Study on the mechanism of hydrate adhesion on the surface of rocks and minerals

Zhe Wei¹,a, Mingzhong Li¹,b*, Yanchen Lu¹,c, Chenwei Liu¹,d, Shuai Wu¹,e, Shuai Zhao¹,f

¹College of Petroleum Engineering, China university of petroleum, Qingdao, Shandong, China

aemail: z19020044@s.upc.edu.cn, cemail: z16020127@s.upc.edu.cn, demail: liuchenwei@upc.edu.cn, eemail: z19020088@s.upc.edu.cn, femail: s19020072@s.upc.edu.cn.com

*Corresponding author: bemail: limingzhong@upc.edu.cn.

Abstract. Natural gas hydrate is mainly enriched in the low temperature and high pressure environment such as the extremely cold permafrost zone and the polar continental shelf, which is a renewable energy with great development value. The analysis of the adhesion mechanical properties of gas hydrate on the surface of rock and mineral is of great significance for the correct evaluation and effective control of the influence of gas hydrate on sedimentary layers. In this paper, an experimental device for visualizing the adhesion of hydrate wall under atmospheric pressure was built to directly test the adhesion strength of hydrate on the rock wall. The influence mechanism of the microstructure of rock wall and the types of rock minerals on the adhesion strength of hydrate was studied. It was found that the adhesion strength of hydrate on the sandstone wall was greater than that of carbonate rock salt. The higher the surface roughness of rock and mineral, the higher the adhesion strength of hydrate.

1. Introduction
Natural gas hydrate mainly refers to a kind of caged crystalline compound generated under low temperature and high pressure, which is enriched in the cracks and pores of sedimentary layers in the extremely cold permafrost zone, polar continental shelf, continental slope, deep sea bottom and deep lake bottom. Because of its advantages of environmental protection, high thermal energy and large potential, it is known as "the most valuable strategic resource for development in the 21st century". The hydrate attached to the surface of rock and mineral and its pore structure will increase the shear strength of hydrate deposits and walls. In turn, the bond between sediment particles is reduced. When the hydrate is decomposed or driven away, the sediment skeleton will be damaged to a certain extent, resulting in the decrease of its strength, and then greatly reduce the stability of the sediment layer.

A large number of studies have shown that the adhesion strength of hydrate on the wall is the key factor to determine the accumulation or detachment of hydrate on the wall, and it is very important to explore the adhesion strength between the growth hydrate and the wall for the quantitative evaluation of the growth pattern of hydrate on the wall. Nicholas [2] and Aspend et al. [3] tested the adhesion between the cyclopentane hydrate particles and the wall surface, and found that in the absence of free water, the force between the particles and the wall was very small. Liu Chenwei tested the adhesion force between hydrate particles and pipe wall in the presence of free water, and found that the presence of water greatly...
increased the adhesion force (at least one order of magnitude) \cite{4-5}. For the growth model of wall hydrate, it is very important to explore the adhesion strength between growth hydrate and wall to quantitatively evaluate the growth model of wall hydrate. The above studies are the tests on the adhesion of hydrate particles formed after settling on the surface of the pipe wall. At present, there are few reports on the tests on the adhesion between hydrate growing on rock minerals and the rock surface \cite{6}.

2. Materials and methods

2.1. Experimental device

A test device for the growth adhesion of rock mineral hydrate was built to measure the microscopic adhesion of the growth hydrate on the surface of rock mineral. The experimental equipment mainly includes circulating refrigeration system, hydrate generation system and adhesive force measurement system. The specific structure is shown in Figure 1.

![Figure1 Hydrate growth adhesion test device](image)

2.2. Experimental method

(1) Start the circulating refrigeration system to provide a low temperature environment for the hydrate generation system, and measure the temperature of the atmospheric pressure hydrate reaction device through the temperature acquisition device until it is adjusted to -3 ℃;(2) Pour 1/2 volume of cyclopentane into the hydrate formation reaction tank, and seal the tank with a cover to cool the cyclopentane for 40 min;(3) The rock sample block is immersed in liquid nitrogen and cooled by liquid nitrogen vaporization and heat absorption. After the rock and mineral are completely cooled, a thin layer of snow-white ice film is formed on the cooled rock wall surface by the condensation of distilled water vapor.(4) The four transparent quartz frames are placed in the quartz frame track on the wall of the cooled rock mineral, and the whole test unit is placed in the cyclopentane in the atmospheric reaction tank, so that the cyclopentane is immersed through the whole test unit;(5) Adjust the circulating refrigeration system, increase the system temperature at the rate of 0.5 ℃/10min to 0 ℃, and maintain the temperature for more than 30 min, and then, temperature rise at the rate of 0.2 ℃/5min until the required temperature is reached;(6) spray three times of distilled water into the hydrate reaction tank with a sprayer every 20-30 min, and add 4-6 mL of cyclopentane into the reaction tank every 2h;(7) After the experiment reaches the required test time, rotate the operating handle on the sliding table to drive the digital display push and pull meter to move back and forth through the movement of the cross sliding table, thus pushing the transparent quartz frame to slide along the quartz frame track. When the hydrate in the transparent quartz frame is peeled off, the maximum value recorded by the digital display push-tension meter is the wall adhesion force of hydrate formation in the liquid phase.
### 3. Experimental results and analysis

#### 3.1. Influence of rock mineral species on hydrate adhesion

Different rock and mineral types have differences in wettability, rock surface energy, surface microstructure and surface sand content, which affect the adhesive force of hydrate formation. In this paper, carbonate rock and sandstone samples polished by 800-mesh sandpaper were selected as rock materials, and quartz glass with original roughness retained was selected as a comparative experiment. The experimental results are shown in Figure 2.

