

PLUGGINGS RISK FOR GAS PRODUCTION BELOW ICE POINT: UNUSUAL SELF-PRESERVATION OF METHANE HYDRATE IN POROUS SEDIMENTS

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ABSTRACT

The self-preservation effect is crucial for hydrate storage, however, may also hinder the decomposition and even results in severe plug of production well for hydrates exploitation below freezing point. In this study, a high pressure micro-differential scanning calorimeter (HP μ -DSC) was used to study the effect of sediment particle size and type on the self-preservation of CH₄ hydrate with low saturation. It was found that there is still a strong self-preservation effect, and the stability of CH₄ hydrate degrades with the reduced sediment particle size as a whole. The CH₄ hydrates, in different sediments, have significant differences of self-preservation phenomena. CCD camera and in-situ raman spectroscopy was used to further investigate the influence mechanism. The experimental results indicate that the ice and bentonite synergistically enhanced the self-preservation effect of CH₄ hydrate, which should be paid great attention to the gas production process of hydrate below freezing point in the future. This is the first investigation on the sediment influence on self-preservation effect of methane hydrate. Our findings are of significance for both risk prevention of hydrate exploitation and a better understanding of self-preservation effect.

Keywords: CH₄ hydrate, self-preservation effect, sediment type, sediment particle size, dissociation

1. INTRODUCTION

Natural gas hydrates (NGHs), a non-stoichiometric crystalline compound, are consisted of cages made of hydrogen-bonded water molecules and small gas molecules [1]. As is known, the existence of the self-preservation phenomenon is crucial to realizing the storage and transportation of natural gas by forming hydrates. It is reported that NGH crystal can be stored for

more than three weeks under thermodynamically unstable conditions at 253 K and atmospheric pressure [2]. However, it will also hinder the hydrate decomposition and even results in severe plug of production well during hydrates exploitation process below freezing point. A large number of sand extraction and hydrate reformation are one of the most urgent problems for field production test of NGHs [3-7]. The sand-containing hydrate, once reformed inside the production well at terrestrial permafrost with ambient temperature lower than 0 °C, will severely impact the production efficiency and safety due to the self-preservation effect. On the other hand, Wang et al. [8] recently proposed a method for high-efficiency hydrates production below quadruple point in marine sediment. It is reported that the gas production rate increased with the drop of production pressure. However, as the pressure was further reduced, the self-preservation effect may undesirably occur.

Ershov and Yakushev [9] presented the existence of CH₄ hydrates self-preservation effect with high saturation in frozen rocks, but did not reported its dissociation dynamics. In this study, a high pressure micro-differential scanning calorimeter (HP μ -DSC) was used to study on the effect of sediment particle size and sediment type on self-preservation effect of CH₄ hydrate with low saturation. To further explore the influence mechanism with different types of sediments, CCD camera and in-situ Raman spectroscopy was used.

2. EXPERIMENTAL SECTION

2.1 Materials

The CH₄, N₂ gases (99.99% purity) were supplied by the Beijing Beifen Gas Industry Corporation. Deionized water was used in all the experiments. The silica sands, sodium bentonite and kaolin were supplied by Yifeng

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Silica Sands Co. Porous silica gels with pore diameters of 15.0 nm was purchased from Sigma-Aldrich Co. The parameter of the media used as the methane hydrate sediments in the experiments are shown in Table 1.

2.2 Experimental apparatus and procedures

The experimental process can be divided into two parts: CH₄ hydrate formation in porous sediments and decomposition below ice point.

To eliminate, as much as possible, the influence of residual ice on the dissociation of CH₄ hydrate. A high pressure micro-differential scanning calorimeter (HP μ -DSC7 Evo, Setaram Inc.) was used by achieving a high hydrate conversion rate. The change of the heat and the dissociation equilibrium temperature were measured. The schematic of this system can be seen in Fig. 1.

