Influence of the granule size and composition uniformity on methane hydrate dissociation

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Abstract. Influence of the granule size and composition on methane hydrate decay was studied experimentally. It was shown that the maximum dissociation rate is achieved for the granule diameter of 0.1 mm and for the uniform powder composition. The dissociation was realized at negative temperatures and in the region of "self-preservation". The granules dissociation rate decreased significantly with increasing the powder layer thickness from 1 mm to 30 mm. It was demonstrated that the nonuniform distribution of granules and the thick layer leads to a decrease in the methane hydrate dissociation and to different kinetic dissociation curves.

1. Introduction
The dissociation of gas hydrates is determined by many key factors: the external temperature and pressure, granules subcooling degree, and granules structural characteristics [1, 2]. There are several main structures of gas hydrates: cubic structures (sI) and (sII), and hexagonal structure (sH) [1]. Methane gas hydrates have cubic structure (sI). The hydrate recovery from marine deposits was discussed in Ref. [3]. The gas hydrates cover both the global resources of energy and the new effective technologies such as the batteries with CP₄ hydrate [4]. Much attention is paid to the problems, related to transportation and storage of raw materials in large containers [5]. The huge tankers carry liquefied natural gas at the temperatures below 110 K. Cryogenic temperatures lead to high natural gas transportation costs. The phenomenon of self-preservation of gas hydrates will ensure the transportation and storage of hydrate raw materials at temperatures above 260 K. These temperatures significantly reduce the storage and transportation costs. The phenomenon of self-preservation is associated with anomalously low rates of the gas hydrate dissociation [6-12]. Low rates of decomposition are caused by the formation of a solid crust of ice on the surface of the granules. The dissociation kinetics depends on the morphology of the ice structures on the surface of the granules [13, 14]. It is necessary to take into account the heat flux, heat transfer coefficient and external turbulence in modeling the kinetics of the decomposition of granules and gas hydrate layers [15, 16]. External turbulence affects transport mechanisms in the mixing layer during gas hydrate combustion [11, 17]. The strength of the ice shell on the surface of hydrated granules depends on the dendritic structures, which also grow rapidly for salt hydrates [18, 19] and suppress heat transfer. The kinetics of crystallizations and hydrated growth varies greatly with a high degree of supercooling [20]. When burning methane hydrate there is a multiphase system (methane-gas hydrate-water-vapor-ice) [21-24]. It is shown that combustion occurs with the decay of a gas hydrate into ice and methane with
formation of a water film on the powder surface. The motion of dissociation front occurs from the granule surface to their center and from the top powder surface to the bottom of the container with solid fuel. It is necessary to take into account external convection in the description of evaporation and hydrate formation [25-27]. The combustion kinetics of methane hydrate was studied in [28, 29]. When the methane hydrate burns, a vapor stream, small drops, and a thin liquid film form on the surface of the hydrate, which leads to a decrease in the combustion temperature of the fuel [30-42].

Thus, the study of the influence of granule size, the uniformity of the particle size and the height of the powder layer is important both for the development of storage and transportation technologies of methane hydrate and for combustion technologies.

2. Experimental method and analysis

The scheme for studying methane hydrate dissociation is shown in Fig. 1. The thermocouples were placed inside the tank (1) and above the powder surface. The external temperature was kept constant. The thermal measurements of granule surface were carried out by the thermal imager (NEC-San Instruments) (4). The hydrate powder temperature varied from 95 to 273 K. Relative measurement error of the thermocouple was within 1.5 K. The difference between the temperatures measured by the thermal imager and the thermocouple did not exceed 2.0 %. The diameter of the tank was 70 mm, and the tank height was 40 mm. There were thermocouples inside the powder layer (2). A change in powder mass depending on the time was determined with the help of the scales (3).

![Figure 1. The scheme for studying methane hydrate dissociation: 1 – the tank for powder; 2 – methane hydrate; 3 – electronic scale; 4 – thermal imager (NEC-San Instruments)](image)

The total mass of extracted methane from the powder corresponded to initial methane concentration (11-12 %). To produce the methane hydrate granules, the ice powder was located into the cooled autoclave, and then, the methane pressure of about 6 MPa was set in the autoclave. The autoclave was maintained at the temperature of +274 K until the pressure drop. Then, it was cooled to the liquid nitrogen temperature. Hereupon, the powder was taken, ground and put into the autoclave again. The external gas pressure of 1bar was constant. The initial sample temperature was 188 K.

