

## Formation experiments of CO<sub>2</sub> hydrate chimney in a pressure cell

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**Abstract:** Experimental investigations were conducted to understand the formation process of CO<sub>2</sub> hydrate the chimney structure by using a gas bubble emission technique in water within a pressure cell. The detailed process was video-recorded and analyzed to study the initiation and growth behavior of hydrate chimney while the cell pressure was increased and gas supply rate decreased gradually with time. In the initial stage of chimney growth, a hydrate crystal started to form in a cup shape at the gas nozzle and ascended together with gas bubbles due to mechanical weakness of the hydrate/nozzle contact. Growth of hydrate chimney occurred with supercooling of 3 K (overpressure of 0.60 MPa) or more, and continued until the top end was closed completely by hydrate.

**key words:** CO<sub>2</sub> hydrate, gas hydrate chimney, bubble emission, supercooling (overpressure), gas supply rate

### 1. Introduction

Gas hydrates are solid crystalline compounds that consist of gas molecules trapped in a framework of hydrogen-bonded water molecules, and are stable under high pressure and low temperature conditions (Sloan, 1998). Natural gas hydrates occur worldwide in submarine sediments in deep oceans and in deep permafrost layers (Kvenvolden, 1993). Submarine gas hydrates in massive, layered, or particle shapes (Suess *et al.*, 1999; Ginsburg, 1993) are thought to be formed by gas diffusion mechanisms in water (Buffett and Zatsepina, 2000). In contrast, globular gas hydrate structures are formed from gas bubbles as shown by Bohrmann *et al.* (1998). A CO<sub>2</sub> hydrate chimney structure was observed in the Mid-Okinawa Trough by Sakai *et al.* (1990). This chimney was a translucent elongated conical pipe standing on the sea floor. CO<sub>2</sub> bubbles were released into seawater through the chimney. Formation of a hydrate chimney is connected with gas transfer in the underlying sediment, and the shape of the hydrate is intimately related to the hydrate chimney formation process. However, little is known about the formation process or stability of the hydrate chimney.

This study was conducted to understand the CO<sub>2</sub> hydrate chimney formation process by using a pressure cell with optical windows.

## 2. Experimental method

### 2.1. Apparatus

A pressure cell with optical windows (pressure cell, A) was especially designed and constructed by Shoji *et al.* (2002). This cell is made of stainless steel (volume capacity of 400 ml) and durable to a maximum pressure of 5.0 MPa (Fig. 1). A schematic view of the experimental apparatus is shown in Fig. 2. Pressure cell A was placed in an ethylene glycol cooling bath kept at 274 K. CO<sub>2</sub> gas was supplied from another pressure cell, B (volume capacity of 120 ml) by decomposition of 'dry ice' (solid CO<sub>2</sub>). A stainless steel tube was connected between cell B and a nozzle (diameter 1.0 mm) fixed at the bottom of cell A. Internal pressures in both cells ( $P_1$ ,  $P_2$ ) and upper and lower temperatures in cell A ( $T_1$ ,  $T_2$ ) were measured by pressure gauges (KEYENCE AP-14, 0–10 MPa range) and platinum resistance thermometers respectively, and recorded automatically.

### 2.2. Procedure

CO<sub>2</sub> gas and 300 ml of pure water were kept in pressure cell A for about one day at

