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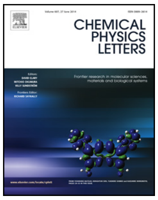

In situ observation of gas hydrates growth hosted in porous media

Jiafei Zhao[a], Lei Yang[a], Kaihua Xue[a,*], Weihaur Lam[b], Yanghui Li[a], Yongchen Song[a,*]

[a] Key Laboratory of Ocean Energy Utilization and Energy Conversion of Ministry of Education, Dalian University of Technology, Dalian 116024, China
[b] Department of Civil Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

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ABSTRACT

Gas hydrates can be free floating in the sediment matrix; contacting, but do not cement; actually cementing and stiffening the sediment. The microstructure and growth of gas hydrates (CH_4 and CO_2) in porous media were observed in situ by Magnetic resonance imaging (MRI). The experimental results confirmed the random nucleation of gas hydrates in porous media. The results show that hydrates are preferentially formed in the pore spaces. Hydrates then occupy the pores of porous media gradually, but do not cement the adjacent glass beads in the final stage. Gas hydrates are believed growing as free-floating model in porous media.

Natural gas hydrate is the global interest due to the potential impact on diversification of world energy resources, seafloor stability, drilling hazard of exploration and impact on climate change as major greenhouse gas [1]. In hydrate-bearing sediments, gas hydrates can be (a) free-floating in the sediment matrix, (b) contacting and existing sediment grains, but not cementing or (c) cementing and stiffening the bulk sediments [2,3]. The porous microstructure of gas hydrates governs the mechanical strength and hydraulic permeability of the hydrate-bearing sediments [4]. Moreover, for exploration of gas hydrates, the velocity and attenuation of compressional and shear waves depend primarily on the spatial distribution of hydrates in the pore space in sediments [5]. Kleinberg et al. (2003) [6] suggested that hydrates tend to replace the water in the pore spaces and form in the centres of the pores rather than as a coating on the grains. Moreover, Kerkar et al. (2009) [7] first directly observed the growth of tetrahydrofuran (C_4H_8O, hereafter THF) hydrate in porous media using synchrotron X-ray computed microtomography, and found THF hydrates nucleates random and grows independently of the grain surfaces. Additionally, methane hydrates were observed to form at different time and different positions by Bagherzadeh et al. (2011) [8]. However, Waite et al. (2004) [9] used rock physics models to differentiate the potential pore-space hydrates distributions and suggested the methane hydrates cement the unconsolidated sediments. Xue et al. (2012) and Song et al. (2013) [5,10] recently investigated THF hydrate growth habit in porous media and found that THF hydrate growth is first modelled by cementing model then the floating model with increasing water concentration. Gas hydrates were mainly formed at high pressure and low temperature, especially methane and carbon dioxide hydrates. Purpose-built equipment is generally needed to form and to study the behaviour of gas hydrate. However, THF could only form hydrate at 4.4 °C and atmospheric pressure. Therefore, THF hydrate is commonly studied as a substitute for natural gas hydrates in laboratory. To date, no direct microscopic measurement was reported to confirm the gas hydrates growth habits in hydrate-bearing sediment.

Magnetic resonance imaging (MRI) is a well-established technique in the medical field used typically for imaging liquid water in porous media. MRI becomes more popular in the field of engineering and materials science. Cheng et al. (2013) [11] observed the formation and dissociation of carbon dioxide hydrate by MRI and obtained the hydrate saturation for different time. The study indicated that MRI signal is strong in free water, but undetectable above the background noise when the water forms a solid hydrate. Daraboina et al. (2013) [12] investigated the formation kinetics of methane/ethane/propane hydrate in the presence of kinetic inhibitors using MRI. The results demonstrate that MRI is a useful tool to visualise and to evaluate the performance of kinetic inhibitors on gas hydrates formation. The methane diffusion and hydrate growth were observed by Susilo et al. (2006) [13] using nuclear magnetic resonance (NMR) spectroscopy and imaging (MRI). In addition, Ersland et al. (2010) [14] monitored the spontaneous exchange of CH_4 with CO_2 within the hydrate structure. They proved that MRI gives excellent information about the rate of the hydrate formation and the rate of CO_2—CH_4 exchange. Moreover, Moudrakovski et al. (1999, 2004) [15,16] studied the methane and carbon dioxide hydrate formation processes inside dispersed water

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[*] Corresponding author.
E-mail addresses: jfzhao@dlut.edu.cn, zhaojiafei@zju.edu.cn (J. Zhao), songyc@dlut.edu.cn (Y. Song).

