Changes in Physical Properties of Hydrate Deposit during Hydrate Formation and Dissociation

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Abstract. The microscopic distribution pattern of hydrates in pores is closely related to the accuracy of seismic data and acoustic data in the exploration of hydrate resources, and has important influence on the permeability and mechanical stability of reservoirs during mining. This study performed macro-micro experiments of tetrahydrofuran (THF) hydrate formation and dissociation in solution and pore space. Dissociation characteristics of pore hydrate with different saturation and distribution pattern were observed, 2D and 3D models were built, fluid and quartz particle migration, channel blockage and reformation were captured and analysed. Results demonstrated that, as the concentration of THF in the solution increases from 19%, 24% to 29%, the main distribution pattern of the hydrate formed in the pores gradually changes from pore filling, particle cementation to skeleton supporting, while the dissociation behaviour of pore hydrate mainly happened at the pore filled area, particle surface and the particle connection area. As the saturation increases, the amount of water generated by dissociation increases, the more obvious the water migration, the greater the impact on the stability of the particles, and the more the formation of channels and blockages. During field methane recovery, controlling the dissociation rate of hydrates and fluid migration rate are helpful to maintain reservoir mechanical stability. Therefore, when temperature and pressure conditions are relatively stable, increasing the drainage channel can effectively reduce the turbulent oscillation, the impact on particle stability and blockage of sand production channel.

Keywords. Gas hydrate bearing sediment; physical properties; pore hydrate; distribution pattern; microscopic pore structure.

1. Introduction
From the first discovery of natural hydrates to Deep Sea Drilling Project (DSDP) [1], Ocean Drilling Program (ODP) [2], and Integrated Ocean Drilling Program (IODP) [3], hydrates have been extensively researched and explored by human beings, which include resource census and exploration, borehole mining, gas recovery, and gas transportation and flow protection [4-6].
The distribution pattern of hydrates has an important influence on the permeability of reservoirs during the mining process and the mechanical stability of nearby formations [7-10]. As the hydrate saturation changes, there will be some changes and transitions between the distribution patterns. During the dissociation of hydrates, the hydrates of different distribution modes cause different macroscopic changes in porosity, permeability and mechanical strength during the dissociation process [7, 11], which have an important impact on the safe and rapid exploitation of hydrate reservoirs, and have gradually become the key to hydrate research [4, 12]. Therefore, research on macroscopic physical properties and microscopic distribution patterns changes during gas hydrate dissociation is indispensable.

This paper first through the self-designed simple hydrate formation device, using different concentrations of THF aqueous solution to form pore hydrates of different distribution patterns, the temperature and resistance changes were monitored to analyze the process of hydrate formation. Then, the drilling sampling was simulated and operated, the samples were heated and laser scanned to observe the thermal dissociation characteristics of the hydrates with different distribution patterns in the pores, and the three-dimensional structure of the local pores before and after the dissociation was measured. This is an important guiding role in exploring the microscopic distribution patterns and dissociation characteristics of hydrates in pores, mastering the migration laws of fluids during heating and mining, and selecting suitable mining processes.

2. Experimental Methods
The experimental process mainly includes the formation of hydrate, the sampling of hydrate bearing sediments and the observation of pore hydrate dissociation, instruments are shown in figure 1, mainly include: VK-X100/200 laser measuring microscope system (Keyence Corporation, Osaka, Japan), temperature collector (Toprie TP700 data collector, Toprie Electronics Co., Ltd., Shenzhen, China), digital bridge (Tonghui TH2817B LCR, Tonghui Electronics Co., Ltd., Changzhou, China), heating sheet, micro sampling tool and self-designed hydrate formation device.

The self-designed hydrate formation device has an inner diameter of 25 mm and an inner height of 70 mm, mainly composed of upper and lower copper electrodes and glass tube. The seal between the lower electrode and the glass tube is achieved by the sealant. No instrument material reacts with reactants. Temperature at 3 points are measured by the temperature collector, the resistance of the whole sediment is measured by the digital bridge.

Experimental materials mainly include natural quartz sand (obtained from Baicheng Beach of Xiamen City, China), natural sodium bentonite (Wuhan Deawon Trenchless Technology Co., LTD, Wuhan, China), tetrahydrofuran solution (99%, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China), sodium chloride powder and distilled water.

**Figure 1.** Schematic of experimental instruments.
3. Results and Discussion

3.1. Temperature and Resistance Changes in the Formation of THF Hydrate in Pore Space and Solution

The temperature and resistance curves over time in the sediment pores with concentration of 19%, 24% and 29% THF solutions forming hydrates are shown in figures 2 and 3. The initial temperature of the three concentrations of solution was 23.8°C, and the initial resistance were 2.1 kΩ, 2.74 kΩ, and 3.7 kΩ, respectively. As the temperature of the solution decreases, the electrical resistance of the deposit gradually increases. When the time is about 12 minutes (point O), the rate of temperature decreased and the rate of increase of resistance value begin to decrease gradually. When the time is 25 minutes (point A), the resistance value begins to decrease rapidly and the temperature decrease rate reduced obviously. The comprehensive analysis of point O and point A can judge the formation of hydrate from point A. The increase of resistance of OA segment is mainly affected by temperature. With the decrease of temperature, the conductivity of sediment decreases and the resistance value increases, the temperature at which the hydrate starts to form is about 6.5°C, which is significantly higher than the phase equilibrium temperature of the hydrate in the THF solution, indicating that the formation of hydrates in the pores of the sediment is easier, the main reason is that the sediment component has the effect of promoting the formation of THF hydrate, and is mainly affected by the porous bentonite [13].

