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Fractal Analysis on Methane Hydrate Formation in Porous Media

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Abstract: The study of the hydrate formation process in porous media is of great significance for hydrate application. In this work, the formation process of methane hydrate in porous media was monitored in situ by a low-field magnetic resonance imaging (MRI) system. The formation characteristics of methane hydrate in porous media and the change of fractal dimension of pore space were studied through the change of residual water saturation and T_2 relaxation time distribution. The experimental results show that the hydrate formation process is divided into two stages: fast and slow. During the formation process, the water in the pores is continuously consumed and transformed into hydrate, and the overall T_2 distribution gradually shifts to the left. In the formation process of hydrate, the pore space becomes more complex, the change of fractal dimension from top to bottom of the reactor gradually increases, and the hydrate formation rate also gradually increases.

Keywords: MRI experiment; Water saturation; Fractal dimension

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1. Introduction

Gas hydrates are cage-type compounds formed at low temperatures and high pressures [1]. There are three known structures of hydrate crystals: structure SI, structure SII, and structure SH. Smaller guest molecules such as methane, carbon dioxide, hydrogen, etc., generally form SI hydrates. As a new type of phase change material, hydrates have an extensive range of applications, such as CO_2 capture [2], gas storage and transportation [3], seawater desalination [4], refrigeration, and air conditioning [5]. It is of great significance to study the formation process of hydrates in porous media for the application of hydrates.

The formation of hydrates in porous media is a complex phase transformation process, and the change of gas-liquid distribution in the pores will affect the formation rate of hydrates. The changes of liquid in the pores during the hydrate phase transition can be monitored by MRI technology, which can more intuitively observe the hydrate formation process. Shakerian *et al.* [6] used MRI technology to study the formation process of gas hydrate in metal core holders and studied the formation rate of hydrate through the change of T_1 and T_2 relaxation time. Zhang *et al.* [7] visualized the change of water saturation during the phase transition of methane hydrate through low-field nuclear magnetic resonance experiments and found that the spatial distribution of gas-water-hydrate during the phase transition of hydrate was not uniform over time. Zhao *et al.* [8] used MRI technology to monitor the formation and decomposition of CO_2 hydrate in porous media in situ, evaluated the phase transition process of hydrate through the change of fractal dimension, and analyzed the variation of liquid distribution in porous media with time during the phase transition.

It is of great significance to study the microstructure changes of hydrate in porous media for understanding the formation characteristics of hydrate. In this paper, a low-field MRI system is used to visually monitor the formation process of hydrate in porous media, and water saturation, T_2 relaxation time, and fractal dimension changes are used to study the formation rule, spatial structure change, and formation rate of hydrate in pore space.

2. Experiment

2.1. Experimental apparatus

The experimental system is shown in **Figure 1**. The reactor is made of self-made non-magnetic polyimide with a length of 50 mm and a diameter of 25 mm. 80-120 mesh quartz sand was used to simulate the porous media environment. The gas cylinder contains 99.9% pure methane, and the gas is injected into the reactor with an air pump. Deionized water is injected using a high-pressure syringe pump. The temperature of the whole system is controlled by a heated circulator, and the temperature-controlled circulating fluid is a fluorine-containing inert liquid that does not contain ^1H atoms and does not interfere with the ^1H MRI signal in the reaction mixture in the fluid state. A temperature sensor with an accuracy of 0.1°C is inserted vertically into the reactor to monitor the temperature in the reactor in real time. The gas pressure controls the pressure in the reactor, and the constant pressure function of the high-pressure syringe pump is used to keep the whole system at a constant pressure. MRI measurements are performed on a benchtop MRI system running at 12.74 MHz with a uniaxial pulsed field gradient. A series of 1D DHK SPRITE profiles and T_2 relaxation time distributions were obtained in successive cycles using advanced GIT software.

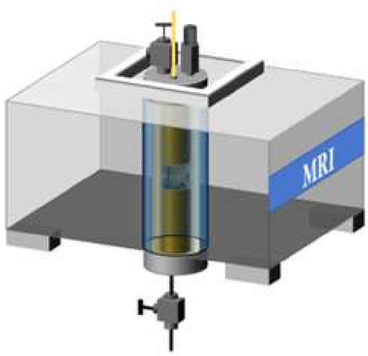

Figure 1. Schematic diagram of the experimental apparatus

2.2. Experimental procedure

Before starting the experiment, connect the pipelines, inject nitrogen to pressurize the reactor and all connected valves, and maintain a pressure of 6 MPa for 12 h for leak detection. The quartz sand is compacted in the reactor, placed vertically in the center of the nuclear magnetic field, and connected to the entire line. The vacuum pump is used to draw the gas out of the reactor. A high-pressure syringe pump is used to inject deionized water into the reactor to completely saturate the pores. CH_4 gas is injected into the reactor with a high-pressure syringe pump to drain part of the free water until the desired initial residual water saturation is reached. CH_4 gas is continuously injected into the sample tube to achieve the desired pressure of 4 MPa and a constant pressure is controlled. Ethylene glycol was used to cool the solution, and the temperature of the whole system was controlled at 273.65 K, and then the hydrate generation experiment began.

