Polar Meteorol. Glaciol., 19, 42–49, 2005

Formation experiments of CO_2 hydrate chimney in a pressure cell

Satsuki Kataoka*, Osamu Kitamura, Kinji Hyakutake, Kiyoshi Abe, Akihiro Hachikubo and Hitoshi Shoji

Kitami Institute of Technology, 165, Koen-cho, Kitami 090-8507
**Corresponding author. E-mail: dse05001@std.kitami-it.ac.jp*

(Received March 31, 2005; Accepted August 1, 2005)

Abstract: Experimental investigations were conducted to understand the formation process of CO_2 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_2 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_2 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_2 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_2 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 m*l*) 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_2 gas was supplied from another pressure cell, B (volume capacity of 120 m*l*) by decomposition of 'dry ice' (solid CO_2). 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_2 gas and 300 m*l* of pure water were kept in pressure cell A for about one day at

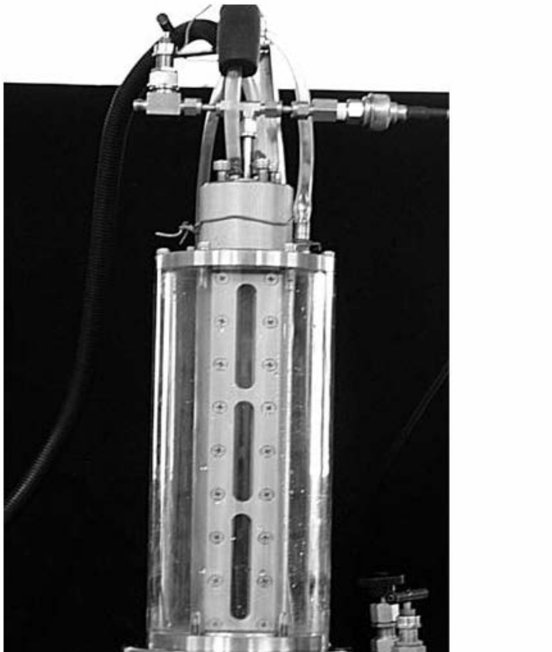

Fig. 1. Pressure cell A for hydrate chimney formation.

