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Effect of depressurization pressure on methane recovery from hydrate–gas–water bearing sediments

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HIGHLIGHTS

- MH dissociation characters were measured for ternary phases sediment.
- Heat transfer is a control factor for MH dissociation pattern and rate.
- There is a maximum depressurization range to make MH dissociation rate increase.
- Methane gas seepage makes liquid water distribution changes.

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ABSTRACT

Natural gas hydrates (NGHs) are a promising energy source with huge reserves. The dissociation characteristics of NGHs need to be clarified further for developing safe and efficient technology for its recovery. In this study, Classes 1 and 2 NGH deposits were simulated by forming methane hydrate (MH) in porous media, and MH dissociation induced by depressurization was investigated using magnetic resonance imaging (MRI). MRI showed the liquid water distribution, which was used to analyze MH formation and dissociation. The vessel pressure was also measured during the experiments, which was compared with the MRI mean intensity of liquid water. MH dissociation processes were measured and analyzed under different backpressures, from 2.2 to 2.8 MPa. It was observed that liquid water hindered methane gas output during gas production; hydrate dissociation caused the movement of some liquid water, which usually led to fluctuations in MRI signal intensity. The experimental results also indicated that the MH dissociation pattern was affected by heat transfer; although a larger depressurization range led to faster dissociation, the average dissociation rate was controlled by heat transfer.

1. Introduction

Natural gas hydrates (NGHs) are ice-like crystalline compounds, wherein water molecules create cavities (hosts) through hydrogen bond formation to engage natural gas molecules (guests) at high pressures and low temperatures. Typical natural gas contains methane (CH_4), ethane (C_2H_6), propane (C_3H_8), and carbon dioxide (CO_2), each of which can form different hydrates [1,2]. A large amount of methane is trapped in NGHs, and methane hydrate (MH) is consequently the most common NGH in natural sediments [3]. MH widely exists in the permafrost and in marine sediments. Usually, NGH deposits are divided into three classes [4–6]: Class 1 deposits contain two layers: an overlying hydrate-bearing layer (HBL) and an underlying two-phase fluid zone containing mobile gas and water; e.g. the hydrate accumulation in the North Slope of Alaska [7]. Class 2 deposits contain a water zone above the HBL; e.g., Nankai Trough, Japan [8,9]. Class 3 deposits involve only an isolated hydrate layer without any contact with the hydrate-free zone; e.g. the Gulf of Mexico [4]. Considering that different NGH sediments have different gas recovery characteristics, clarification of hydrate dissociation characteristics and development of exploration technologies need to be carried out separately for each class.

NGH dissociation is a complicated process, and is usually accompanied by phase change, multiphase flow, mechanics, mass and heat transfer, etc. [10,11]. The popular methods for triggering hydrate dissociation are thermal stimulation, inhibitor injection, and depressurization [12–14]. Moreover, some exceptional methods such as CO_2 replacement [15] and gas lift [16] have been proposed to meet the enhanced safety and economy requirements of commercial NGH production. Thermal stimulation increases the

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MH sediment temperature so that it exceeds the MH phase equilibrium temperature [17]. Inhibitor injection lowers the MH phase equilibrium pressure [18], while depressurization decreases the sediment pressure so that it is below the MH phase equilibrium pressure [19,20]. Wang et al. experimentally investigated the gas/water production, efficiency, recovery, and production rate during thermal stimulation and thermal huff and puff [21]; after comparing thermal stimulation, depressurization, thermal huff and puff, etc., they concluded that thermal stimulation should be combined with depressurization [22,23]. Depressurization is generally considered the most feasible and promising method for NGH exploration because of its cost-effectiveness [24].

Although field-scale depressurization was first tested at the Mallik site of the Mackenzie Delta in Northwest Territories, Canada [25], followed by larger-scale field tests at the same site in 2007 and 2008 [26], many issues with actual production are yet to be resolved [27]. Consequently, there have been many studies on hydrate dissociation and gas production in porous media by depressurization. Tang et al. investigated the characteristics of gas production by depressurization in hydrate reservoirs of different sizes, and proved that hydrate dissociation kinetics have a considerable effect on laboratory-scale hydrate reservoirs, and that this effect can be ignored in field-scale reservoirs because of the flow ability dominating [14]. Haligva et al. also studied the kinetics of hydrate decomposition by depressurization, and suggested that the rate of methane recovery from hydrates is affected by the laboratory sample [28]. Moreover, different hydrate saturations and permeabilities of the hydrate zone in porous media impact the gas production rate and dissociation characteristics [29,30]. Simulation methods have also been used to study MH recovery by depressurization. Li. et al investigated the kinetics and gas production characteristics of MH decomposition under depressurization with low gas saturation using both experimental methods and numerical simulations [31]. A comparison of the simulated and experimental data showed that the rate of decomposition increases with decreasing pressure. Using the inverted five-spot water flooding method, Li et al. also evaluated the energy efficiency ratio and verified the equilibrium model with the experimental data [32]. Besides, as the other mathematical description, the kinetic model is always described with Kim–Bishnoi model [33]. Recently, a field-scale simulation of methane recovery from marine hydrate deposits was carried out using the TOUGH + HYDRATE code [34]. The full 3D simulation covers an area of 38 km^2, and aids in the simulation of coupled flow, mass and heat transport, thermodynamics, and the phase behavior for large-scale hydrate sediments.

