Influence of CO_2 Hydrate on Liquid CO_2 Hydrodynamics for CCS under Ocean Floor

Yuji Takagi[1], Akiko Kaneko[1], Yutaka Abe[1] & Kenji Yamane[2]

[1] Engineering Mechanics and Energy, University of Tsukuba, Ibaraki, Japan

[2] Osaka Blanch, National Maritime Research Institute, Osaka, Japan

Correspondence: Yuji Takagi, Engineering Mechanics and Energy, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba, Ibaraki, Japan. Tel: 81-29-853-5498. E-mail: ytakagi@edu.esys.tsukuba.ac.jp

Abstract

The purpose of the present study is to reveal the influence of CO_2 hydrate on the flow of liquid CO_2 injected in a packed bed as simulating seabed. In order to reveal the influence of CO_2 hydrate, differential pressure and temperature are measured under both condition of CO_2 hydrate formation and no-formation. As the result, under the condition of the hydrate formation, differential pressure at the inlet of the packed bed become large compared with that under the condition of no-formation. The amount of the hydrate estimated from the temperature suggested increasing as the initial temperature of the test section lowers. Friction factor is also estimated. As the result, in the upstream part of packed bed, the difference of the friction factor between the hydrate formation and no-formation condition become small with increase of Reynolds number.

Keywords: global warming, CO_2 storage, CO_2 clathrate hydrate, packed bed

1. Introduction

In the method of CCS (carbon dioxide capture and storage), storage of CO_2 under the seabed such as aquifers has been expected as one of the effective options for reducing CO_2 emissions into the atmosphere. Under the condition of pressure higher than 4.5 MPa and temperature lower than 283.4 K, CO_2 clathrate hydrate is formed. CO_2 hydrate prevents liquid CO_2 from dissolving into water. In the sea around Japan, there is the region with sufficient environment of CO_2 hydrate formation. Therefore, liquid CO_2 injected in seabed sediments in those regions reacts with pore water and forms CO_2 hydrate. The hydrate-filled sediments (hydrate sealing) are expected to serve as an article cap rock, and prevent the escape of CO_2. Thus, the method of CO_2 storage under the seabed is a little influence on the marine environment and long term storage is possible (Koide et al., 1997). However, when liquid CO_2 is injected into seabed in those regions, there is at risk of choking liquid CO_2 flow due to CO_2 hydrate formation in a pipe arrangement and seabed. Therefore, it is important to clarify the influence of the hydrate on CO_2 storage under the seabed.

The previous studies of the hydrate formation in a packed bed have mainly performed under the condition that the flow rate of CO_2 is low such as the generation of seal layer by the hydrate formation. However, there is little knowledge about the aquifer storage under the condition of the flow rate when CO_2 injection in the pipe arrangement. And, in the previous studies of CO_2 Hydrate, Yamane et al. (2000) shows that the strength of CO_2 hydrate membrane is very strong just below the dissociation temperature. This phenomenon suggests the factor of the further obstruction of liquid CO_2 flow. And, Uchida et al. (2000) shows that the propagation rate of CO_2 hydrate on the interface is greater as the temperature lowers. Therefore, under the condition of the hydrate formation, it is considered that the influence of the hydrate on the flow of liquid CO_2 changes according to the temperature of surrounding environmental.

The purpose of the present study is to reveal the influence of CO_2 hydrate on the flow of liquid CO_2 injected in a packed bed as simulating seabed. In order to reveal the influence of CO_2 hydrate, differential pressure and temperature are measured under both condition of CO_2 hydrate formation and no-formation. From the temperature rise due to CO_2 hydrate formation, we estimate the amount of the hydrate formation. Friction factor is also estimated. Friction factor is compared with the Ergun's equation (1952) proposed for single-phase flow in a packed bed.

2. Experimental Sections

2.1 Experimental Apparatus

A schematic diagram of experimental apparatus is shown in Figure 1. The apparatus is mainly composed of a test section, a CO_2 buffer cylinder, CO_2 bombs, a water tank, a pump, a compressor, a silicon heater and measurement instruments. The test section is made by stainless steel (the length is 2.0 m, the inner diameter is 97.1 mm), here, downstream direction is defined as z-axis as shown in Figure1. Pressure gauges, thermocouples and windows for observation are installed at z = 0.1, 0.7, 1.3 and 1.9 m. A cylinder of stainless steel for CO_2 buffer (the length is 1.0 m, the inner diameter is 97.1 mm) is set on the test section, and installed one window for observation.

