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FORMATION AND DISSOCIATION OF METHANE HYDRATE IN MARINE SEDIMENTS CONSIDERING CONFINING PRESSURE

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ABSTRACT

Methane hydrate (MH) is considered as one of the most promising energy source. It is necessary to understand the characteristics of methane hydrate formation and dissociation in marine sediments. In this study, the marine sediments from the South China Sea were employed to remold sediment core samples containing methane hydrates. Then, the MH-bearing sediment was dissociated by depressurization. The experimental results indicated that with the continuous supply of gas source, it is easier to nucleate and grow for methane hydrate in marine sediments under confining pressure. However, hydrate formation may lead to grain-coating or contact-cementing pore, thereby not contributing to the gas flow. Thus, as the continuous gas injection causes the hydrate saturation to increase, the time required for inlet pressure raised to equal outlet pressure becomes longer and longer. In the later stage of depressurization, under the influence of confining pressure and fluid flow driving, water production and gas production in marine sediments are extremely difficult.

Keywords: methane hydrate, formation, dissociation, marine sediment, confining pressure

NOMENCLATURE

Abbreviations	
MH	Methane hydrate
Symbols	
m_s	The quality of the dried marine soil
m_w	The quality of ultrapure water
P_0	Confining pressure
P_1	Inlet pressure
P_2	Outlet pressure
t	Time
ω	Water content

1. INTRODUCTION

MH is widely distributed in permafrost regions and shallow sediments on marine continental margins [1]. Especially in marine sediments, there is abundant energy reserve of MH. However, marine sediments as the hydrate carrier are rarely studied in laboratories [2, 3].

Related scholars have carry on some numerical simulations and experimental researches on the formation and dissociation of MH in porous media, and they have made considerable progress [4]. However, few experiments and numerical simulations on formation and dissociation of MH in marine sediments, especially without considering the effects of confining pressure. The favorable geologic conditions for gas hydrate formation are usually low temperatures (<300 K) and high pressures (>0.6 MPa) [5]. This determines the deposition of natural gas hydrates below 600 m of sea level or 200-1100 m of permafrost [6]. Therefore, for the field exploitation and commercial application of the gas recovery from hydrate reservoirs in the marine sediments, it is necessary to consider the influence of confining pressure. In this case, studying the formation and dissociation characteristics of MH in marine sediments are more meaningful for hydrate-related researches and hydrate flied exploitation.

In this study, the marine sediments from the South China Sea were employed to remold methane hydrate-bearing sediments. In order to give an improved basis for predicting actual behavior of hydrates in an oceanic environment, formation and dissociation characteristics of MH in marine sediments considering confining pressure were analyzed.

2. EXPERIMENTAL SECTION

2.1 Experimental apparatus

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An experimental setup was built for the formation and dissociation of MH in marine sediments, as shown in Fig. 1. The experimental system consists of four sub-systems, namely, the pressure-control system, the low-temperature cooling system, the core holder and the data collection system.

The cylindrical core holder submerged in the sink, 215 mm in length with 50 mm internal diameter. An end plug attached to the top of the core holder is movable to suit the volume of samples. The surrounding of the core is covered by a rubber sleeve to apply the lateral confining pressure. The temperature of core holder was indirect controlled by a water bath. The pressure-control system contained a high-pressure ISCO pump (260D, Teledyne ISCO Inc., Lincoln, NE, America) that injected methane, a control valve (Fisher–Baumann) coupled with a self-tuned PID controller (OMEGA CN2120 Ramp/Soak Controller), and confining-pressure pump that injected water. The A/D module (Advantech Co., Ltd. Milpitas, CA, USA) that recorded the signals of pressure and temperature in real time during the experiments. The uncertainty of T-type thermocouple and pressure gauges was ± 0.1 K and ± 0.01 MPa, respectively. The gas flux was monitored by a gas flux meter supplied by Bronkhorst High-Tech B.V.