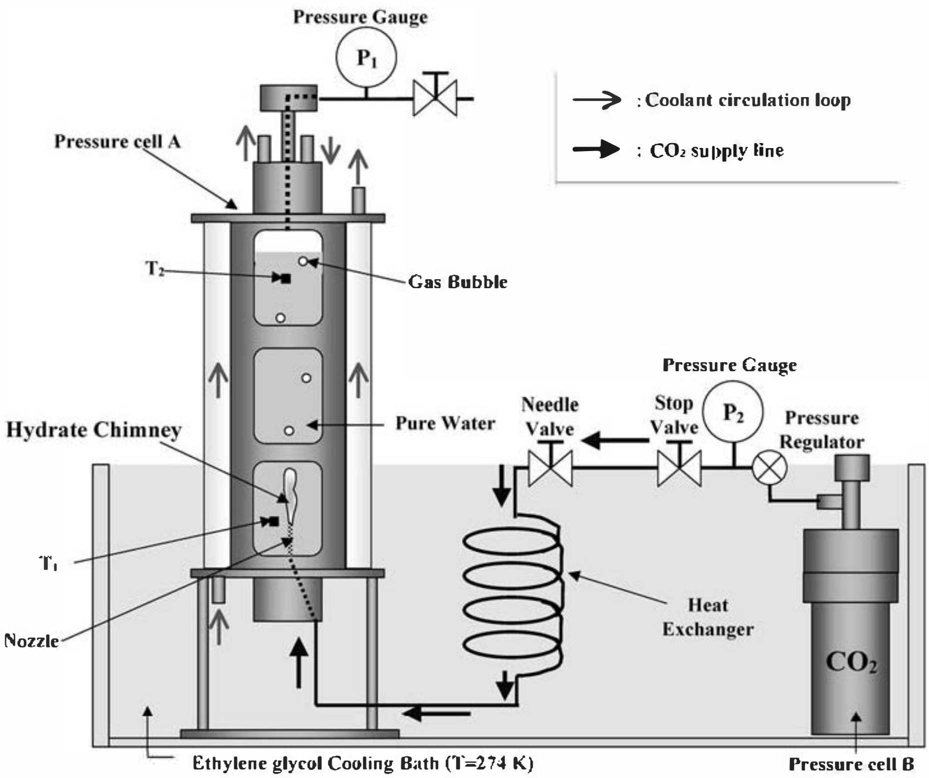

Fig. 2. A schematic view of the experimental apparatus.

274 K and 1.00 MPa to allow pre-experimental dissolution of 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 CO_2 hydrate at 274 K in pure water. In stage 2 (P_1 ranges from 1.56 MPa to 2.40 MPa) CO_2 hydrate started to form at the nozzle in a cup shape (Fig. 4b).

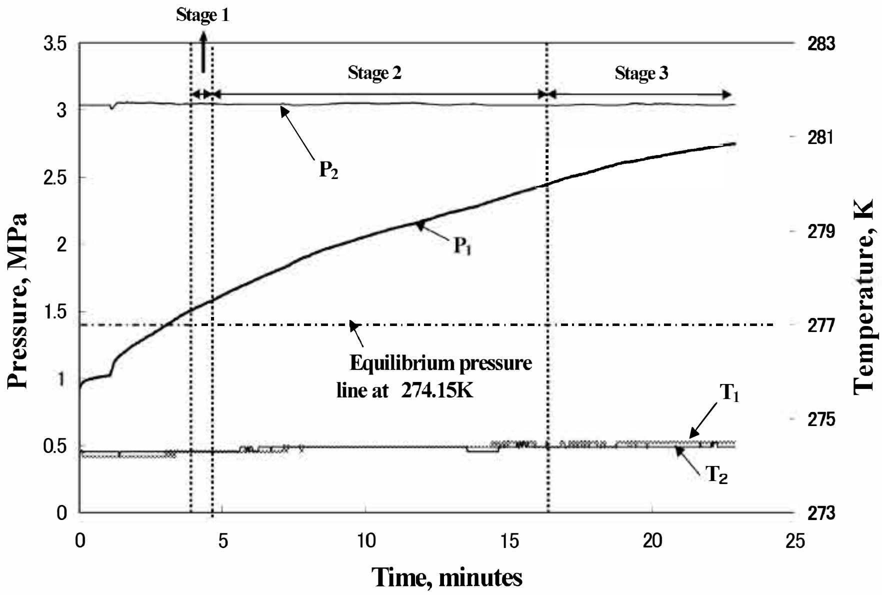

Fig. 3. Typical time-changes of temperature (T_1 and T_2) and pressure (P_1) during a test run. Stages 1, 2, and 3 correspond to the hydrate formation periods of globular, cup and chimney structures, respectively.

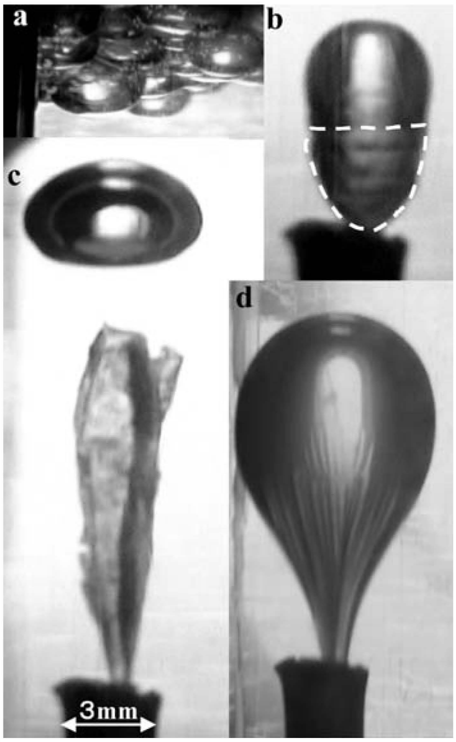

Fig. 4. Classification of hydrate shapes observed in this study (a: globular, b: cup, c: chimney, d: balloon).

