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## Full Length Article

## Methane hydrate crystal growth on shell substrate

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## ABSTRACT

Hydrate crystals growth on the surface of methane bubble (hydrate film) in pure water was studied by using a high-pressure visible microscope under the conditions of subcooling  $\Delta T = 5.44\text{--}13.72\text{ K}$  and methane concentration difference  $\Delta C = 2.92\text{--}8.19\text{ mol}\cdot\text{L}^{-1}$ . It was found the hydrate film is porous and the hydrate crystals grow towards the liquid phase on the film substrate. The crystal morphology and growth rate are affected by  $\Delta T$  and  $\Delta C$ . When  $\Delta T < 8.82\text{ K}$  and  $\Delta C < 4.12\text{ mol}\cdot\text{L}^{-1}$ , the hydrate grows into scattered columnar crystals, and the axial growth rate of the crystal gradually decreases. When  $\Delta T > 8.82\text{ K}$  or  $\Delta C > 4.12\text{ mol}\cdot\text{L}^{-1}$ , the hydrate crystals grow in dendritic shape, and the axial growth rate increases first and then decreases. The perimeter and area of the growing hydrate crystals were measured, and the fractal dimension of hydrate crystal under different  $\Delta C$  and  $\Delta T$  was calculated. The results show that the fractal dimension of columnar hydrate crystal is greater than 3. When  $3.87\text{ mol}\cdot\text{L}^{-1} < \Delta C < 4.20\text{ mol}\cdot\text{L}^{-1}$  and  $7.4\text{ K} < \Delta T < 8.8\text{ K}$ , the fractal dimension of columnar hydrate crystal is greater than 4; The fractal dimension of dendritic hydrate crystal is less than 3. When  $\Delta C > 4.77\text{ mol}\cdot\text{L}^{-1}$ ,  $\Delta T < 8.52\text{ K}$ , the fractal dimension of dendritic hydrate crystal is less than 2.

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## 1. Introduction

Natural gas hydrate (NGH) is a type of non-stoichiometric clathrate crystal compound formed by natural gas and water under low temperature and high pressure conditions. NGH is also called methane hydrate due to the main component of natural gas [1].

Due to its huge resources, NGH is considered to be an important alternative energy source in the future. During the trial production of NGH in the sea area, it was found that hydrate re-formed on bubbles in the drainage pipeline, which hindered the trial production. In conventional oil and gas production, in low-temperature and high-pressure wellbore and gathering pipelines, hydrates usually form on the surface of bubbles, and then accumulate and block, seriously threatening the flow safety [2]. In addition, gas hydrates have large gas storage capacity, could separate gas mixtures, and have high latent heat. These properties are expected to be used in the development of new technologies, such as the transportation and storage of hydrogen and natural gas, separation of mixed gases, and secondary refrigeration. In all the above applications, hydrate form and grow on the surface of the bubbles. In order to

develop NGHs, ensure the safety of oil and gas flow, and develop hydrate-based technologies, people need to understand the growth characteristics of hydrate crystals on the bubble surface (film substrate) [3,4].

The growth of gas hydrate is a complex crystallization process. Morphological research could help to understand the growth mechanism of hydrate crystals. Ohmura *et al.* [5] conducted a study on the formation and growth of methane hydrate crystals in methane saturated water under the conditions of 273.5 K and 6–10 MPa by visual observation. They found the hydrate crystals grow in liquid water based on the hydrate film. The morphology of the crystals changes significantly with pressure. At a pressure of 6–8 MPa, the hydrate crystals are columnar; at a pressure of 10 MPa, the columnar crystals are replaced by dendrites. The hydrate crystal growth morphology might depend on the mass transfer controlled driving force. Melikhov *et al.* [6] found that, in the early stage of methane hydrate film formation in solution, the hydrate crystals and their aggregates move at a speed of  $2\text{--}5\text{ mm}\cdot\text{s}^{-1}$ , and the crystal aggregates rotate and collide at a rate of  $\Omega \sim 0.2\text{--}2\text{ rad}\cdot\text{s}^{-1}$ . A hydrodynamic model is used to explain the movement of crystals and aggregates. The relationship between the strong chemical reaction force accompanying the formation of hydrate crystals and the crystal size, shape, and growth rate is revealed. Freer *et al.* [7] studied the formation of hydrates at

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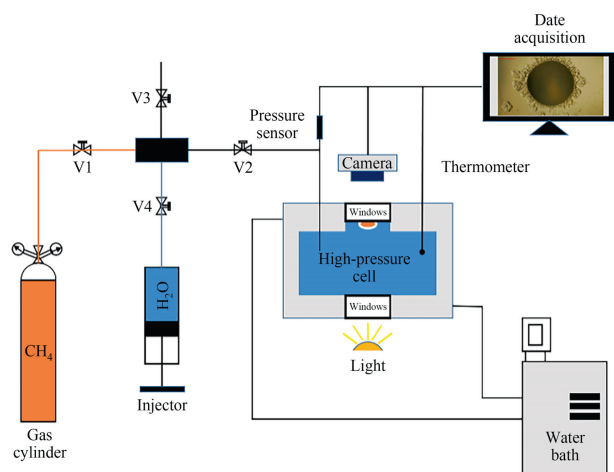


Fig. 1. A schematic of the high pressure visible reactor system.

the methane-water interface at 1.0–4.0 °C and 3.55–9.06 MPa by using an optical microscope. They found that the hydrate growth rate is directly proportional to the degree of subcooling. The influence of the driving force on the growth rate is analyzed, and a possible mechanism of molecular adhesion is proposed by observing the crystal morphology, and a model that combines interface adhesion kinetics with convective heat transfer is developed. Li *et al.* [8] visualized the hydrate crystals under different gas compositions and subcooling. The results show that the growth of hydrate films is controlled by the growth of single crystals at low degrees of subcooling. At higher degrees of subcooling, the lateral growth rate is controlled by both the seeding rate of crystal seeds and the growth rate of a single crystal.

Besides the pure methane-water system, Lee *et al.* [9] studied the growth of methane-propane hydrate crystals on the surface of liquid water under different subcooling conditions. They found the growth of the hydrate phase always starts from the formation of a hydrate film on the surface of the liquid water, and the detailed characteristics of crystal nucleation, migration and growth in the reactor were observed with a microscope. The results show that the degree of subcooling is a key parameter to control the morphology of the hydrate crystal on the hydrate film, and it affects the growth rate and structure of the crystal. Ozawa *et al.* [10] visually observed the hydrate morphology formed by methane and tetrahydropyran. Pits were observed on the hydrate crystals formed under high subcooling, and the hydrate crystals formed under low subcooling are relatively smooth. Hayama *et al.* [11] studied the growth morphology of methane hydrate at the gas-liquid interface under different sodium dodecyl sulfate (SDS) concentrations and different subcoolings. They found in the SDS

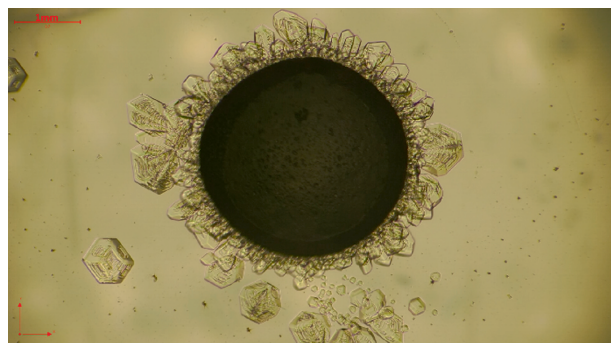


Fig. 2. Methane hydrate crystals on film substrate.

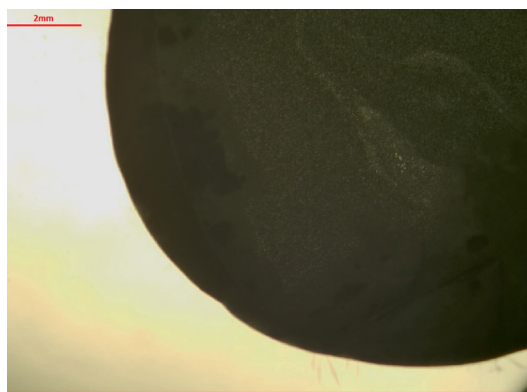


Fig. 3. Formation of hydrate film at gas liquid interface.

solutions, the size of a single hydrate crystal is smaller than in pure water. As the subcooling increases, the hydrate crystals gradually become slender. When the subcooling is extremely high, the hydrate grows into upright crystal fibers. Veluswamy *et al.* [12,13] used a non-stirred reactor to study the morphology of methane hydrate in the presence of 5.6% (mol) tetrahydrofuran (THF) solution and 0.1%–0.5% (mass) amino acid, and observed the methane hydrate formed in the presence of THF is needle-shaped, and the methane hydrate formed in the presence of amino acid is fluffy and flocculent.

Except for methane hydrate, Hussain *et al.* [14] studied the kinetics and morphology of ethane hydrate formation under the conditions of 270–280 K and 8.83–16.67 bar using a batch reactor. They found the formation kinetics depends on pressure, temperature, subcooling and stirring rate. Morphological studies have shown the appearance of ethane hydrate is similar to thread or cotton. Ohmura *et al.* [15] studied the macroscopic morphological changes of carbon dioxide hydrate crystals in liquid water. The results show that as the system subcooling increases, the carbon dioxide hydrate crystals changes from thick polyhedral crystals to fine dendrites. The increase in system subcooling leads to an increase in the driving force for guest substance (carbon dioxide) dissolved in the water to transfer to the surface of the hydrate crystal, thereby increasing the crystal growth rate, and the crystal growth rate determines the crystal morphology. Saito *et al.* [16] observed the formation and growth of clathrate hydrate crystals on the surface of water droplets exposed to mixed gas (containing methane, ethane and propane), and classified the hydrate crystal morphology according to the system subcooling. The lateral growth rate of hydrate crystals was measured. The results show that when the subcooling  $\Delta T_{\text{sub}} \geq 3.0$  K, the hydrate crystals are

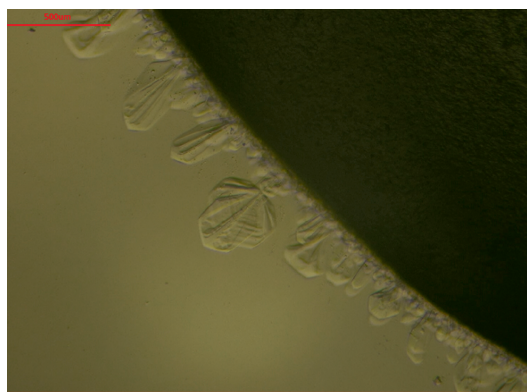


Fig. 4. Hydrate crystals grow towards the liquid phase on the film substrate.