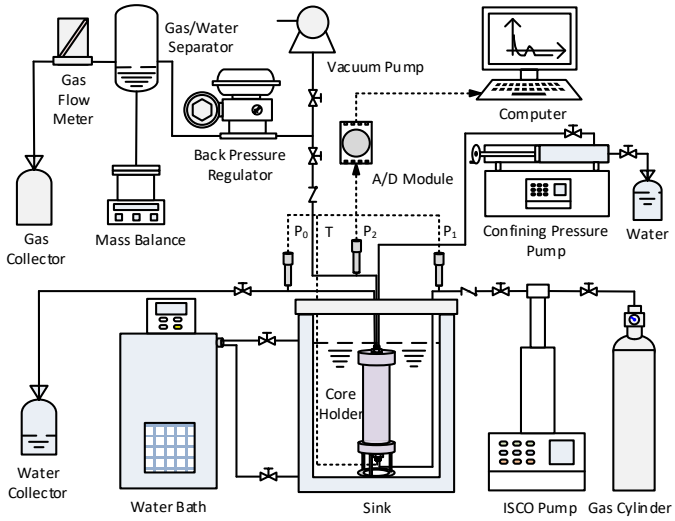

Fig. 1 Schematic diagram of the experimental system

2.2 Materials

The purity of methane gas was 99.99 % (molar fraction), which was provided by Dalian Special Gases Co., Ltd., China. The deionized water was prepared by our laboratory.

In experiments, the core samples with or without hydrate were prepared using marine sediments. The marine sediments was supplied by China National Offshore Oil Corporation, sampled at the 122 m depth layer in South China Sea. Before experiments, the particle size of the remolded sediments was measured and analyzed by Bettersize laser particle size analyzer (9300T). The main ions of the marine sediment was detected by an ion chromatograph (ICS-5000, Thermo Fisher Scientific). Table 1 shows the main properties of remolded sediments used in this study.

Table 1 The main properties of remolded sediments

Parameters	Properties
Porosity	38 %
Dry density	2.75 g·mL^{-1}
Specific surface area	794.10 m^2·kg^{-1}
Particle size distribution	0.20-108.20 μm
Median grain size(D50)	5.82 μm
Composition	Clay, silt, fine sand
Main ions	Na^+, K^+, Ca^{2+},Cl^-, SO_4^{2-}

2.3 Experimental procedure

In order to remove the residual moisture, the marine sediments were kept in drying box at 368 K for 24 h. The crushed sediments were mixed with quantitative ultrapure water using a stirrer. The water content of remold sediments was calculated by the Equation (1):

$$\omega = \frac{m_w}{m_s} \times 100\% \quad (1)$$

where ω is the water content (%), m_w is the quality of ultrapure water (g), m_s is the quality of the dried marine soil (g). In this study, the water content of remold sediments is about 30.57 %.

Then, the sediment samples were compacted by a sampler with 50 mm internal diameter. When the sediment sample was compacted into cylindrical with 57 mm in length and 50 mm internal diameter, it was loaded in core holder. Afterwards, the sample temperature was maintained at 276 K by a water bath. Injecting water through a confining pressure pump to increase the confining pressure of the core sample. In order to form MH, methane gas was injected into the core holder and the pore pressure was about 8 MPa. According to the gas consumption of hydrate formation, it is need to inject methane gas multiple times to 8 MPA. After a week period of hydrate formation, sufficient hydrate existed in the sediments. Finally, the MH-bearing sediment sample was dissociated by depressurization using a back pressure regulator. During the entire experiment of MH formation and dissociation, the confining pressure is always higher than the pore pressure.

3. RESULTS AND DISCUSSION

3.1 Formation characteristics of MH in marine sediments considering confining pressure

Fig. 2 shows the formation process of MH in marine sediments under the effect of confining pressure.