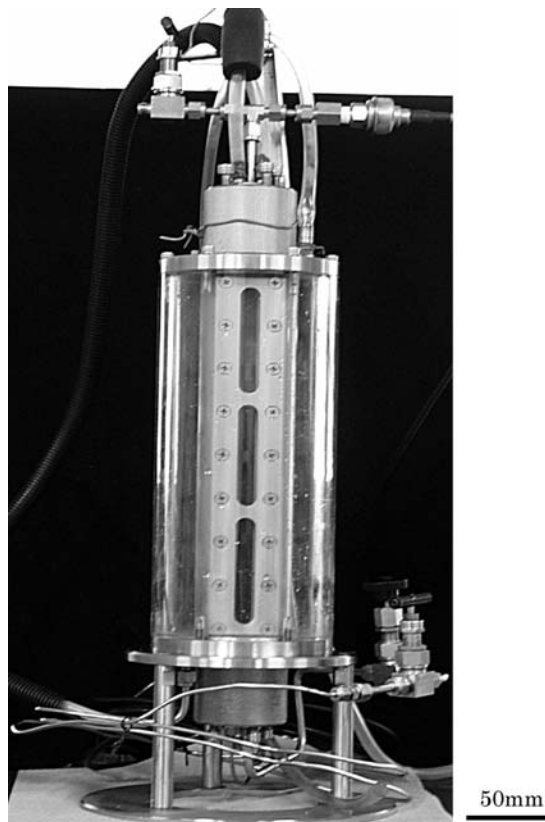


Fig. 1. Pressure cell A for hydrate chimney formation.

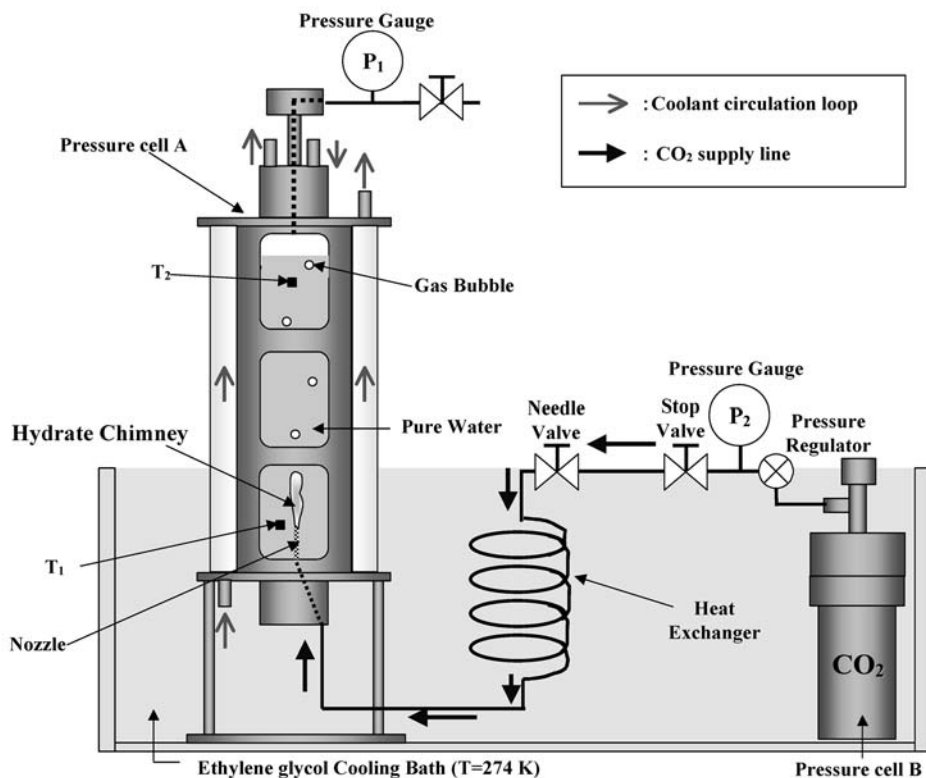


Fig. 2. A schematic view of the experimental apparatus.

274 K and 1.00 MPa to allow pre-experimental dissolution of  $\text{CO}_2$  gas into water. The gas supply pressure ( $P_2$ ) was kept between 1.50 and 3.00 MPa by using a pressure regulator during each test run. Therefore, the pressure in cell A ( $P_1$ ) increased and the rate of gas supply decreased gradually with time after the onset of each experiment. Formation processes of hydrate chimney on the nozzle were continuously recorded by a video camera through the window.

### 3. Results and discussion

#### 3.1. The change of hydrate structure with pressure

Eighteen experimental runs were conducted with four pressure levels,  $P_2$ , for gas supply. Each run took between about 2 min and one hour.