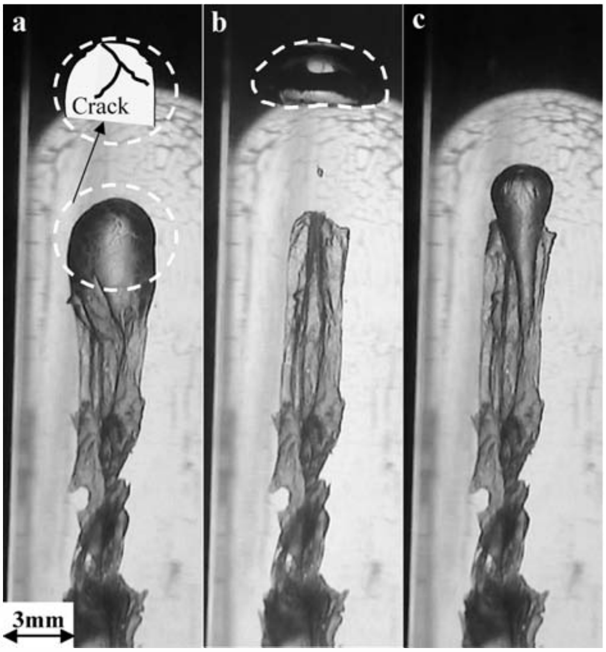

Fig. 5. Sequential photographs of chimney structure growth. A crack appeared at the top of the closed chimney (a), and a bubble ascended through the top hole (b). The top of the chimney was closed by hydrate film again after some chimney growth (c).

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 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_2 in pressure cell B	Intiation pressure, P_1 in pressure cell A			
		Globular	Cup	Chimney	Balloon
1		1.49	1.56	2.40	—
2		—	1.84	2.42	—
3	3.00	1.64	2.07	2.94	—
4		1.69	1.89	2.69	—
5		1.75	2.25	2.64	—
6		1.65	1.82	—	2.48
7		1.63	1.89	—	2.49
8		1.70	1.82	2.13	2.47
9	2.50	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		1.71	1.86	—	—
14	2.00	1.78	1.92	—	—
15		1.83	1.86	—	—
16		1.89	1.92	—	—
17	1.50	—	—	—	—
18		—	—	—	—