2.3. Calculation of fractal dimension

The T_2 relaxation rates of pore fluids include T_2 free relaxation, T_2 surface relaxation, and T_2 diffusion relaxation. In this experiment, the effects of T_2 free relaxation and T_2 diffusion relaxation are negligible, so the relaxation rate of the pore fluid can be expressed in terms of T_2 surface relaxation:

$$T_2 = \frac{1}{\rho}\left(\frac{V}{S}\right) = \frac{r}{\rho F_S} \tag{1}$$

where F_S is the geometric shape factor, and for spherical and cylindrical holes, F_S is equal to 3 and 2, respectively, and r is the hole radius.

From petrophysics, there is a relationship between capillary pressure and pore size in porous media:

$$P_C = \frac{2\sigma \cos\theta}{r} \tag{2}$$

where P_C is the capillary pressure when the pore size is r, σ is the surface tension of the pore fluid, and θ is the contact angle between the pore fluid and the pore surface.

According to the fractal theory of porous media, the fractal expression of the capillary pressure curve of reservoir rock is as follows:

$$S_v = \left(\frac{P_C}{P_{C\min}}\right)^{D-3} \tag{3}$$

where $P_{C\min}$ is the capillary pressure corresponding to the maximum pore size $r_{\max}$ in the porous medium.

From equations (1), (2), and (3), the expression for S_v can be deduced as follows:

$$S_v = \left(\frac{T_{2\max}}{T}\right)^{D-3} \tag{4}$$

Taking the logarithm of both sides of equation (4) yields:

$$\lg S_v = (3-D)\lg T_2 + (D-3)\lg T_{2\max} \tag{5}$$

S_v is the percentage of the pore accumulation volume in the porous medium with lateral relaxation time less than T_2 in the total pore volume, and D is the fractal dimension of the pore structure of the porous medium.

3. Results and discussion

3.1. Residual water saturation

Figure 2 shows the 1D DHK SPRITE measurements for the hydrate generation experiment. The left end of the curve corresponds to the bottom end of the sand-filling model, the right end corresponds to the top end of the sand-filling model. The decomposition of hydrate mainly occurs at -2.5 cm to 2.5 cm. The curve shows the change in residual water saturation over 50 minutes of hydrate formation, and the change in residual water saturation over time can be divided into two phases. The first 10 minutes were the first stage with a faster generation rate, and the residual water saturation decreased from 32.94% to 19%. The second stage with a slower generation rate in the last 40 minutes, with the residual water saturation reduced to 9.71%. The residual water saturation of the first stage decreased by 13.94%, and that of the second stage by 9.29%. The water consumption rate of the first stage was much faster than that of the second stage, mainly because a hydrate film was formed on the gas-water contact surface at the time of hydrate formation. The heat and mass transfer between gas and water is hindered by the gradually thickening hydrate, and the formation rate of hydrate gradually decreases.

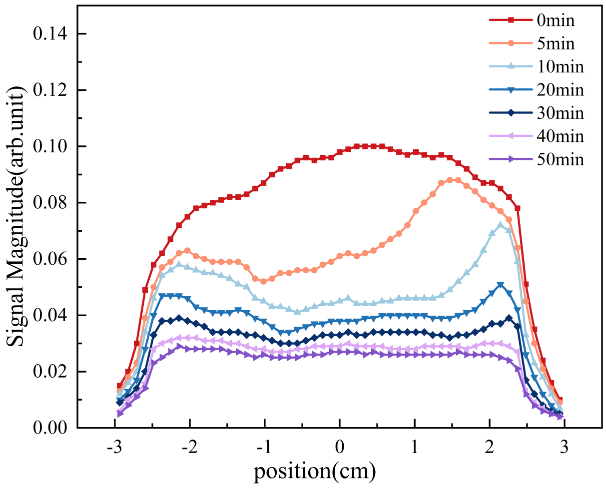

Figure 2. 1D DHK SPRITE measurement results during hydrate formation

3.2. T_2 relaxation distribution

Figure 3 shows the change in the T_2 distribution during hydrate formation. Before hydrate formation, there are two peaks in the T_2 distribution, and the peak on the right is relatively large, indicating that the initial water is mainly distributed in macropores. During hydrate formation, the peak values of the two peaks are gradually decreasing, indicating that the water in the pores is gradually consumed to form hydrate. The peak value decreases fastest in the first 10 minutes, which shows that the water consumption rate and hydrate formation rate are faster in the first 10 minutes. For 10–50 minutes, the water content in the pores is gradually decreasing, and the hydrate formation rate is uniformly reduced. In the process of hydrate formation, the distribution of the T_2 peak gradually moves to the left. Because solid hydrate is gradually generated in pores, it occupies a part of pore space, turning macropores into micropores. A decrease in the surface-to-volume ratio of the pore also results in a decrease in the relaxation time of the water in the pore.