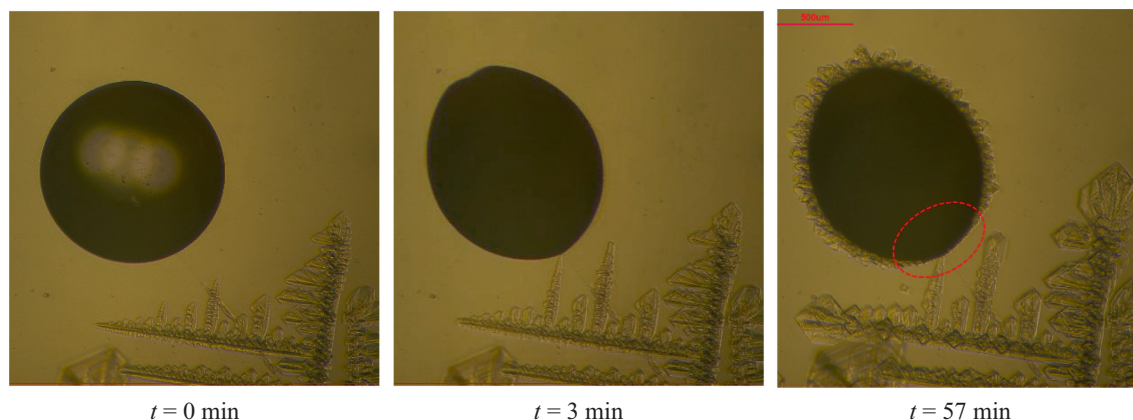


Fig. 5. Seed induced formation of hydrate shell substrate. The given time is the start recording time,  $T = 3.8\text{ }^{\circ}\text{C}$ ,  $P = 8.19\text{ MPa}$ .

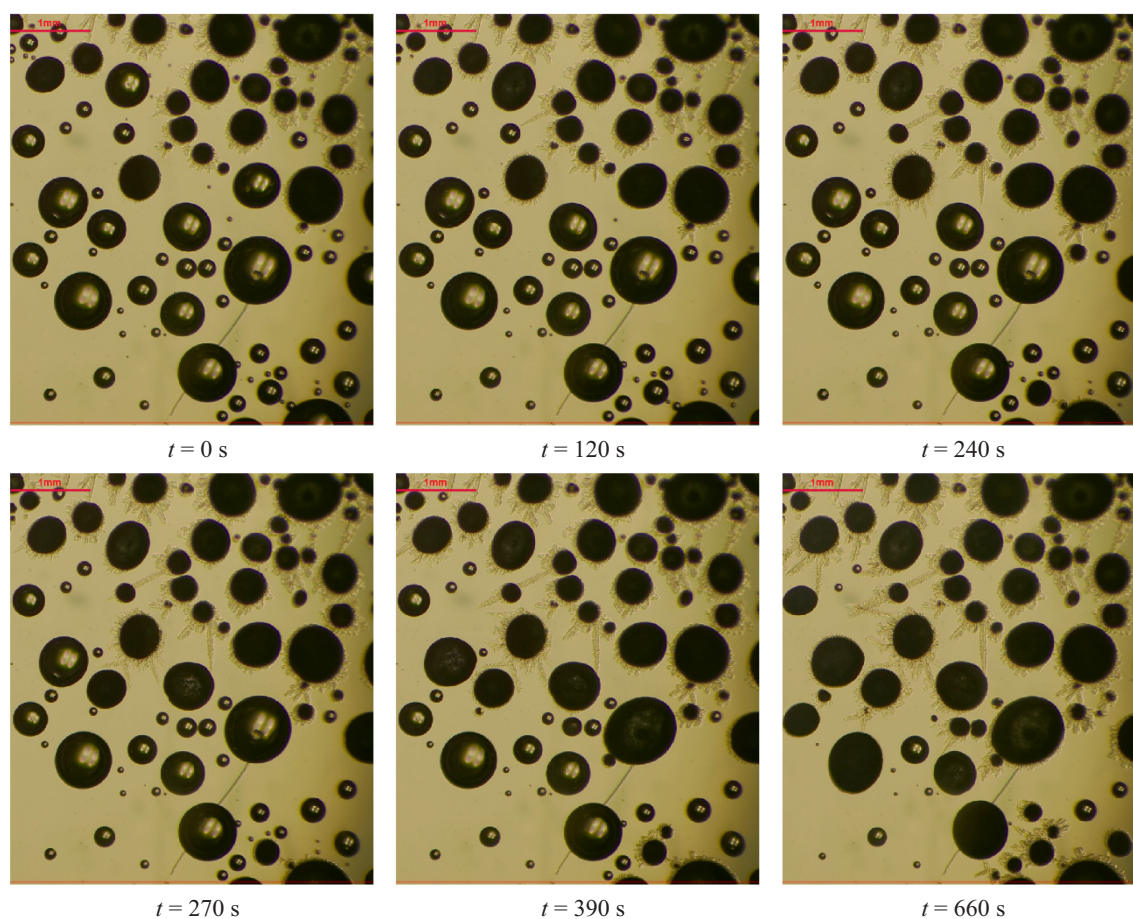


Fig. 6. Hydrate crystals induce hydrate formation on the surface of other bubbles. The given time is the start recording time,  $T = 3.8\text{ }^{\circ}\text{C}$ ,  $P = 8.72\text{ MPa}$ .

usually sword-shaped or triangular. When  $3.0\text{ K} > \Delta T_{\text{sub}} > 2.0\text{ K}$ , the hydrate crystals become a polygon, and then a larger-sized polygon. The length of one side of the polygon is usually  $0.5\text{--}1.0\text{ mm}$ . The size of hydrate crystal decreases with the increase of subcooling, and the lateral growth rate of hydrate crystal increases with the increase of subcooling. Huang *et al.* [17] observed the formation process of THF hydrate in situ with a high-resolution atomic force microscope and found the subcooling is a key factor affecting the hydrate morphology. They observed the special dendrites and protrusions on the edge of the hydrate crystal. Wang *et al.* [18] con-

ducted a THF hydrate formation experiment under flow conditions in a visualization reactor, analyzed the changes in the microscopic morphology of THF hydrate, and obtained a microscopic model of the THF hydrate formation and agglomeration process. In addition, statistical methods were used to study the different forms of THF hydrate, and the particle size changes and distributions during their formation were analyzed. Zheng *et al.* [19] studied the morphology and formation kinetics of methane-carbon dioxide mixture and 2.57% (mol) TBAB/TBPB formed semi-clathrate. They found the needle-like and columnar hydrate crystals are formed

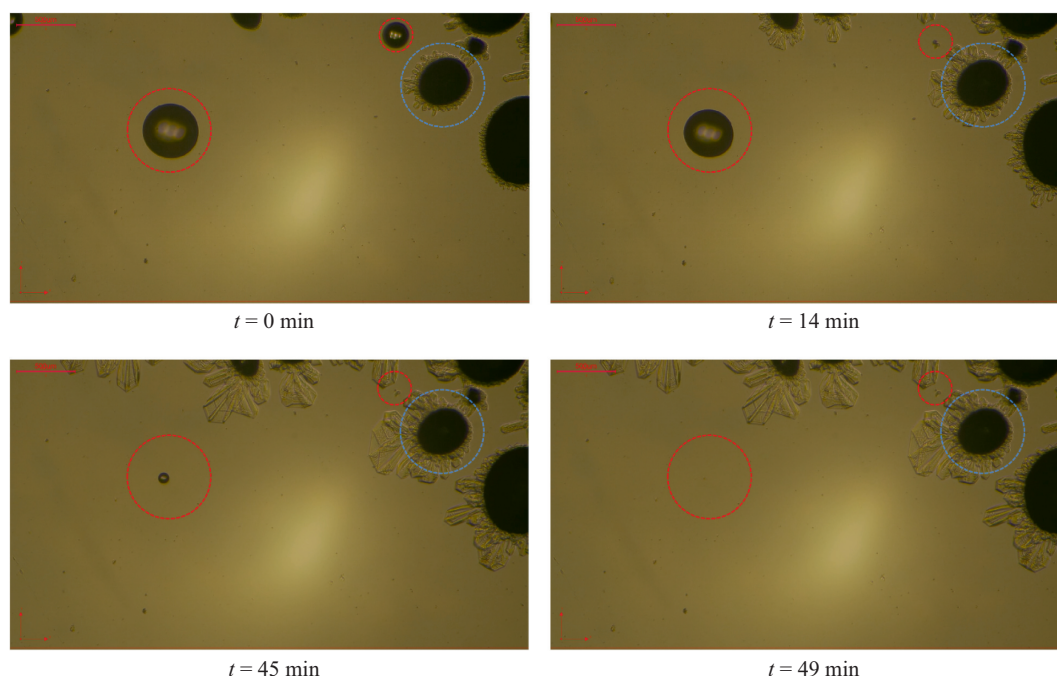


Fig. 7. Bubbles dissolve and disappear during adjacent hydrate crystals grow. The given time is the start recording time,  $T = 3.8\text{ }^{\circ}\text{C}$ ,  $P = 8.72\text{ MPa}$ .

near the gas-liquid interface, and the columnar hydrate crystals become thicker and thicker over time. Zhao [20] observed the formation process of HCFC-141b refrigerant gas hydrate through experiments, and calculated the growth rate of hydrate crystals using microscopic images.