Figure 3 shows a typical time-change of pressure and temperature during the run. When  $P_2$  was 1.50 MPa ( $P_1$  was much lower than 1.50 MPa), no hydrate formation was observed. When  $P_2$  was about 2.00 MPa or more, and  $P_1$  was about 1.50 MPa or more, gas bubbles beneath the water surface transformed into globular-shape hydrates (stage 1) as shown in Fig. 4a. This means that a minimum pressure of about 1.50 MPa is required to form  $\text{CO}_2$  hydrate at 274 K in pure water. In stage 2 ( $P_1$  ranges from 1.56 MPa to 2.40 MPa)  $\text{CO}_2$  hydrate started to form at the nozzle in a cup shape (Fig. 4b).

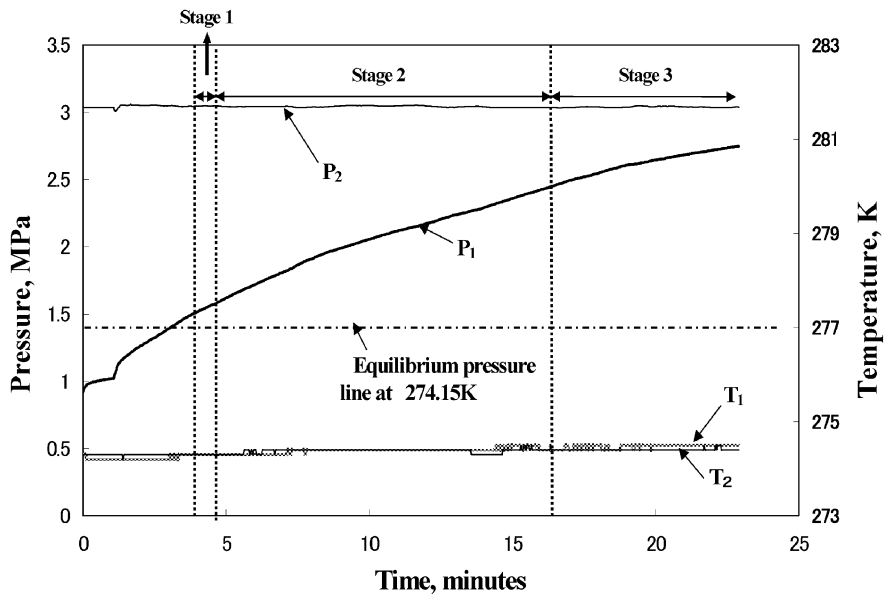


Fig. 3. Typical time-changes of temperature ( $T_1$  and  $T_2$ ) and pressure ( $P_1$ ) during a test run. Stages 1, 2, and 3 correspond to the hydrate formation periods of globular, cup and chimney structures, respectively.

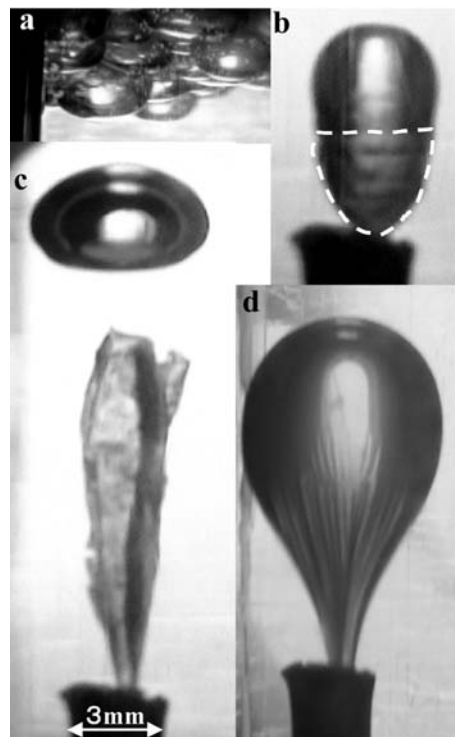


Fig. 4. Classification of hydrate shapes observed in this study (a: globular, b: cup, c: chimney, d: balloon).