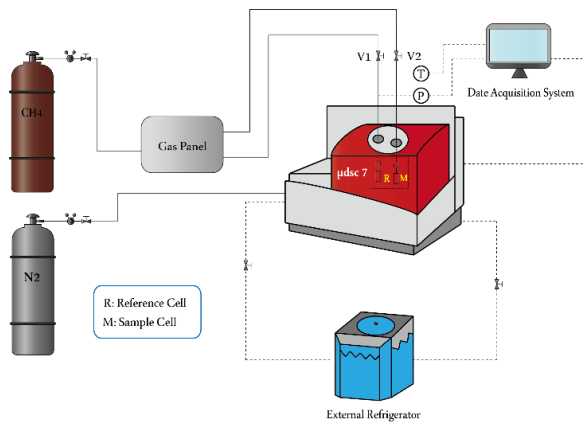


Fig 1 Schematic diagram of DSC setup.

In the DSC experiment, approximately 0.2 mL of partially water-saturated sediment media were charged to the sample cell. The accurate amount of charged and remainder water were both calculated through the endothermic thermogram of ice melting using an ice melting enthalpy of 333.33 J/g. The cells were pressurized to 10 Mpa with CH₄ gas for hydrate formation. To achieving the high hydrate conversion

rate, a multicycle mode of cooling-heating was adopted, which is presented in fig.2. After a period of time for temperature stabilizing at 267.15 K, the CH₄ gas in the cells was discharged to atmospheric pressure for hydrate dissociation process. Finally, the temperature is heated from 267.15 K to 293.15 K for complete decomposition of ice and hydrate.

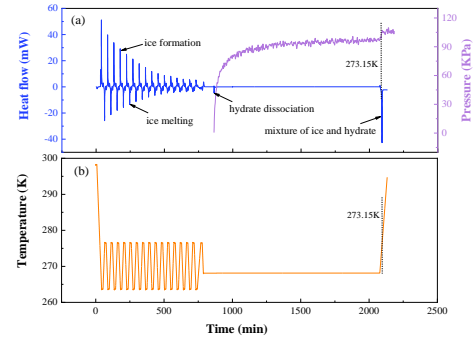


Fig 2 Changes in heat flow, pressure and temperature during hydrate formation and dissociation process. Only the pressure change, during the decomposition process, is shown here. (a) heat flow change; (b) temperature change.

In the CCD and Raman experiment, a high-pressure optical cell (HPOC) with two sapphire windows was used. The effective volume of the HPOC chamber is approximately 1.4 mL. The HPOC was initially charged with 1.2mL of partially water-saturated sediment media for CH₄ hydrate formation. More details descriptions of the HPOC and Raman have been provided in our previous studies [10].

3. RESULTS AND DISCUSSION

A summary of experimental conditions and results are listed in Table 1. The temperature, during hydrate dissociation process, was maintained at 268.15K for all the experiments. The initial water content for all the experiments is approximately 30 vol%.

Table 1. Summary of experimental conditions and results

Runs	Sediment content (vol %)	particle diameter range (μ m)	water conversion to hydrate (mol %)	dissociation ratio (mol %)
1	silica sand	25-38	100	99.34
2	silica sand	80-109	98.84	74.33
3	silica sand	120-150	99.28	64.84
4	silica sand	380-830	98.31	63.74
5	silica gel	80-200	100	91.28
6	70% silica sand+30%bentonite	19-26 for bentonite	86.59	11.36
7	70% silica sand+30%kaolin	21-30 for kaolin	89.36	80.2
8	70% silica sand+15%bentonite	19-26 for bentonite	95.08	10.73
9	pure water	/	92.02	18.23

3.1 Effect of the particle size of medium

Four groups of experiments (Run 1-4) were performed to investigate the effect of quartz sand particle size on the self-preservation effect of CH₄ hydrates, as shown in fig. 3. Fig. 3a shows the heat flow change over time after the pressure in the cells was discharged to atmospheric pressure. It can be seen that the endothermic peak become larger with the smaller size of sediment particle, that is, more hydrate decomposes. This could be attributed to the enhance specific surface effect. Fig. 3b illustrates the variation of decomposition ratio with time calculated from pressure, which is almost consistent with fig. 3a. It should be mentioned that the final decomposition ratio for Run3 and 4 is similar, indicating that, in addition to the specific surface of sediments, there are other factors that simultaneously affect the self-preservation effect of CH₄ hydrate.

