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In-situ visual observation for the formation and dissociation of methane hydrates in porous media by magnetic resonance imaging

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ABSTRACT

In this work, magnetic resonance imaging (MRI) was employed to observe the in-situ formation and dissociation of methane hydrates in porous media. Methane hydrate was formed in a high-pressure cell with controlled temperature, and then the hydrate was dissociated by thermal injection. The process was photographed by the MRI, and the pressure was recorded. The images confirmed that the direct visual observation was achieved; these were then employed to provide detailed information of the nucleation, growth, and decomposition of the hydrate. Moreover, the saturation of methane hydrate during the dissociation was obtained from the MRI intensity data. Our results showed that the hydrate saturation initially decreased rapidly, and then slowed down; this finding is in line with predictions based only on pressure. The study clearly showed that MRI is a useful technique to investigate the process of methane hydrate formation and dissociation in porous media.

1. Introduction

Natural gas hydrate, an ice-like crystalline structure, in which molecules of gas (mainly methane) are contained in a lattice formed by water molecules, widely exists in nature and is becoming more widely accepted as a promising energy resource [1–3]. The total amount of this hydrate is thought to be at least double that of the entire exploitable hydrocarbon contained in the reserves identified to date [4–6]. The hydrates can form gas reservoirs in the gas hydrate stability zone, including the marine or freshwater sediments at water depths greater than 300 m and the permafrost under the land [7–9]. In 2007, a gas hydrate drilling campaign was carried out in the Shenhu area (South China Sea), and the presence of gas hydrate was confirmed [10]. Gas hydrates also appear in conventional oil and gas pipelines because the high pressures and low ambient temperatures in the pipelines may lead to rapid hydrate growth. This would completely block the flowline and cause operational and safety hazards [11]. Moreover, hydrates have a significant impact on energy recovery, transportation, and climate change [12,13].

These facts are closely related to the formation and dissociation of hydrates. Thus, researchers are directing efforts towards understanding the behavior of the hydrate. Like other crystallization processes, hydrate formation is not governed by thermodynamic laws, but is rather stochastic [14,15]. The features of gas hydrate growth and dissociation depend on several parameters, including the contact area between phases, pressure, temperature, supercooling degree, gas and salt concentrations in water solution, structural characteristics of the sample and gas solubility in water [16]. Methane hydrates usually nucleate and grow along the gas–water interface [17], and continued growth is supported by the methane dissolved in water. Induction time is an important parameter for the process of hydrate formation. The elapsed time for the hydrate nuclei to achieve a critical size for initiating the hydrate growth is considered to be the induction time [18,19]. The rate at which hydrates nucleate and grow is related to the thermodynamic driving force; subcooling and supersaturation are the most common driving forces [20,21]. Linga *et al.* [22] conducted a series of experiments about gas hydrate formation in a variable volume bed of silica sand particles. They found that an initial slow growth was followed by a rapid hydrate growth rate of equal magnitude for nearly all experiments. McCallum *et al.* [23] discussed the impact of the size of the hydrate formation vessel on the induction time and hydrate formation/decomposition. They discovered that the large volume of the vessel can provide more locations for hydrate nucleation to occur. Recently, Mohebbi *et al.* [24] investigated the gas hydrate formation from a natural gas mixture using a stirred-reactor tank. Their results indicated that the rate of gas consumption is exponentially related to over-pressurizing of the system. On the other hand, visual observation by digital macrophotography [25] proposed that the solid fraction increased by the

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formation of additional primary crystals rather than by the growth of existing particles. In addition, the hydrate crystals are believed to be wetted with the aqueous liquid at all times during dissociation, confirming a strong hydrophilic character. Akhfash *et al.* [26] studied the methane hydrate formation rate and resistance to flow. In their study, a transition from a homogeneous to heterogeneous particle distribution was observed directly through three independent measurements showing good agreement with each other. It was proposed that the properties of natural hydrates are different significantly from the properties of artificial hydrates, which also has an effect on the dissociation curves [16,27]. In particular, the dissociation rate of natural samples is lower than that of the artificial powders; the dissociation mechanism is dependent not only on the driving forces, but also on the structural characteristics of micro-grains and the diameters of sample spheres [28].

Magnetic resonance imaging (MRI), a well-established technique routinely employed in the medical field, is becoming more widely used in engineering and materials science. MRI can map the proton with high-space resolution in three dimensions non-invasively. The MRI signal is poor for the hydrogen in solid hydrates, but is strong for liquid water. Water and solid can be distinguished easily by the MRI images. Therefore, hydrate spatial distribution, saturation and the rate of hydrate formation and dissociation can be determined. MRI can provide visual data and accurate information, making it a useful tool for the study of hydrates [29–32]. Moreover, Ersland *et al.* [33] monitored the spontaneous exchange of methane with CO_2 within the hydrate structure. They proved that MRI could provide clear information about the rate of the hydrate formation and the rate of the CO_2–CH_4 exchange.

Despite the relevance of this topic, few studies [30,32] have been proposed that use MRI to directly observe the formation and dissociation of methane hydrate. In order to gather more information about this critical point, we propose in this contribution a method for a direct visual observation performed with MRI to investigate nucleation, growth, and decomposition of methane hydrate. The validity of our method has been proven by comparing the saturation obtained from MRI data and from calculating pressure.