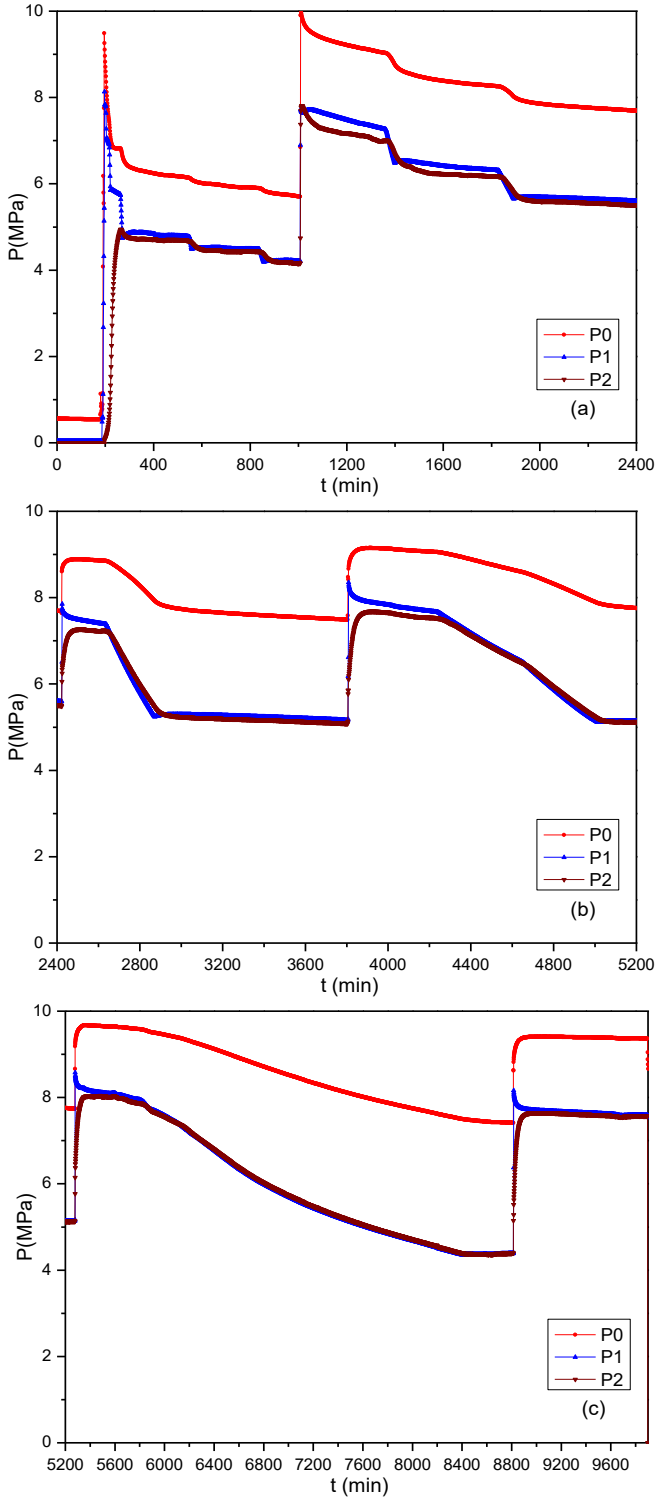

Fig. 2 The gas injection and MH formation process at 276 K: (a) 1st and 2ed of gas injection; (b) 3rd and 4th of gas injection; (c) 5th and 6th of gas injection.

The formation characteristics of methane hydrate-bearing marine sediment after each gas injection are shown in Table 2.

Table 2 The formation characteristics of methane hydrate-bearing sediment.

Gas injection	t_1 (min)	ΔP_1 (MPa)	t_2 (min)	P_3 (MPa)
1st	77	0.04 0.09	9 20	4.16
2ed	0.83	0.59 0.52	40 65	5.51
3rd	63	2.13	235	5.09
4th	80	2.45	770	5.13
5th	82	3.59	2744	4.39
6th	105	0	0	7.57

Note: t_1 represents the time required for the outlet pressure to increase to equal the inlet pressure; ΔP_1 is the pressure drop caused by hydrate formation; t_2 represents the duration of the pressure drop; and P_3 is the lowest pore pressure after stabilization.

