

Formation Kinetics Studies of CH₄ Hydrate in Brine and Porous Sediments by Micro-Differential Scanning Calorimeter

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ABSTRACT

The formation of gas hydrates in porous sediments composed of fine-grained media with a larger specific surface should be imaginatively faster, while why do hydrates in natural conditions tend to accumulate in coarse particles? In view of the controversy over the influence of sediment conditions on hydrate formation kinetics, in this work, a high pressure micro-differential scanning calorimeter (HP μ -DSC) with small reactor volume and high precision was specially used to systematically investigate the effects of quartz sand particle size, initial water content, and sediment medium type on the formation kinetics of CH₄ hydrate in porous sediments. The results show that the CH₄ hydrate formation rate, on a whole, increases with the decreased quartz sand particle size and initial water content. However, it is not completely monotonous, and the difference and degree of the influence for one factor on the hydrate formation depends on the choice of another factor. Moreover, the addition of kaolin or bentonite even with smaller particle size and larger specific surface, however, relatively hinders the formation of CH₄ hydrate. By directly observing the formation process of CH₄ hydrate in different porous sediments, it was found that the rapid hydrate growth in porous sediments relies greatly on the continuous diffusion and growing of hydrates towards adjacent media. In addition, some interesting phenomena for bentonite wetting and cracking have also been observed. The discoveries in this work provide a systematic and unique insight into the natural gas hydrates formation in porous sediments.

Keywords: CH₄ hydrate, formation kinetics, porous sediments, HP μ -DSC

1. INTRODUCTION

Natural gas hydrates (NGHs) are ice-like crystalline solids formed mainly by CH₄ gas and water under thermodynamically suitable conditions [1]. The total CH₄ reserve in NGHs is estimated to be between 3×10^{15} and 1.55×10^{18} m³ at standard temperature and pressure [2, 3]. The huge energy potential has attracted a large number of scholars to develop this resource. However, the NGH reservoir properties in different locations are various, which largely influences the exploitation efficiency. Thus, the understanding of NGHs formation and their interactions with host sediments is significant whether for the selection of suitable development ways, or the hydrate resource detection and estimation.

Compared with a large number of NGH exploitation studies, the investigation focusing on hydrate formation kinetics in porous sediments is relatively limited. Moreover, in most of the reports on the hydrates formation, either the water used in experiments was mainly deionized water, or glass beads were used as porous media. The characteristics of these systems are quite different from those in nature which are porous sediments and seawater mixing systems. Heeschen et al. [4] reported that the surfaces of different sediment media in nature are accompanied with mineral changes, which can significantly affect the hydrate nucleation and growth. Uchida et al. [5] considered that NaCl might accumulate at the hydrate growth interface and change the hydrate growth mode.

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In addition, regarding the influence of sediment characteristics on hydrate growth, some conclusions are still controversial. For example, Bagherzadeh et al. [6] found that CH_4 hydrate formation rate is faster in a bed with lower water content and smaller particle size. However, the results of Zhang et al. [7] indicated the lower hydrate formation rate with small sand grains. For sediment systems with finer media, there are larger gas-liquid contact surfaces, which should accelerate the gas hydrates formation to a greater extent. However, many geological exploration surveys have also shown that NGHs tend to accumulate in coarse-grained sand deposits. So how exactly is this difference caused?

In this study, by using a high pressure micro-differential scanning calorimeter (HP μ -DSC) with small reactor volume and high resolution specially, the effects of sediment particle size, initial water content and medium type on the CH_4 hydrate formation kinetics in brine and porous sediments were systematically investigated. Due to the small volume of the DSC reactors, the influences of spatial differences and water migration on the experiment results could be reduced. In addition, the nucleation and growth process of CH_4 hydrate in porous sediments were directly observed through an optical cell. The finding in this work provide a systematic and unique insight into the natural gas hydrates formation in porous sediments.

2. EXPERIMENTAL SECTION

2.1 Materials

The CH_4 , N_2 gases (99.99% purity) were supplied by the Beijing Beifen Gas Industry Corporation. The quartz sands, kaolin and bentonite were purchased from Yifeng Silica Sands Co. The brine (3.35 wt% NaCl solution) was prepared in laboratory.

2.2 Experimental apparatus and procedures

A high pressure micro-differential scanning calorimeter (HP μ -DSC7 Evo, Setaram Inc.) was used to detected the heat flow change during CH_4 hydrate formation process. The schematic diagram of μ -DSC setup is illustrated in Fig. 1. Before the formation experiments, approximately 0.2 mL of partially water-saturated sediment media was charged to the sample cell. The temperature was then cooled to 274.15 K. Both of the two cells were vacuumed and then pressured to 9.6 MPa by CH_4 gas. After that, the DSC started to measure.

