

# The kinetics of methane hydrate formation study in different sediments based on the "Haima" cold seep environment #

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## ABSTRACT

The characteristics of hydrate transformation of deep-sea seepage methane in sediments affect the fate of methane and have a great impact on the global climate. However, there are many kinds of deep-sea sediments with complex compositions, as one of the main seafloor sediments, the mechanism of chlorite's influence on hydrate formation is not clear. This study aims to investigate the effects of chlorite and quartz sand on the kinetics of methane hydrate formation. The experimental results show that when the sediment particle size is the same, the change of initial water saturation has a certain effect on the formation rate of hydrate and the final water conversion rate, however, when the initial water saturation of sediments is the same, the change of particle size has little effect on the final water conversion. Although the sediments with a high specific surface area can provide more nucleation sites for hydrate to promote the formation of hydrate, they can also absorb more water, leading to a decrease in water activity and slowing down the formation of hydrate. In addition, the results of this study provide a further understanding of the conversion characteristics of methane hydrate in sediments.

**Keywords:** natural gas hydrate exploitation, kinetics, methane leakage, free gas, porous sediments

## 1. INTRODUCTION

In today's world, the problem of global warming is becoming more and more serious. Methane is a key factor leading to global warming because its greenhouse effect is several orders of magnitude higher than carbon dioxide [1]. Seafloor methane seeps are widespread worldwide and affect the ocean and atmospheric carbon

budget [2]. As seeped methane migrates from the seafloor to the atmosphere, it is blocked by a series of complex reactions, such as dissolution in seawater, microbial oxidation, and formation of hydrates in seafloor sediments [2, 3]. In these processes, the rate of methane hydrate formation in sediments is faster, so the characteristics of methane hydrate conversion in seafloor sediments have an important impact on the final destination of methane. There are many kinds of sediments in the South China Sea, such as quartz sand, calcite, pyrite, feldspar, and so on [4]. Gas hydrates mainly exist in sand and clay sediments, but the formation and distribution of gas hydrates in sand and clay sediments have different characteristics. The properties and compositions of sediments are key factors affecting the kinetics of hydrate formation. For example, compared with sand, clay sediments have the characteristics of smaller particle size [5], larger specific surface area, lower permeability, and stronger water absorption. Therefore, understanding the effect of the properties of sediments on the kinetics of hydrate formation is crucial for understanding the characteristics of hydrate transformation in sediments. Although many studies have focused on the conversion characteristics of methane in quartz sand, montmorillonite, kaolin, and other sediments [6-8], there are few studies on the mechanism of chlorite's influence on hydrate formation. Chlorite is one of the important components of seafloor sediments. Therefore, based on the two main mineral components in the sediments of the Haima cold seep area, this study investigated the effects of the particle size and initial water saturation of chlorite and quartz sand on the kinetics of hydrate formation. The research results will help to further understand the transformation characteristics of methane hydrate in

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different sediments, and provide a more in-depth scientific basis for dealing with global warming.

## 2. EXPERIMENTAL SECTION

### 2.1 Materials

The methane gas (purity: 99.9%) used in the experiments was purchased from Guangdong DATE Yuejia Gas Co., Ltd., and chlorite and quartz sand were purchased from Guzhang Shan Lin Shi Yu Mineral Co., Ltd. The particle size distribution of the sediment is shown in Figure 1, and the physical properties are shown in Table 1

Table. 1 Physical properties of sediment

Medium	Particle size(um)	BET(m <sup>2</sup> /g)
Chlorite	15-25,75-90	29.5
Quartz sand	15-25,75-90	0.92

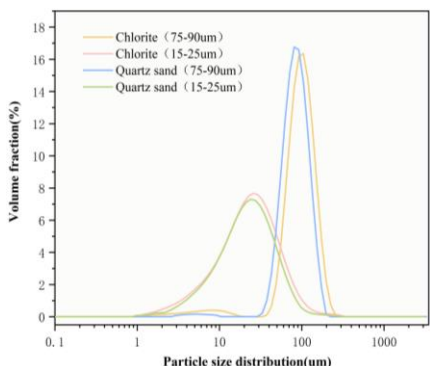


Fig. 1 Particle size distribution of quartz sand and chlorite

### 2.2 Experimental apparatus

As shown in Figure 2, the main component of the device is a visual reactor made of transparent sapphire, which enables the camera to capture the entire process of hydrate formation inside the reactor at a fixed time interval. The reactor has an effective volume of 26 ml and can withstand a pressure of 11 MPa. The reactor is equipped with a thermocouple sensor (accuracy 0.1 K), two pressure sensors (accuracy 0.001 MPa), and a data acquisition system for monitoring real-time temperature (T) and pressure (P) data within the reactor. The entire reactor assembly is placed in a transparent water bath, the temperature is controlled by an external circulating cooler, and the data acquisition system collects experimental data at fixed intervals of 10 seconds.