As shown in Fig. 2 and Table 2, after the second gas injection, the outlet pressure quickly rises to the same as the inlet pressure. It seems possible that this result is due to the pore and throat of marine sediment to be opened by the first gas injection. After that, as the continuous gas injection causes the saturation of the hydrate in the sample to increase, the time required for the inlet pressure to rise to equal the outlet pressure becomes longer and longer. There are significant pressure drop, that is, obvious phenomena of hydrate formation, in addition to the last time gas injection. Same as reported in the literature [4, 7, 8], a decrease in the permeability for an increase in the hydrate saturation. Hydrate formation results in grain-coating or contact-cementing pore, thereby not contributing to the gas flow.

The experimental results show that as the number of gas injections increases, the pressure drop caused by hydrate formation larger. Correspondingly, the rate of the pressure drop becomes slower, and the pressure drop lasts for a longer period of time. In other word, with the continuous supply of gas source, it is easier to nucleate and grow for methane hydrate in marine sediments under confining pressure. The minimum pressure for methane hydrate formation is approximately 4.2 MPa. A possible explanation for this might be that the marine sediments contain various ions (see Table 1) that may inhibit hydrate nucleation

After continuous formation of methane hydrate up to 45.7 h, the gas was injected to 8 MPa again. The pressure drops only about 0.1 MPa within 15 hours, so the end of hydrate formation can be considered.

3.2 Dissociation characteristics of MH in marine sediments considering confining pressure

After a week period of hydrate formation, the MH-bearing sediment was dissociated by depressurization using a back pressure regulator. In the first stage of depressurization, the back pressure valve is set to 3.0 MPa; in the second stage of depressurization, the back pressure valve is set to 0.0 MPa. Fig. 3 shows the dissociation characteristics of MH-bearing marine sediments by depressurization.

In the initial stage of depressurization, the core outlet pressure drops directly to atmospheric pressure, and gas output is about 0.02 L. Free gas, the dissociated water and gas will flow driven by the pressure difference effect. Since the outlet pressure is lower than the set value of the back pressure, the inlet pressure slowly drops and the outlet pressure rises. Back pressure valve drops from 3 MPa to 0 MPa when inlet pressure and outlet pressure are near. In the second stage of depressurization, the total water production is 19.52 g. In the later stage of depressurization, water production and gas production are extremely difficult. There are several possible explanations for this result. Owing to the decrease of pore pressure, the fluid flow driving is insufficient [9]. As the increase of pressure difference between confining pressure and pore pressure, the appearance volume and pore volume of the core could be reduced and deformed, and some particles may even be cemented, which not conducive to permeability of the reservoir.

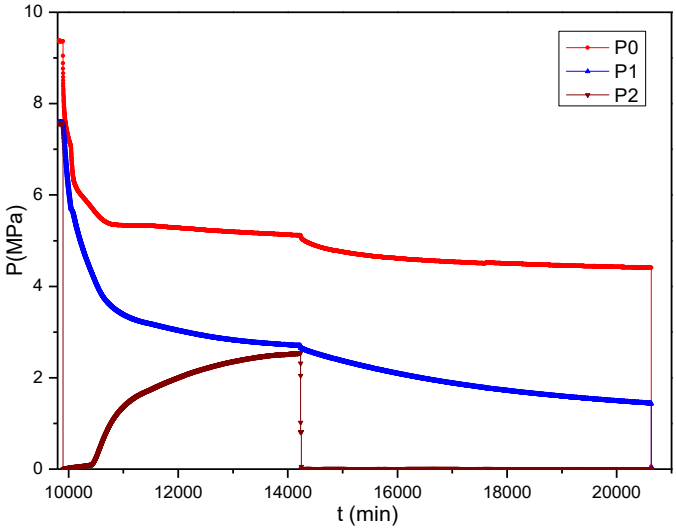

Fig. 3 The dissociation process of MH-bearing sediments by depressurization

4. CONCLUSIONS

In this study, formation and dissociation characteristics of MH in marine sediments considering confining pressure were analyzed. In the stage of hydrate formation, the presence of confining pressure can contribute to hydrates formation, and further improve hydrate saturation. Under the influence of confining pressure and fluid flow driving, water production and gas production by depressurization in MH-bearing marine sediments are extremely difficult.

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