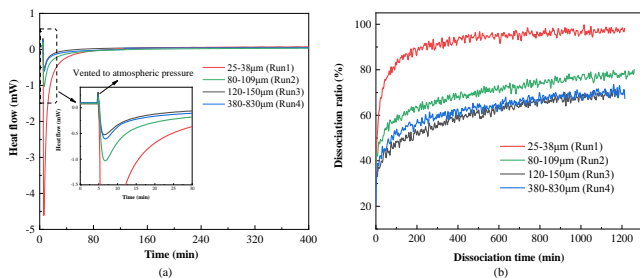


Fig 3 Effect of the particle size of quartz sand on the change of heat flow and dissociation ratio. (a) heat flow change; (b) dissociation ratio change

3.2 Effect of the sediment type

Fig. 4. displays the variations of pressure with dissociation time for different types of sediment medium. As can be seen, the pressure of Run6 with 30 vol% bentonite hardly rises, and is significantly lower than Run3 with quartz sand before heating. It was unexpected because of the much smaller particle size of bentonite, however, the extremely strong stability of CH₄ hydrate. For Run7 with 30 vol% kaolin, the pressure also remained almost unchanged until 298 min with a skyrocketing, indicating that the CH₄ hydrate was stable at first, but then suddenly decomposed. For comparison, Run8 with 15 vol% bentonite and Run 9 with pure water equal to 30% moisture content in porous sediments were conducted. The experimental results show that the hydrates were still highly stable even if the content of bentonite was decreased in Run8. While for Run9, the hydrate decomposed obviously once the pressure was vented to atmospheric pressure. To investigate if the

increased porosity creates the strong self-preservation of methane hydrate in bentonite, Run5 with porous silica gel was conducted. It was found that the hydrate decomposition rate was the fastest, which weakens the self-preservation effect of CH₄ hydrate, instead. It should be noted that the final pressure after heating, is much greater than the maximum pressure for Run6-8, which indicate that there are gases may in other forms inside the sediment. This could be one important reason for the strong self-preservation effect.

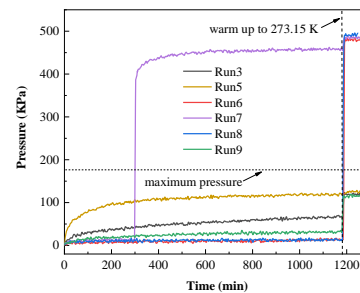


Fig 4 Variations of pressure with dissociation time for different type of medium. The maximum pressure refers to the pressure that can be achieved assuming complete decomposition of methane hydrate without loss during the venting process.

3.3 Study on the influence mechanism of medium

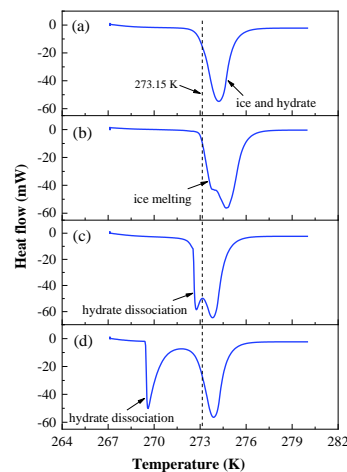


Fig 5 Diversity of endothermic peaks during the heating process from 267.15 K to 293.15 K. (a) Run 3; (b) Run 9; (c) Run 6; (d) Run 8.

Fig. 5 shows the diverse DSC endothermic peaks in different sediment systems during warming from 267.15 K to 293.15 K. Fig. 5a illustrates the quartz sand system with only one endothermic peak that can be attributed to the simultaneous ice melting and CH₄ hydrate decomposition. Fig. 5b presents the pure water system with ice melting following by hydrate decomposes. The hydrate dissociation in quartz sand and bentonite mixed

system is shown in Fig. 5c-d. A endothermic peak appeared before ice melted, presumably due to partial decomposition of CH₄ hydrate. As the content of bentonite reduced, the corresponding temperature for the first endothermic peak also decreases, that is, becomes less stable.

To further investigate the influence mechanism of medium types on the self-preservation effect of CH₄ hydrate, CCD camera was used to observe the morphological change of CH₄ hydrate sediments during dissociation process.