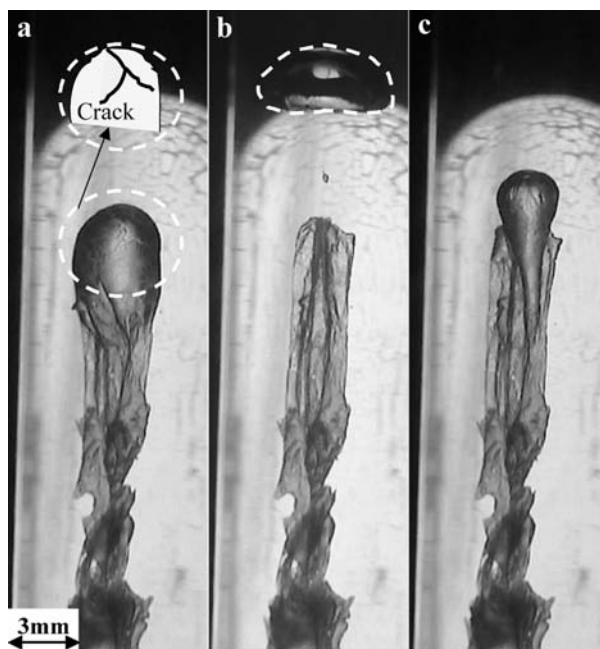


Fig. 5. Sequential photographs of chimney structure growth. A crack appeared at the top of the closed chimney (a), and a bubble ascended through the top hole (b). The top of the chimney was closed by hydrate film again after some chimney growth (c).

But gas bubbles with cup-shaped hydrates ascended up to the water surface, apart from the nozzle without forming chimney structures. Chimney structures (Fig. 4c) started to form in stage 3 when  $P_1$  was higher than about 2.00 MPa. When the pressure difference between  $P_1$  and  $P_2$  was lower than 0.10 MPa (lower gas supply rate), balloon shaped hydrates sometimes occurred (Fig. 4d). When a hydrate chimney was closed by hydrate film, cracking and/or breaking of hydrate at/near the top sometimes allowed the chimney to grow more (Fig. 5).

### 3.2. Factors affecting formation of hydrate chimney

The pressure conditions for each type of hydrate structure are summarized in Table 1. The formation of a hydrate chimney was observed in pressure cell A when the pressure in pressure cell A was high. However, the important point to notice is that  $P_2 = 2.00$  and 1.50 MPa did not form a hydrate chimney when the gas flow to pressure cell A was decreased. So it appears that two factors, fast hydrate growth and strength of hydrate at the nozzle, are very important for hydrate chimney formation.

The supercooling, that is the deficiency of the equilibrium temperature under the experimental pressure, and the overpressure, that is the deficiency of the equilibrium pressure under a given temperature, can be calculated from  $P_1$ ,  $T_1$  and phase equilibrium data for  $\text{CO}_2$  hydrate (Larson, 1955). The supercooling and overpressure correspond to the driving force of hydrate growth. All experimental data were plotted in Fig. 6 to

Table 1. Initiation pressure values for each type of hydrate structure.

Run No.	Pressure, P <sub>2</sub> in pressure cell B	Initiation pressure, P <sub>1</sub> in pressure cell A			
		Globular	Cup	Chimney	Balloon
1	3.00	1.49	1.56	2.40	—
2		—	1.84	2.42	—
3		1.64	2.07	2.94	—
4		1.69	1.89	2.69	—
5		1.75	2.25	2.64	—
6	2.50	1.65	1.82	—	2.48
7		1.63	1.89	—	2.49
8		1.70	1.82	2.13	2.47
9		1.78	2.02	2.30	—
10		1.75	1.76	—	—
11		1.67	2.09	2.27	2.47
12	1.67	1.98	—	2.45	
13	2.00	1.71	1.86	—	—
14		1.78	1.92	—	—
15		1.83	1.86	—	—
16		1.89	1.92	—	—
17	1.50	—	—	—	—
18		—	—	—	—

