

Effect of Ca-MMT with different water content on methane hydrate kinetics in sandy environments

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ABSTRACT

The kinetic characteristics of methane conversion to hydrates in deep-sea cold seep sediments have a significant impact on hydrate accumulation and resource distribution. Consequently, they have important implications for the assessment of carbon sequestration and hydrate extraction potential. Nevertheless, the impact of clay minerals in cold seep sediments on the kinetics of methane hydrate formation in sandy environments remains uncertain. To investigate this, quartz sand was employed to simulate a sandy environment, allowing the effect of varying levels of calcium-based montmorillonite on the kinetics of methane hydrate formation in porous media to be studied. The results demonstrated that the initial rate of hydrate formation increased, while the final methane consumption decreased as the mass fraction of calcium-based montmorillonite (MMT) increased in comparison to the pure quartz sand system. The observed effects were mainly attributed to the high specific surface area of MMT and its capacity for adsorbing water. This work contributes to our understanding of the mechanism by which calcium-based montmorillonite affects the transformation of hydrates at varying water contents. Furthermore, it provides scientific support for the estimation of marine carbon sink capacity and carbon sequestration.

Keywords: South China Sea cold seep, Methane leakage, Formation kinetics, Calcium-based montmorillonite

1. INTRODUCTION

Natural gas hydrates are ice-like crystalline solids that form from gases such as methane and water at low temperatures and high pressures [1]. The potential of

natural gas as an energy source has been the subject of considerable interest, given the substantial resource reserves, high energy density and clean combustion properties associated with it [2].

Concurrently, the emission of methane, as a greenhouse gas, has also resulted in an increase in global carbon emissions and a growing trend of global warming, with methane contributing approximately 30% to global warming thus far [3]. Consequently, in recent years, the international community has signed a series of documents calling for a global reduction and mitigation of methane emissions. It has been demonstrated that, in addition to human activities such as the oil and gas industry, landfills and waste disposal, which represent the primary sources of methane emissions, the quantity of methane released from the oceans into the atmosphere should not be overlooked. As the world's largest methane reservoirs, seafloor methane seepage from deep-sea sediments is a relatively common phenomenon, typically resulting from processes such as the fermentation of organic matter or the decomposition of unstable natural gas hydrates [4]. The leakage of methane from the seabed to the surface occurs in the form of a plume of bubbles [5], which is subsequently released into the atmosphere, thereby increasing the atmospheric concentration of carbon. Therefore, attention must be paid to methane leakage from the seabed.

As an important part of the global cold spring system, the South China Sea Cold Seep, with its unique geographical and geological advantages, is an ideal place to study the methane seepage from the cold seep and its impact on the environment [6]. In recent years, with the in-depth investigation and study of the South China Sea Cold Seep system, people have gained a more

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Table. 1 The summary of experimental conditions and results.

Run	Medium	Water quality (g)	Clay/water content (wt%)	Initial pressure (Mpa)	Initial temperature (°C)	Induction time (min)	CH ₄ consumption (mmol CH ₄ /mol H ₂ O)
1	quartz	15	0	8	14.5	121	152.7
2	Quartz / montmorillonite	15	20	8	14.5	139	151.2
3	Quartz / montmorillonite	15	100	8	14.5	117	146.7
4	Quartz / montmorillonite	15	400	8	14.5	112	97.1

comprehensive understanding of the methane leakage mechanism and its impact on the environment. In addition, it has been found that NGH in the South China Sea (SCS) is mainly deposited in clay-rich reservoirs [7]. Expanded clay minerals (e.g. montmorillonite and kaolinite) are abundant in methane hydrate-bearing sediments (MHBs) and have an important influence on methane hydrate formation and dissociation. The question of whether clay minerals facilitate or hinder hydrate growth kinetics and the mechanisms involved is still controversial. Some work has been done to study the effect of different levels of clay minerals in the suspension on the kinetics of hydrate formation, showing that montmorillonite can reduce the hydrate nucleation time but delays the kinetics of hydrate formation. However, since it is a suspension agitation system, there is a high probability that hydrate formation can be promoted in the initial stage, and also in the later stage, due to the large amount of hydrate formation, the agitation gets obstructed, which also greatly restricts the gas-liquid mass transfer, and so it may have a certain influence on the experimental results.