In the visual observation experiment, an optical cell with two sapphire windows was used. The effective volume of the cell chamber is approximately 10 mL. The cell was initially charged with 2 mL of partially water-saturated sediment media which was pressed on one of the sapphire windows. Then the cell was cooled to 274.15 K, and CH_4 hydrate was formed at 9.6 MPa. More information about the apparatus were detailed elsewhere in literatures [8, 9].

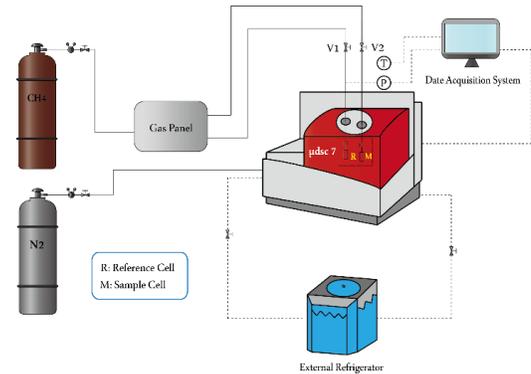


Fig. 1. Schematic diagram of DSC setup

3. RESULTS AND DISCUSSION

3.1 DSC heat flow change for hydrate formation

Fig. 2a and 2b show the DSC heat flow change during CH_4 hydrate formation process with different quartz sand particle size and initial water content, respectively. The positive heat flow value represents heat release, indicating the formation of CH_4 hydrates. The time spent for the initial arisen of exothermic peak is the hydrate nucleation time. It can be found from both figures that the exothermic heat quickly soared to maximum after the nucleation. Subsequently, the heat flow decreased slowly and there were extended peaks with a long time span. In Fig. 2a, the largest exothermic peak appeared corresponding to the smallest particle of quartz sand with 25-38 μm . In addition, the extension peak was also obviously larger, and there were more distinct multi-exotherm peaks. These peaks may be originated from other newly nucleated points, or the growth of hydrates at different points. Therefore, the particle size could not only affect the initial reaction rate, but also the intensity for subsequent reactions. For the 25-38 μm particle diameter but different water content, the exothermic curves were also obviously different. That is, the appearance of different exothermic forms was not only related to the particle size, but also closely to the moisture content. There may be different mechanisms for the effect of particle size and water content on CH_4 hydrate formation.

Table 1. Summary of experimental conditions and results

Run	Medium	Particle diameter range (μm)	Initial water content (vol%)	Duration of experiments (min)	Induction time (min)	Water conversion to hydrate (mol %)
1	quartz sand	25-38	20	2450	10.5	75.80
2	quartz sand	25-38	50	3600	17.9	76.92
3	quartz sand	25-38	100	5980	139.1	6.78
4	quartz sand	80-109	20	2460	73.3	79.14
5	quartz sand	80-109	50	6200	239.1	75.96
6	quartz sand	80-109	100	6070	401.7	14.60
7	quartz sand	180-250	50	4190	10.6	47.38
8	quartz sand	180-250	100	6680	55.3	11.68
9	quartz sand	380-830	20	2670	165.0	42.82
10	quartz sand	380-830	50	3670	192.9	18.32
11	quartz sand	380-830	100	5740	216.4	17.33
12	quartz sand/ kaolin	80-109/21-30	20	4250	42.9	61.84
13	quartz sand/ bentonite	80-109/19-26	20	4250	204.5	33.09

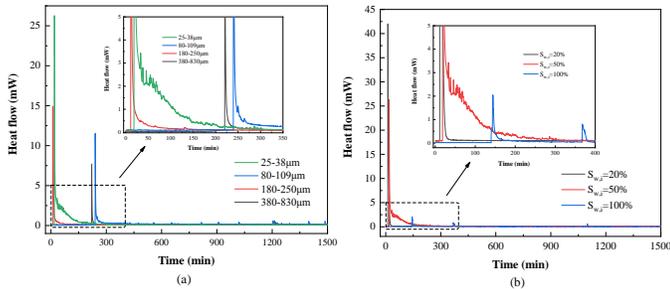


Fig. 2. Heat flow change during the CH₄ hydrate formation process. (a) with 50 vol% initial water content and different quartz sand particle size, (b) with 25-38 μm particle size and different initial water content

3.2 Effect of sediment conditions on hydrate formation

The percentage of water conversion to hydrate can be obtained by integrating DSC exothermic curve. Fig. 3 shows the change of water conversion ratio with normalized time. When the initial water content was 50 vol%, the formation rate of CH₄ hydrate increased significantly with the decreased quartz sand particle size, as is presented in Fig. 3a. This can be explained by specific surface. However, the influence mechanism of specific surface area seemed to be unsuitable when the water content was 100 vol%, that there was no linear correlation between the CH₄ hydrate formation rate and sediment particle size, as is displayed in Fig. 3b.