Although many scholars have conducted visual studies on the crystal growth and morphology of methane hydrate, their research observations are carried out at a single condition, and the detailed features of the hydrate crystals are still unclear. In this work, the influence of subcooling and methane concentration differences on the growth of hydrate crystals is studied, the methane hydrate crystals growth on the shell substrate is observed, and the morphology of methane hydrate crystals is analyzed. The growth rate of hydrate crystals under different conditions are measured. In order to quantify the morphology of hydrate crystals, the fractal theory was applied, and the relationship between the formation conditions, crystal morphology and fractal dimension was obtained.

## 2. Experimental

A high-pressure visual reactor system is used for the experiment (Fig. 1). The main body of the high-pressure reactor is a 245 ml stainless steel cylindrical cavity wrapped by a temperature-controlling jacket. High pressure resistant glass made windows are installed on the upper and lower side of the reactor. There is a  $\phi 3\text{ cm} \times 1\text{ cm}$  cylindrical depression on the top of the reactor. The depression makes the bubbles completely gathered in the visible area during the experiment. The methane gas used in the experiment was provided by Qingdao Xinkeyuan Technology Co., Ltd., with a purity of 99.999%. The pressure is measured by using a TRAFAG sensor (8251 type, 0–16 MPa,  $\pm 0.05\text{ MPa}$ ). The temperature is measured by using a PT100 platinum resistance sensor ( $\pm 0.1\text{ K}$ ).

During the experiment, the following steps were adopted: (1) flush the reactor and pipeline with methane gas to discharge residual air (open V1, V2 to inject gas into the reactor, then close V1, open V3 to vent, repeat three times); (2) inject a certain amount

of methane into the reactor (gas pressure is controlled by valve switches V1 and V3), close V2, and temporarily seal the reactor; (3) inject water and pressurization (open V2 and V4, and inject a certain amount of liquid into the kettle, so that methane will gather into bubbles in the visible window, the bubble rises to the inner surface of the window as a result of buoyancy. The bubble remains stationary because the liquid phase in the system is not flowing, and the kettle will reach a certain pressure); (4) turn on the water bath and start to cool down; (5) turn on the light source and microscope, and start to observe the bubbles.

In the experiment, a stereo microscope (Osway, T1-HD228S) was used to observe the formation and growth of hydrate crystals on the shell substrate.

## 3. Results and Discussion

The growth of methane hydrate is believed to be controlled by heat and mass transfer. In this work, the subcooling  $\Delta T$  and the methane concentration difference  $\Delta C$  are used as control factors to study the growth law of hydrate crystals on the surface of bubbles in pure water.

The subcooling is the temperature difference for crystal growth and is calculated by Eq. (1) [21]:

$$\Delta T = T_{\text{eq}} - T_{\text{exp}} \quad (1)$$

In Eq. (1),  $T_{\text{eq}}$  represents the hydrate phase equilibrium temperature, calculated by Chen-Guo model, K;  $T_{\text{exp}}$  represents the experimental temperature, K.

The methane concentration difference is another driving force for crystal growth, which is calculated by Eq. (2):

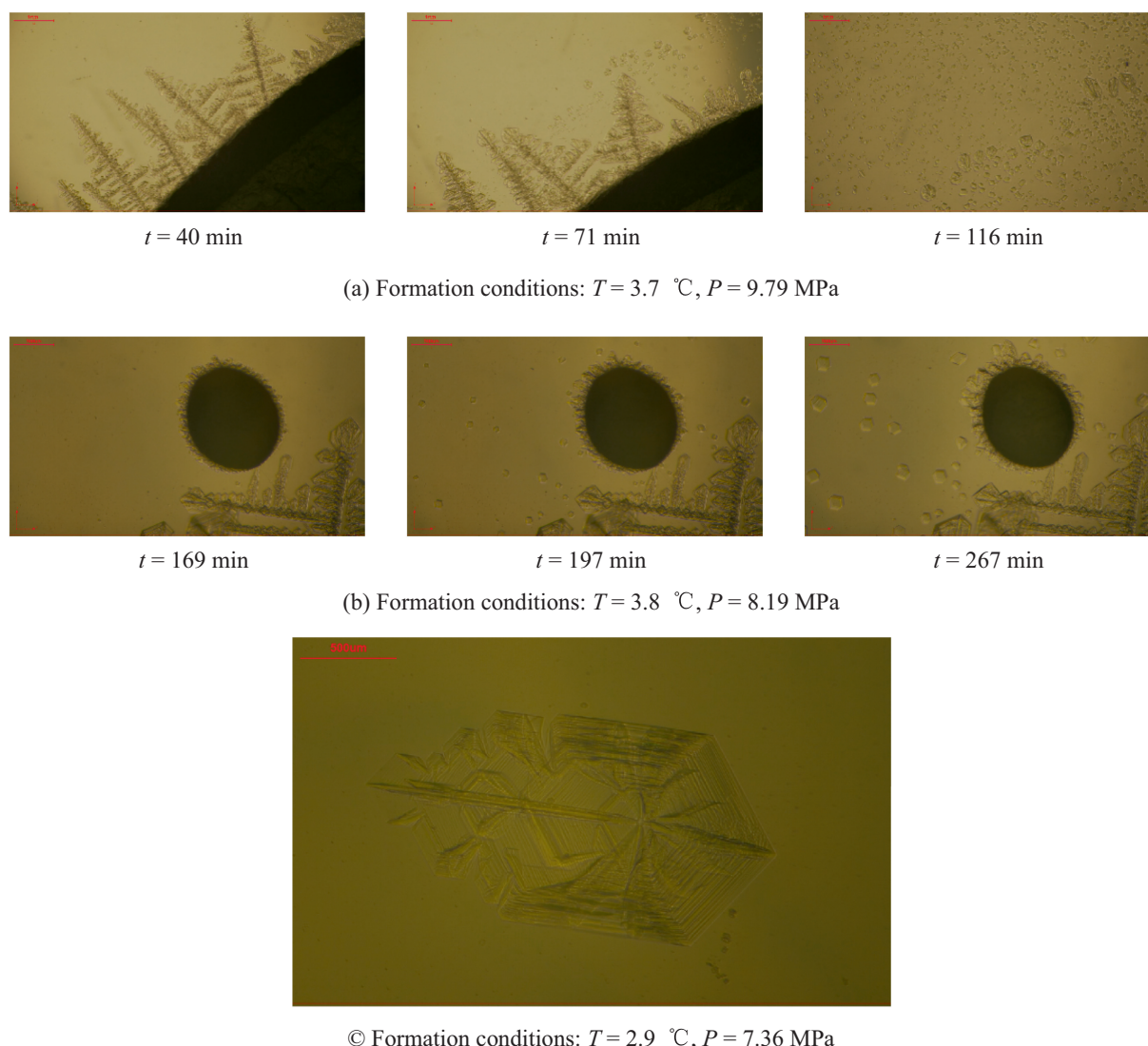
$$\Delta C = C_{\text{bubble}} - C_{\text{H}} \quad (2)$$

In Eq. (2),  $C_{\text{bubble}}$  represents the concentration of methane in the bubble,  $\text{mol}\cdot\text{L}^{-1}$ ;  $C_{\text{H}}$  represents the solubility of methane in water in the presence of hydrate [21],  $\text{mol}\cdot\text{L}^{-1}$ .

$C_{\text{H}}$  is calculated from Eq. (3):

$$C_{\text{H}} = \exp[15.4802 + 0.0191P - (4996.2 + 6.6488P)/T] \quad (3)$$





**Fig. 8.** The individual hydrate crystal in liquid phase. The given time is the starting time of hydrate crystal growth.

In Eq. (3),  $P$  represents the pressure in the system when containing hydrate, MPa;  $T$  represents the temperature in the system when containing hydrate,  $^{\circ}\text{C}$ .

In the experiments, the  $\Delta T$  range is 5.44–13.72 K, and the  $\Delta C$  range is 2.92–8.19 mol·L $^{-1}$ . Within the range, the hydrate crystals growth on the surface of methane bubbles are visually observed at micron scale, and a series of images of hydrate crystals were obtained (Fig. 2). According to the observed images, the growth law of hydrate crystals on the shell substrate was analyzed. The hydrate crystals were classified according to the morphology. The perimeter and area of the hydrate crystals were measured, and the fractal dimensions of hydrate crystals under different  $\Delta T$  and  $\Delta C$  conditions are calculated.

### 3.1. The formation mechanism of shell substrate and hydrate crystals

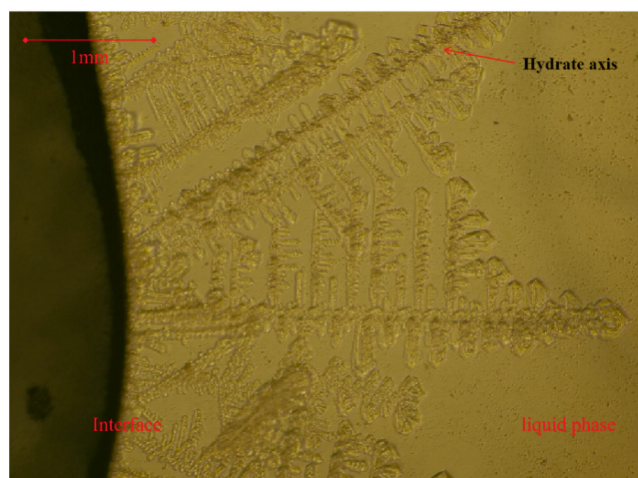
#### 3.1.1. The formation mechanism of hydrate shell substrate

After reaching the temperature and pressure conditions for hydrate formation, if there is no external seeding trigger, methane bubbles in the water need to pass a certain induction period to form hydrate at the gas–liquid interface. Once the hydrate formation started, the gas–liquid interface is quickly covered, forming a

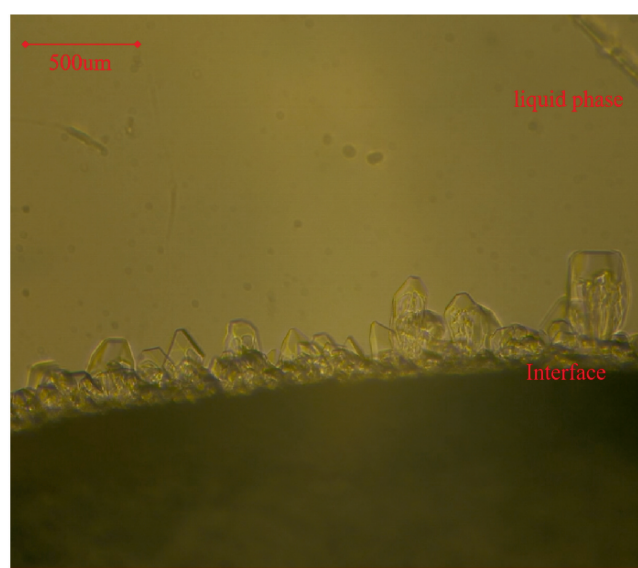
hydrate film, and then the hydrate crystals grow toward the liquid phase on the film substrate (Figs. 3 and 4).

