

# Formation Kinetics Characteristics of CH<sub>4</sub> Hydrate in “Haima” Cold Seep Environment With Varied Dissolved Methane Concentration

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## ABSTRACT

Seabed methane seeping is widespread around the world, affecting the ocean and the global carbon cycle. Natural gas hydrate (NGH) is an important physical way to have leaked CH<sub>4</sub> sequestration. Hydrate formation kinetics is one of the key factors affecting methane capture efficiency. Varied dissolved CH<sub>4</sub> concentrations due to different methane flux differences may affect the kinetic characteristics of hydrate formation, which is necessary to be unveiled. In this work, the effect of initial dissolved CH<sub>4</sub> concentration on hydrate formation in static system was investigated by constructing different CH<sub>4</sub> leakage flux conditions in simulated “Haima” cold spring environment. The experimental results showed that the increase of initial dissolved CH<sub>4</sub> concentration accelerated hydrate formation, while the obvious promoting effect may depend on the higher dissolved CH<sub>4</sub> concentration. Morphology experiments showed that under the condition of relatively high concentration of dissolved CH<sub>4</sub>, a large number of flocculent hydrates formed in the liquid phase, and induced the growth of CH<sub>4</sub> hydrate toward the liquid phase. Combined with CH<sub>4</sub> gas consumption analysis, it is believed that this phenomenon was related to the formation of porous CH<sub>4</sub> hydrate. The results obtained in this study have important reference significance for understanding the mechanism of hydrate formation and evolution in the CH<sub>4</sub> seeping environment.

**Keywords:** CH<sub>4</sub> hydrate formation, dissolved methane concentration, morphology, “Haima” cold seep

## 1. INTRODUCTION

In the trend of increasing global carbon emissions, more and more attention has been paid to controlling carbon emissions. CH<sub>4</sub>, as the second largest greenhouse gas affecting global warming, limiting its emissions has far-reaching significance for global climate change [1].

Natural gas hydrate (NGH) is an ice-like compound, mainly composed of methane molecules and water

molecules, which is an important part of the global carbon cycle [2]. The total resource of NGH is estimated to be twice as much as the total amount of all proven fossil fuels around the world, with NGH endowed in the ocean accounting for more than 95% of global NGH and playing a much important role in methane sinks [3].

Methane seeps from the seafloor all the time, and this geological phenomenon of methane-rich fluids leaking from the surface of marine sediments is also called “cold seep” [4, 5]. “Cold seep” are existed all over the world and contain not only free methane gas, but dissolved methane. Most of these methane-bearing fluids rising from submarine sediments form NGH in the sediments to be sequestered, while some leak into the water column [6]. The rate and efficiency of hydrate formation is one of the important factors in determining the rate of methane sequestration.

Temperature, pressure, subcooling and salinity et al. can affect the kinetics of NGH formation in the marine environment, which are also the focus of previous studies and have been reported more frequently [7-9]. In addition, different methane seepage fluxes can significantly affect the formation characteristics of NGH. Furthermore, changing the gas-liquid contact area affects hydrate formation directly, and the dissolved amount of methane in different intensity seepage zones under the same temperature and pressure conditions is also different, which can affect hydrate nucleation and growth. Li et al. [10] found experimentally that in a high-subcooling, free-gas-containing environment of CH<sub>4</sub> hydrate formation, hydrates may nucleate first in the aqueous phase rather than at the gas-liquid interface with high CH<sub>4</sub> concentration. The experimental results of Li et al [11] suggest that the formation characteristics of hydrate triggered by CH<sub>4</sub> dissolved gas in the mobile aqueous phase are clearly influenced by the spatial distribution and flow path of dissolved gas. However, the current study is not clear about how CH<sub>4</sub> dissolved gas content affects and couples with free gas to influence the characteristics of CH<sub>4</sub> hydrate formation kinetics.

In this paper, at the in situ environment of the "Haima" cold seep, a typical active cold seep with the water depth of 1200-1400 m in the Western area of the northern slope of the South China Sea is aimed [12]. The effect of dissolved methane concentration on hydrate formation kinetics in a static environment with the same 1350 m ocean depth and temperature, but with different methane leakage fluxes, is investigated using high-pressure visual reactor simulations. The formation rates of CH<sub>4</sub> hydrate at different dissolved gas amount were calculated by temperature and pressure variations, and the corresponding morphological change characteristics were recorded.