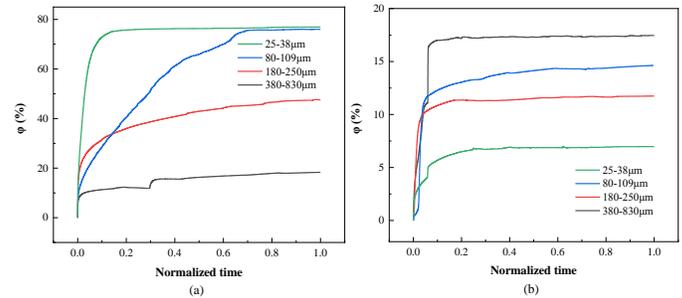


Fig. 3. Effect of particle size on the CH₄ hydrate formation (a) with 50 vol% initial water content, (b) with 100 vol% initial water content

The effect of initial water content on the formation of CH₄ hydrate is shown in Fig. 4. For particle size in the range of 180-250 μm , the difference between the formation rate and conversion ratio of CH₄ hydrate under different water content is the largest, as presented in Fig. 4c. However, with the decreased or increased particle size, the disparity in hydrate formation rate, especially in conversion ratio, gradually reduces. It can be concluded that the formation rate of CH₄ hydrate was simultaneously restricted by both the particle size and the initial water content by combining Fig. 3 and Fig. 4. The effect of a single factor on the formation of CH₄ hydrate also depends on the choice of another factor.

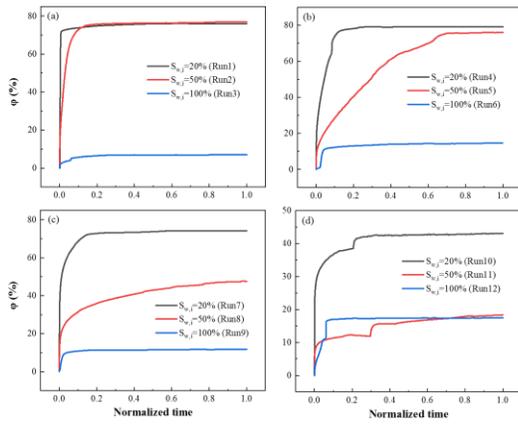


Fig. 4. Percentage of the water conversion to CH₄ hydrate with different initial water content in quartz sand sediments with particle size in the range of (a) 25-38 μm, (b) 80-109 μm, (c) 180-250 μm and (d) 380-830 μm

Fig. 5 shows the effect of different sediment media on the formation of CH₄ hydrate. After 50 vol% of clay was added, the hydrate formation rate and conversion ratio decreased significantly. In addition, the effect of clay types on CH₄ hydrate formation was quite different. The hydrate formation rate in system with the bentonite was significantly slower than that in the system with the kaolin.

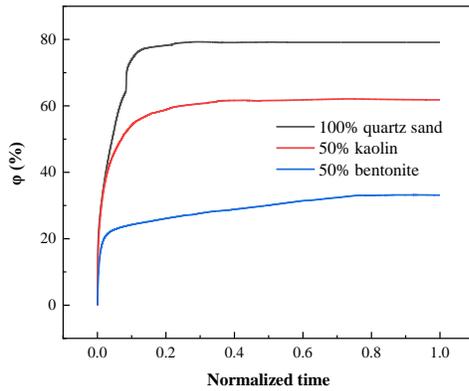


Fig. 5. Effect of medium type on the CH₄ hydrate formation

3.3 Visual observation on hydrate formation in porous sediment

To further understand the CH₄ hydrate formation in porous sediments, the growth process of CH₄ hydrates in an optical cell was directly recorded, as is illustrated in Fig. 6 and 7. Once a nucleation point emerged, the CH₄ hydrate diffused and grew along the adjacent quartz sand particles, with which the reaction specific surface gradually increased, as shown in Fig. 6. New nucleation sites were also observed during this process, however, the rapid growth of hydrates seemed to depend mainly on the growth and diffusion of CH₄ hydrate.