If a seed crystal is triggered, the hydrate film substrate will form almost instantaneously. As shown in Fig. 5, the bubbles become dark instantly after being contacted by the hydrate crystals, that is, the bubbles rapidly form a hydrate film. At the same time, during the hydrate crystal growth process, as observed in Fig. 5, no hydrate crystals growth was observed at the around of the contact point. On the other side, the large chunk crystal near the shell grew obviously. Considering the growth of the small crystals on shell and the large chunk as a whole, we believe the ‘no crystal growth around the contact point’ should be caused by the Ostwald ripening. Hydrate tends to form on large chunk to minimize the total energy of the system. As shown in the right image in Fig. 5, no crystal growth was found around the contact point, while a large number of hydrate crystals grew towards the liquid phase in other areas.

When there are multiple similar bubbles in the liquid phase, the induced seed formation shown in Fig. 5 will occur in a chain. Fig. 6 shows the chain reaction of hydrate film substrate formation induced by seed crystals. The chain reaction occurred in 660 seconds. The hydrate crystals grow on one hydrate film substrate,



(a) Dendritic hydrate



(b) Columnar hydrate

Fig. 9. Hydrate morphology.

once the crystal contact with the adjacent bubble, hydrate formation will be quickly triggered and the bubble will be covered soon. New hydrate crystals grow on the newly formed hydrate shell. The repeated crystal growth and shell formation enabled the chain reaction.

### 3.1.2. The formation mechanism of hydrate crystals

The growth of hydrate crystals consumes methane. The methane supply mechanism have an important influence on the growth of hydrate crystals. Experiments have found that during the growth of hydrate crystals, in addition to the consuming of methane in the hydrate shell, it will also absorb methane in nearby bubbles. As shown in Fig. 7, the diameter (major axis) of the hydrate shell in the blue dashed circle is reduced from 0.42 mm at  $t = 0$  min to 0.40 mm at  $t = 49$  min. The bubbles in the red dotted circle gradually dissolve and disappear with the growth of nearby hydrate crystals.

In addition to growth of columnar or dendritic crystals from the shell substrate, hydrate crystals will also appear in the liquid phase as independent crystals. Fig. 8 shows the images of independent hydrate crystals gradually emerging in the liquid phase after the

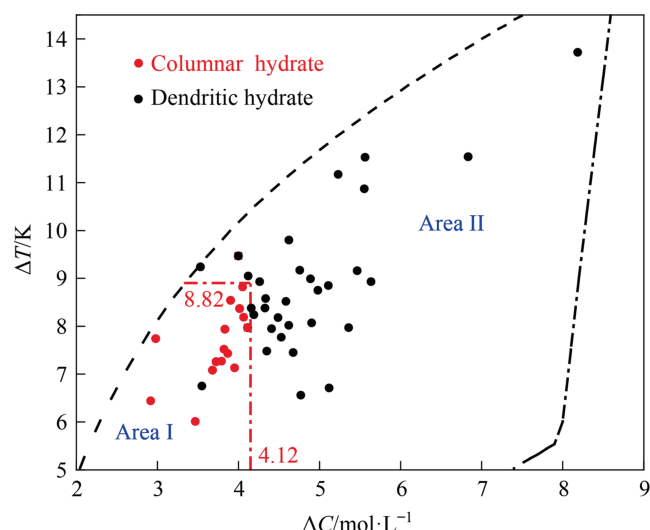


Fig. 10. Regional division of dendritic hydrate and columnar hydrate.

hydrate crystals on the shell surface have grown for a certain period of time under different temperatures and pressures. It could be seen from Fig. 8 that the crystals have regular edges. The surface of the individual crystal particles with a smaller particle size is smooth, and there are depressions on the surface of the larger individual crystal. The independent crystal should be mainly due to heterogeneous nucleation which occurs due to suspended and dissolved impurities and this crystal growth defect facilitates the storage of solvent inclusions (water saturated with methane).

## 3.2. Morphology and growth rate of hydrate crystals

### 3.2.1. Morphology of hydrate crystals

In this work, 42 groups of experiment for hydrate crystal growth on independent methane bubbles were carried out. The initial thickness of the hydrate layer and the shape of hydrate crystals are quite varied due to distinct driving factors [22]. According to the images, the methane hydrate crystals containing the hydrate axis are classified as dendritic hydrates (Fig. 9(a)), and the methane hydrate crystals without the hydrate axis are classified as columnar hydrates (Fig. 9(b)). Taking  $\Delta T$  and  $\Delta C$  as the influence parameters, the formation condition regions of the two hydrate crystals were divided (Fig. 10).

In Fig. 10, the abscissa is the methane concentration difference during the formation of methane hydrate crystals, while the ordinate is the subcooling during the formation of methane hydrate crystals. The black dashed line is the maximum and minimum subcooling margin that could be obtained under this methane concentration difference. It can be seen from Fig. 10 that the morphology of hydrate crystals has a clear relationship with subcooling and the methane concentration difference. When in the range of Region I, that is,  $\Delta T < 8.82$  K and  $\Delta C < 4.12$  mol·L<sup>-1</sup>, methane hydrate crystals on the shell substrate grow in a columnar shape. When  $\Delta T > 8.82$  K or  $\Delta C > 4.12$  mol·L<sup>-1</sup> in the Region II, the methane hydrate crystals on the shell substrate grow in a dendritic shape.

The independent crystals formed in the liquid phase also present dendritic or columnar characteristics. Two independent crystals are shown in Fig. 11. Independent crystal 1 is in symmetrical leaf-like shape with obvious growth spindles and could be classified as a dendritic shape. The independent crystal 2 is a hexagonal fragmented crystal, and no obvious growth axis could be seen. By adjusting the focal length of the microscope, we find that the inde-



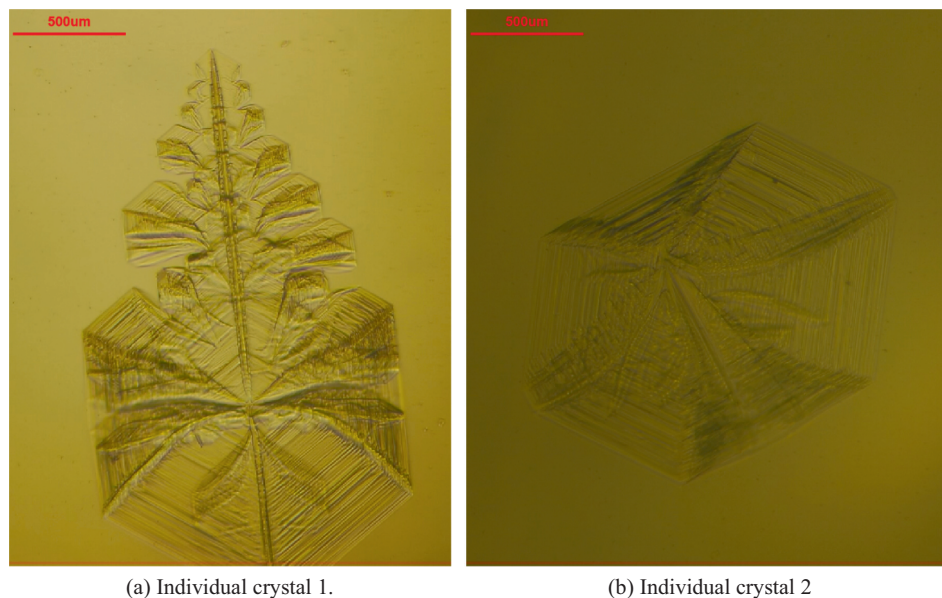


Fig. 11. The individual hydrate individual crystal formed in liquid phase at  $T = 2.9\text{ }^{\circ}\text{C}$  and  $P = 7.36\text{ MPa}$ .