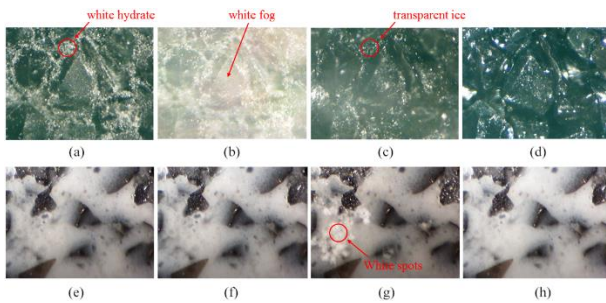


Fig 6 Morphological change of methane hydrate sediments during dissociation process in sediments with different medium. (a)-(f) in silica sands and (e)-(h) in 70% silica sand+30%bentonite, in which (a) and (e) before venting, (b) and (f) venting to atmospheric pressure, (c) and (g) 24h after vent, (d) and (h) heating for complete decomposition of hydrate. The temperature was 267.15 K for hydrate dissociation before heating.

As is shown in fig. 6a before depressurization, white hydrates presented in the quartz sand gap and surface can be clearly observed. When vented to atmospheric pressure, a large amount of white fog appeared in the silica sand sediments, shown in fig. 6b. After 24 h, the transparent ice film appeared, which can be seen in fig. 6c. While for fig. 6e-f, it was difficult to distinguish the position of hydrates, and there was almost no change during the venting process. Fig. 6g shows that white spots appeared on the bentonite after 24 hours, but the morphology was significantly different from the transparent ice in fig. 6c.

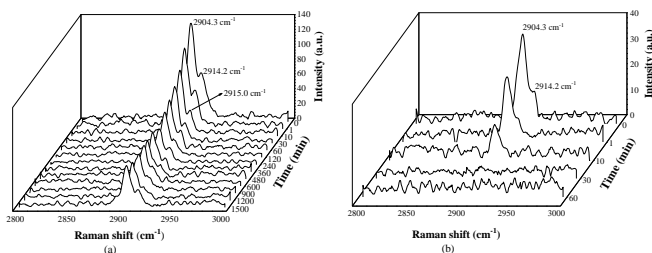


Fig 7 Time-resolved Raman spectra during CH₄ hydrate dissociation process in sediments with different medium at 267.15 K and atmospheric pressure. (a) silica sands; (b) 70% silica sands + 30% bentonite.

Time-resolved Raman spectra were used to examine the change of methane hydrate on the surface of sediments, as shown in fig. 7. The two peaks centered at 2904.3 cm⁻¹ and 2914.2 cm⁻¹ could be assigned to C-H stretching frequencies of CH₄ trapped in large (5¹²6²) and small (5¹²) cages of sl hydrate, respectively. As shown in Fig. 7a, the decomposition of CH₄ hydrate gradually slows down and begins to stabilize after 120 minutes in the quartz sand system. There is no transition of the hydrate structure during the decomposition process with still in sl type, however, peak shift occurs after 10 min. Fig. 7b show that the weak Raman signal of CH₄ hydrate on the surface of bentonite (perhaps on the quartz sand, or the gaps between quartz sand and bentonite. Because only a very small part of the entire surface on the sediment can the CH₄ hydrate Raman signal being observed) has not been observed after 30 min, and there is also no structure transition during the decomposition process.

4. CONCLUSION

In this study, a high pressure micro-differential scanning calorimeter (HP μ -DSC) was used to study the effect of sediment particle size and sediment type on the self-preservation effect. It was found that there is still a strong self-preservation effect for the sediment systems with low methane hydrate saturation. The stability of CH₄ hydrate degrades with the reduced sediment particle size as a whole, in which the specific surface of sediments could be one of the important reasons. The CH₄ hydrates, in different sediments, have significant differences of self-preservation phenomena. CCD camera and in-situ Raman spectroscopy results indicate that the decomposition mechanisms of CH₄ hydrate in quartz sand and bentonite may be different. Ice and bentonite can synergistically enhance the self-preservation effect, perhaps because of pressure bearing effect. This could also be the main reason for the existence of hydrates self-preservation effect in pure water system.

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