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Full Length Article

Methane hydrate formation in mixed-size porous media with gas circulation: Effects of sediment properties on gas consumption, hydrate saturation and rate constant

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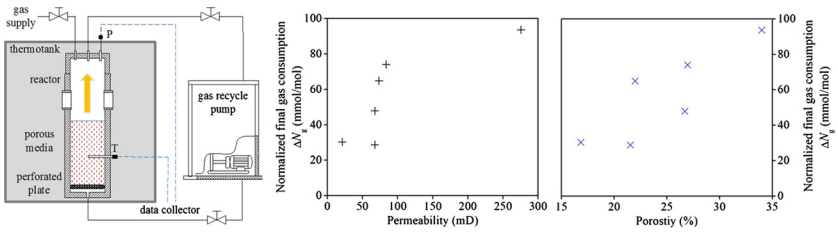
GRAPHICAL ABSTRACT



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ABSTRACT

Being a promising potential source for natural gas, methane hydrate (MH) is attracting increasing interest due to its great amount and diverse geographic distribution. The formation of MH is significantly influenced by the properties of sediment media such as porosity and permeability. In this study, in order to have a better understanding on the relationship between MH formation behavior and sediment properties, as well as to synthesize representative hydrate samples, MH was formed in six different sets of mixed-size porous media composed of clay, silt and fine sand, with saline water and circulating methane gas to reflect MH formation with free methane flux in marine sediment. The sediment composition, experimental pressure (15 MPa) and temperature (286.2 K) were chosen based on the SH2 drilling site in the Shenhu area in South China Sea. A two-stage growing behavior was observed for all systems. The gas consumption and hydrate formation rate exhibited positive relations with the permeability and porosity of the sediments. Furthermore, hydrates were found to be preferably formed in the bottom layer of the sediment, which could be attributed to the drastic drop of permeability at the early stage of hydrate formation. Lastly, the hydrate formation rate constant was calculated based on the intrinsic kinetic model and found to be a good reflection of the mass transfer properties of different porous media.

1. Introduction

Methane hydrates (MH) is a non-stoichiometric crystalline compound with snowy-ice like structure consisting of hydrogen bonded network of host water molecules and entrapped methane guest molecules [1]. About 98–99% of the methane hydrates in nature are located

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in the deep marine shelf and on the oceanic slope in the coastal areas, and 1–2% are in the permafrost regions of the subarctic parts of continents [2–4]. The amount of natural gas sequestered in the hydrate form is estimated to be around 3000 TCM, which is about an order of magnitude higher than the estimate for conventional gas [5]. Due to such a great amount and diverse geographic distribution, MH has attracted considerable attention from governments and scientists [6–8]. While many attentions have been focused on the development of feasible methods to recover natural gas from MH, it is the cornerstone to know how MH forms because the synthesized hydrate-bearing porous media samples are the precondition for the laboratory and numerical studies of hydrate dissociation.

A number of laboratory studies on the relationships between the sediment and MH formation behaviors have been conducted. Kumar et al. [9] studied the effect of silica sand/clay ratio and the water saturation on hydrate formation under 274.5 K/6.0 MPa. They discovered that the presence of clay reduced the hydrate formation kinetics significantly. Ruffine [10] also employed the mixture of clay (composed of 75 wt% kaolinite, 18 wt% illite and 7 wt% quartz) and silica sand as the geologic matrix and formed MH under 274.15 K/4.9–7.5 MPa. It was found that the morphology of MH bearing sediment changed with the increasing proportion of clay. Heeschen et al. [11] investigated the gas hydrate growth within glass beads, silica powder, and clay minerals under 274.0 K/7.0 MPa and found that a high concentration of fine sands with a grain size < 125 μm led to explicitly faster gas hydrate formation compared to coarser sand. Linga et al. [12] studied the effect of silica sand bed size (particle size of the sand in the range of 150–630 μm) on the hydrate formation under 277.15 K/8.0 MPa. They found that the bed size was an important factor that would affect the rate of hydrate formation in a porous bed. Bagherzadeh et al. [13] also investigated methane hydrate formation in different silica sand beds (particle size including 210–297, 125–210, 88–177, and < 75 μm) under 274.15 K/8.0 MPa and observed that hydrate formation was faster in a bed with lower water content and smaller particle size. Chong et al. [14] examined the size effect of silica sand including four different sizes ranging from sand-silt cut off size (0.063 mm) to granular pebble (3.0 mm) on MH formation under 277.2 K/8.0 MPa. Significant amount of methane hydrate was observed to form on top of the porous media instead of dispersed within the coarse sands (0.56–1.3 mm) and granular samples (1.5–3.0 mm). These results from the literature highlight the importance of selecting an appropriate porous medium and experimental approach to synthesize representative artificial methane hydrate in laboratory.

