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Dynamic behavior of methane hydrates formation and decomposition with a visual high-pressure apparatus

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ABSTRACT

A new visual high-pressure apparatus, with an internal volume of about 1.6 L, was installed in the present study to investigate the dynamic behavior of gas hydrate formation and decomposition. A series of experiments have been conducted for collecting the dynamic data of methane hydrate formation at specific temperature and pressure and those of hydrate decomposition at temperatures from 274 K to 285 K as pressure decreasing from high pressure to ambient pressure. A first-order reaction model represents well the dissociation behavior of methane hydrates. In addition to the visual inspection of the phase transition through transparent windows, the dynamic temperature distribution, pressure, and the total volume change of the released methane provide valuable data to verify and improve the performance of software for simulating the methane hydrate formation and the gas production from the natural gas hydrate reservoir with depressurization process.

1. Introduction

Natural gas hydrate has been recognized as one of potentially alternative energy resources in the future since the estimated amount of the gas in hydrate form is even greater than that in conventional natural gas wells (Makogon et al. [1], Moridis and Sloan [2]). In addition to the phase equilibrium properties of the gas hydrate systems (*e.g.*, Marshall et al. [3], Dholabhai et al. [4], Adisasmito et al. [5], Yang et al. [6]), the dynamics behavior during the gas hydrate decomposition are fundamentally important to develop the gas production technology from hydrates. There are several possible ways to induce gas hydrate destabilization, for example, by thermal treatment (Moridis et al. [7], Cranganu [8], Fitzgerald et al. [9]), depressurization (Sun and Chen [10], Zhou et al. [11], Lee et al. [12], Su et al. [13], Li et al. [14], Wang et al. [15]), and chemical stimulations (Sloan [16], Demirbas [17], Park et al. [18]). Among the above-mentioned techniques, Ji et al. [19] claimed that the depressurization could be economically attractive for natural gas hydrates production in comparison with other methods.

Regarding the studies on the methane hydrate decomposition through depressurization, Sun and Chen [10] used a sapphire cell to measure the kinetic data of methane hydrate dissociation by depressurization method at various temperatures and pressures. They found that hydrate dissociation was controlled by gas diffusion and thus the hydrate dissociation process can be considered as a moving boundary problem. Based on the experimental and simulation results, Zhou et al. [11] suggested that methane hydrate formed initially at the top zone of the reactor and followed by forming around the lower part of the sediment. They also reported that ice formation in the transition regime when the cell's temperatures are below zero during the depressurization process. Lee et al. [12] investigated the hydrate decomposition of a Berea sandstone core, which have lengths of 30.4 cm and diameters of 3.81 cm. The results showed that the degree of depressurization is a crucial factor for gas production rate. Su et al. [13] installed a 3-D device to investigated methane hydrate formation and decomposition. The temperature distribution curves revealed that the hydrate in the top and bottom of reactor dissociated faster than in the inner. This study also found that decomposed position and sequence could be identified by the temperature variation during the depressurizing. Li et al. [14] and Wang et al. [15] also explore the heat transfer and methane production behavior by using a 3-D 117.8 L pressure chamber (Pilot-Scale Hydrate Simulator, PHS). These studies found that the mass and heat transfer processes mainly govern the hydrate dissociation and concluded that the synergistic effect of depressurization and heat stimulation could increase the hydrate dissociation rate. In addition to temperature, pressure, and released gas volume measurements, more sophisticated instruments have also been employed to gas hydrate studies such as *in-situ* Raman Spectroscopy (Komai et al. [20]), X-ray computed tomography (CT) (Kneafsey et al. [21] and Kneafsey and Moridis [22]), magnetic resonance imaging (MRI) (Wang et al. [23] and Yang et al.

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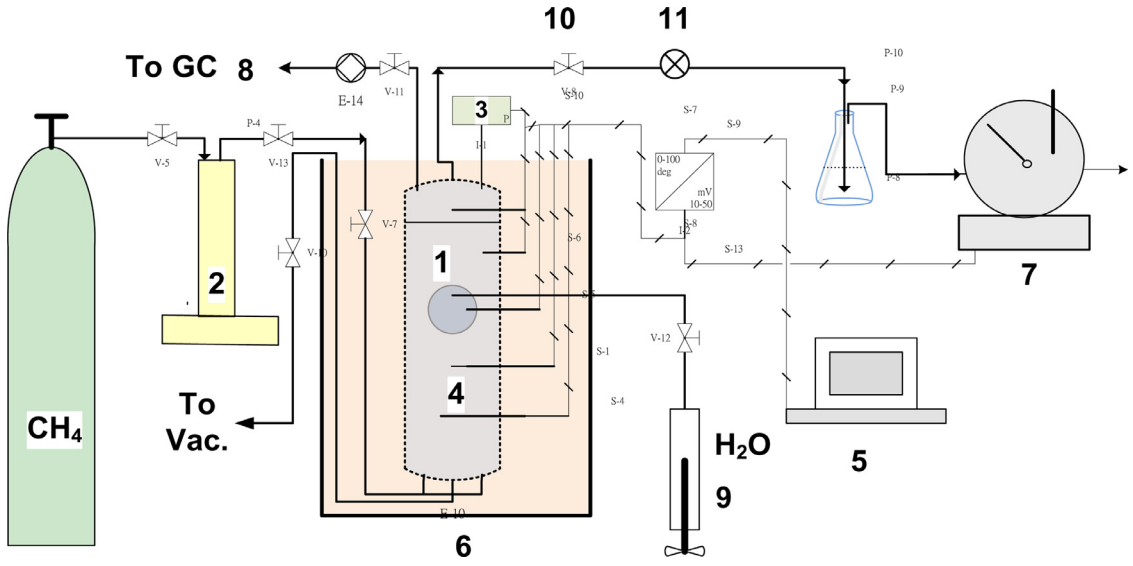