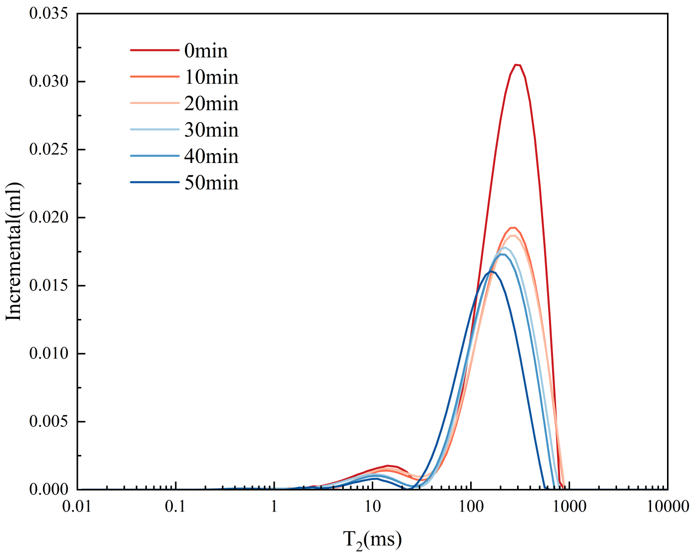

Figure 3. T_2 relaxation time distribution

3.3. Fractal dimension

The complexity of the pore space can be expressed by the fractal dimension. The larger the fractal dimension, the more complex the structure in the pore. **Figure 4(a)** is a schematic diagram of fractal dimension fitting calculation, linear regression analysis is carried out on lgS_v and lgT_2, and the fractal dimension D of the pore structure can be calculated by linear slope K. **Figure 4(b)** shows the fractal dimension changes of five positions in the reactor during hydrate formation. The initial water content in pores at each position is different, so the fractal dimension at the initial moment is also different, which does not affect the change of the fractal dimension. In the process of hydrate formation, the water in pores is gradually transformed into hydrate, and the spatial structure of pores becomes more complicated, and the fractal dimension gradually increases. In the first 10 minutes, the fractal dimension increases rapidly, and after 10 minutes, it increases slowly. The variation of fractal dimension at each position in the reactor indicates that the hydrate formation process at each position is also different. The fractal dimension corresponding to the five positions of the reactor gradually increased, indicating that the hydrate formation rate of each position of the reactor gradually increased from top to bottom.

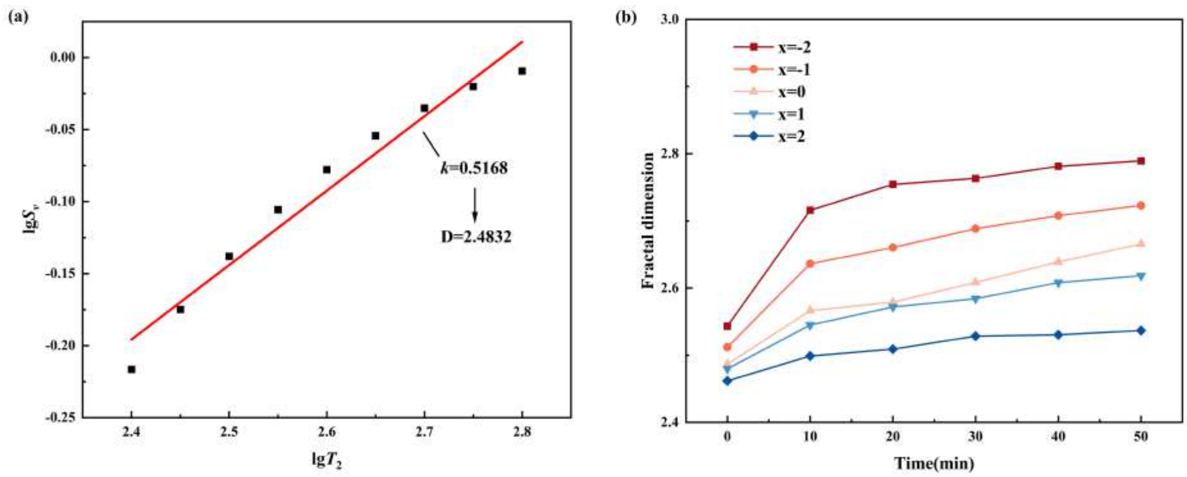

Figure 4. Fractal dimension calculation and variation

4. Conclusion

The formation process of methane hydrate in porous media was studied by MRI experiments. The variation of hydrate formation rate with time and the complexity of pore space during hydrate formation were compared and analyzed. The experimental results are as follows:

(1) During hydrate formation, the residual water saturation decreased by 13.94% in the first 10 minutes and by 9.29% in the last 40 minutes. The hydrate formation process was divided into two stages: fast and slow.

(2) Hydrate is mainly generated in macropores, and the formation of hydrate occupies pore space, gradually shifting the T_2 distribution to the left.

(3) When hydrate is formed, the pore space becomes more complex, and the fractal dimension of each position changes differently. The hydrate formation rate is fast at the location where the fractal dimension changes greatly.

Disclosure statement

The authors declare no conflict of interest.

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