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Phase behavior of methane hydrate in silica sand

Shi-Cai Sun [a,c,*], Chang-Ling Liu [b], Yu-Guang Ye [b], Yu-Feng Liu [a]

[a] Shandong Provincial Key Laboratory of Civil Engineering Disaster Prevention and Mitigation, Shandong University of Science and Technology, Qingdao 266590, China
[b] Qingdao Institute of Marine Geology, Qingdao 266071, China
[c] State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdou 610500, China

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ABSTRACT

Two kinds of silica sand powder with different particle size were used to investigate the phase behavior of methane hydrate bearing sediment. In coarse-grained silica sand, the measured temperature and pressure range was (281.1 to 284.2) K and (5.9 to 7.8) MPa, respectively. In fine-grained silica sand, the measured temperature and pressure range was (281.5 to 289.5) K and (7.3 to 16.0) MPa, respectively. The results show that the effect of coarse-grained silica sand on methane hydrate phase equilibrium can be ignored; however, the effect of fine-grained silica sand on methane hydrate phase equilibrium is significant, which is attributed to the depression of water activity caused by the hydrophilicity and negatively charged characteristic of silica particle as well as the pore capillary pressure. Besides, the analysis of experimental results using the Gibbs–Thomson equation shows that methane hydrate phase equilibrium is related to the pore size distribution of silica sand. Consequently, for the correct application of phase equilibrium data of hydrate bearing sediment, the geological condition and engineering requirement should be taken into consideration in gas production, resource evaluation, *etc.*

1. Introduction

Naturally occurring gas hydrate in marine sediment or permafrost widely around the world is the focus of a special attention as a potential energy resource. Some methods for gas production from hydrate reservoirs have been proposed, such as depressurization, thermal stimulation and inhibitor injection, *etc.* [1], the reliability and economy of which need to be investigated further.

Gas hydrate reservoirs also provide a carbon dioxide sink through sequestration with simultaneous conversion of in situ solid gas hydrates into gaseous fluid. Such method can overcome the economic impediments of gas hydrate exploitation and carbon dioxide sequestration [2,3]. Due to the large storage capacity (about 184 volumes of methane gas per volume of methane hydrate), gas hydrate can be used as a potential method for gas storage, and the gas storage capacity of hydrate can be increased by the presence of porous media [4]. For the issues above, hydrate formation and dissociation in porous media or sediments should be understood, which is dependent on the medium property. Generally, gas hydrates occur in the form of segregated nodules, lenses, pellets or sheets in fine particle sediments, but an interstitial pore-filling between particles in coarse particle sediments [5]. Natural sediments hosting gas hydrates are generally characterized by mineral particle, organic debris, pore water, mud and clay, *etc.*, so it is very difficult to specify the impact of each factor. Because the deposition of sediment particles with different size controls the pore space, the amount of pore water and free gas, *etc.*, the particle size plays an important role in affecting hydrate morphology and distribution [6,7].

Unlike hydrate formation/dissociation in bulk water, the hydrophilic surface and interfacial effect of solid particles may affect hydrate equilibrium in sediment. Studies have shown that hydrate phase equilibrium temperature is not changed in the coarse-grained sediment [8–10], while the equilibrium temperature in various fine-grained sediments such as porous silica gel [11,12], porous glass [13,14], glass sand [15] and marine sediment [16,17] is lower than that in bulk water. According to the solid-solution theory, hydrate phase equilibrium is dependent on the water activity. Due to the depressed water activity in fine-grained sediment, hydrate occurs at a lower temperature or a higher pressure. This phenomenon may explain why the bottom of gas hydrate stability zone (GHSZ) is (40 to 100) m shallower than the bottom simulating reflector (BSR) in Ocean Drilling Program (ODP) Leg 164 drilling [18].

In most literatures, the measured hydrate phase equilibrium commonly corresponded to the average diameter of particle/pore size. We think that this approach is debatable. Natural sediment usually has a wide range of particle/pore size distribution. Consequently, the sediment has not necessarily the same size

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* Corresponding author at: Shandong Provincial Key Laboratory of Civil Engineering Disaster Prevention and Mitigation, Shandong University of Science and Technology, Qingdao 266590, China. Tel.: +86 532 86057593.
E-mail address: qdsunsc@163.com (S.-C. Sun).

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distribution with the same average diameter of particle/pore size. Owing to the different constraint condition in different size pore, the phase behavior of gas hydrate is distinguishing in sediments of different particle size. *e.g.*, the capillary of small pore is larger than that of large pore to result in a more significant depression of hydrate equilibrium temperature. Therefore, a good understanding of the *p*-T trace of hydrate formation and dissociation in natural sediment with a particle size distribution is necessary for the proper engineering application of equilibrium data. For gas production and resource evaluation, it is important to determine when hydrates bearing specific sediment begin to dissociate and when dissociate completely. According to such information, we can accurately evaluate the resource of hydrate reservoirs or calculate the injection of external energy (hot water, chemical reagents, *etc.*) or pressure drop for hydrate dissociation. Otherwise, the trouble or danger may occur. In this work, the coarse-grained silica sand and fine-grained silica sand was used to investigate the phase behavior of methane hydrate, respectively, which helps to understand the relationship between the particle/pore size and hydrate phase equilibrium.