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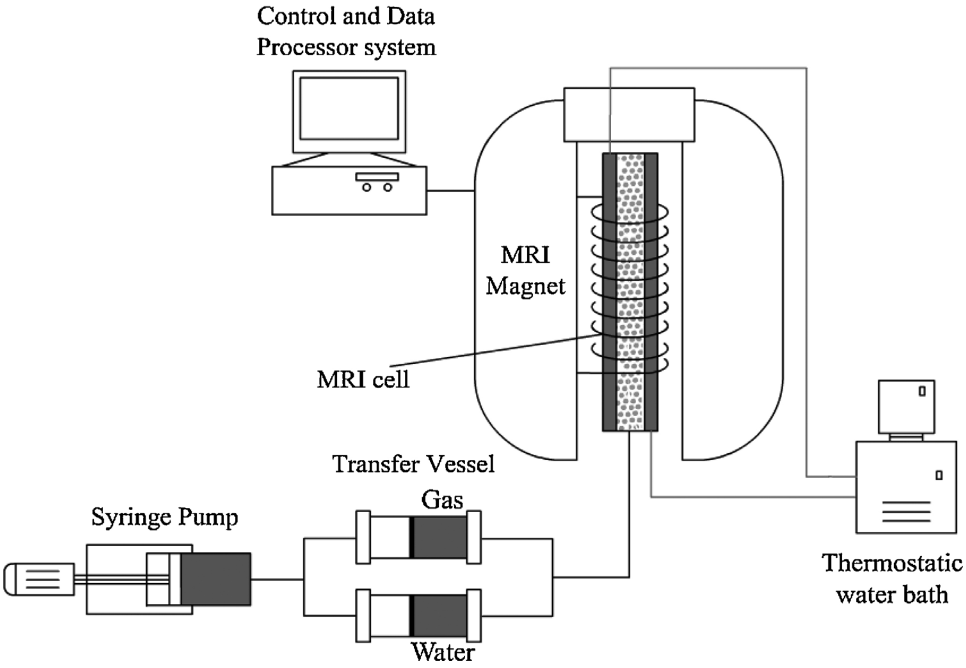

Figure 1. Schematic diagram of the experimental apparatus.

droplets and the interaction of methane gas with ice surfaces using ^1H magnetic resonance microimaging. However, the utilisation of MRI to monitor the growth habit of methane or carbon dioxide hydrates in porous media has not been reported.

In the present study, an MRI experimental system was established for in situ observation of the microstructures of methane and carbon dioxide hydrates in porous media. Quartz glass beads (AS-ONE, Co., Ltd., Japan) BZ-4 (3.962–4.699 mm, average 4.5 mm) were used to simulate the porous media in MRI cells. The experimental system is illustrated in Figure 1. The MRI system was from Varian, Inc. 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 to observe the growth of gas hydrates. Images were collected with 256 points for read-out and phase-encoding. The field of view was set to be 40 mm × 40 mm. The fluorinert was used as the coolant in the MRI system. Since the fluorinert cannot be visualised by MRI, the interference on the imaging system can be minimised. The temperature controller was a high-precision circulator with a range from −28 °C to 200 °C at a precision of ±0.01 °C. The hydrate formation and dissociation were achieved by controlling the temperature of the coolant. The coolant continuously circulated around the sample through the MRI cell. After cleaning the quartz glass beads and the MRI cell with deionised water, the MRI cell was filled with glass beads to simulate porous media. To eliminate the influence of the other gases, the whole system is evacuated before the gas and water injection. In each experimental run, the deionised water was saturated with carbon dioxide (99.999% purity) or methane (99.99% purity) at specific temperatures (3 °C for CO_2, 1 °C for methane) and initial pressures (5 MPa for CO_2, 7 MPa for methane) for hydrate formation. The whole progress was continuously monitored by MRI. Since the crystal growth of hydrate is random and the sample container is larger than the field of view, each experiment was repeated several times and monitored by MRI.

Based on our previous investigations in the porosity and saturation of gas hydrates using MRI [11], the sample porosity and saturation were determined. The porosity (φ) was 38.9% and is comparable with the 38% theoretical porosity (φ_{th}) of a random dense pack of uniform spheres. The carbon dioxide hydrate saturation (S_h) increased from 0% to 33.6% at approximately 1080 min. Figure 2a shows the CO_2 hydrate growth in the longitudinal section of the porous media. The growth was observed for 24 h. The CO_2 hydrates formed after 270 min, but hydrate growth ceased after 17 h. Prior to the formation of hydrates, CO_2 is at the top of the visual field, and the black areas in the images represent the quartz glass beads and the white areas represent free water. The images of the longitudinal section indicate that the formation of gas hydrates is stochastic in the porous media. They prefer to grow at the interface of the water and CO_2 and subsequently grow around the glass beads as shown in Figure 2a. The formation of hydrates starts from the upper part of the visual field (arrowheads at the 270 min image of Figure 2a), and propagates downwards. The results suggest that hydrate growth is influenced by the solubility of CO_2. These observations are consistent with our previous visual observations on THF hydrate growth [10] and the random nature of the nucleation process. During hydrate growth, the water layer exists between the glass beads and the hydrates as shown in image of 1080 min in Figure 2a. Moreover, Figure 2b shows the growth of the hydrates in one of the cross sections. As shown at the hydrate point (arrowhead) at 720 min, the hydrates were initially formed in the pores. With the growth of the hydrates, they gradually occupied the pore space. However, hydrates do not cement the adjacent glass beads; a free water layer is observed between the hydrates and glass beads at 1080 min, as shown in Figure 2b. The carbon dioxide hydrates grow in pores in a manner similar to the free-floating or pore-filling models described by Kingston et al. (2008) [17].

In addition, Figure 3a and b shows the MRI signal intensity along the line in Figure 2b before and after CO_2 hydrate formation, respectively. The MRI process is a non-invasive scan, and the MRI data obtained can be used to determine the distribution of hydrogen density. The intensity of data reflects the actual hydrogen distribution in free water. The peaks around the glass beads indicate the existence of free water layer. This result shows that the CO_2 hydrates grow as a free-floating model in porous media.

The same process was repeated for methane hydrate formation. Figure 4 shows the process of the CH_4 hydrate growth on quartz glass beads. In the image of 570 min in Figure 4a, the hydrate point first forms in the pore as indicated by the arrow. After 6 h, the hydrates form in the pore space at the lower part of the MRI