It is shown that an increase in the thickness of the powder layer leads to a sharp decrease in the decay rate. The decrease in the intensity of dissociation is due to the fact that a transverse temperature gradient forms in the thick layer of the powder and the central region of the layer is in the "self-preservation" regime for a long time. The highest dissociation rates are achieved for a thin layer, the thickness of which is equal to 1-2 diameters of the granules. Fig. 1 shows the experimental data for the dissociation rate \( J \) for different compositions of methane hydrate granules. As can be seen, \( J \) has a maximum value for a homogeneous composition of granules with a minimum particle diameter (curve 2). The lowest decomposition rate corresponds to an inhomogeneous composition with a large share of large granules (curve 3). When the composition and size of the granules change, the position \( t \) for the maximum \( J \) changes. The width \( \Delta t \) also changes, which characterizes the total decay time. The smallest value of \( \Delta t \) corresponds to curve 2. Fig. 2 (a-c) shows thermal images of the temperature change of the powder surface with different granules diameter.
Figure 2. A change in methane flow depending on the different granular composition: 1) 60% mass for $d = 0.1$ mm and 40% mass for $d = 1$ mm; 2) 100% mass for $d = 0.1$ mm; 3) 30% mass for $d = 0.1$ mm; 30% mass for $d = 1$ mm and 40% mass for $d = 3$ mm.

Figure 3. (a-c) Thermal images: a) $d = 6$ mm; b) $d = 3$ mm; c) $d = 0.1$ mm; d) The methane mass flux for different granules diameters ($m_0 = \text{const}$): 1) $d_1 = 0.1$ mm; 2) $d_2 = 0.5$ mm; 3) $d_3 = 3$ mm; 4) $d_4 = 5$ mm; 5) 6 mm.

It is seen that for large granules there is an extremely uneven temperature field. The characteristic size of the temperature unevenness is the same as the average diameter of the granule. For granules with a diameter of 0.1 mm, the temperature field is uniform for the entire surface of the powder, and the temperature change along the tank diameter is related only to the longitudinal heat flux directed to the side wall of the reservoir. The change of the methane mass flux with time for different diameter of granules is presented in Fig. 2(d). As can be seen from graphs, the characters of the dissociation kinetics of small particles differ from the granules of larger size. For the granules with small particles ($d = 0.1$ mm), the dissociation of the methane hydrate begins much earlier, the amplitude of curve is substantially greater and the maximum width of the dissociation time is 10 times lower than for the large granules with $d = 6$ mm. Thus, the change in the powder composition of the methane gas hydrate leads to different kinetic dissipation curves.
Conclusion
Thus, the experimental study of nonisothermal dissociation of methane hydrate granules has been realized. Influence of the granule size in a wide range of diameter from 0.1 to 6 mm has been studied experimentally. The influence of the granule composition on methane hydrate decay has been established.

The maximum dissociation rate was achieved for the small granule diameter and for the uniform powder composition (100 % mass for granules with $d = 0.1$ mm). The dissociation curves had the essentially nonlinear character. All curves for the dissociation rates had an extremum.

Reduction in dissociation rate was associated with the curvature of the granules and was due to self-preservation. For the granules with small particles ($d = 0.1$ mm), the methane hydrate dissociation begins much earlier and the curve amplitude is substantially greater; the maximum width of the dissociation time is 10 times lower than for the large granules with $d = 6$ mm.

The dissociation rate of methane hydrate granules decreases significantly with increasing the powder layer thickness from 1 mm to 30 mm.

The obtained experimental data show that for storage and transportation technologies it is necessary to use granules of the largest size (4-6 mm and more) and the thick layer of powder (30 mm and more), since these conditions ensure a minimum dissociation rate. For the combustion technology, high decay rates and small particles with the small powder layer height are necessary.

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