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Methane hydrate formation/reformation in three experimental modes: A preliminary investigation of blockage prevention during exploitation

Yongchen Song, Pengfei Wang, Lanlan Jiang, Yuechao Zhao, Mingjun Yang*

Key Laboratory of Ocean Energy Utilization and Energy Conservation of Ministry of Education, Dalian University of Technology, Dalian 116024, China

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ABSTRACT

Methane hydrate (MH) is a clean energy source with significant potential. However, the hydrate formation/reformation characteristics during the natural gas hydrate (NGH) exploration process must be elucidated. In this study, methane hydrate was formed/reformed in three different modes to simulate the mining of NGH sediment. The experimental results indicated that when the hydrate forms in partly water saturated porous medium in a flow of methane gas, the methane gas flow rate does have a significant effect on hydrate saturation. Hydrate could be formed in larger amounts and faster by the methane displacement of the water-saturated porous medium than in any other experimental mode. However, the pressure curves fluctuated strongly in this mode. When the hydrate was reformed at a constant pressure in partly water-saturated porous medium, the hydrate saturation maxima increased. However, when the hydrate was reformed by flowing methane through the partly water-saturated porous medium, the hydrate saturation maxima decreased.

1. Introduction

Energy and the environment are two topics of global importance, especially with the rapid increase in the energy demand and the generation of ever-increasing amounts of air pollutants (Stocker, 2013). Clean energy policies and stringent pollution controls can reduce the global atmospheric air pollution (Brown et al., 2001; Ebi et al., 2014; Rogelj et al., 2014). A number of institutions are dedicated to developing clean energy sources such as nuclear, wind, and solar (Zhao et al., 2012, 2009). Natural gas hydrates are a new potential source of clean energy, and methane is the major hydrocarbon constituent of gas hydrates (Ginsburg and Soloviev, 1997; Goel, 2006). The volume of gas stored in hydrates is large (Chong et al., 2015; Milkov and Sassen, 2002). For instance, the total amount of carbon in hydrates is reported to be twice that in all conventional resources, including coal, oil, and natural gas (Lee and Holder, 2001; Li et al., 2007). However, estimates of this volume vary widely (Frye et al., 2012; Milkov, 2004). In addition, the volume of natural gas hydrates that can reach surface waters vary with the ocean depth (Barnard et al., 2015; McGinnis et al., 2006). Over the past two decades, many countries have investigated methane hydrate (MH) as an energy source (Matsumoto et al., 2011; Sain and Gupta, 2012).

Gas hydrates are insertion compounds that are formed from water and light hydrocarbons (Bishnoi and Natarajan, 1996; Giavarini et al., 2008). Different hydrate-forming gases can result in structure I (S-I), structure II (S-II), and structure H (S-H) types hydrate (Kang et al., 2001; Sloan, 1998). MH (S-I) exists mainly in permafrost (including the continental shelves) and is commonly found in marine sediment voids/cracks or rocks with good permeability. This means that the hydrate forms during the migration of fluids (Max and Johnson, 2014; Max and Lowrie, 1996). With respect to the exploitation of MH, the latent heat required for the dissociation of the hydrate and the hydrate pore habit of the hydrate-bearing sediments are of significant importance (Jung and Santamarina, 2012). Hydrate decomposition causes a decrease in the local temperature, which may cause secondary hydrate formation, resulting in the clogging of the penetration path, which can affect the long-term recovery efficiency (Haligva et al., 2010; Vafaei et al., 2012; Zhang and Lu, 2014). In the case of fine-grained sediments, hydrate formation can readily block pore throats and reduce the permeability to seal-free gas. This hydrate formation process can trap gases and

* Corresponding author.
E-mail address: yangmj@dlut.edu.cn (M. Yang).

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cause the gas pressure to rise until it exceeds the overburden stress and drives the gases through the regional hydrate stability zone (Liu and Flemings, 2007; Waite et al., 2009). The driving of gases through the regional hydrate stability zone results in stress redistribution, sediment creeping, and collapse and/or landslides in the upper strata, and can even lead to the release of large volumes of methane from the hydrate into the ocean and the atmosphere (Liu and Flemings, 2006; Seo et al., 2014). Owing to the flexibility, safety, and economy associated with natural gas storage and transportation, using hydrate technology is also a potential method (Gerami and Pooladi-Darvish, 2007). Most studies on MH have aimed to improve the storage efficiency and capacity. Further, most studies on hydrate formation have involved static experiments and not those performed under dynamic seabed-simulating conditions (Hao et al., 2008; Kang et al., 2009; Lv et al., 2012). Therefore, in order to be able to exploit MH resources, it is important to elucidate the hydrate formation characteristics in porous media under dynamic conditions (Bishnoi and Natarajan, 1996; Talaghat, 2009).