After point A, the resistance of the AB segment decreases rapidly, and the rate of temperature decrease is significantly reduced, indicating that the hydrate is rapidly formed and is constantly exothermic. The change trend of the resistance in this process is opposite to the change trend of the resistance in the pure solution (figures 4 and 5), and the decrease is rapid. The main reason is that the THF rapidly consumes the extremely poor conductivity of THF, which enhances the conductivity of the solution and thus the resistance is rapidly reduced. Besides, there is no obvious temperature increase in the formation of hydrates in the pores of the sediment, and there is slight fluctuation in the formation of hydrates only in 29% of the solution (red circle in figure 4), mainly because the amount of hydrate formed in the pores is much less than in the solution. The BC segment is a continuous formation stage of hydrates, the temperature is gently reduced, the resistance value fluctuates drastically, and the pores and throats are blocked by the formation of hydrates, which affects the connectivity of the solution. After point C, the temperature remains unchanged, and the resistance value is also stable. Only the resistance value of the 29% THF solution fluctuates, which can be explained by the migration of water and THF solution. At this time, the formation of hydrate can be considered to be basically finished. The final temperature was maintained at around 4.3°C and the resistance values were maintained at 2.65 kΩ, 2.95 kΩ, and 3.96 kΩ, respectively.

To sum up, the formation process of hydrate in THF solution is in good agreement with the phase equilibrium curve, and the concentration has a great influence on the resistance of hydrate formation. In the rapid formation stage of hydrate, the temperature variation range in different concentration solutions is significantly different. The phase equilibrium curve of hydrate in sediment pores is affected by bentonite and porous conditions, and the phase equilibrium temperature is shifted by about 1.1°C. At the same time, the effect of concentration on the resistance value during hydrate formation is also obvious, but it has no obvious effect on the temperature variation. There is a difference between the formation process of hydrates in sediment pores and in solution. Although the amount of hydrate formation in sediments is much less than that of pure solution, the formation process of hydrates in core pores also undergoes slow generation period, rapid generation period, growth stagnation period and pore water migration, the hydrate formation is good and can be used for subsequent observation experiments.
3.2. Dissociation Characteristics of Hydrates in Pore and the Influence on Pore Passage

The hydrate bearing sediment in the THF hydrate formation device was taken out by the sampling tool and placed on mesh workbench of the laser measuring microscope system, the hydrate distribution and dissociation process were observed by the laser scanning. 2D and 3D maps of the pores were measured and reconstructed. The results are shown in figures 6-8, the pore maps of the hydrates formed in the pores of the sediments corresponding to 19%, 24% and 29%.

In figure 6, the different colors represent different elevations. The red circle, white circle and black circle are respectively the hydrate filled in the pore, on the surface of the quartz particle and hydrate between the two adjacent quartz particles, the blue circle area whose color gradually deepens is the pore channel, while the blue circle area with more uniform color is the water surface of the pore water. From the pore hydrate distribution map before and after dissociation, it can be intuitively found that the pore-
filled hydrate in the red circle decomposes after heating and is obvious, and there is also a certain amount of hydrate dissociation in the white circle, and the hydrate decomposed in the black circle. The amount is not much, and the overall saturation of the hydrate is small. At the same time, the range of the pore water after dissociation is also increased before the dissociation, and the height difference of the three-dimensional map in the two processes before and after is decreased by 6.9 μm, which can be regarded as the thickness of the hydrate which is decomposed on the surface of the particle.

Figure 6. Pore structure of hydrate bearing sediment formed by 19% THF solution. (a) 2D, before dissociation; (b) 3D, before dissociation; (c) 2D, after dissociation; (d) 3D, after dissociation.

Figure 7 shows the dissociation of the pore hydrate formed by the THF solution in a concentration of 24%. It can be found that the particle diameter is much smaller than the diameter of the particles in figure 6, this is because the sediments used quartz sand particles with good grain size gradation during the preparation process. Comparing the two-dimensional and the three-dimensional map, it can be found that the saturation of the hydrate in figure 7 is significantly greater than the hydrate saturation in figure 6. At the same time, it can be intuitively found that a large amount of hydrates in the pores are decomposed, including hydrates in the middle of the pores, between adjacent particles, and on the surface of the particles. The red circle and the black circle show a large amount of hydrate dissociation. According to the three-dimensional map, it can be clearly found that the elevation difference between adjacent particles is more obvious after dissociation, indicating that the adjacent particles are mainly in the heating process. The hydrate between them decomposes, the amount and degree of dissociation of hydrate in figure 7 is
significantly increased relative to the dissociation of the pore intermediate hydrate in figure 6, and mainly occurs between adjacent particles.

