, the hydrate formation process turns to the diffusion control stage, and the shell surface forms bulges during the hydrate formation process and gradually thickens. This causes the pore channels between the ice powder to become smaller and cement gradually. These results demonstrated that, the agglutination among the smaller particle size ice powder hindered the diffusion process of gas in the mixture system of quartz sand and ice powder. The smaller the particle size of ice powder was, the more serious the effect would be.

In addition, the larger throat among the large ice powder was avail to migration and diffusion of gas, and it improved the mass transfer of CO$_2$ gas in the mixed system of quartz sand and ice powder during the experiment. Then the formation process of hydrate was promoted to some extent. So the final pressure drops are different from the trend at the beginning of the hydration reaction. Interestingly, the final pressure drop was the smallest in porous media with ice particle size of 500 µm among the three experiments. This indicates that both the small-sized ice powder with larger specific surface area and the large-sized ice powder with larger pore size could effectively promote the formation process of CO$_2$ hydrate under a certain conditions. However, when the particle size of ice powder is in the middle value, it is considered that the specific surface area and pore size have weak effect on promoting the formation process of hydrate in porous media to some extent.

3.3 Effects of temperature and ice powder particle size on the formation rate of hydrate

Figure 6 shows the evolutions of the formation rate for CO$_2$ hydrate in porous media under different temperature conditions (Exp. 1–3 in Table 1). In the experiments, the initial pressure and the particle size of ice powder were the same. And the comparison of the average formation rate
for CO₂ hydrate is shown in Table 2. Clearly seen from Figure 6, the formation rate was highest at the beginning of the experiment when the temperature was 270.15 K in porous media below the freezing point. And the formation rate of hydrate was always the maximum in the first 20 h of the experiment. After 25 h, the formation rate of CO₂ hydrate was almost unanimously. It indicated that the formation process was mainly controlled by the diffusion process of CO₂ in the stage. Obviously, temperature had a significant influence on the formation process of CO₂ hydrate in porous media below the freezing point. Moreover, according to the mentioned above, when the temperature was in the range of 268.15 K–272.15 K, it did not mean that the formation rate was higher under the condition of lower temperature. During the formation process of hydrate, the degree of supercooling is one of the influencing factors. But the thickness of “the quasi-liquid layer” varied with temperature also has a significant impact on the formation rate of CO₂ hydrate in porous media below the freezing point. During the experiment, it can be noticed that the pressure occurred the secondary rapid drop and the formation rate increased significantly (as shown in Figures 4 and 6 at 60–80 h). According to the experiment, the largest average formation rate of hydrate was attained $3.68 \times 10^{-4}$ mol h⁻¹ when the experimental temperature was 270.15 K.

Figure 7 shows the evolutions of the formation rate for CO₂ hydrate in porous media with different particle size of ice powder (Exp. 2, 4 and 5 in Table 1). And the comparison of the formation rate for CO₂ hydrate is shown in Table 2. The average formation rate of hydrate was the slowest when the ice particle size was 500 µm. In addition, as shown in Figure 7, there was obvious difference on the formation rate of CO₂ hydrate in the first 20 h of the experiment. The formation rate of hydrate was the largest when the particle size of ice powder was 250 µm at the initial time in the experiment. This was because it had the larger specific surface area in the porous media with the smaller ice particle size in the experiments. At the beginning of the hydration reaction, the contact area between CO₂ gas and ice powder was relatively large and it provided more opportunities for gas molecules to come into contact with the ice surface. So the formation rate of CO₂ hydrate was greater to some extent. However, as the reaction progressed, the agglutination among the smaller particle size ice powder hindered the diffusion process of gas in the mixture system of quartz sand and ice powder. The formation rate of hydrate was always the largest when the particle size of ice powder was 700 µm during the stage of 2.5–20 h in the experiment. This was because the larger pore size between porous media is favorable to the gas diffusion process of CO₂ gas. Simultaneously, the formation rate of hydrate remained basically the same after 30 h of the experiment. The results indicated that there was evident difference on the formation rate of CO₂ hydrate during the early stage of the experiment under the condition of different particle size of ice powder. This was the main reason for the difference the conversion rate and gas storage capacity of CO₂ hydrate in porous media below the freezing point.

### 3.4 Effects of temperature and ice powder particle size on the hydrate conversion rate

Figure 8 shows the evolutions of the conversion rate for CO₂ hydrate in porous media under the condition of different temperature and ice powder particle size. As shown in Figure 8, it can be obviously realized that the conversion
rate of hydrate is the lowest when the temperature was 268.15 K under the same pressure and particle size conditions. The results further illustrated that, temperature has an important influence on the conversion rate of water to hydrate below freezing point. Under the condition of different temperature (Exp. 2, 4 and 5 in Table 1), the conversion rate of hydrate attained 19.24%, 40.47%, and 37.91% when the temperatures were 268.15 K, 270.15 K and 272.15 K, respectively. Clearly seen from Figure 8, the conversion rate of hydrate increased at the early stage of the experiment. And then the increment decreased with the temperature increasing in the range from 268.15 K to 272.15 K. Interestingly, the conversion rate is higher at 272.15 K than that of 270.15 K during the stage of 75–105 h in the experiment. This was because the thickness of the QLL was thicker at higher temperature as the temperature approached the freezing point.39-42