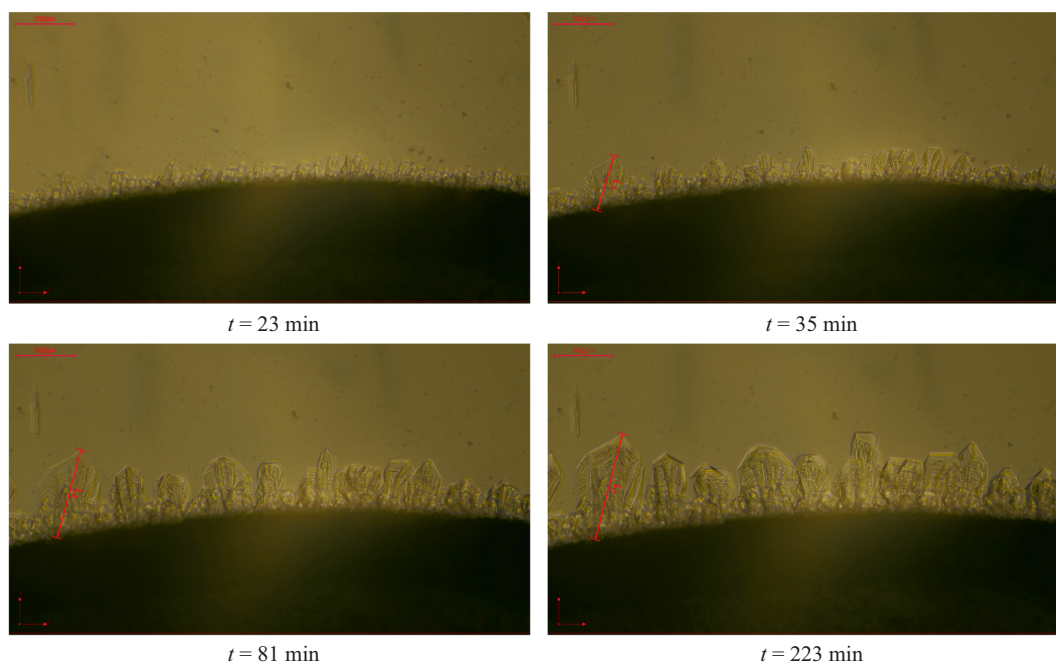


Fig. 12. The growth process of columnar hydrate crystal on bubble surface at  $\Delta T = 7.97\text{ K}$  and  $\Delta C = 4.11\text{ mol}\cdot\text{L}^{-1}$ . The given time is the starting time of hydrate crystal growth.

pendent crystal 2 is not plane. Therefore, it could be speculated that the independent crystal has a polyhedral structure. Both of these two types of crystals have obvious crystal growth defects (i.e., dents on the crystal) which are conducive to the storage of solvent inclusions.

### 3.2.2. Growth rate of hydrate crystals

By photographing, the growth rate of methane hydrate on the shell substrate under different subcooling and methane concentration differences was experimentally studied. Take a set of experiments as an example to illustrate the research method.

Fig. 12 shows the growth images of methane hydrate crystals on the shell substrate at different times under the conditions of  $\Delta C =$

$4.11\text{ mol}\cdot\text{L}^{-1}$  and  $\Delta T = 7.97\text{ K}$ . It could be seen from Fig. 12 that the growth of hydrate crystals changes significantly from 23 min to 81 min, and the length of the hydrate crystals does not increase significantly after growing to a certain extent. In the image shown at 223 min, the hydrate crystals change little and hardly grow, and the overall growth process is very slow. Columnar hydrates are mostly irregular prisms in shape, and there are dents on the crystal surface. This kind of crystal defects is conducive to the storage of solvent inclusions.

Fig. 12 shows the growth process of hydrate crystals at various time points. The hydrate growth rate could be calculated:

$$v_i = \frac{L_i}{t_i} \quad (4)$$

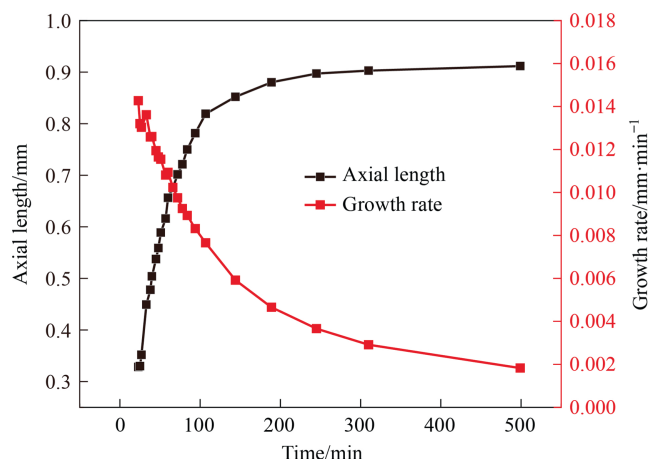


Fig. 13. The radial length and growth rate of columnar hydrate versus time at  $\Delta C = 4.11 \text{ mol}\cdot\text{L}^{-1}$  and  $\Delta T = 7.97 \text{ K}$ .

In Eq. (4),  $t_i$  represents the hydrate crystal growth time, min.  $L_i$  represents the axial length of the hydrate at time  $t_i$ , mm.

After processing the crystal growth images obtained in the experiment, the axial length of the columnar hydrate crystal and the growth rate with time under this condition ( $\Delta C = 4.11 \text{ mol}\cdot\text{L}^{-1}$ ,  $\Delta T = 7.97 \text{ K}$ ) was obtained, as shown in Fig. 13. It could be seen from the Fig. 13 that the maximum growth rate of columnar hydrate under this condition is  $0.0143 \text{ mm}\cdot\text{min}^{-1}$ . The growth rate decrease gradually over time. The reason could be explained as below: with the thickening of hydrate film, the mass transfer of methane gas is gradually restricted, therefore the growth rate of the hydrate axis length gradually decreases with time going. However, due to the porosity of the hydrate film, the mass transfer of methane gas is restricted but not prohibited, so the hydrate crystals continue grow until the driving force (concentration difference) no longer exists.

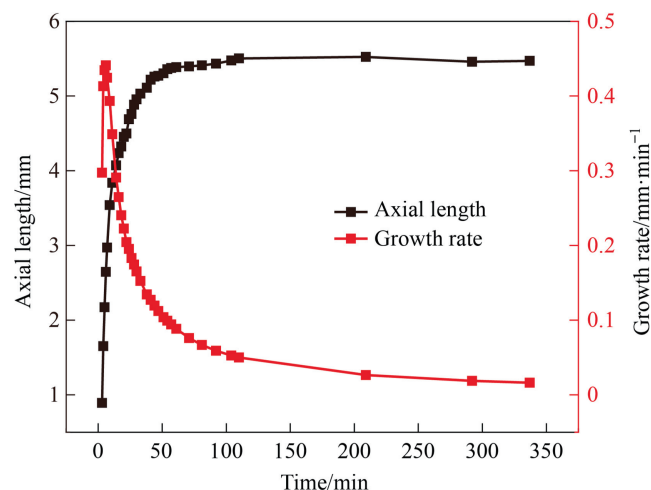


Fig. 15. Axial length and growth rate of dendritic hydrate with time when  $\Delta C = 5.55 \text{ mol}\cdot\text{L}^{-1}$  and  $\Delta T = 10.87 \text{ K}$ .

Compared with columnar hydrates, dendritic hydrates grow faster and produce more hydrates. When  $\Delta C = 5.55 \text{ mol}\cdot\text{L}^{-1}$  and  $\Delta T = 10.87 \text{ K}$ , after a period of induction time, a hydrate film is formed at the gas–liquid interface first. After the hydrate film covers the entire bubble, dendritic hydrates gradually formed on the shell substrate toward the liquid phase. Fig. 14 shows the growth of dendritic hydrate crystals at different times. It could be seen from Fig. 14 that the hydrate crystal length grows to 2 mm in 5 min, the growth rate is extremely fast. The hydrate crystal length reaches 5.0 mm in 33 min, and the growth rate decreases slowly until 292 min, the final length is close to 5.5 mm. Except the axial length, but hydrate crystals also grow in branches and leaves. The branches and leaves become thicker and stronger.

The method for calculating the growth rate of dendritic hydrate crystals is the same as that of columnar. The crystal growth images

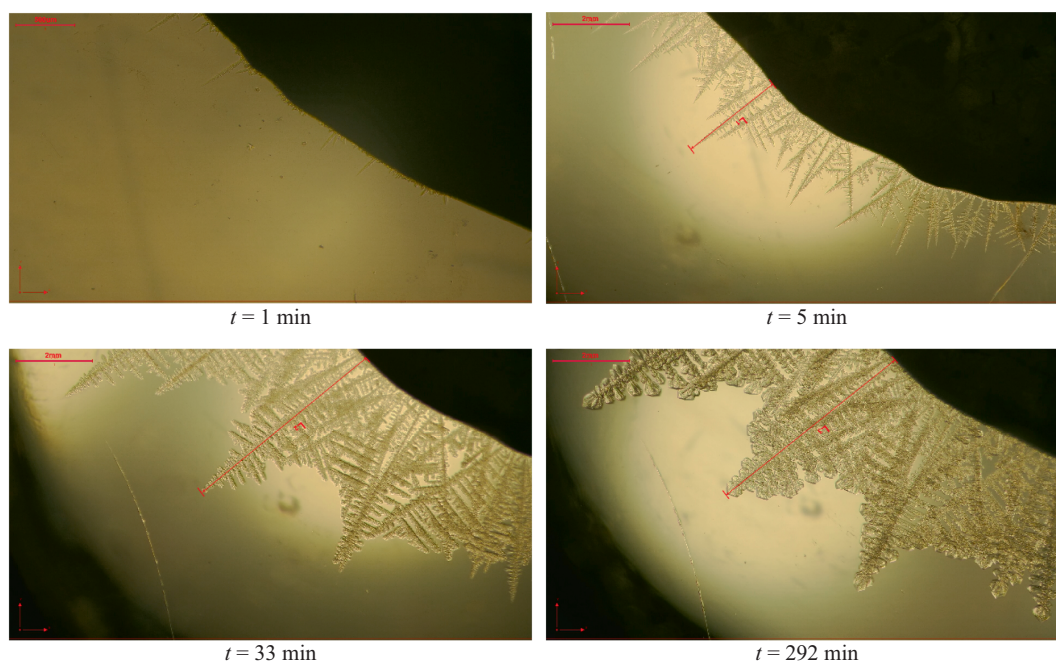


Fig. 14. The growth process of dendritic hydrate crystal on bubble surface under the conditions of  $\Delta T = 10.87 \text{ K}$  and  $\Delta C = 5.55 \text{ mol}\cdot\text{L}^{-1}$ . The given time is the starting time of hydrate crystal growth.