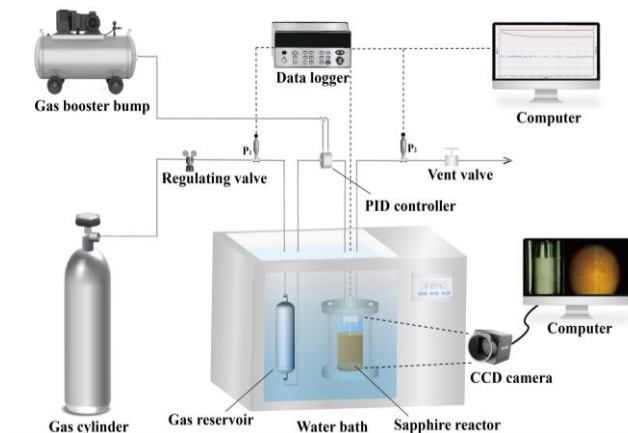


Fig. 2 Experimental device diagram

### 2.3 Experimental procedures

The experimental procedures are as follows:

(a) Rinse the reactor three times with deionized water and dry completely.

(b) After the sediment and water are evenly mixed in a certain proportion, they are loaded into the reactor, and the sediment is compacted in the reactor with a piston.

(c) The reactor was sealed and put into a water bath at 4 °C. Methane was injected into the reactor to 0.5 MPa and emptied, and the process was repeated three times.

(d) After the temperature and pressure in the reactor are stable, open the buffer tank and quickly inject CH<sub>4</sub> to 9.6 MPa into the reactor, and then stop the gas injection.

## 3. RESULTS AND DISCUSSION

The summary of experimental conditions and results is shown in Table 2. Table. 2 Summary of experimental conditions and results.

Run	Medium	Particle diameter range (μm)	Initial water content (vol%)	Water conversion to hydrate (%)
1	quartz sand	15-25	30	76.5
2	quartz sand	15-25	60	70.1
3	quartz sand	75-90	30	75.3
4	quartz sand	75-90	60	72.4
5	chlorite	15-25	30	78.2
6	chlorite	15-25	60	70.2
7	chlorite	75-90	30	77.9
8	chlorite	75-90	60	68.2

### 3.1 The influence of sediment-water saturation on the kinetics of hydrate formation

Figures 3a and 3b show the change of water conversion rate in sediments with the same particle size when the initial water saturation of sediments is 30 vol% and 60 vol%. It can be seen that both the hydrate formation rate and the final water conversion rate decrease with the increase in water saturation, whether it is 15-25  $\mu\text{m}$  or 75-90  $\mu\text{m}$ . The water conversion of chlorite with an initial water saturation of 30 vol% was always slightly higher than that of quartz sand, while the water conversion of chlorite with an initial water saturation of 60 vol% began to be lower than that of quartz sand after 50 min, which can be explained by the gas-liquid contact area theory. As can be seen from Table 1, the specific surface area of chlorite is larger than that of quartz sand, so chlorite can provide more nucleation sites for hydrate formation so that the initial growth rate of hydrate is greater than that of quartz sand. When the water saturation is 60 vol%, in the initial stage of hydrate growth, although chlorite with a high specific surface area provides more nucleation sites for the growth of hydrate, the high water saturation results in the accumulation of sediment pore water, which reduces the methane concentration in the pore. Therefore, in the later stage of hydrate growth, methane dissolved in water is needed to sustain the growth of hydrate, which greatly slows down the growth rate of hydrate, this is also consistent with Xie's study [7]. It is worth noting that although the specific surface area of chlorite is much larger than that of quartz sand when the sediment particle size is 15-25  $\mu\text{m}$ , the hydrate formation rate and the final water conversion rate are almost the same regardless of the initial water saturation of 30 vol% or 60 vol%. When the sediment particle size is 75-90  $\mu\text{m}$  and the water saturation is 60 vol%, after 200 min of the experiment, the hydrate formation rate and final water conversion rate in quartz sand are higher than that of chlorite. It can be seen that the sediment with a high specific surface area does not promote the hydrate formation all the time. We can speculate that although chlorite with a high specific surface area provided hydrate nucleation sites, it also adsorbed more water molecules on its surface, resulting in lower water activity, therefore, the final water conversion rate of chlorite system is lower than that of quartz sand. Therefore, we can think that the increase in water saturation slows down the kinetics of hydrate formation. In addition, the change in water saturation has different effects on the hydrate formation kinetics of quartz sand and chlorite,

and the effect on the chlorite system is slightly higher than that of quartz sand.