## 2. MATERIAL AND METHODS

### 2.1 Materials

The methane gas (purity: 99.9%) used in the experiments was purchased from Guangdong DATE Yuejia Gas Co., Ltd. and deionized water with conductivity less than 10<sup>-4</sup> S·m<sup>-1</sup> was used.

### 2.2 Experimental apparatus and procedures

The schematic diagram of experimental apparatus is shown in Figure 1. Briefly, the main part of the device is a reactor, with a quartz window at the front and back respectively. The effective volume is 121.0 mL and the maximum load pressure is 15 MPa, and the hydrate formation can be observed through the front and rear windows. An *in-situ* Raman spectrometer was used to measure initial CH<sub>4</sub> concentration in the water phase. The Raman spectra was collected by a LabRAM Odyssey Raman system. 600 grooves/mm grating and 532 nm wavelength laser were employed.

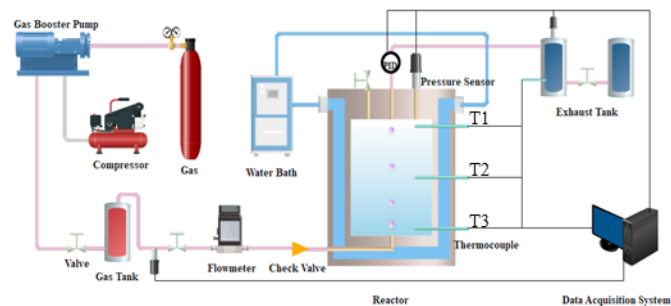


Figure 1 Schematic diagram of experimental apparatus.

The reactor was firstly cleaned before the experiment, and then 80 g of deionized water was added into the reactor, after which the system temperature was cooled to 277.15 K and kept constant. After the temperature was stable, CH<sub>4</sub> gas was injected from the

bottom to enter the system in the form of CH<sub>4</sub> bubble leakage. The injection rate of CH<sub>4</sub> gas was controlled by a high-pressure flow meter, and after the system pressure reached 13.5 MPa, the outlet valve of the reactor was opened and the system pressure was kept constant by the PID (Proportion Integration Differentiation) at the outlet. In this experiment, different CH<sub>4</sub> leakage rates were controlled to simulate different intensity methane leakage zones in the "Haima" cold spring area, and the injection time was 120 min for each experiment. Then the inlet and outlet valves were closed to let CH<sub>4</sub> hydrate nucleate and grow rapidly through the top gas-liquid interface perturbation. The purpose of the above controlled methane leakage is to form liquid phase systems with different dissolved methane contents in order to examine the effect of dissolved methane concentration on the kinetics of CH<sub>4</sub> hydrate formation in a static environment. In addition, one set blank experiment without methane leakage process was conducted. In this set of experiment, hydrate formation was made rapidly by top rapid gas injection and perturbing the gas-liquid interface. The total time from gas injection to hydrate formation was about 2 min. This set of experiments was used to simulate an environment with very low initial dissolved methane content. The concentration of dissolved methane in the liquid phase is quantified by Raman spectroscopy at the end of the methane dissolution process and before hydrate formation. After hydrate formation, the process of hydrate formation in the system is recorded by temperature and pressure and morphological changes.

## 3. RESULTS AND DISCUSSION

In this study, three sets of experiments were conducted to form three systems with different initial dissolved methane contents by controlling the methane bubble leakage flux and time. The dissolved methane content from high to low corresponds to simulate strong methane leakage, medium leakage and low leakage zones, respectively. In this study, the effect of initial dissolved methane concentration on the kinetics of CH<sub>4</sub> hydrate formation in the static system was investigated, and the specific experimental conditions and results are shown in Table 1. Figure 2 shows the initial dissolved CH<sub>4</sub> content in water before hydrate formation in the three groups of systems. The values are the average values of dissolved methane in the upper, middle and lower parts of the aqueous phase. It should be noted that for Run2 and Run3 in the process of methane leakage, the dissolved methane concentration gradually decreases

from top to bottom, but the difference is not obvious. For the Run1 injected with gas at the top, it only contains a very small amount of dissolved methane in the liquid

phase at the top. Therefore, it can be considered that there is almost no dissolved methane in the water phase before hydrate formation.