Figure 1. Schematic diagram of the experimental apparatus

2.2 Experimental Procedures and Conditions

In order to simulate the flow structure in seabed, the test section was filled with glass beads at the range of z = 0.12-2.0 m. The diameter of glass beads is 0.85-1.0 mm. The experimental procedure is showed below. Ion-exchanged water is supplied to the test section from the water tank by using the pump and the compressor. Liquid CO_2 is supplied to the position of the observation window of the CO_2 buffer cylinder. The interface of water and liquid CO_2 is confirmed in the observation window at z = 0.1 m and the temperature of the test section is set according to conditions. After the temperature reaches a constant value, in order to make the pressure constant when liquid CO_2 is injected, the test section is pressurized with a CO_2 bomb which heated with the silicon heater. After pressure reaches a prescribed value, by opening the valve at the bottom of the test section, liquid CO_2 flows through the packed bed. The fluid behaviour of liquid CO_2 is observed at the windows, and temperature and differential pressure are measured simultaneously. Finally, when the front of liquid CO_2 arrive at z = 2.0 m, the valve at the bottom of the test section is closed and the flow stops. And, the amount of water flowing out of the test section is measured.

In this study, porosity of the test section is about 0.39. The mass flow rate of water is 0.04 to 0.46 kg/s. The injection pressure of liquid CO_2 is about 6 MPa. In 6 MPa, dissociation temperature of CO_2 hydrate is about 283.4 K (Sloan et al., 2007). In order to investigate the influence of CO_2 hydrate on the flow of liquid CO_2 when liquid CO_2 injected in the packed bed, experiments are conducted under both condition of CO_2 hydrate formation and no-formation. An initial temperature T_{ini} is set at 278.2, 280.2 and 282.2 K under the condition of CO_2 hydrate formation. On the other hand, T_{ini} is set at 287.6 K under the condition of no-formation.

The snapshots of the interface of water and liquid CO_2 at z = 0.1 m are shown in Figure 2. Figure 2 (a) shows the snapshot of T_{ini} = 280.2 K under the condition of CO_2 hydrate formation, and we identified that the thin hydrate membrane was formed at the interface of the liquids. Figure 2 (b) shows the snapshot under the condition of no-formation. There was no hydrate membrane at the interface. In this study, the experiments under condition of CO_2 hydrate formation are conducted after confirming the hydrate exiting at the interface.

(a) T_{ini} = 280.2 K   (b) T_{ini} = 287.6 K

Figure 2. Interface of water and liquid CO_2 under the condition of CO_2 hydrate formation (a) and no-formation (b)

3. Results and Discussion

3.1 Time Variation of Differential Pressure and Temperature

3.1.1 Condition of No-formation

Figure 3 shows the time variation of differential pressure and temperature under the condition of no-formation. The flow rate Q_w is about 0.13 kg/s and initial temperature of the test section T_{ini} is 287.6 K. In Figure 3 (a) and (b), the horizontal axis represents the elapsed time until the front of liquid CO_2 reach at the bottom of the test section from the time when the drain valve is opened and flow of liquid CO_2 starts. In Figure 3 (a), the differential pressure in z = 0.1-0.7 m increased from 0 s. Similarly, the differential pressure in z = 0.7-1.3 m and z = 1.3-1.9 m increases from about 11 s and 20 s, respectively. It is considered that the increase of these differential pressures is influenced by the flow resistance of water and liquid CO_2 two-phase flow in the packed bed. And, the maximum values of the differential pressure in each section are almost same value 0.035 MPa.

Figure 3 (b) shows the time variation of temperature. It is confirmed that temperatures at each position are not changed.

(a) Differential pressure   (b) Temperature

Figure 3. Time variation of differential pressure (a) and temperature (b) under the condition of no-formation (d_p = 0.85-1.0 mm, T_{ini} = 287.6 K, Q_w = 0.13 kg/s)

3.1.2 Condition of CO_2 Hydrate Formation

Figure 4 shows the time variation of the differential pressure and the temperature under the condition of CO_2 hydrate formation. The flow rate Q_w is about 0.11 kg/s and initial temperature of the test section T_{ini} is 280.2 K. According to Figure 4 (a), the differential pressure in z = 0.1-0.7 m increased from 0 s as is the case in Figure 3 (a). The differential pressure in z = 0.7-1.3 m and z = 1.3-1.9 m increased from 12 s and 22 s, respectively.