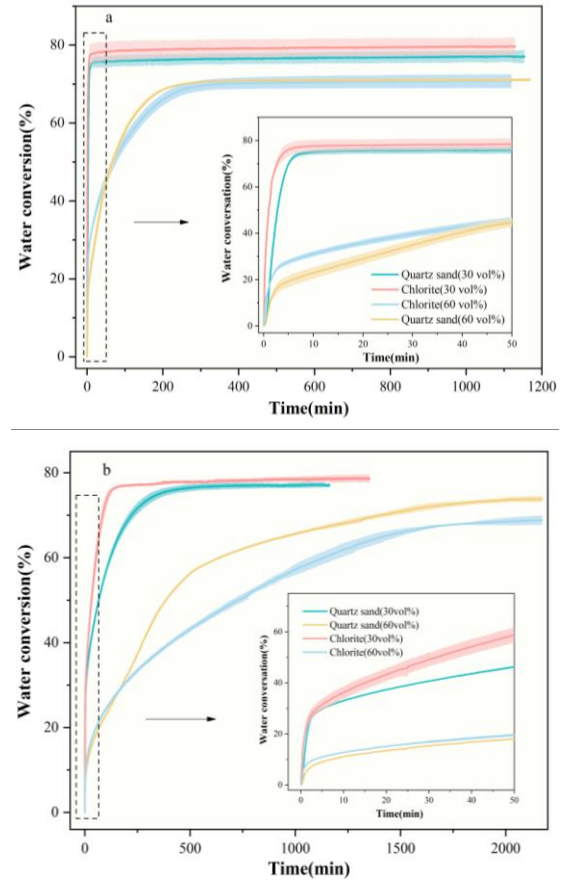


Fig. 3 Percentage of the water conversion to  $\text{CH}_4$  hydrate with different initial water content in quartz sand sediments with particle size in the range of (a) 15-25  $\mu\text{m}$ , (b) 75-90  $\mu\text{m}$

### 3.2 The influence of sediment particle size on the kinetics of hydrate formation

Figures 4a and 4b show the changes in water conversion rate in sediments with the same water saturation when the sediment particle size is 15-25  $\mu\text{m}$  and 75-90  $\mu\text{m}$ . It can be seen that when the initial water saturation is 30 vol%, with the increase of sediment particle size, the hydrate formation rate and water conversion rate in the sediment decrease in the first 400 min, but after 800 min, the hydrate formation in the two types of sediments has ended, and the final water conversion rate of the large-size sediment is almost equal to that of the small-size sediment. When the initial water saturation is 60 vol%, within 1200min, with the increase of the sediment particle size, both the water conversion and hydrate generation rate in the sediment decrease. This is because generally, it is believed that the specific surface area of the sediment with small particle size is larger than that of the sediment with large particle

size. Therefore, the larger specific surface area of small particle-size sediments can provide more nucleation sites for hydrate formation. Interestingly, when the experiment is conducted for a long time, under the condition of the same initial water saturation of sediments, the final water conversion rate is almost the same for both large and small particle size sediments, but the difference is the formation rate of hydrate. Therefore, it can be seen that the change in particle size has little influence on the final water conversion rate. Moreover, with the increase in particle size, the decreasing trend of the hydrate formation rate of the chlorite system is higher than that of quartz sand. In conclusion, when the water saturation is the same, the change in particle size does not have a significant effect on the final water conversion rate but has a significant effect on the hydrate formation rate. Among them, the increase in particle size has a greater effect on the hydrate formation rate in chlorite sediments than that in quartz sand.

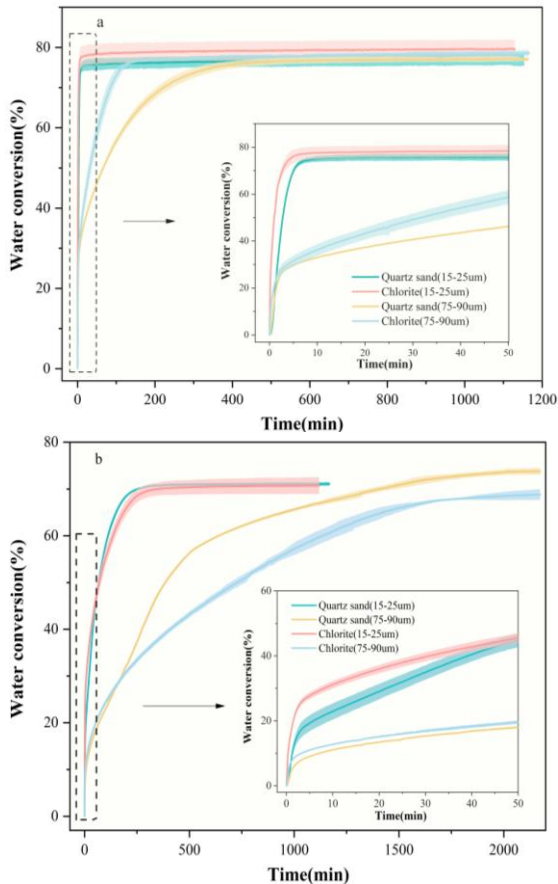


Fig. 4 Effect of particle size on the  $\text{CH}_4$  hydrate formation (a) with 30 vol% initial water content, (b) with 60 vol% initial water content

#### 4. CONCLUSION

This study systematically investigated the effects of particle size and initial water content of quartz sand and

chlorite on the kinetics of  $\text{CH}_4$  hydrate formation in porous sediments. For sediments with the same particle size, the formation rate and final conversion rate of hydrate decrease with the increase of water saturation, which slows down the growth kinetics of hydrate. For the sediments with the same initial water saturation, the change in particle size has little effect on the final water conversion but has a greater effect on the hydrate formation rate. However, sediments with high specific surface area do not always promote the kinetics of hydrate formation, because although sediments with high specific surfaces can provide more nucleation sites, they can also absorb more water, resulting in lower water activity, thus slowing down the formation of hydrate.

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