Table 1 Experimental Conditions and Results in this study

Run	methane flux (mol/min)	injection time (min)	Initial dissolved methane content (mol/L)	Methane consumption (mmol CH <sub>4</sub> /mol water)
1	0	0	0.0001	0
2	0.002	120	0.0624	0.0948
3	0.029	120	0.2103	2.2800

\*System temperature, 277.2 K; initial pressure, 13.5 MP

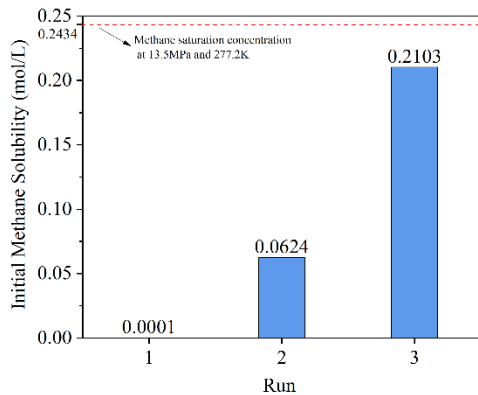


Figure 2 Initial dissolved methane concentration in water phase

### 3.1 Analysis of temperature and pressure variation and gas consumption in hydrate formation process

Figure 3 shows the change of the system pressure and temperature over time during hydrate formation for different initial methane solubility conditions. For the three groups of experiments, the pressure in the system gradually decreased during hydrate formation due to the consumption of methane gas. In the initial formation stage of hydrate, the pressure drop rate is relatively fast, and with the reaction proceeding the pressure drop rate gradually slows down, indicating that the growth rate of the hydrate slows down. This is due to the fact that the hydrate film formation of a gas-liquid interface increases the resistance of CH<sub>4</sub> molecules or water molecules to

another phase through mass transfer, and as the hydrate film thickens, the mass transfer resistance gradually increases. Comparing the pressure drop trend at the beginning of hydrate growth, it can be found that for the high initial dissolved CH<sub>4</sub> concentration in Run3, the rapid pressure drop phase lasted the longest, lasting about 100 min. In addition, after the nucleation of CH<sub>4</sub> hydrate, the temperature T2 located at the gas-liquid interface showed a significant increase for about 15 minutes, with a maximum temperature rise of about 0.5 K. Because of exothermic of hydrate formation, so the hydrate is rapidly formed at the gas-liquid interface during this period. Since there are mainly differences in the content of the initial CH<sub>4</sub> dissolved gas in the three sets of experiments, it can be inferred that the occurrence of this phenomenon is also related to the high concentration of initial CH<sub>4</sub> dissolved gas. In the initial dissolved CH<sub>4</sub> concentration experiment of Run2, two small increases in temperature also occurred at 200-300 min. Due to T1 is located in the gas phase, its temperature rise may be mainly caused by water climbing the wall of reactor to the temperature measurement point and generating hydrate exothermic heat. However, during the temperature rise, the pressure does not drop significantly, but increases with the temperature. Thus, the hydrate is formed in only a small amount. However, due to the low sensible heat and low thermal conductivity of the gas phase, the temperature T1 has increased.