**Figure 7.** Pore structure of hydrate bearing sediment formed by 24% THF solution. (a) 2D, before dissociation; (b) 3D, before dissociation; (c) 2D, after dissociation; (d) 3D, after dissociation.

In addition, it can be seen that there is a significant change in the blue region. From the previous analysis, it is known that the blue circle region where the color gradually deepens is the pore channel, and the color is more uniform is the pore water surface. The area indicated by the arrow in figure 7a is the pore water channel in circulation. After the dissociation occurs, it becomes a pore-water surface with uniform color, indicating that the original pore channel is blocked, and the water generated by the dissociation is not immediately transported out. The reason for the blockage is mainly caused by the movement of quartz particles or bentonite. The decrease of cohesion is the main reason for the looseness of the particles. Due to the small grain size of the sand, the quartz particles and bentonite migrated under the movement of a large amount of water generated by the dissociation. On the contrary, the area indicated by the arrow in figure 7c is mainly the pore water surface before the dissociation occurs, and a large number of pore channels appear after dissociation, indicating that the quartz particles and bentonite are loosened and transported with pore water to form pores, or the dissociation of the hydrate in the pores allows the pore channels to pass through. At the same time, it can be determined that the pore channel is larger and the aqueous solution transport speed is faster. The elevation difference of the three-dimensional map before and after dissociation is 25.5 μm, which is larger than the elevation difference in figure 6.
Figure 8. Pore structure of hydrate bearing sediment formed by 29% tetrahydrofuran solution. (a) 2D, before dissociation; (b) 3D, before dissociation; (c) 2D, after dissociation; (d) 3D, after dissociation.

Figure 8 shows the before and after dissociation of the pore hydrate formed by a 29% THF solution. The elevation difference of the three-dimensional map before and after dissociation is 396.1 μm, which is much larger than the elevation difference in figure 7, indicating that the dissociation amount of the hydrate is large. Also, due to the large grain size of the observation zone, a larger pore structure is formed. The saturation of the hydrate in figure 8 is higher relative to figure 7. It can be clearly seen from the comparison before and after the dissociation that in figure 8, the large amount of hydrate between the particle surface and the adjacent particles is decomposed, and in figure 7 is mainly the dissociation of the hydrate between the adjacent particles. The white circle area has obvious changes before and after dissociation. According to the three-dimensional pore map, the main reason for the color change is the dissociation of the hydrate on the surface of the particle. Before the dissociation, the difference in elevation between the particles is large, and the dissociation produces a large amount of water, which is filled into the pores between the particles, and the channel is small, and the generated water is not quickly migrated, so that there is a large amount of pore water between the particles, resulting in a decrease in the elevation difference after dissociation.

It is worth noticing that the large area of the blue area in figure 8c is mainly pore water, and there is no obvious phenomenon of pore blockage and formation of new pores. Compared with figure 7, the grain size and hydrate saturation of the observation area in figure 8 are large, and a large amount of water is
generated without causing more obvious particle migration, thereby indicating that the particles having a smaller grain size are decomposed by the hydrate. The effect of pore water migration is more pronounced, resulting in a significant decrease in bond strength and migration.

It can be seen that the dissociation of the hydrate reduces the bond strength between the particles and has a greater influence on the bond strength between the sand particles having a smaller particle size. At the same time, the dissociation of high-saturation hydrate has a greater influence on the mechanical strength of the core than the dissociation of low-saturation hydrate. Relative to the particle surface and pore intermediate hydrate, when the hydrates which act as bonding between adjacent particles decompose, the influence on the mechanical strength of the core is most obvious, the particles are easy to loosen and move, and the particles and bentonite are driven and washed under the pore water migration, blocking the pores, so that the water produced by the dissociation cannot be immediately discharged. Therefore, in the actual hydrate formation mining process, when the temperature and pressure conditions are relatively stable, the reservoir drainage channel can be appropriately increased to reduce the turbulent oscillation caused by water and gas migration, reduce the impact on the particles and reduce the sand production. Blockage of the passage helps maintain the mechanical stability of the well wall. In addition, the gas production rate and immediate drainage should be strictly controlled to prevent safety problems caused by excessive loss of mechanical strength of the hydrate formation.

4. Conclusions
The microscopic distribution pattern of hydrates in pores is closely related to the accuracy of seismic data and acoustic data in the exploration of hydrate resources, and has an important influence on the permeability and mechanical stability of reservoirs during methane recovery. In this paper, 2D and 3D maps of hydrate bearing pores were reconstructed in simple way, changes in macroscopic and microscopic physical properties of simulated marine sediment during hydrate formation and dissociation were studied.

As the concentration of THF in the solution increases, the saturation of the formed hydrate in the pores increases, and the distribution pattern is gradually shifted from the pore filling, particle cementation to the skeleton supporting. The dissociation of pore hydrate reduces the cohesion between the particles, accompanied by fluid formation, while the influence degree depends on the distribution pattern of the hydrate. Decreased cohesion and water migration will cause the movement of quartz particles, resulting in blockage of pore channels.

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