In conclusion, although some studies have been conducted on the role of clay minerals in the formation of NGHs, relatively few studies have been conducted on the hydrate formation dynamics of sediments in sandy environments. Therefore, it is necessary to further investigate the mechanism of clay minerals in sandy environments in the South China Sea to provide scientific support for the rational development and exploitation of NGH resources. In this experiment, quartz sand was used as a porous medium for the seafloor sandy sediment environment to study the effect of calcium-based montmorillonite on the formation kinetics of methane hydrate by changing its content. It is of great importance to promote the understanding of the mechanism of clay minerals in cold seep sediments on the formation of hydrate from methane seepage.

2. MATERIAL AND METHODS

2.1 Materials

The CH₄ gas possess a purity level of 99.99 %, was procured from Guangdong Yuejia Gas Corporation. Deionised water was prepared in this laboratory. The quartz sand (with a particle size ranging from 250 to 400 μm) and the calcium-based montmorillonite (with a particle size ranging from 5 to 15 μm) used in the experiments was purchased from Shanghai Macklin Biochemical Technology Co.. The detailed particle size distribution of the sediment media, such as quartz sand, is shown in Fig. 1.

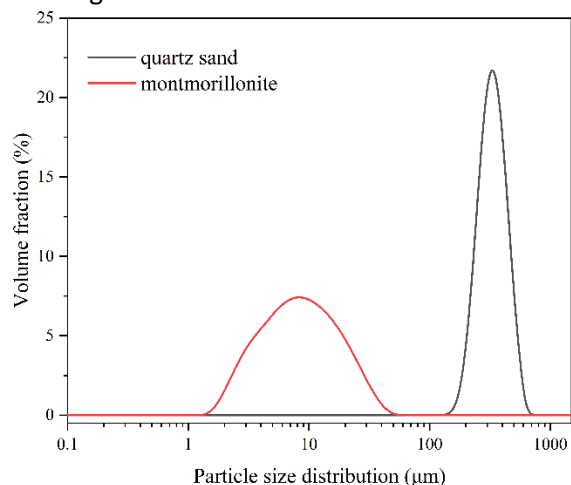


Fig. 1 Particle size distribution of the experimental sediments.

2.2 Experimental Apparatus

Figure 2 presents a schematic representation of the reactor system employed for methane hydrate formation. The autoclave reactor has an effective volume of 550ml, an internal diameter of 8cm, a height of 101.5cm, and is equipped with nine temperature sensors with an accuracy of $\pm 0.1^\circ\text{C}$ and an operating temperature range of -10°C to 40°C . Furthermore, the apparatus is furnished with a pressure sensor exhibiting an accuracy of 0.001 MPa and an operational pressure

range of 0 – 25 MPa. For purposes of reference, a schematic diagram of the device is provided in Figure 1. Two sapphire windows were incorporated into the reactor for the purpose of facilitating visual observation. The reactor was immersed in a water bath circulator, specifically designed for this purpose, in order to maintain a constant temperature. All experimental data were recorded on a computer at 20-second intervals.

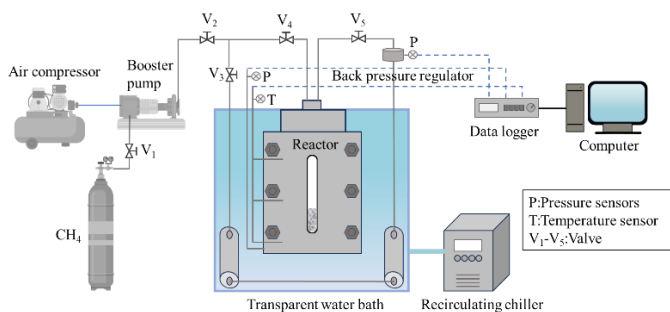


Fig. 2 Schematic diagram of the experimental setup.

2.3 Experimental Procedures

Prior to the commencement of the experiment, the reactor was cleaned and tested for gas tightness in order to ensure that it remained dry and airtight. Following this, the reactants were prepared. In order to purify the gas, the reactor was purged with low-pressure methane gas (1.0 MPa) for three cycles, after which methane gas was added and pressurized to 8 MPa. The reactor was then allowed to stabilize, with the water bath temperature maintained at 15 °C throughout this process. The data acquisition system was activated to commence real-time recording of the temperature-pressure changes. Following a two-hour period during which the pressure was allowed to stabilize, the temperature of the reactor was reduced to 4°C by means of cooling the water bath.

3. RESULTS AND DISCUSSION

In this work, methane consumption is defined as the number of millimoles of methane consumed per mole of water. The mass fractions shown in the article are all montmorillonite over water. The summary of experimental conditions and results are listed in Table 1. To facilitate the comparison of the water conversion rates of different mass fractions of MMT at the same time, t_{500} is used in this paper to denote the water conversion rate at 500 minutes as an analogy to t_{2250} .