Most experimental investigations have been carried out to analyze gas production and heat transfer in a closed vessel, and the traditionally used optical method cannot be used for sediments. In order to further study the characteristics of MH decomposition, X-ray computed tomography (CT) and magnetic resonance imaging (MRI) have been used to visualize MH dissociation in porous media. Timothy et al. used X-ray CT to compare MH dissociation in different hydrate samples [35]; some researchers have measured the physical properties of gas hydrates during formation and decomposition [36,37]. MRI has been applied for studying the in situ formation and dissociation of methane and CO_2–CH_4 hydrates in porous media [38,39]. Baldwin et al. [40] and Ersland et al. [41] have also used MRI to study gas hydrate formation, the conversion of methane hydrates into CO_2 hydrates through exchange with CO_2, and to obtain the spatial distribution of hydrate growth.

Overall, although there is a great deal of progress in understanding the thermodynamic and kinetic characteristics of MH hydrate dissociation by depressurization, some inherent mechanisms still need to be clarified. In this study, we focus on the dissociation of MH from Classes 1 and 2 hydrate deposits, wherein both mixed gas (free gas and hydrate dissociation gas) saturation and liquid water saturation are high during gas production. MRI images have been obtained to analyze the influence of different backpressures on gas production from MH deposits. The results provide some basic visual data for the kinetics of MH dissociation in porous media, along with a reference for future NGH exploration.

2. Experiments

2.1. Apparatus and materials

The experimental apparatus consisted of an MRI system (Varian, Inc., USA), a high-pressure vessel, two high-pressure pumps (260D, Teledyne Isco Inc., USA), a thermostated bath (FL300, JULABO technology, Germany), a data acquisition system, and a backpressure regulator (BP-2080-M, JASCO, Tokyo, Japan). Details regarding the experimental apparatus are provided in a previous paper [39]. A water container and pump were also used for water injection. The MRI system (operating at 400 MHz) was used to visualize MH formation and dissociation in porous media. The basic principle is that MRI can detect the ^1H in liquids and produce liquid distribution images, while the ^1H in solids is not detected and thus solids are not visualized in the images. A spin echo pulse sequence was applied with TR = 500 ms, TE = 1.63 ms, and slice thickness = 4 mm. The field of view (FOV) was 30 × 30 mm and the MRI image matrix was 128 × 128 pixels. The high-pressure vessel was made of polyimide (a nonmagnetic material) and had a design pressure of 12 MPa. The total size of the cylindrical vessel was ∅38 × 314 mm. In order to maintain a stable vessel temperature, a thermostated bath filled with Fluorinert (FC-40, 3 M Company, USA) was used to cool the vessel jacket. High-pressure pumps were used to inject water and methane gas into the vessel. The backpressure control valve was connected with the vessel outlet to control the backpressure. The vessel pressure was measured with an accuracy of 0.1 MPa using a pressure transducer (Nagano Co. Ltd., Japan) connected to the vessel. A thermocouple was used to monitor the jacket temperature. A middle container was used to store water, which was maintained at specified temperature using a glycol bath (F38-EH, JULABO Technology, Germany). This constant-temperature water was then injected into the vessel. BZ-02 glass beads (0.177–0.250 mm; As-One Co., Ltd. Japan) with porosity of about 35.4% were packed into the vessel to simulate the porous media. Deionized water was used in all experiments.

2.2. Procedure

The BZ-02 glass beads were evenly and tightly packed into the vessel, and then placed into the magnetic body of the MRI system. After evacuating the vessel, deionized water was slowly injected into the vessel until the pressure reached 6 MPa. Once the pressure became stable, which indicated that the glass beads were fully saturated, high-pressure nitrogen was injected to make space for methane injection by displacing the pore water, and the amount of displaced water was recorded. The vessel was evacuated again. Subsequently, methane gas (99.99%, Dalian Special Gases Co., LTD, China) was slowly injected at the design pressure of 6 MPa and the thermostated bath was set at 274.15 K to trigger hydrate formation. After the pressure and temperature became stable, images could be continuously obtained using MRI.

In order to simulate natural MH sediments during gas production, we injected liquid water into the porous media to discharge some of the residual gas before MH dissociation. The water temperature was maintained at 273.65 K by the thermostated bath, and this water was injected until the water flowed out and the