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# An experimental study on gas production from fracture-filled hydrate by $CO_2$ and $CO_2/N_2$ replacement

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ABSTRACT

The fracture-filled gas hydrate commonly occurs in marine fine-grained sediments and the fracture of rock in permafrost regions. Gas production from fracture-filled methane hydrate by the $CO_2$ replacement method has been investigated. The reservoir condition of permafrost-associated gas hydrate in Muri Basin, Qilian Mountains was taken as an example to set up the experimental parameters. $CO_2$, $CO_2/N_2$ (3:1) and $CO_2/N_2$ (1:3) were selected for gas replacement. Based on the results from six sets of laboratory experiments, we can learn that the factors affecting gas replacement included gas composition for replacement, pressure and the morphology of the hydrate. When the pressure was lower than the equilibrium pressure of $CO_2/N_2$ binary hydrate and the equilibrium pressure of methane hydrate, there was a rapid decomposition process of methane hydrate and might be a transient water freezing process at the first few minutes. The ice around methane hydrate might inhibit the further decomposition of methane hydrate. A higher replacement rate and accumulative methane recovery ratio can be obtained when the morphology of methane hydrate was well distributed thin layer, which could be obtained with the ice layer by gradually increasing its temperature. The thin layer of hydrate is the main morphology of the fracture-filled gas hydrate found in the Qilian Mountain permafrost. Therefore, the gas production from hydrate by $CO_2/N_2$ (3:1) replacement might be a good choice for gas production from hydrate in Muri Basin, Qilian Mountain.

## 1. Introduction

Natural gas hydrate (NGH) is one kind of cage compound formed by natural gas (mainly $CH_4$) and water under low-temperature and high-pressure coexisting conditions [1]. NGH, known as the most commercial and perspective new clean energy, is widely distributed in permafrost regions as well as along the continental margins in the oceans [2,3]. Technically recoverable global volumes of gas hydrates are estimated to be on the order of $3 \times 10^{15}\,m^3$ [4]. Nevertheless, it is still enormous as compared to the conventional gas resources ($4 \times 10^{14}\,m^3$) and shale gas ($2.04–4.56 \times 10^{14}\,m^3$) [5]. Gas production from NGH in clayey silt sediments was technically successful in the Shenhu area of South China Sea in 2017, and the cumulative gas production in 60 days was more than $3 \times 10^5\,m^3$ [6].

According to the principle of gas production from the NGH, production methods can be divided into three categories [7]. The first is dissociating NGH through breaking down its phase equilibrium by changing the temperature, pressure and salinity conditions using the techniques of thermal stimulation, depressurization and chemical inhibitor injection [5,8]. The second category is based on the replacement of guest molecule, in which one or more types of gases (such as $CO_2$, $CO_2/N_2$, and $CO_2/H_2$) are injected into the NGH reservoirs to replace $CH_4$ [9–11]. In the last category, we take NGH as usual solid mineral resource, and gas production is mainly during the transportation process from reservoirs to the surface. The solid fluidization development principle of NGH stored in shallow layers of deep water provided by Zhou is one kind of the third category, which has been also successfully tested at the station of LW3 in the northern part of South China Sea in 2017, and the total gas production is 81 $m^3$ [12].

The methods discussed above have their advantages and disadvantages. The depressurization production is the best economical and simple method. However, it works slowly, and the NGH reformation

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could occur easily [13,14]. The thermal stimulation production has the advantage of the obvious effect and the high production rate but its thermal energy efficiency is relatively lower [15,16]. The production with inhibitor stimulation is simple, but it is expensive and may damage the environment [17]. In addition, gas production from NGH with the first and the third category may induce submarine geological hazard, because the cementation form of the sediments may be disturbed [18,19]. However, the new mixture hydrate formed during NGH production using gas (such as $CO_2$) replacement will maintain the formation stability. At the same time, it will achieve the $CO_2$ storage, just like $CO_2$-EOR (Enhanced Oil Recovery) [20]. So, gas production from NGH by gas replacement has become a hot topic. The successful application of this method on the Alaska North Slope in 2012 has verified the feasibility of this method in the field [21].

The feasibility of gas production from hydrate by $CH_4$-$CO_2$ replacement was first verified by Ohgaki in laboratory [9]. This reaction can be carried out spontaneously in the feasibility of thermodynamics and kinetic [22,23]. With the addition of $N_2$ into $CO_2$, the $CH_4$ recovery rate from methane hydrate by the replacement rises to 85% from 64% [10]. In order to analyze the mechanism of replacement and to select the parameters of replacement, the hydrate equilibria of $CO_2$/$CH_4$, $CO_2$/$N_2$ and $CH_4$/$CO_2$/$N_2$ mixture gases and cage occupancy behaviors are measured and investigated [24–27]. With the increase of $N_2$, the hydrate phase equilibrium pressure will increase. Without the gas composition for replacement, temperature, pressure and salinity, the size and distribution of sediment particle, permeability, water saturation and gas hydrate saturation also influence the replacement results in porous media [28–35]. In order to further enhance $CH_4$ recovery and $CO_2$ storage, depressurization, thermal stimulation or $CO_2$ Swap are combined in $CH_4$ production from gas hydrate by $CH_4$-$CO_2$ replacement [36–40].