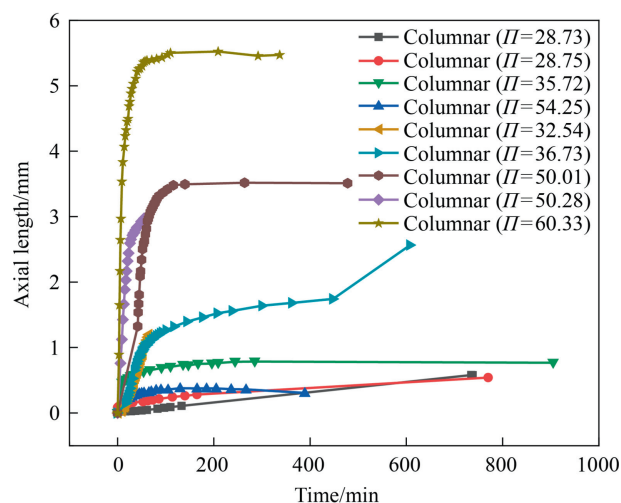


Fig. 16. Time dependence of radial growth of some experimental hydrate crystals.

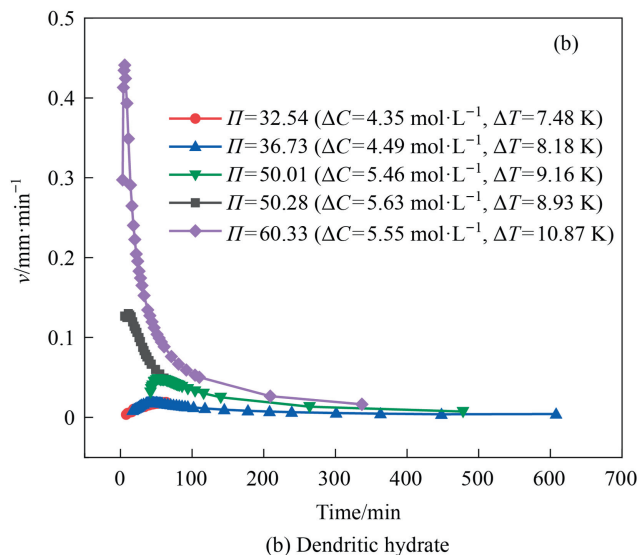
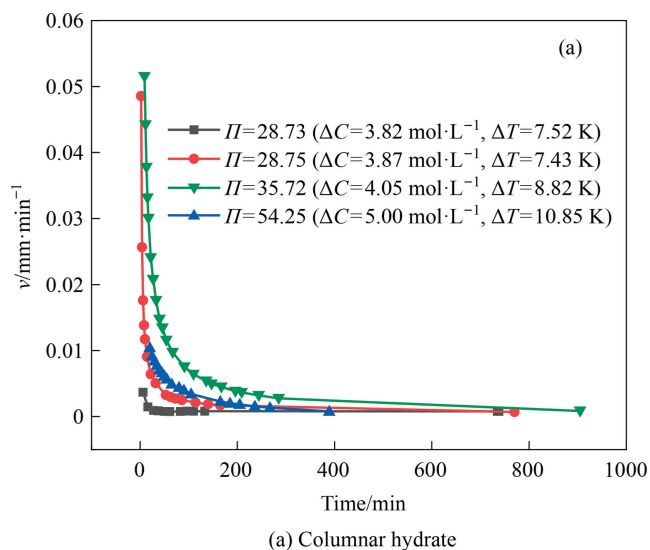


Fig. 17. Curve of growth rate of partial hydrate crystal with time.

obtained in the experiment are processed to obtain dendritic hydrate crystals growth rate. The length in the axial direction and the growth rate with time is shown in Fig. 15. It could be seen from Fig. 15 that the maximum growth rate of dendritic hydrate under this condition is  $0.4410 \text{ mm} \cdot \text{min}^{-1}$ . Compared with columnar hydrates, the growth of dendritic hydrate crystals is much faster, and the growth rate increases first and then decreases. The reason is that after the crystal grows to a certain length, with the progress of the hydration reaction, the hydrate film gradually thickens, the mass transfer of methane gas is gradually limited, and the crystal growth rate gradually decreases. However, because the hydrate film has certain pores, the mass transfer of methane gas is limited but not prohibited, so hydrate crystals will continue grow.

In this work,  $\Delta T$  and  $\Delta C$  are used as the controlling factors of crystal growth. let  $\Pi = \Delta T \times \Delta C$ , it could be seen from Fig. 16, generally speaking, the larger the  $\Pi$ , the longer the final length of the hydrate crystals, and generally dendritic hydrates are longer than columnar hydrates. Fig. 17 is a curve of the growth rate of partial hydrate crystals with time. The larger the  $\Pi$ , the faster the growth rate of hydrate crystals. Generally, the growth rate of dendritic hydrates is one order of magnitude higher than that of columnar hydrates. With the growth of hydrate crystals, the hydrate film gradually thickens, and the diffusion of methane gas from the bubbles to the liquid phase is gradually inhibited.

### 3.3. Fractal characteristics of hydrate crystals growth on the membrane substrate

Fractal growth refers to the growth following a certain self-similar law everywhere as time goes by, which is always carried out in a certain form that reflects the law of self-similarity, and the fractal dimension is constant during the growth process. The formation of snowflakes and the growth of branches in nature are both the process of generating certain fractal dimensions [20]. By observing the overall structure of methane hydrate dendrites (Fig. 18), it can be found that the entire growth process of methane hydrate has three main characteristics (Fig. 19): (1) There are branches on the main stem (hydrate axis), and the growth of the main stem and the branches proceed simultaneously (2) There are sub-branches growing on the branches (3) The growth is inhibited when the branch meets the main trunk or branch. The crystal growth is with typical self-similarity, which is the characteristics of fractal growth.

The hydrate crystal growth is a typical fractal growth-viscous finger extension process. Viscous finger extension refers that in a quasi-two-dimensional system, when a low-viscosity fluid enters into a high-viscosity fluid, the interface between the two fluids changes from a plane to an irregularly bifurcated interface. During hydrate crystal growth, methane supply might be the rate-determining step. The low-viscosity methane gas in bubble diffuses into the high-viscosity liquid phase, the methane transportation process could be equivalent to a quasi-two-dimensional system. Due to hydrate formation, the methane concentration in the liquid on crystal surface is equal to  $C_H$ , which is lower both than the methane solubility and the methane concentration in bubble  $C_{\text{bubble}}$ . Therefore, as long as hydrate crystal form in the liquid, methane gas can be continuously transported from the bubbles. The methane concentration difference between bubbles and crystal surface is equivalent to the external driving force of the viscosity index [23].

The growth dimension is exhibited by the growth speed and compaction degree of hydrate crystals at certain external conditions. In this work, the principle of perimeter-area method is used

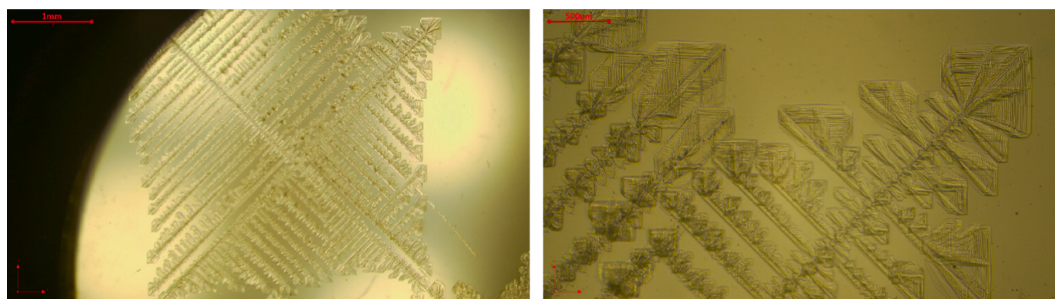


Fig. 18. Overall structure of hydrate dendrites.

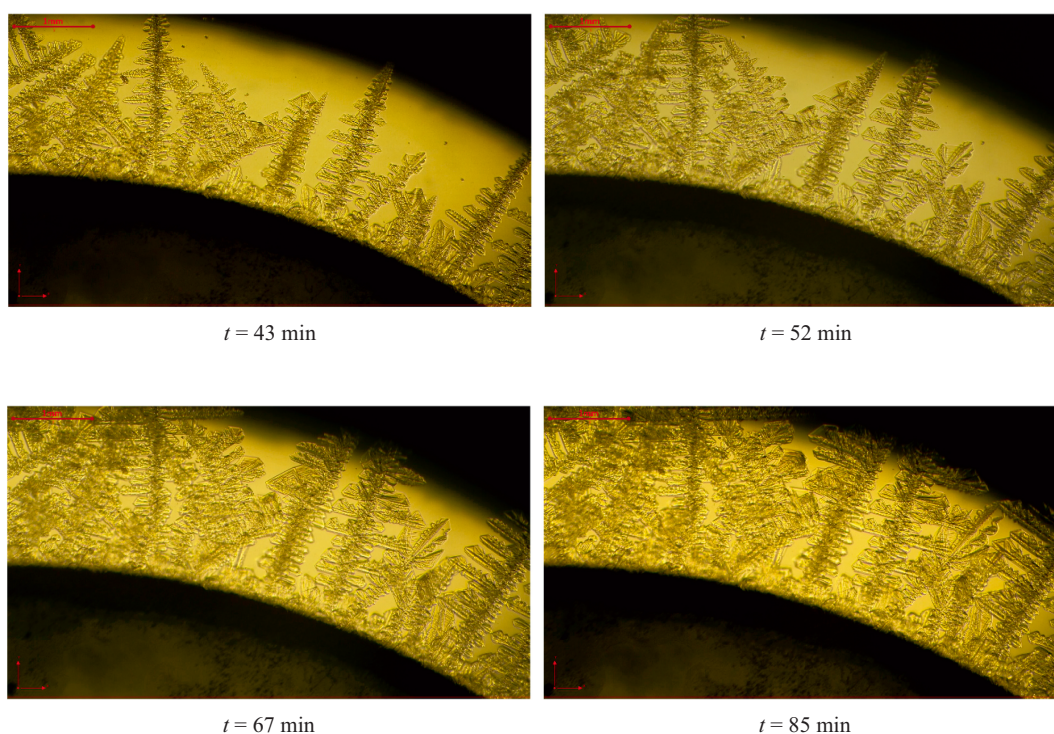


Fig. 19. Backbone and branches in hydrate crystal growth. The given time is the starting time of hydrate crystal growth.

to calculate the fractal dimension of the hydrate crystal morphology by using an ImageJ image analysis software [24]. The perimeter  $Pe$  and area  $A$  of the hydrate crystal was measured by ImageJ. In one experiment, the area  $A$  and perimeter  $Pe$  of different crystal branches was measured at different times. The perimeter and area data was plotted in double logarithmic and regressed in linear. Taking Fig. 20 as an example, by measuring the perimeter and area of different dendrites at different times under the same generation conditions, and Table 1 is obtained.