2. Experimental

2.1. Experimental equipment

The experimental equipment employed in this work has been described by Sun *et al.* [17] as shown in figure 1. The high-pressure vessel with a net volume of 150 mL was immerged into a temperature-adjustable air bath/water bath. A pressure transducer (~0.1 MPa) and a platinum resistance thermometer sensor (±0.1 K) were used to measure the variation of the pressure and temperature during hydrate formation and dissociation, respectively. In addition, the temperature and pressure data during the experiments were recorded by the data acquisition in real time.

2.2. Experimental materials

Silica sand is a typical component of natural sediment hosting gas hydrate, and gas hydrate may occur in sediment with different particle size [19]. In this work, two kinds of silica sand power (coarse-grained and fine-grained) supplied by Lingshou-BaoLei Mineral Processing Co., Ltd. were used to investigate hydrate phase behavior. Although sII and sH gas hydrates have been identified in nature, the majority of gas hydrate samples recovered up to now are sI methane hydrate, *e.g.*, Liu *et al.* [20] reported that methane gas accounts for more than 99% on the basis of laser micro-Raman spectroscopy analysis on the hydrate sample from Shenhu Area of South China Sea. As to this result, methane gas (99.99% purity) provided by Qingdao Ruifeng Gas Co., Ltd. was used to synthesize hydrate. The deionized water made in laboratory was used in all experiments. Before experiments, the particle size of silica sand was measured by Malvern MS2000 Laser particle size analyzer, as shown in table 1.

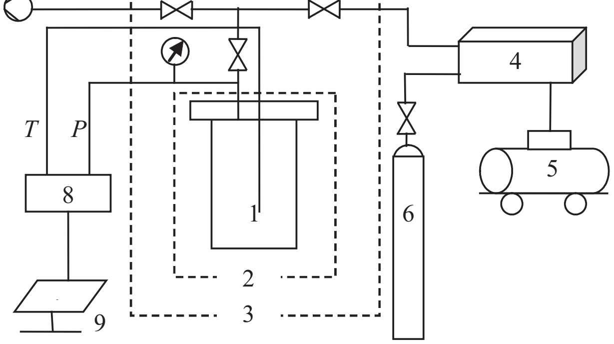

FIGURE 1. Experimental setup for hydrate equilibrium measurement [17]. (1) vessel; (2) water bath; (3) air bath; (4) pressurized system; (5) air compressor; (6) cylinder; (7) vacuum pump; (8) data acquisition; (9) computer.

2.3. Experimental method and procedure

In experiments, the isochoric multi-step heating dissociation method was used to investigate the phase equilibrium of methane hydrate since it was more reliable and repeatable than the conventional continuous-heating method [21–23]. The experimental process follows the following principles: (1) a certain amount of methane gas was firstly charged into the vessel and methane hydrate equilibrium was obtained at a relatively higher temperature–pressure range. After that, a portion of gas was slowly released from the vessel, and then methane hydrate equilibrium at a relatively lower temperature–pressure range was measured, and so on. This method can conveniently obtain methane hydrate equilibrium at a wide range of temperature–pressure, eliminating the need for repeated evacuation and gas injection. Furthermore, the silica particles is in a relatively more stable packing-state, ensuring the same structure for all the measured equilibrium data of methane hydrate. (2) Methane hydrate formation and dissociation may affect the packing state of silica sand, such as the pore size, permeability, *etc.* and the change of physical properties of silica sand would affect the hydrate phase equilibrium [5,24]. Consequently, for a more accurate result, each run of experiments was repeated several times (at least five times in this work) to provide a relatively more stable packing-structure of silica sand. And the experimental results of the last time were regarded as the final results which reflect the actual packing state of silica sand. (3) Additionally, the enough time was given in each run of experiments for synthesizing adequate methane hydrate. During hydrate dissociation, sufficient time (between (12 and 24) h, it may be longer based on the experimental condition) was also given to allow the system to reach equilibrium state after each temperature increment of (0.2 to 0.5) K. When the stable state of the system was reached, the corresponding pressure and temperature was the equilibrium condition of hydrate in pores of a certain size. The procedure was described in detail in the literature [17].

3. Results and discussion

3.1. p-T trace of methane hydrate phase behavior in silica sand

When the silica sand sample is added into hydrate system, solid particles act as the third interface to provide more nucleation centers accelerating the clustering of methane molecule and water molecule. In general, the silica particles can promote hydrate formation, *i.e.*, a shortened induction time and enhanced formation rate [8,25,26]. However, if the particle size or pore size of silica sand is too small, it will affect the diffusion rate and concentration of methane gas, and then hinder hydrate nucleation [27]. Figure 2(a) shows the *p*-T trace of phase behavior of methane hydrate bearing coarse-grained silica sand. In A–B segment, the system is cooled, and the pressure linearly drops associated with thermal contraction. While in B–C–D segment, the temperature firstly increases suddenly, then decreases gradually. This indicates that a lot of methane hydrate occurs. At this stage, the mixture of methane gas and water fluid with a higher energy is transform into solid methane hydrate with a lower energy. In D–E segment, the system is heated, and the pressure linearly increases associated with thermal expansion, suggesting that methane hydrate does