Apart from the host sediment, the fluid movement is another factor that would significantly affect the MH formation. Based on the methane sources, three common theories have been suggested for hydrate formation in nature, namely the in situ biogenic methane, dissolved methane in water, and free gas bubbles in water [15]. Laboratory experiments need to be carefully designed to make representative hydrate-bearing sediments for each case. In particular, for the third case where hydrate is formed from free gas bubbles, a good laboratory hydrate-bearing sediment synthesis system should be able to reflect the free gas migration during hydrate formation [16]. However, only a few laboratory studies have paid attention to synthesize hydrate samples in the presence of fluid migration. Seol and Kneafsey [17] investigated the multiphase flow through hydrate-bearing silica sand (U.S. Silica F110, mean diameter ~120 μm), and suggested that the permeability change was caused not only by the presence of hydrate as a component within the pore space, but also by the preferred location of hydrate accumulation. Su et al. [16] employed a 196 L natural gas hydrate physical simulation device to investigate the behavior of hydrate formation in quartz sand (0.18–0.42 mm) with a gas seeping system. They found that the hydrate distribution in sediment with gas seeping was very different compared with the static system. In their system, hydrate trap was present in the middle of the specimen, preventing the growth of hydrate upwards, and then the trap gradually extended downward. McCallum et al. [18] compared the overpressures and induction times of hydrate formed by bubbling methane gas into bulk water and bentonite in a Seafloor Process Simulator (SPS) (72 L) and Parr vessel (450 mL). Subsequent experiments employing the same facility but bubbling methane gas into sediment suggested that in porous media systems containing free methane gas, bubble pathways and accumulation points were likely to control the location and habit of massive hydrate deposits [15,19]. Note that pure water was used in their experiments. Therefore, it may not be a good reflection of the marine MH deposits. The above studies highlight the significant effect of free methane migration on the MH formation behavior compared with a quiescent system. Thus, in order to be more representative of the MH formation associated with free methane flux, we deployed the methane gas circulation method for all the experiments in this study.

In China, methane hydrate deposits also have emerged as an attractive potential energy source [6,20]. In recent years, several drilling projects have been carried out in South China Sea (SCS) and Qinghai-Tibetan Plateau permafrost regions in China [21]. In the Shenhu area in SCS, gas hydrate samples were detected at three of the five sites that were cored (Sites SH2, SH3 and SH7). The grain size analysis of the hydrate-bearing sediment showed that SH2 site was mainly composed of clay (< 0.004 mm, 15.68–40.16%), silt (0.004–0.063 mm, 53.74–81.35%), and sand (> 0.063 mm, 0.5–11.87%) [22]. The presence of intense methane seepage was found in some sites of the northern SCS, which would cause different behavior of MH formation and accumulation [22,23].

Nevertheless, most of the previous laboratory studies formed MH in quiescent systems with relatively uniform sediment media mainly composed of silica sands, while the natural MH bearing sediments are typically a mixture of clay, silt, and sand. In order to have a better understanding on the relationship between MH formation behavior and sediment properties, it is necessary to synthesize more representative hydrate samples in a system closer to the natural circumstances, including the sediment composition, saline water, free gas migration, pressure (P), and temperature (T), etc. Considering these factors, in this study, we formed MH in mixed-size porous media composed of silica sand, silt and clay with methane circulation to reflect the case where hydrate is formed from free methane flux. Six sets of porous media with different porosity and permeability were employed. The sediment composition, experimental temperature (286.2 K) and pressure (15 MPa) were chosen based on the real environmental conditions of the SH2 drilling site in the Shenhu area in SCS [22]. Note that the P/T conditions employed in this work were quite different from the experimental conditions in the studies mentioned in the second paragraph, which are mostly in the range of 274.0–277.2 K and 4.9–8.0 MPa. Saline water of 3.5 wt% NaCl solution and methane circulation with a rate of 5 mL/min were employed. We studied the MH formation kinetics, MH saturation and distribution in sediment, and variation of rate constant during MH formation. To the best of our knowledge, this is the first work employing mixed-size sediment media, saline water, and gas circulation together to investigate MH formation behavior at near real P/T conditions of MH drilling region. The results would contribute to a better understanding on the typical MH formation behavior with mixed-size porous media and free methane flux. The hydrate formation method employed in this work could also provide some guidelines for synthesizing representative MH samples, which is essential to the studies on energy recovery from MH.

2. Experimental

2.1. Materials

Silica sand and silty clay were supplied by Shengli Silica Sands Co., Ltd. Methane gas with purity of 99.9% was supplied by Liming Gas Co., Ltd. Sodium chloride (NaCl, 99.5% purity) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Deionized water was used for all