3.1 Effect of Ca-MMT on induction time

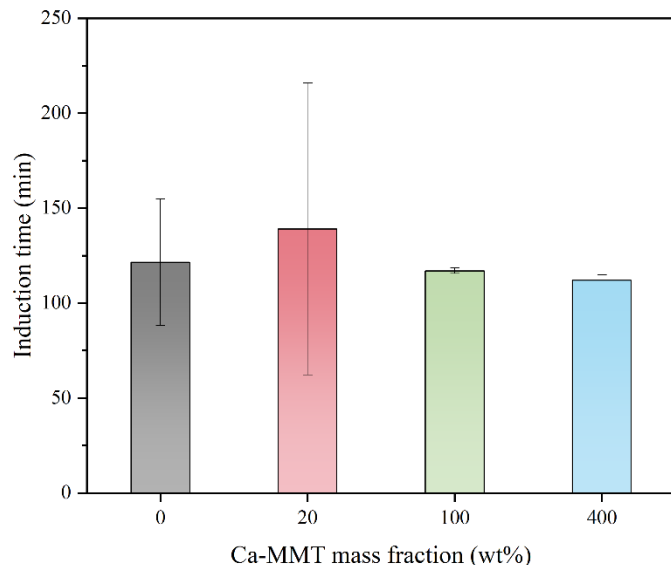


Fig. 3 Comparison of the average induction times for hydrate formation in sandy sediments with Ca-MMT over water mass fractions of 0-400 wt%.

As shown in Figure 3, when 0-400 wt% Ca-MMT was added, the induction time of the hydrate first increased and then decreased, and at a mass fraction of 20 wt%, the induction time increased by about 14% compared to that of the pure water system, whereas when the mass fraction was increased to 100 wt%, the induction time decreased by about 4% compared to that of the pure water system, and by almost 8% at 400 wt%. The above results show that only when the mass fraction of MMT is increased to 20 wt% in small amounts, the induction time of the hydrate changes very significantly. Some literature has suggested that the presence of porous media can increase the water-gas surface area and improve the heat transfer rate, thereby promoting the nucleation of CH₄ hydrate. However, this experiment shows that the addition of a small amount of MMT to the pore water of a porous medium delays hydrate nucleation and that only a sufficiently high content of MMT can have some promoting effect on hydrate nucleation. This is attributed to the high specific surface area of MMT as well as the increased salinity in the pore water; at low MMT, its dissolution in the water increases the salinity of the solution, which inhibits hydrate nucleation, whereas as the MMT content increases, the promotion of nucleation by its high specific surface area begins to predominate, leading to a multiple effect of MMT content on hydrate nucleation.

3.2 Effect of Ca-MMT with different water content on MH growth kinetics

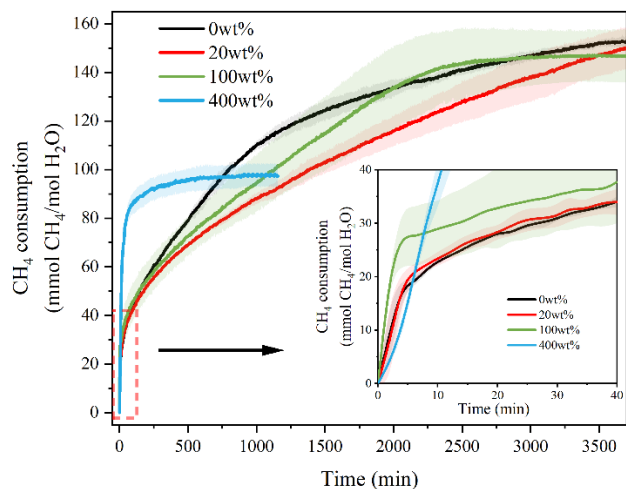


Fig. 4 Methane consumption for hydrate production in sandy sediments with the same initial conditions and Ca-MMT with a mass fraction of water between 0 and 400 wt%.