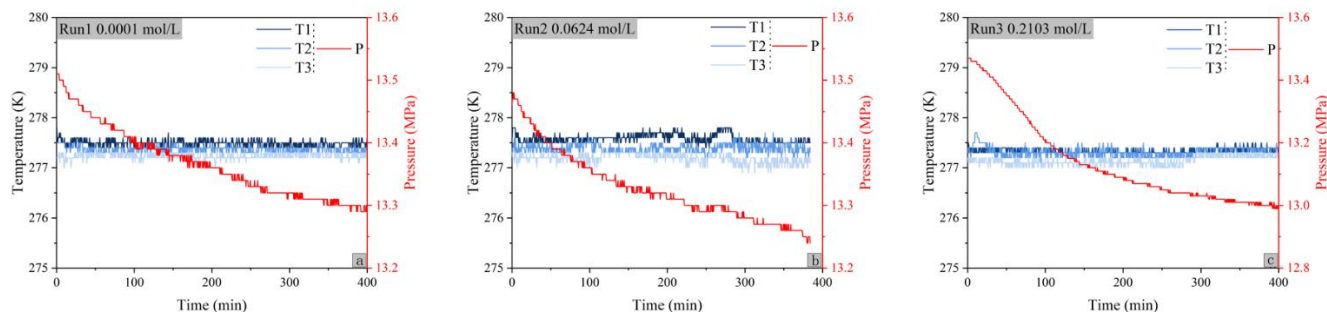


Figure 3 Variations of system pressure and temperature during hydrate formation

In different initial methane dissolved gas systems, the comparison of pressure changes during hydrate formation is shown in Figure 4a. It can be found that for Run3 with the high initial dissolved methane concentration, the pressure drop is most obvious, and in the whole experimental period, the instantaneous hydrate conversion rate is maintained. For Run2, although there is also a low content of dissolved  $\text{CH}_4$ , the pressure drop trend is consistent with Run1, which is almost no dissolved gas. Figure 4b shows the change of gas consumption due to hydrate formation with each group of systems. It can be seen that the relatively high dissolved  $\text{CH}_4$  content of 0.2103 mol/L can significantly promote hydrate formation, while the  $\text{CH}_4$  consumption curve in the 0.0624 mol/L system coincides with the  $\text{CH}_4$  consumption curve in the almost dissolved methane

system. It shows that the relatively high content of dissolved methane in the aqueous phase is more conducive to the continuous formation of hydrates, and it is possible that the initial dissolved methane concentration reaches a certain value to have a more obvious promotion phenomenon. People might think that the reason why hydrates are produced faster in high-concentration dissolved  $\text{CH}_4$  systems is because more dissolved gas is used for hydrate conversion. However, it should be noted that the curve in Figure 4b. is a growth rate curve obtained by only the gas-phase methane being consumed, the presence of a large amount of dissolved methane in water can indeed promote the conversion of gas-phase methane to hydrate. So why?

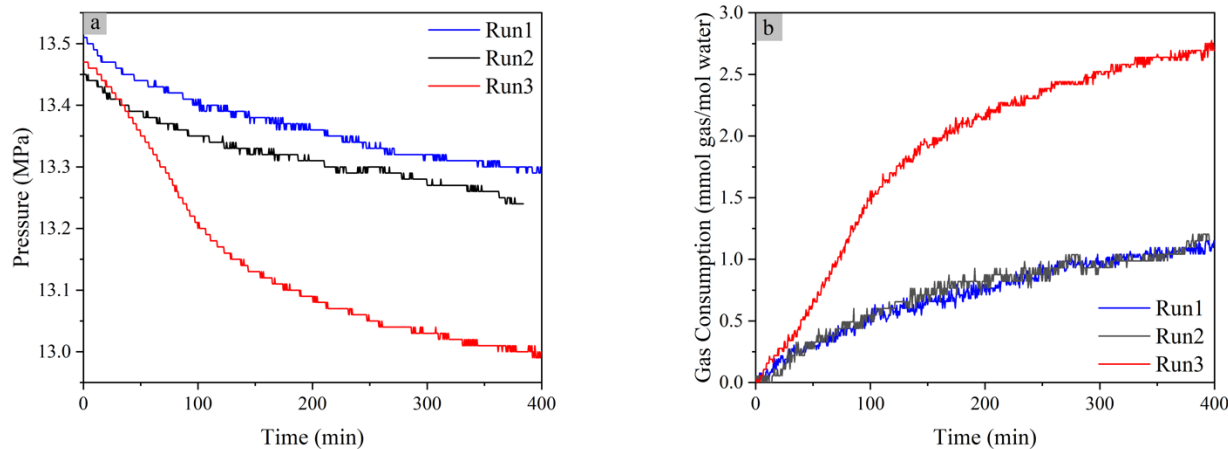


Figure 4 Variations of pressure and Methane dissolution consumption rate during hydrate formation