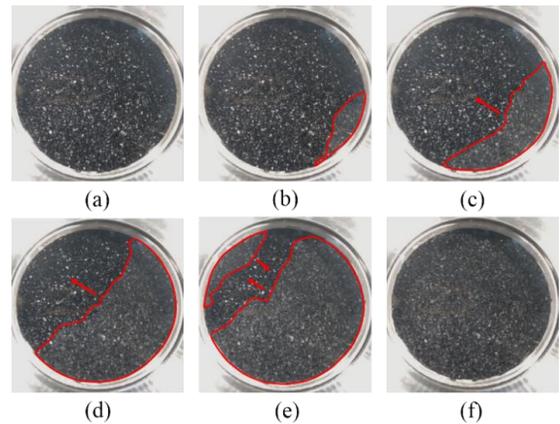


Fig. 6. The process of CH₄ hydrate formation in quartz sand with 20 vol% initial water content. (a) before nucleation, (b) 5 s after nucleation. The nucleation occurred near the boundary of the cell firstly. (c) 10 s and (d) 25 s after nucleation. The CH₄ hydrate rapidly grew around adjacent media particles. (e) 35 s after nucleation. A new nucleation point appeared. (f) 40 s after nucleation. The CH₄ hydrate spread over the surface of the porous sediment. The white substance inside red circle represents CH₄ hydrate

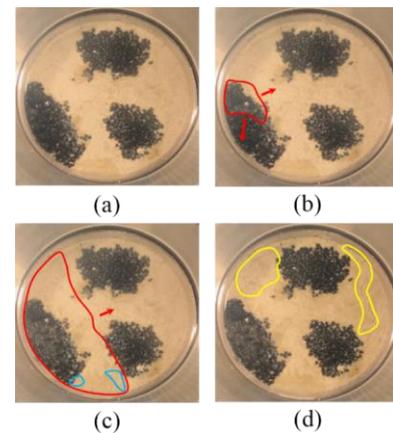


Fig. 7. The process of CH₄ hydrate formation in bentonite system with inlaid quartz sand on the surface with 20 vol% initial water content. The mosaic quartz sand is designed to make it easier to distinguish the growth of hydrates. (a) before nucleation, (b) 5 s after nucleation. (c) 30 s after nucleation. Liquid water appeared on the bentonite surface during the growth of hydrates. (d) 4 min after nucleation. Obvious cracks appeared in the bentonite. Blue circles represent liquid water, and yellow circles are cracks

The process of CH₄ hydrate formation in bentonite system with inlaid quartz sand on the surface was presented in Fig. 7. The similar hydrate diffusion mode but slower rate to quartz sand sediment was also found in the bentonite system. This phenomenon indicates that even in the bentonite with strong water absorption, there is still a close connection among these media, and the hydrate nucleation at one point can also affect the conversion of nearby water. In addition, the phenomena

of wetting and bentonite cracking were observed. The wetting should be caused by the migration of free water. It is worth noting that these water were not obviously converted to hydrates within 12 hours, which will further hinder the transportation of gas and make the reaction more difficult to proceed downward. The occurrence of cracks may be due to uneven local stress. The force may be caused by the further expansion of bentonite with the formation of CH₄ hydrate, or by the cementation of the clay due to the hydrate formation on one side.

4. CONCLUSION

In this study, the effects of quartz sand particle size, initial water content, and sediment medium type on the formation kinetics of CH₄ hydrate in porous sediments were systematically investigate. The results show that the CH₄ hydrate formation rate increases with the decreased quartz sand particle size and initial water content as a whole. However, it is not completely monotonous, and the difference and degree of the influence for one factor on the hydrate formation depends on the choice of another factor. The direct reason for this phenomenon is the different gas-liquid contact area. In addition, the water retention capacity of quartz sand with different particle sizes may also has an effect on it.

The addition of kaolin or bentonite even with a smaller particle size, however, relatively hinders the formation of CH₄ hydrate. This indicates that, in addition to the specific surface, there are other mechanisms affecting the CH₄ hydrate formation kinetics in porous sediments. By directly observing the formation process of CH₄ hydrate in different porous sediments, it was found that the rapid hydrate growth in porous sediments relies greatly on the continuous diffusion and growing of hydrates towards adjacent media. In addition, some interesting phenomena for bentonite wetting and cracking have also been observed. The systematic knowledge gained in this work can explain the phenomenon that gas hydrates in nature tend to be enriched in coarse sand, and, to a certain extent, can also explain the conclusion difference of CH₄ gas hydrate formation kinetics in some previous experiments.

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