![Figure 2: Comparison of hydrate adhesion strength in liquid phase in different rock samples used in the experiment](image)

As can be seen from the above chart, the average adhesion strength of hydrate formation on the surface of sandstone minerals in the liquid phase system is the largest, which is divided into 460 kPa. The average adhesion strength of hydrate formation on the surface of carbonate rocks is 378 kPa. The adhesive strength of hydrate formation on the surface of quartz glass sample is 178 kPa.

One of the main reasons for the difference in adhesion strength is that the three rock and mineral samples have their own surface energy, which determines their wettability. Van Oss et al. [7] believe that the surface energy of a solid is composed of its Lewis acid-base component and the Van der Waals force component, as shown in Formula (1).

$$\gamma_i = \gamma_i^{LV} + 2\sqrt{\gamma_i^+ \gamma_i^-}$$  \hspace{1cm} (1)

Where, $\gamma_i^{LV}$ is the van der Waals force component; $\gamma_i^+$ is the acid component; $\gamma_i^-$ is denoted by the base component.

In addition, Fowkes et al. [8] also proposed the composition method of the free energy of solid surface expressed in Equation (2).

$$\gamma = \gamma^d + \gamma^n$$ \hspace{1cm} (2)

Where, $\gamma$ is the total surface energy, $\gamma^d$ and $\gamma^n$ represents the dispersion force and non-dispersion force caused by London force between molecules respectively.

The surface energy of carbonate rock and sandstone are both high, and the wetting property of solid surface is related to its surface energy. The larger the surface energy is, the easier the liquid spreads on the solid surface, and the smaller the contact Angle is, the better the wetting effect is. The contact Angle of droplets measured on the surface of carbonate rock and sandstone is 57.6° and 52.3°, respectively. Therefore, the larger the contact area of droplet of the same volume on the rock and mineral surface with high surface energy is, the higher the adhesion strength between hydrate and wall surface will be. In addition, the sandstone wall contains a high percentage of sand, which can induce the formation of hydrate and reduce the induced nucleation period of hydrate. Therefore, under the same undercooling degree and hydrate formation time, the higher the degree of hydrate transformation, the higher the shear...
strength of hydrate formation on the surface. At the same time, there are peak-like papillae formed by tiny rock particles on the surface of both carbonate and sandstone samples, which can increase the contact area between droplets and the wall surface, enhance mass transfer and promote the generation of hydrate. The reason for the low adhesion strength of quartz glass is that although its surface has good wettability and the contact Angle of liquid droplets on the surface of quartz glass is 61.8°, its surface is relatively smooth, there is no sandy particles, and the surface morphology of microstructure is more subtle. The actual contact area between hydrate formation and the wall surface is smaller than that on the surface of carbonate rock and sandstone samples, so the shear strength is lower and the adhesion force is the least.

3.2. Influence of rock wall microstructure on hydrate adhesion

The surface of rock and mineral is not smooth, but there are a large number of tiny peaks and valleys formed by a large number of small rock particles. This microscopic geometric feature can be described as the wall roughness. Different roughness conditions will affect the wetting degree of the rock wall, and then affect the crystal morphology of droplets on the wall. The difference of rock and mineral surface roughness can reflect the different wetting characteristics. In this section, 100-mesh, 800-mesh and 2000-mesh sandpaper were used to grinding the rock wall, respectively, so that it presented different wall microstructure, thus causing differences in wettability. For example, the wettability characteristics of the rock wall in the liquid phase were shown in Fig. 3, and the measured contact angles were 33.6°, 57.6° and 71.8°, respectively.

![Figure 3 Diagram of wetting characteristics caused by microstructures of different rock surfaces in liquid phase](image)

Under the conditions of supercooling degree of 6.7 ℃ and hydrate formation time of 360 min, the adhesion force of hydrate formation on rock and mineral surface was measured. In order to ensure that the roughness of the rock mineral surface is uniform and the wettability is consistent, the rock wall surface is sanded for more than 20 minutes. The test results of hydrate adhesion on the rock wall in the liquid phase system are shown in Figure. 4.

![Figure 4 Comparison of hydrate adhesion strength under different rock wall surfaces in liquid phase](image)
The average adhesion strength of hydrate formation on the rock wall surface after sanding with 100 mesh sandpaper is 536 kPa. The average adhesion strength of hydrate on the rock wall surface polished by 2000 mesh sandpaper is 285 kPa. The smoother the surface is, the smaller the adhesion strength of hydrate is. The microstructure of rock and mineral surface affects its wettability, and the contact angle can directly reflect its wettability. Assuming that there are microstructures with different roughness on the solid surface, the liquid phase can contact with the rough structure on the surface completely, then the contact area of the two phases will be larger than that of the liquid phase on the smooth surface. At the same time, the more obvious the microstructure of the solid surface is, the more hydrophobic the hydrophobic surface is and the more hydrophilic the hydrophilic surface is. Because the surface of rock and mineral is hydrophilic, the more obvious the mountain-like microstructure on the surface is, the greater the degree of concave and convex is, and the better the wetting effect is. The existence of this microstructure will cause capillary action. Under the attraction of capillary action, the droplets infiltrate into the cracks of the wall of the microstructure, which increases the contact area between the droplets and the rock and mineral surface, and results in the increase of the adhesion strength between the hydrate and the wall.

4. Conclusion
Under the same surface roughness, the adhesion strength of hydrate generated on the surface of sandstone is greater than that of carbonate, and the obvious surface microstructure is the main reason that the adhesion strength of hydrate on the surface of rock and mineral is greater than that of quartz glass.

As the surface roughness of rock and mineral increases, the more obvious the surface microstructure is, the stronger the hydrophilicity is, and the larger the contact area between the droplet and the surface of rock and mineral becomes, leading to the larger the adhesion strength of hydrate.

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