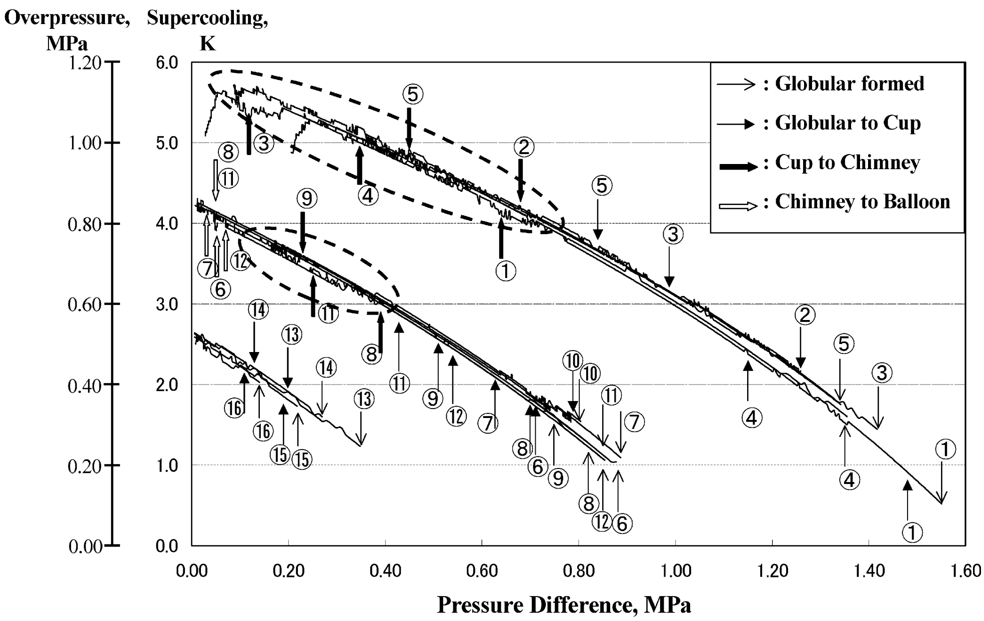

Fig. 6. Onsets of various types of hydrate formation. Pressure difference is a measure of gas supply rate. Note that a chimney structure only appears at supercooling values higher than 3 K (corresponding to overpressure values higher than 0.60 MPa).
①~⑯: Run number. : Formation area of the hydrate chimney.

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_2 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_2 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_2 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_2 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 over-pressure) is required for CO_2 gas hydrate formation within the limit of the present study conditions.

References

Bohrmann, G., Greinert, J., Suess, E. and Torres, M. (1998): Antigenic carbonates from the Cascadia subduction zone and their relation to gas hydrate stability. Geology, **26**, 647–650.

Buffett, B.A. and Zatsepina, O.Y. (2000): Formation of gas hydrate from dissolved gas in natural porous media. Mar. Geol., **164**, 69–77.

Ginsburg, G.D., Soloviev, V.A., Cranston, R.E., Lorenson, T.D. and Kvenvolden, K.A. (1993): Gas hydrate from the continental slope, offshore Sakhalin Island, Okhotsk Sea. Geo-Mar. Lett., **13**, 41–48.

Kvenvolden, K.A. (1993): Gas hydrate - geological perspective and global change. Rev. Geophys., **31**, 173–187.

Larson, S.D. (1955): Phase studies of the two–component carbon dioxide–water system, involving the carbon dioxide hydrate. Ph.D. thesis, University of Illinois, Doctoral Dissertation Published No. 15235, University Microfilms.

Sakai, H., Gamo, T., Kim, E.S., Tsutsumi, M., Tanaka, T., Ishibashi, J., Wakata, H., Yamamoto, M. and Oomori, T. (1990): Venting of carbon dioxide-rich fluid and formation in Mid-Okinawa trough back-arc basin. Science, **248**, 1093–1096.

Shoji, H., Hachikubo, A., Miyamoto, A., Hyakutake, K., Abe, K., Bohrmann, G. and Kipfstuhl, S. (2002): Construction of a pressure cell for visual observations on pressures of globular gas hydrate. Yokohama, Proceedings of the Fourth International Conference on Gas Hydrate, **2**, 839–843.

Sloan, E.D. (1998): Clathrate Hydrates of Natural Gases. 2nd ed. New York, Marcel Dekker, 705 p.

Suess, E., Torres, M., Bohrmann, G., Collier, R.W, Greinert, J., Linke, P., Rehder, G., Trehu, A., Wallmann, K., Winckler, G. and Zuleger, E. (1999): Gas hydrate destabilization: enhanced dewatering, benthic material turnover and large methane plumes at the Cascadia convergent margin. Earth Planet. Sci. Lett., **170**, 1–15.

Vlahakis, J.G., Chen, H.S., Suwandi, M.S. and Barduhn, A.J. (1972): The growth rate of ice crystals-properties of carbon dioxide hydrate, a review of properties of 51 gas hydrates. Syracuse U. Research and Development Report 830, prepared for US Department of the Interrior.