Fig. 1. Schematic diagram of the mid-scale apparatus for observing gas hydrate formation and decomposition.

[24]). Those experimental results provided valuable information of local properties changes during the gas hydrate formation and decomposition.

Based on specific experimental purposes, many types of apparatus have been developed for investigating the kinetic behavior of gas hydrate formation and decomposition. As a representative case, Ruffine et al. [25] constructed a volume-variable cell, whose internal volume can be changed from 20 cm^3 to 65 cm^3 by adjusting the position of piston. This high-pressure cell was equipped with sapphire-windows and connected to Raman spectrometer and GC–MS for observing the dynamic behavior of mixtures in the cell and analyzing the composition of samples taken from the cell, respectively. Another extreme case is that Fitzgerald et al. [9] developed a pilot-scale reactor with the internal volume of 7.0 L. This reactor is a blind-vessel embedded with a pile of thermocouples for monitoring the temperatures at different positions in the reactor. A thermal conductivity gas analyzer was also connected to the reactor for continuously monitoring the gas concentration. This large-scale reactor was mainly used to test the methane production via *in-situ* thermal stimulation dissociation. In the present study, a mid-scale visual high-pressure cell with 1.6 L interior volume was installed for investigating the dynamic behavior of the gas hydrate formation and especially for the gas hydrate decomposition induced by depressurization. Using this apparatus, we are able to collect wide variety of dynamic data, including video, digital images, temperature profiles, pressure, and the total volume changes of the gas during the hydrate formation and destabilization courses. These dynamic data are useful in improving the software performance for simulating the methane hydrates formation and the natural gas production from the hydrate reservoir via depressurization process.

2. Experimental section

2.1. Chemicals

Methane (purity: 0.99 in mass fraction) was purchased from Acros (USA). This chemical was used as received. Deionized water was obtained from NANO pure-Ultra pure water system with resistivity of 18.3 MΩ cm.

2.2. Apparatus and procedure

Fig. 1 is the schematic diagram of the apparatus installed in the present study. High-pressure cell (**1**, manufactured by Metal Industries Research & Development Centre, Taiwan) is the main part of this equipment as shown in Fig. 2. Its dimension is 100 mm (I.D.) × 200 mm (height) and 1.6 L internal volume. This unit is operable at temperatures from 273 K to 373 K and pressures up to 200 bar. For visual observation, a pair of high-pressure glass windows (25 mm diameter) was mounted on the cell's body. Additionally, six RTD temperature sensors (**4**, from T1 to T6, PT-100, accuracy: ±0.1 K) were inserted in the high-pressure cell at different positions. These sensors measure the temperature profile at the center of the cell through the courses of gas hydrate formation and decomposition. Two pressure transducers (**3** in Fig. 1 or **P1** and **P2** in Fig. 2, UNIK 5000, 0 bar–300 bar, accuracy: ±0.1%, GE Druck, UK) detect the pressure in the cell. The whole cell is immersed in a thermostatic bath (**6**, 253 K –373 K, stability: ±0.5 K).

In each experimental run, temperature of bath is maintained at a specific value and the cell was evacuated first. Water is then charged into the cell with a hand pump (**9**, Model 62-6-10, High Pressure Equipment Co., USA) until the water level reaching around the middle of the windows. Subsequently, methane was injected into the cell using a syringe pump (**2**, 500D, max. 255 bar, Teledyne Isco, USA) from the bottom of the cell. The injection was continued until a specific pressure to be attained. As pressure higher than liquid-gas-hydrate three-phase coexistence pressure, methane hydrates started to form. During the hydrate formation, the syringe pump was operated at a constant-pressure mode. Fresh methane can be introduced instantaneously into the cell by the syringe pump to maintain constant pressure as methane gas transfers gradually into hydrate phase. The reading of total volume of make-up methane was monitored by a digital video camera through the entire course.

After the rate of hydrate formation approaching to zero, the experimental run of gas hydrate decomposition by depressurization is followed. The pressure in the hydrate cell reduces dramatically upon opening the metering valve (**10**) at a given back pressure, adjusting by a regulator (**11**). The methane hydrates dissociate and thus methane gas releases as cell's pressure decreases. The accumulated volume of the released methane is measured by using a wet test meter (**7**, Model 8, TG 1, accuracy: ±0.2 %, Ritter, Germany).

All the dynamic histograms, including temperature profile (from T1 to T6), pressure, and the total volume of released methane gas, were recorded by the data acquisition system (5) during the experimental runs. A digital camera took the images of phase states in the cell through the windows.