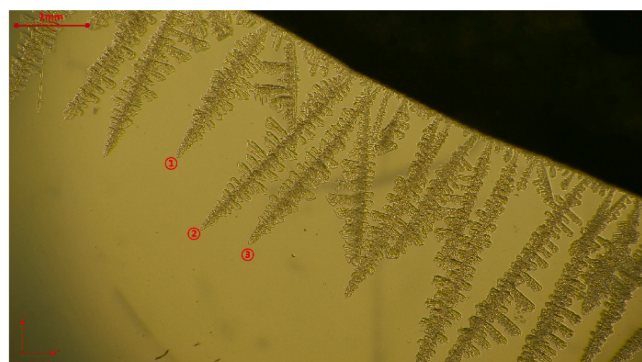
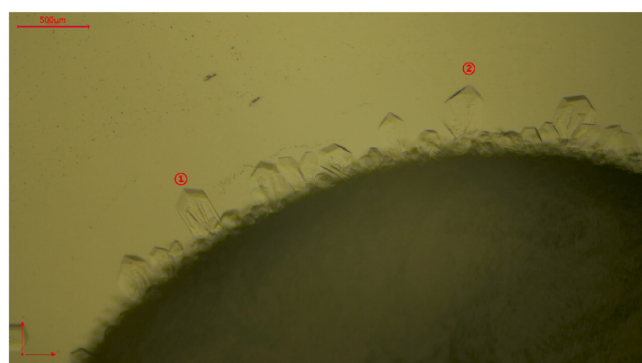
Fitting the  $\lg Pe$  and  $\lg A$  data in Table 1 to a straight line, the slope of the straight line could be obtained, and the fractal dimension of hydrate crystals is the twice of the slope of the regression line (Fig. 21). Under the conditions of  $\Delta C = 5.46 \text{ mol}\cdot\text{L}^{-1}$  and  $\Delta T = 9.16 \text{ K}$ , the slope of the fitted straight line is 1.041, then the fractal dimension of the dendritic hydrate crystal is 2.082. Under

the conditions of  $\Delta C = 4.05 \text{ mol}\cdot\text{L}^{-1}$  and  $\Delta T = 8.82 \text{ K}$ , the slope of the fitted straight line is 1.813, then the fractal dimension of the columnar hydrate crystal is 3.626.

A total of 18 sets of experiments were processed, and the fractal dimensions of hydrate crystals under various temperature and pressure conditions were obtained. The fractal dimension cloud maps under different temperature and pressure conditions is shown in Fig. 22. In the Fig. 22, Area I represents columnar hydrate, Area II represents dendritic hydrate, and the upper left part above the white dashed line is the theoretically unreachable area.

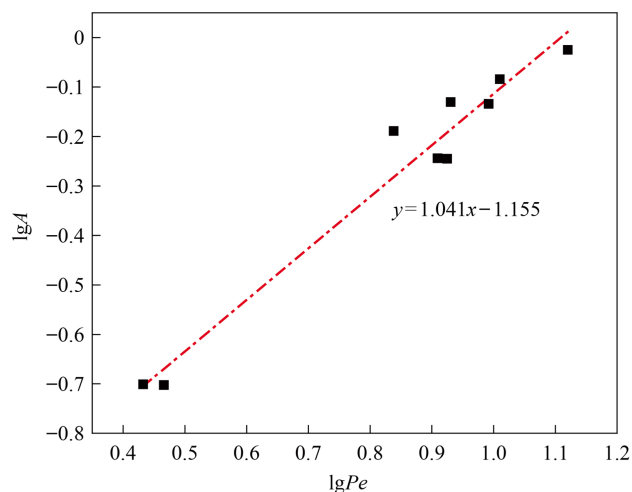
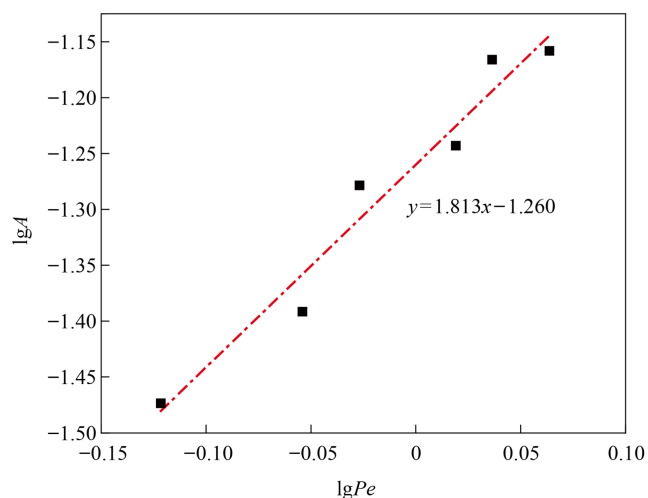
It could be seen from Fig. 22 that the fractal dimension margin between dendritic and columnar hydrate crystals is 3. The fractal dimension of columnar hydrate crystals is greater than 3, that is, area I. The edge of area I becomes darker inward. When



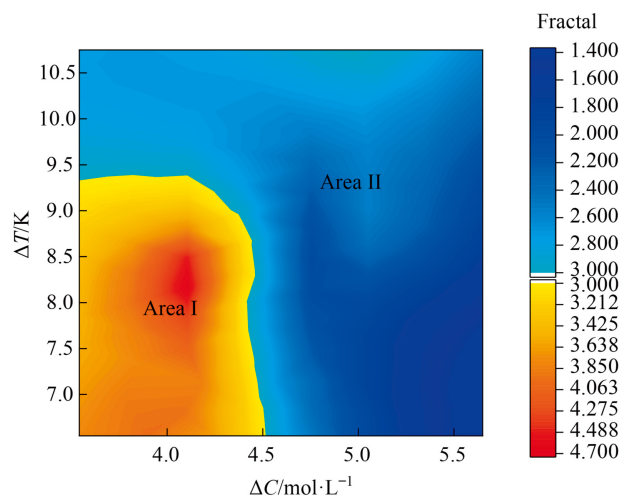
(a) Dendritic hydrate crystal at  $\Delta C = 5.46 \text{ mol}\cdot\text{L}^{-1}$  and  $\Delta T = 9.16 \text{ K}$ .(b) Columnar hydrate crystal at  $\Delta C = 4.05 \text{ mol}\cdot\text{L}^{-1}$  and  $\Delta T = 8.82 \text{ K}$ .**Fig. 20.** Hydrate crystals under different conditions.**Table 1**  
Hydrate crystal perimeter and area parameters

| Crystal perimeter and area parameters of dendritic hydrate at $\Delta C = 5.46 \text{ mol}\cdot\text{L}^{-1}$ and $\Delta T = 9.16 \text{ K}$ |          |                 |         |
|-----------------------------------------------------------------------------------------------------------------------------------------------|----------|-----------------|---------|
| $Pe/\text{mm}$                                                                                                                                | $\lg Pe$ | $A/\text{mm}^2$ | $\lg A$ |
| 2.71                                                                                                                                          | 0.4324   | 0.20            | -0.7012 |
| 2.92                                                                                                                                          | 0.4661   | 0.20            | -0.7027 |
| 8.41                                                                                                                                          | 0.9248   | 0.57            | -0.2451 |
| 9.82                                                                                                                                          | 0.9920   | 0.73            | -0.1340 |
| 13.19                                                                                                                                         | 1.1202   | 0.94            | -0.0250 |
| 6.89                                                                                                                                          | 0.8382   | 0.65            | -0.1890 |
| 8.11                                                                                                                                          | 0.9092   | 0.57            | -0.2439 |
| 8.52                                                                                                                                          | 0.9306   | 0.74            | -0.1304 |
| 10.23                                                                                                                                         | 1.0099   | 0.82            | -0.0844 |
| Crystal perimeter and area parameters of columnar hydrate at $\Delta C = 4.05 \text{ mol}\cdot\text{L}^{-1}$ and $\Delta T = 8.82 \text{ K}$  |          |                 |         |
| $Pe/\text{mm}$                                                                                                                                | $\lg Pe$ | $A/\text{mm}^2$ | $\lg A$ |
| 0.94                                                                                                                                          | -0.0268  | 0.05            | -1.2786 |
| 1.09                                                                                                                                          | 0.0364   | 0.07            | -1.1661 |
| 1.16                                                                                                                                          | 0.0637   | 0.07            | -1.1582 |
| 0.76                                                                                                                                          | -0.1215  | 0.03            | -1.4736 |
| 0.88                                                                                                                                          | -0.0540  | 0.04            | -1.3916 |
| 1.04                                                                                                                                          | 0.0191   | 0.06            | -1.2430 |

$3.87 \text{ mol}\cdot\text{L}^{-1} < \Delta C < 4.20 \text{ mol}\cdot\text{L}^{-1}$ ,  $7.4 \text{ K} < \Delta T < 8.8 \text{ K}$ , the fractal dimension of columnar hydrate is greater than 4. The fractal dimension of dendritic hydrate crystals is less than 3, that is, area II. On the whole, the smaller the  $\Delta T$  and the larger the  $\Delta C$ , the deeper the blue and the smaller the fractal dimension. When

(a) Dendritic hydrate crystals at  $\Delta C = 5.46 \text{ mol}\cdot\text{L}^{-1}$  and  $\Delta T = 9.16 \text{ K}$ (b) Columnar hydrate crystals at  $\Delta C = 4.05 \text{ mol}\cdot\text{L}^{-1}$  and  $\Delta T = 8.82 \text{ K}$ **Fig. 21.** Relationship between  $\lg A$  and  $\lg Pe$  in hydrate crystals.