2. Experiments

2.1. Apparatus and materials

The experimental apparatus employed in this work [34] is illustrated in Fig. 1. An NMR system (400MHZ, Varian, Inc., U.S.) was used to observe the formation and dissociation of methane hydrate. A fast spin echo multi slice (FSEMS) pulse sequence with time of repetition (TR) = 1000 ms and time of echo (TE) = 10.14 ms was used. The thickness of the slices was set to 1 mm. Images were set to be collected with 256 × 256 points. The field of view (FOV) was 40 mm × 40 mm. In order to investigate the effect of the pore size on hydrate formation and dissociation, three different sizes of quartz beads (AS-ONE, Co. Ltd., Japan), BZ-1 (particle diameter 990-1400 μm, average 1200 μm), BZ-04 (particle diameter 350–500 μm, average 400 μm), and BZ-01 (particle diameter 80–120 μm, average 100 μm), were used to simulate three different porous media, respectively. It was assumed that the quartz particles have the same surface roughness. The simulated porous media exhibit a similar porosity (about 38%). Fig. 1 also shows the cell used inside the MRI system. The cell has a design pressure of 12 Mpa, and the effective dimension of the cell is 15 mm in diameter and 200 mm in length. The part of the cell detected by MRI consists of polyimide, while the two caps were made of titanium and joint by taper thread. The thermostatic bath system was a circulator (F25-ME, Julabo Inc., Germany) which has a temperature control range from −28 °C to 200 °C and a precision of ±0.01 °C. Fluorinert FC-40 (produced by 3 M, MN, US) was chosen as the coolant because this fluid does not contain imaginable hydrogen and has low dielectric properties to minimize RF losses. A thermocouple (SAKAGUCHI E.H VOC CORP, Japan) to monitor temperature was inserted into the coolant jacket. All the pipes were wrapped with insulation coverings to reduce the heat loss. The temperature difference between the coolant jacket and the circulator is about 0.5 °C. The high-precision syringe pump (Teledyne ISCO Inc., US) was used to inject water or methane. The estimated errors of temperature and pressure measurements are ±0.1 K and ± 0.01 MPa, respectively. Methane of 99.9% purity (provided by Dalian Special Gas Co., Ltd., China) and deionized water were used in the whole experiments.

2.2. Procedure

The clean glass beads were firstly packed into the cell, and then a vacuum pump was used to discharge the gas in the cell. After water was injected into the cell, methane gas was slowly injected into the cell until the pressure achieved the design value of 9 MPa. Then the cell was closed and kept at a steady temperature of 1 °C. At the same time, MRI was acquiring images continuously. When hydrate forms in the cell, the intensity of the MRI signal changes. Hydrates formations were directly observed for more than 18 hours, and were considered complete when the MRI signal intensity and the pressure of the system became stable and did not change for longer than 3 hours [31,32]. The hydrate was then decomposed by increasing the temperature of the thermostatic bath to 16 °C. The pressure in the vessel was continuously monitored. Each experiment was repeated several times, and the averages were calculated to reduce the errors caused by randomness.

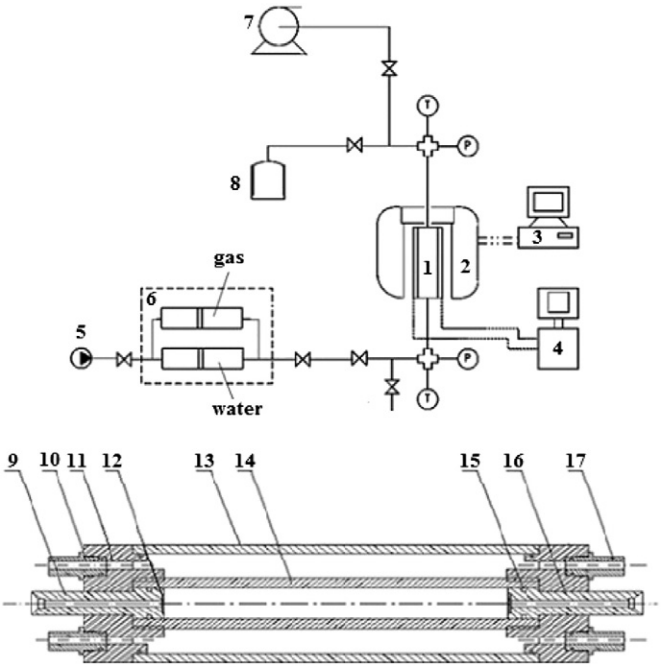

Fig. 1. Schematic description of the experimental apparatus. 1, MRI cell; 2, MRI system; 3, output system; 4, thermostatic bath system; 5, syringe pump; 6, transfer vessel; 7, vacuum; 8, gas collecting bottle; 9, upper head; 10, coolant outlet; 11, upper cap; 12, sieve; 13, vacuum sleeve; 14, inner-sample container; 15, sealing O-ring, 16, lower head; 17, coolant inlet.