Fig. 4 shows the methane consumption under the same initial conditions and Ca-MMT ratio water for the mass fraction of the 0-400 wt% system, with mass fractions corresponding to water contents of 100%, 83%, 50% and 20% in that order. From the local enlarged graphs, it can be seen that the methane consumption in the initial stage gradually increased with the increase of Ca-MMT content from 0 to 100 wt% at the limit of 5 min, while the methane consumption in the same time period became minimum when the mass fraction reached 400 wt%. It shows that when the water content of Ca-MMT is more than 50%, the initial methane hydrate formation rate increases with the increase of MMT content, and when the water content of Ca-MMT decreases, the hydrate formation rate decreases at the same time. However, it should be noted that the duration of the rapid generation phase for 0-100 wt% Ca-MMT is the same, which is about 5 min, while the duration of the rapid generation phase for 400 wt% is up to 20 min. It demonstrates that the MMT mass fraction up to 400 wt% is very uniformly distributed in the silica sand and that a large amount of free and weakly bound water can be completely reacted in almost the same time.

From the overall kinetic curves, the addition of Ca-MMT inhibited the overall growth kinetics of methane hydrate in the range of 0-20 wt%, and in the range of 100-400 wt%, the rate of hydrate formation in the early stage was greatly enhanced with increasing Ca-MMT content, but the final methane consumption was greatly reduced. In order to analyse the effect of different MMT contents on the methane hydrate formation characteristics at different times, the water conversion rates at 500 min and 2250 min were selected for comparison. From Fig. 5, it can be seen that the trend of

water conversion rate at t_{500} is decreasing and then increasing, from 0 wt% to 400 wt% in the order of 47.5%, 41.2%, 43.7% and 57.1%, and the water conversion rate at 400 wt% is increased by about 20% compared with that of the pure water system, and 20 and 100 wt% are decreased by 15% and 8%, respectively, compared with that of the pure water system. This is mainly because the addition of a small amount of Ca-MMT inhibits the kinetics of hydrate formation in the early stage, leading to a decrease in the water conversion rate, but Ca-MMT at 400 wt% can provide a large number of nucleation sites and promote the formation of a large amount of hydrate. t_{2250} shows that the water conversion rate at 100 wt% has the largest increase and exceeds that of the water-only system, suggesting that the rate of its formation is higher than that of the water-only system in the later stage. This is mainly attributed to the increase in gas-liquid contact area by Ca-MMT, as the pore space decreases with hydrate formation, but the addition of MMT promotes gas-liquid contact and thus formation at the later stage. However, the water conversion of 400 wt% is almost unchanged compared to 500 min, indicating that the reaction is essentially complete and the remaining water in the system is mainly strongly bound water that does not participate in hydrate formation. This is mainly due to the large specific surface area of Ca-MMT and the strong adsorption of water. When the MMT content is low, Ca-MMT can be dissolved in the pore water, which improves the salinity of the water and has an inhibitory effect on hydrate formation, and at a later stage it can provide a large number of nucleation sites, which improves the rate of hydrate formation. When the Ca-MMT content is high, the free water is converted into strongly bound water by adsorption on the Ca-MMT surface, and the strongly bound water is not involved in hydrate formation, thus reducing the water conversion rate.

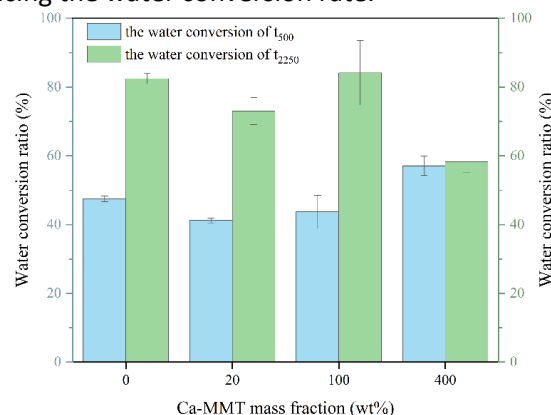


Fig. 5 Water conversion of Ca-MMT with mass fractions ranging from 0-400 wt% at 500 and 2250 min under the same initial conditions

4. CONCLUSIONS

In this work, quartz sand was used to simulate a sandy environment and the effect of Ca-MMT on the kinetics of methane hydrate formation at different water contents was investigated by varying the mass fraction of MMT over water. The conclusions obtained from the experiments are as follows.

(1) When the mass fraction of Ca-MMT is small (<20 wt%), it significantly increases the induction time relative to the pure aqueous system, and conversely, when the mass fraction is large (>100 wt%), it promotes hydrate nucleation.

(2) The addition of MMT had a significant enhancing effect on the initial rapid growth phase of methane hydrate compared to the pure water system and was proportional to the amount of MMT. As the MMT content increased from 0 to 400 wt%, the duration of the initial rapid growth phase increased from 5 to 20 min.

(3) As the MMT content increases, the water content decreases and the strong adsorption of MMT leads to a decrease in free water, which in turn leads to a decrease in the final water conversion rate.

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