With the advancement of investigations on $CH_4$ production from gas hydrate by $CH_4$-$CO_2$ replacement, studies have extended to enhance the replacement rate and efficiency and to explore replacement mechanism from the replacement feasibility validation and the gas hydrate equilibria measurement [41,42]. However, studies on $CH_4$-$CO_2$ replacement are mainly focused on gas hydrate in water or porous media. There are few investigations on gas production from fracture-filled hydrate by $CH_4$-$CO_2$ replacement. A series of $CH_4$-$CO_2$ replacement experiments were performed with an artificial fracture held open by a spacer, however, the main goal of the fracture was to allow easy transport of gases or liquids [33]. The fracture-filled gas hydrate (layers, nodules, veins and so on) commonly occurs in both marine fine-grained sediments and the fracture of rock in permafrost regions, as shown in Fig. 1 [43–47]. In this paper, we performed a total of six sets of experiments on the fracture-filled gas hydrate by $CH_4$-$CO_2$ replacement to study the influencing factors of replacement rate (such as the morphology of gas hydrate, pressure and gas composition). In our experiments, we took the reservoir condition of permafrost-associated gas hydrate in Muri Basin, Qilian Mountains of Western China as an example to set up the experimental parameters for the first time. The fracture-filled hydrate is the main type of gas hydrate found in the Qilian Mountain permafrost, which fills the fractures of siltstone, mudstone and oil shale as thin layer and agglomerates in a few millimeters [47]. Therefore, we used the mudstone core to create the fracture, and the target thickness of hydrate layer was set at 1.5 mm and 3.0 mm in the experiments. Based on the range of gas hydrate sample (124.1–396 m) and the thickness of permafrost (95 m), we can get the formation pressure is about 2.0–4.7 MPa [7,48]. Therefore, the replacement pressure was set at 3 MPa, and the temperature was 2 °C accordingly. In addition, 5 MPa was for comparation.

## 2. Experimental setup and methods

### 2.1. Materials

$CH_4$ and $N_2$ with purities of 99.99% and $CO_2$ with purity of 99.9% were supplied by Beifang Special Gas Industry Corporation. The ratios of $CO_2$/$N_2$ were 75.3/24.7 and 24.9/75.1, whose phase equilibrium pressure were lower and higher than the phase equilibrium pressure of methane hydrate, respectively. The water was distilled twice. The mudstone core was 48 mm in diameter, whose porosity was less than 1%.

### 2.2. Apparatus

Fig. 2 shows the schematic diagram of the experimental apparatus, which mainly consists of a set of gas supply system, the reactors, a data acquisition system (temperature and pressure), a water bath, a gas chromatograph, and so on.

Two experiments were conducted in two high-pressure reactors constructed with stainless steel with an effective volume of 240 mL and a maximum working pressure of 15 MPa. The quick opening structure is used for the reactor to observe the occurrence of hydrate in the core fracture. The water bath is filled with 30% ethylene glycol aqueous solution to maintain a constant temperature within the range of −17 to 100 °C, whose temperature fluctuation is 0.01 °C. The gas pressure in the reactors will be controlled by the piston cylinders and a hand pump. The gas chromatograph (Agilent 7890B) was calibrated with standard gas before measuring gas consumption. The uncertainties of temperature and pressure measurements in the system are 0.1 K and 0.02 MPa, respectively.

### 2.3. Procedures

The experimental process mainly has two parts: formation of fracture-filled methane hydrate, and gas replacement for $CH_4$ recovery and $CO_2$ storage.

#### 2.3.1. Formation of fracture-filled methane hydrate

In order to simulate the fracture-filled hydrate as found in the Qilian Mountain permafrost, we used the sediment core to simulate the fracture. The core was cut into 10 mm thickness slices with the diamond wire cutting machine, and the slices were cleaned with distilled water and dried in the drying cabinet. The space of two adjacent slices fixed with tape was 5 mm, which was used for simulating the rock fracture. Then the distilled water was injected into the space to form a certain thickness of water layer, and there should no water leak along the wall of the slice, as shown in Fig. 3. Thereafter, the sample was put into the reactor carefully, and the reactor, gas pipelines and sensors were assembled gently. After being vacuumed for approximately 20 min, the reactor was pressurized with $CH_4$ to the desired pressure (about 8 MPa). Until the pressure in the reactor was stable at the room temperature, the reactor was put in the water bath, which had been set up to a temperature of 2 °C. After several hours, the fracture-filled methane hydrate would form. If the pressure of the reactor was stable more than 12 h, as shown in Fig. 4, the process of hydrate formation was considered to be completed. Except run 2-2, all the others experiments were conducted based on this procedure. In run 2-2, the water layers were frozen into ice before vacuuming, then the temperature was set up to −1 °C and the cooled methane through the coil pipe which was placed in the water bath was injected into the reactor to 6.69 MPa. The temperature of water bath was increased slowly (as shown in Fig. 5) to form methane hydrate. The experimental conditions and results of methane hydrate formation are listed in Table 1.

#### 2.3.2. Gas replacement for $CH_4$ recovery and $CO_2$ storage

After the formation of methane hydrate, the temperature of water