Simultaneously, as shown in Figure 8, the ice particle size also has a significant effect on the conversion rate of CO2 hydrate in porous media below the freezing point. When the particle size of quartz sand was 700 µm and the ice particle size was different in the mixed system (Exp. 2, 4 and 5 in Table 1), the conversion rate of CO2 hydrate reached 38.07%, 43.16%, and 49.69%, respectively. It is indicated that the final conversion rate of CO2 hydrate is the highest in the experiments when the ice powder particle size also was 700 µm in the mixture system. This was because the CO2 gas could be quickly and fully contacted with the surface of the ice particles in the mixed system of ice and quartz sand. It provided larger pore channels for diffusion process of CO2 gas in the mixture of 700 µm ice particles and 700 µm quartz sands. Furthermore, the increment of conversion rate for CO2 hydrate was the highest in the first 17 h of the experiment when the particle size of ice powder was 250 µm. This is because it has the smallest particle size and the largest surface area in porous media with ice particle size of 250 µm. It was conducive to the rapid formation of CO2 hydrate in the initial stage. However, with the hydration reaction continuing, the agglutination among the ice particles was enhanced due to hydrate formation. And the diffusion process of CO2 gas was hindered and the increment of conversion rate slowed down gradually. Meanwhile, the smaller particle size of ice powder is not conducive to increasing the

| Exp. No. | Quartz sand particle size (µm) | Ice particle size (µm) | Ti (K) | gas storage (L/L) | Average formation rate (mol h⁻¹) | Conversion rate (%) |
|---------|-------------------------------|-----------------------|-------|-------------------|-------------------------------|--------------------|
| 1       | 700                           | 500                   | 268.15| 35.72             | 1.74 x 10⁻⁴                  | 19.25             |
| 2       | 700                           | 500                   | 270.15| 75.09             | 3.68 x 10⁻⁴                  | 40.47             |
| 3       | 700                           | 500                   | 272.15| 70.35             | 3.46 x 10⁻⁴                  | 38.15             |
| 4       | 700                           | 250                   | 270.15| 80.09             | 4.45 x 10⁻⁴                  | 43.16             |
| 5       | 700                           | 700                   | 270.15| 92.19             | 4.80 x 10⁻⁴                  | 49.69             |
3.5 Effects of temperature and ice powder particle size on gas storage

The gas storage capacity is an important parameter for CO₂ sequestration and storage in the form of hydrate in porous media. In this work, the gas storage capacity was defined as the volume of CO₂ gas stored in the form of hydrate per unit volume under certain conditions. According to the experiments, as shown in Figure 9, the final gas storage capacity can be calculated and reached to 35.72 L/L, 75.09 L/L and 70.35 L/L when the temperatures were 268.15 K, 270.15 K and 272.15 K, respectively. The results showed that the temperature has an extremely important influence on the storage capacity of hydrate in porous media below the freezing point. When the temperature is 270.15 K and 272.15 K, the gas storage capacity of hydrate was almost twice than that at 268.15 K. Thus, these results are expected to provide an important and actual guidance for storing CO₂ in porous media below the freezing point.

Furthermore, the experimental results showed that the final gas storage capacity of CO₂ hydrate was different in the porous media with different ice particle sizes. As shown in Figure 10, the gas storage capacity of hydrate attained 75.09 L/L, 80.09 L/L and 92.19 L/L when the ice particle sizes were 500 µm, 250 µm and 700 µm, respectively. And the gas storage capacity of CO₂ hydrate in a porous media system below the freezing point is higher than that above the freezing point.27 Actually, both ice powder and quartz sand are solid particles with a certain particle size. When the quartz sand and ice powder were fully mixed together in the mixed system, the particle size of ice powder would not only determine how the hydration reaction proceeded, but also determine the characteristics of porous media when it mixed with a certain particle size of quartz sand. For example, they were fully mixed and evenly filled in the space when the particle size of ice powder and quartz sand were 700 µm. And a certain number of ice particles would be agglomerated in the pores of the quartz sand particles when the particle size of ice powder was 250 µm and the particle size of quartz sand was 700 µm. On the other hand, ice powder was easily to gel during the formation process of CO₂ hydrate, which hindered the diffusion process of gas in the mixture of quartz sand and ice powder. Therefore, although it has the larger specific surface area in the porous media with ice particle size of 250 µm, the conversion rate of CO₂ hydrate was lower than that in porous media with ice particle size of 700 µm. And the final gas storage capacity of CO₂ hydrate was the largest in porous media when the ice particle size was 700 µm in the experiment.

4 CONCLUSIONS

In this work, the formation process of CO₂ hydrate was experimentally studied in porous media below the freezing point under the condition of different temperatures and ice particle sizes. The formation behavior and storage characteristics of CO₂ hydrate were investigated through experiment. The results indicated that temperature had an important influence on the formation characteristics of CO₂ hydrate in porous media below the freezing point. The results showed that did not mean that the higher the degree of supercooling was, the better the hydrate formation would be. The formation rate and conversion rate of hydrate were relatively higher when the temperature approached to the freezing point. In addition, the formation rate and conversion rate of CO₂ hydrate attained 3.68 × 10⁻⁴ mol h⁻¹ and 40.47% at the temperature of 270.15 K. Furthermore, the ice particle size of the porous media has a significant effect on the formation process of CO₂ hydrate. The formation rate and conversion rate of hydrate were 4.80 × 10⁻⁴ mol h⁻¹ and 49.69% when the ice particle size was 700 µm mixed with quartz of 700 µm under the temperature of 270.15 K. In addition, the higher temperature was favorable to increase the gas storage capacity of hydrate when it approached to the freezing point. And the gas storage capacities were 70.35 L/L and 75.09 L/L when the temperature was 272.15 K and 270.15 K, respectively. And the gas storage capacity of CO₂ hydrate reached the maximum when the ice particle size was 700 µm mixed.
with quartz sand of 700 µm under the temperature of 270.15 K. And gas storage capacity of hydrate reached to 92.19 L/L in the porous media system during the experiment. These finding would provide important theoretical guidance and reference for CO₂ sequestration and storage in sediments natural gas hydrate exploitation in permafrost regions.

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