### 3.2 Morphology Characteristics during $\text{CH}_4$ hydrate formation processes

In order to further explain the reasons for the occurrence of the above phenomena, the morphological change process of the three groups of experimental

hydrates was analyzed, as shown in Figure 5. For Run1 and Run2,  $\text{CH}_4$  hydrate first appeared wall-climbing phenomenon obviously after nucleation at the gas-liquid interface, and the gas phase side of the window was completely covered by hydrate about 60 min. For the gas

phase consumption in Figure 4b, the migration of the liquid phase to the gas phase and the conversion of the hydrate possibly make a greater contribution to the final gas absorption. After 183 min, the overall morphology of the hydrates of Run1 and Run2 almost no longer changed. In contrast, the hydrate's morphology of Run3 showed obvious differences with Run1 and Run2. At 10 min of hydrate formation, a pronounced flocculent hydrate appears in the liquid phase, which is mainly formed by dissolved methane. Hydrate formation induced by the transfer of mass from the gas phase to the liquid phase seems to play a more crucial role in the consumption of the gas phase than the growth of hydrate caused by the wall-climbing of the liquid phase. At 10 min, snow-white hydrate have appeared in the liquid phase, and 60 min is a significant increase in this type of hydrate. It can be found that the flocculent hydrate in the liquid phase is still obviously visible at this time. By 122 min, the snow-white hydrate was almost in the aqueous phase, and flocculent floating hydrate were almost invisible. Subsequently, until the end of the reaction, there was no significant change in the morphology of the hydrate. This is also basically consistent with the timing of the inflection point of gas phase consumption in Figure 4b. Only by analyzing the morphology of hydrate growth, the amount of hydrate generated in Run3 may be even dozens of times more than that of the other two groups, but it can be found from gas phase analysis that it is only less than 3 times. Based on this, it is speculated that this snow-white hydrate is consistent with the hydrate formed by SDS, which is a very porous hydrate, and there are a large number of pores in the hydrate, and it is the presence of these pores that ensures a consistently fast hydrate formation rate. The presence of these pores is closely related to the formation of flocculent hydrates.

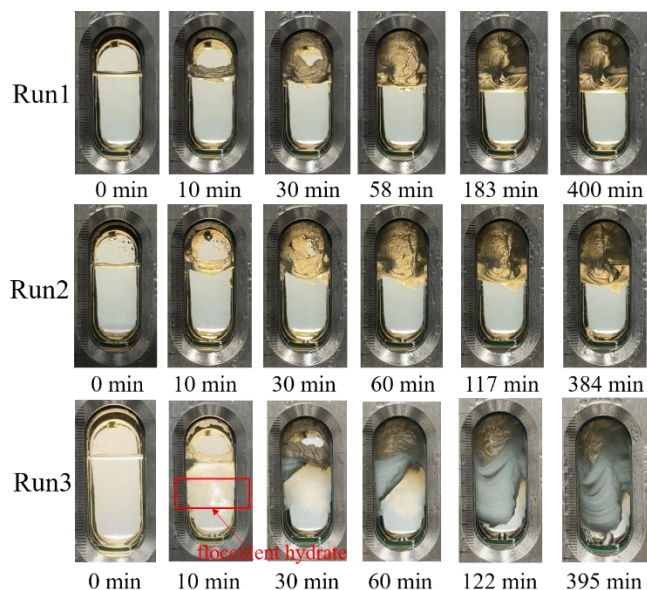


Figure 5 Morphology Characteristics during CH<sub>4</sub> hydrate formation process

#### 4. CONCLUSIONS

In this work, the effect of initial dissolved CH<sub>4</sub> concentration on hydrate formation in static system was investigated by simulating different leaked CH<sub>4</sub> flux in "Haima" cold seep environment. The experimental results showed that the increased initial dissolved CH<sub>4</sub> concentration accelerated the formation of hydrate and resulted into the increase of local temperature due to the heat release from of hydrate formation. However, the promoting effect of hydrate formation was not obvious for the dissolved amount of dissolved CH<sub>4</sub> concentration. The critical value may be related to the equilibrium concentration of dissolved methane in the three phase of gas-liquid-hydrate. Morphology experiments showed that a large number of flocculent hydrates formed in the liquid phase under the condition with relatively high dissolved CH<sub>4</sub> concentration. The further growth of CH<sub>4</sub> hydrate toward the liquid phase may be induced by these flocculent hydrates. However, despite the visible formation of a large number of snow-white hydrates, these hydrates may be porous though the combination of the low CH<sub>4</sub> gas consumption analysis. The results obtained in this study have important reference significance for understanding the mechanism of hydrate formation and evolution in the submarine CH<sub>4</sub> leakage environment.

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