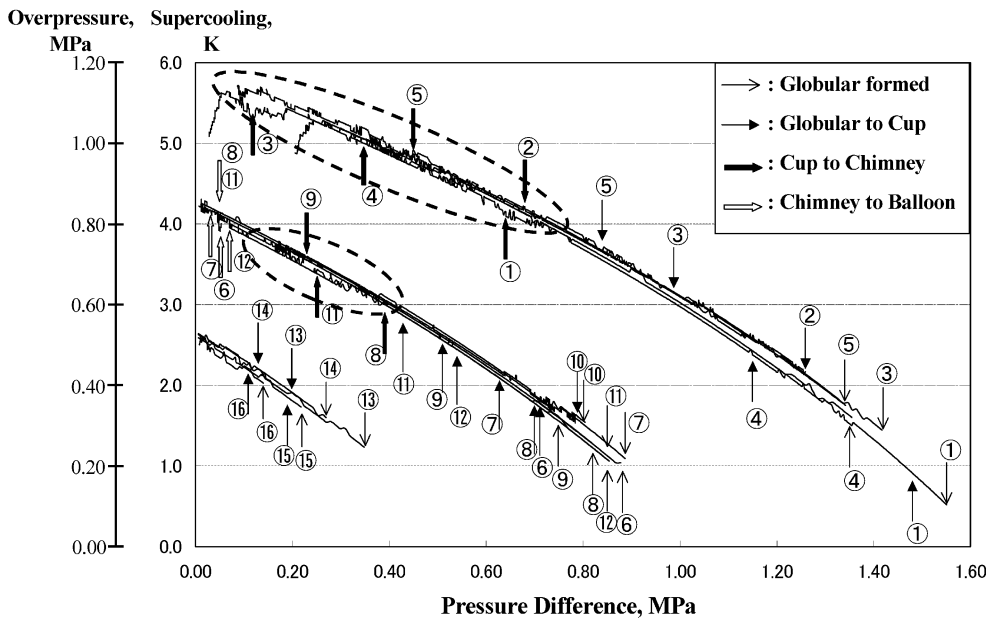


Fig. 6. Onsets of various types of hydrate formation. Pressure difference is a measure of gas supply rate. Note that a chimney structure only appears at supercooling values higher than 3 K (corresponding to overpressure values higher than 0.60 MPa).

①~⑯: Run number.  $\dashrightarrow$ : Formation area of the hydrate chimney.

examine the relationship between supercooling and overpressure/pressure-difference and the appearance of each type of hydrate structure. Supercooling of more than 3 K (overpressure of 0.60 MPa) is required for hydrate chimney formation. The pressure difference ( $P_2 - P_1$ ) determines the flow rate of CO<sub>2</sub> gas from the nozzle. When the pressure difference is lower, bubbles can stay on the nozzle longer and stronger hydrate film is formed at the nozzle. However, a much lower pressure difference (much lower gas supply rate) may lead to balloon formation and closing of the hydrate chimney. One of the important findings is that hydrate chimney formation is limited to a higher pressure and lower gas supply rate condition. Gas bubbles emitted from the nozzle will simply ascend into the water above when supercooling is lower than 3 K (overpressure is 0.60 MPa). The majority of gas in bubbles cannot be fixed in gas hydrate even during chimney formation.

Since this paper reports on experimental results for hydrate chimney formation in pure water the effect of the NaCl solution on chimney growth at the sea floor should be considered. The equilibrium pressure of CO<sub>2</sub> hydrate formed in 4.6 wt% NaCl solution increases by about 0.4 MPa compared with pure water (Vlahakis *et al.*, 1972). A similar degree of pressure difference can be expected for chimney formation at the sea floor.

These findings suggest that the observation of chimney structure may imply a continuous and relatively constant supply of CO<sub>2</sub> emitted from the sea floor in the Mid-Okinawa Trough.

#### 4. Conclusions

Experimental investigations were conducted to understand the hydrate chimney formation process. The CO<sub>2</sub> hydrate chimney structure was successfully formed in a pressure cell. Higher pressure enhances the hydrate crystal growth rate, while a lower pressure difference causes a lower gas supply rate and ensures the growth of strong hydrate contact at the nozzle. More than 3 K of supercooling (0.60 MPa of overpressure) is required for CO<sub>2</sub> gas hydrate formation within the limit of the present study conditions.

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