$4.77 \text{ mol}\cdot\text{L}^{-1} < \Delta C$  and  $\Delta T < 8.52 \text{ K}$ , the fractal dimension of dendritic hydrate is less than 2.

**Fig. 22.** Fractal dimensions of methane hydrate crystals under different  $\Delta C$  and  $\Delta T$  conditions.

#### 4. Conclusions

The growth process of methane hydrate crystals on the shell substrate was experimentally studied, main conclusions could be draw as follows:

- (1) The hydrate film on the surface of methane bubbles in water could be formed in two ways. One is the spontaneous nucleation and growth after a certain induction period. The other one is the rapid growth triggered by the external crystal seeding. The hydrate film is porous.
- (2) Hydrate crystals grow towards the liquid phase on the shell substrate. The hydrate crystal morphology on the shell substrate could be divided into two types. One is a dendritic with a main axis, the other one is a columnar shape without a spindle. The subcooling  $\Delta T$  and the methane concentration difference  $\Delta C$  are the major factors that determine the morphology of hydrate crystals. When  $\Delta T < 8.82$  K and  $\Delta C < 4.12$  mol·L<sup>-1</sup>, hydrate crystals grow in columnar shape. When  $\Delta T > 8.82$  K or  $\Delta C > 4.12$  mol·L<sup>-1</sup>, hydrate crystals grow in a dendritic shape.
- (3) During hydrate crystals growth, methane gas in nearby bubbles is consumed, causing the bubbles to shrink and disappear. The growth rate of dendritic hydrates accelerates first and then slows down, the growth rate of columnar hydrate gradually slows down. The larger the product of subcooling  $\Delta T$  and methane concentration difference  $\Delta C$ , the faster the growth of hydrate crystals. The growth rate of dendritic hydrate is an order of magnitude higher than that of columnar hydrate.
- (4) In addition to the dendritic and columnar hydrates on the shell substrate, independent hydrate crystals could also formed in the liquid phase. The edges of the individual crystals are regular, with the characteristics of dendritic and columnar hydrate crystals. There are dents on the surface of the crystals.
- (5) The growth of hydrate crystals has self-similarity and shows the characteristics of fractal growth. The fractal dimension of columnar hydrate is greater than 3, when  $3.87$  mol·L<sup>-1</sup>  $< \Delta C < 4.20$  mol·L<sup>-1</sup> and  $7.4$  K  $< \Delta T < 8.8$  K, the fractal dimension of columnar hydrate is greater than 4. The fractal dimension of dendritic hydrate is less than 3, When  $4.77$  mol·L<sup>-1</sup>  $< \Delta C$  and  $\Delta T < 8.52$  K, the fractal dimension of dendritic hydrate is less than 2.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Nomenclature

|                     |                                                                                |
|---------------------|--------------------------------------------------------------------------------|
| $A$                 | area, mm <sup>2</sup>                                                          |
| $C_{\text{bubble}}$ | concentration of methane in the bubble, mol·L <sup>-1</sup>                    |
| $C_{\text{H}}$      | solubility of methane in water in the presence of hydrate, mol·L <sup>-1</sup> |
| $\Delta C$          | concentration difference of methane, mol·L <sup>-1</sup>                       |
| $L_i$               | axial length of the hydrate crystal at time $t_i$ , mm                         |
| $P$                 | pressure, MPa                                                                  |

|                  |                                                                  |
|------------------|------------------------------------------------------------------|
| $Pe$             | perimeter, mm                                                    |
| $T$              | temperature, °C                                                  |
| $T_{\text{eq}}$  | temperature of the hydrate phase equilibrium, K                  |
| $T_{\text{exp}}$ | temperature of the experimental temperature, K                   |
| $\Delta T$       | subcooling, K                                                    |
| $t$              | time                                                             |
| $t_i$            | time of hydrate crystal growth, min                              |
| $u_i$            | hydrate growth rate at time $t_i$ , mm·min <sup>-1</sup>         |
| $\Pi$            | the product of $\Delta T$ and $\Delta C$ , K·mol·L <sup>-1</sup> |

#### References

- [1] G.J. Chen, C.Y. Sun, Q.L. Ma, Gas Hydrate Science and Technology, Chemical Industry Press Co., Ltd., Beijing, 2008 (in Chinese).
- [2] E.D. Sloan, C.A. Koh, Clathrate Hydrates of Natural Gases, third ed., CRC Press, Boca Raton, 2007.
- [3] R. Tanaka, R. Sakemoto, R. Ohmura, Crystal growth of clathrate hydrates formed at the interface of liquid water and gaseous methane, ethane, or propane: Variations in crystal morphology, *Cryst. Growth Des.* 9 (5) (2009) 2529–2536.
- [4] C.X. Cheng, Y.J. Tian, F. Wang, X.H. Wu, J.L. Zheng, J. Zhang, L.W. Li, P.L. Yang, Experimental Study on the Morphology and Memory Effect of Methane Hydrate Reformation, *Energy Fuels* 33 (4) (2019) 3439–3447.
- [5] R. Ohmura, S. Matsuda, T. Uchida, T. Ebinuma, H. Narita, Clathrate hydrate crystal growth in liquid water saturated with a guest substance: Observations in a methane + water system, *Cryst. Growth Des.* 5 (3) (2005) 953–957.
- [6] I.V. Melikhov, Y.F. Makogon, E.F. Simonov, V.E. Bozhevol'nov, Motion of Agglomerates on the Surface in the Formation of Methane Hydrate Crystals, *Russian J. Phys. Chem. A* 81 (8) (2007) 1307–1313.
- [7] E.M. Freer, M.S. Selim, E.D. Sloan Jr., Methane hydrate film growth kinetics, *Fluid Phase Equilibria* 185 (1–2) (2001) 65–75.
- [8] S.L. Li, C.Y. Sun, B. Liu, Z.Y. Li, G.J. Chen, A.K. Sum, New observations and insights into the morphology and growth kinetics of hydrate films, *Sci. Rep.* 4 (2014) 4129.
- [9] J.D. Lee, M. Song, R. Susilo, P. Englezos, Dynamics of Methane–Propane clathrate hydrate crystal growth from liquid water with or without the presence of n-heptane, *Cryst. Growth Des.* 6 (6) (2006) 1428–1439.
- [10] K. Ozawa, R. Ohmura, Crystal growth of clathrate hydrate with methane plus partially water soluble large-molecule guest compound, *Cryst. Growth Des.* 19 (3) (2019) 1689–1694.
- [11] H. Hayama, M. Mitarai, H. Mori, J. Verrett, P. Servio, R. Ohmura, Surfactant effects on crystal growth dynamics and crystal morphology of methane hydrate formed at gas/liquid interface, *Cryst. Growth Des.* 16 (10) (2016) 6084–6088.
- [12] H.P. Veluswamy, A.J.H. Wong, P. Babu, R. Kumar, S. Kulprathipanja, P. Rangsunvigit, P. Linga, Rapid methane hydrate formation to develop a cost effective large scale energy storage system, *Chem. Eng. J.* 290 (2016) 161–173.
- [13] H.P. Veluswamy, Q.W. Hong, P. Linga, Morphology study of methane hydrate formation and dissociation in the presence of amino acid, *Cryst. Growth Des.* 16 (10) (2016) 5932–5945.
- [14] S.M.T. Hussain, A. Kumar, S. Laik, A. Mandal, I. Ahmad, Study of the kinetics and morphology of gas hydrate formation, *Chem. Eng. Technol.* 29 (8) (2006) 937–943.
- [15] R. Ohmura, W. Shimada, T. Uchida, Y.H. Mori, S. Takeya, J. Nagao, H. Minagawa, T. Ebinuma, H. Narita, Clathrate hydrate crystal growth in liquid water saturated with a hydrate-forming substance: Variations in crystal morphology, *Philos. Mag.* 84 (1) (2004) 1–16.
- [16] K. Saito, M. Kishimoto, R. Tanaka, R. Ohmura, Crystal growth of clathrate hydrate at the interface between hydrocarbon gases mixture and liquid water, *Cryst. Growth Des.* 11 (1) (2011) 295–301.
- [17] X. Huang, Y.J. Deng, Z.C. Li, W.J. Cai, L.J. Gu, H.L. Lu, Study of THF Hydrate Crystallization Based on in Situ Observation with Atomic Force Microscopy, *Cryst. Growth Design* 20 (5) (2020) 2921–2929.
- [18] W.C. Wang, S. Liu, X.Y. Wang, Y.X. Li, G.C. Song, S.P. Yao, Experimental study on the formation and agglomeration of tetrahydrofuran hydrate under flowing condition, *Int. J. Refrig.* 118 (2020) 504–513.
- [19] Z. Li, D.L. Zhong, W.Y. Zheng, J. Yan, Y.Y. Lu, D.T. Yi, Morphology and Kinetic Investigation of TBAB/TBPP Semiclathrate Hydrates Formed with a CO<sub>2</sub> + CH<sub>4</sub> Gas Mixture, *J. Cryst. Growth* 511 (2019) 79–88.
- [20] Y.L. Zhao, Formation process and fractal growth model of HCFC-141b refrigerant gas hydrate, *Sci. China Ser. B* 45 (2) (2002) 216.
- [21] W.J. Ou, W.J. Lu, F.L. Ning, X.G. Wu, Measurement of methane solubility in pure water in equilibrium with hydrate by using high-pressure optical capillary cell, *Mar. Chem.* 212 (MAY 20) (2019) 74–82.
- [22] S.L. Li, C.Y. Sun, B. Liu, X.J. Feng, F.G. Li, L.T. Chen, G.J. Chen, Initial thickness measurements and insights into crystal growth of methane hydrate film, *AIChE J.* 59 (6) (2013) 2145–2154.
- [23] T. Vicsek, H. Gould, Fractal Growth Phenomena, second ed., World Scientific, Singapore, 1992.
- [24] Z.X. Xiong, Fractal Study of Ceramic Materials, Science Press Co., Ltd., Beijing, 2000. (in Chinese).