The mechanisms of methane migration as well as those of the accumulation of the associated hydrate have been considered previously (Ginsburg and Soloviev, 1997). Nuclear magnetic resonance (NMR) was used to determine the pore-scale growth habit of MH in sandstone. It was found that the hydrate forms where the reactant, gaseous methane, is most abundant, namely, in the largest pore spaces (Kleinberg et al., 2003). Further, magnetic resonance imaging (MRI) has also been used to study hydrate formation (Hiraia et al., 2000). The performance of MRI is not affected by porous media (Baldwin, 2003; Yang et al., 2011). Birkedal et al. performed MH growth and dissociation experiments in partially water- and gas-saturated sandstone using MRI and used the TOUGH + HYDRATE code to predict the empirical nonmonotonic dissociation behavior (Birkedal et al., 2014). In addition to experimental studies, heat and mass transfer models have also been used. Liu et al. developed a model for free gas migration through the regional hydrate stability zone as well as a multicomponent multiphase fluid and heat flow model to describe hydrate formation in marine sediments (Liu and Flemings, 2006, 2007). To quantify the interacting physical processes, mathematical models have been developed for hydrate formation in porous media (Rempel and Buffett, 1997). Dynamic measurements of hydrate-based gas separation in water-saturated porous media have also been performed (Yang et al., 2014b, 2013). However, most of these studies have focused on hydrate formation in a static system, and there have been few reports on hydrate formation in a flowing system; this is particularly true for hydrate reformation.

The purpose of this study was to examine MH formation/reformation in porous medium under dynamic conditions, so that the results can serve as a safety guide for gas hydrate exploration and help improve the efficacy of hydrate-based technologies. MRI was used to image the ^{1}H contained in liquid water (Yang et al., 2013). Given that relaxation time of ^{1}H in hydrate crystals is smaller, MRI can be used effectively to distinguish between solid hydrates and the liquid phase of the hydrate formers (Cha et al., 2015). The effects of the methane flow rate and the initial water saturation level on MH formation in different modes were investigated experimentally. The hydrate saturation level, the residual water saturation (RWS) level (i.e., the percentage of residual water in the pore volume after methane displacement), and the variation in the pressure were measured, and the process of hydrate formation was visualized. This was done to obtain critical data that can not only help prevent hydrate reformation during gas hydrate exploration but also improve hydrate-based natural gas storage and transportation technologies.

2. Experimental

2.1. Materials and methods

The experimental system used consisted of five primary subsystems: (A) the MRI system for visualizing MH formation; (B) a high-pressure vessel; (C) the data acquisition system that recorded the pressure and temperature variations within the high-pressure vessel; (D) high-pressure pumps that injected methane and deionized water and a back-pressure control pump; and (E) a low-temperature cooling system containing two thermostat baths to keep the vessel and the methane injection pump at the required temperature. A schematic diagram of the experimental system is shown in Fig. 1. The high-pressure vessel was made of a nonmagnetic material (polyimide), in order to minimize the effects of the radiofrequency field generated by the MRI system. This high-pressure vessel had a relatively large inner volume and was designed to handle a pressure of 15 MPa. Its effective dimensions were 15 (diameter) × 200 mm, while the overall dimensions were 38 (diameter) × 314 mm. The vessel was surrounded by a jacket in which the coolant circulated continually, in order to heat or cool the vessel. The MRI system (Varian, Inc., Palo Alto, CA, USA), which was operated at a resonance frequency of 400 MHz, was used to image the MH formation process. The intensity of the magnetic field produced by the magnet was 9.4 T, while the maximum gradient strength of the gradient coils was 50 G/cm. The MRI system could image and quantify the distribution of the liquid in the porous media.

In this study, the MRI images were constructed using a spin echo multislice pulse sequence (Song et al., 2013; Yan et al., 2014); the experimental parameters used were the following: echo time of 13.82 ms, repetition time of 560 s, image data matrix = 128 × 128, field of view (FOV) = 30 mm × 30 mm (4.0 mm in thickness), and sequence acquisition time of 1 min. Three high-precision syringe pumps (260D, Teledyne Isco Inc., Lincoln, NE, America) were used in the experiments. Two of these pumps were used to inject methane and deionized water. The third pump was used to control the back pressure during hydrate formation. The pressure transducer (Nagano Co., Ltd., Nagano-ken, Japan) was connected to the vessel. The estimated errors in the pressures were ±0.1 MPa. A temperature transducer (Yamari Industries, Takatsuki-Shi, Osaka, Japan) with an estimated error of ±0.1 K was connected to the vessel jacket. The pressure and temperature signals acquired by the thermocouples and pressure sensors were collected by the A/D module (Advantech Co., Ltd. Milpitas, CA, USA). The collected data were sent to the PC and processed by the monitor and control system. The temperature of the high-pressure vessel and the methane injection pump were controlled within ±0.1 °C using thermostat baths (FL300 and FL 25, JULABO, Seelbach, Germany) filled with Fluorinert (FC-40, 3M Company, Paul, MN, USA).

2.2. Experimental procedures

The glass beads used in this study were produced by As-One Co., Ltd., Japan. Methane (99.9%) was provided by Dalian Guangming Specialty Gas Co., Ltd., China. Three different experimental procedures were performed to simulate hydrate formation: cooling at a given pressure and temperature in a partly water-saturated porous medium in the absence of a constant flow of methane (Case 1); cooling at a given pressure and temperature in a partly water-saturated porous medium in a constant flow of methane (Case 2); and cooling in a fully water-saturated porous medium at a given pressure and temperature under a constant flow of methane (Case 3). For Case 1, the glass beads were packed into the high-pressure vessel. Next, the high-pressure vessel was placed within