However, unlike Figure 3 (a), there is a difference in maximum value of the differential pressure in each section. The maximum value of the differential pressure in z = 0.1-0.7 m is 0.02 MPa higher than it of other sections. In this study, the experiments under condition of the hydrate formation are conducted after confirming the hydrate exiting at the interface at z = 0.1 m. And, under the condition of no-formation as shown in Figure 3 (b), the maximum values of the differential pressure in each section are almost same value. Therefore, it is suggested that choking of liquid CO_2 flow occur due to CO_2 hydrate formation in the packed bed. And, it is considered that particle layer acts as a filter in upstream part of the test section, and the flow resistance by the influence of the hydrate is large in the upstream part compared with other sections.

In Figure 4 (b), the temperature at z = 0.1, 0.7, 1.3 and 1.9 m rose from 0, 12, 22, 33 s, respectively. These temperature rises is caused by the formation heat of CO_2 hydrate (exothermal reaction). In addition, according to Figure 4 (a) and (b), it is confirmed that the temperature at z = 0.7 m increased from the time that the differential pressure in z = 0.7-1.3 m increased. Similarly, the temperature at z = 1.3 m increased from the time that the differential pressure in z = 1.3-1.9 m increased. From these result, it is confirmed that there are correlation between the time when differential pressure rise and temperature rise. Therefore, it is suggested that CO_2 hydrate is expected to form at the front of liquid CO_2.

Furthermore, the temperature at z = 0.7 m indicated a constant value from 14 s, and the temperature rose again from 18 s. This result suggests that not only the front of liquid CO_2 but also after passing the front, remained water and liquid CO_2 in the packed bed react to form the hydrate.

(a) Differential pressure   (b) Temperature

Figure 4. Time variation of differential pressure (a) and temperature (b) under the condition of CO_2 hydrate formation (d_p = 0.85-1.0 mm, T_{ini} = 280.2 K, Q_w = 0.11 kg/s)

3.2 Estimation of the Amount of CO₂ Hydrate Formation

3.2.1 Water Saturation

The relation between the flow rate of water and water saturation is shown in Figure 5. Water saturation is volume ratio of water and pore which exist in the test section when the front of liquid CO_2 is reached at z = 2.0 m and defined as follows:

$$S_w = \frac{V_w}{V_p} \tag{1}$$

$$V_w = \frac{m_{w,set} - m_{w,out}}{\rho_w} \tag{2}$$

$$V_p = \varepsilon \times V \tag{3}$$

where V_w is the volume of the water in the test section when the front of liquid CO_2 is reached at z = 2.0 m, V_p is the volume of pore, $m_{w,set}$ is the mass of water set in the test section before experiments start, $m_{w,out}$ is the mass of water flowing out from the test section, ρ_w is the density of water, ε is the porosity, V is the volume of the test

section. And, solid and open plots indicate the condition of CO_2 hydrate-formation and no-formation, respectively. According to Figure 5, the water saturation indicates approximately range from 0.20 to 0.45 in all experimental conditions.

Figure 5. Relation between the flow rate and water saturation

3.2.2 Estimation of the Amount of CO_2 Hydrate Formation

In this section, we estimate the amount of the hydrate formation using the result of the water saturation as shown in Figure 5 and the temperature rise due to the hydrate formation. First, we assume that the water saturation is uniform with respect to the height position of the test section. Next, the mass of water, liquid CO_2 and glass beads which exist in the test section when the front of liquid CO_2 is reached at the bottom of the test section is obtained by the following formulas:

$$m_w = S_w \times V_p \times \rho_w \tag{4}$$

$$m_{CO_2} = (1 - S_w) \times V_p \times \rho_{CO_2} \tag{5}$$

$$m_g = (1 - \varepsilon) \times V \times \rho_g \tag{6}$$

where ρ_w, ρ_{CO2}, ρ_g is the density of water, liquid CO_2 and glass beads, respectively. Q is the amount of heat that water, liquid CO_2 and glass beads which exist in the test section are necessary for a temperature rise ΔT and defined as follow:

$$Q = (m_w c_w + m_{CO_2} c_{CO_2} + m_g c_g) \Delta T \tag{7}$$

where c_w, c_{CO2} and c_g are specific heat of water, liquid CO_2 and glass beads, respectively, ΔT represents the value of temperature rise.

$$\Delta T = T_{e,max} - T_{ini} \tag{8}$$

where $T_{e,max}$ is the maximum value of the temperature in all measurement position when the front of liquid CO_2 reached at $z = 2.0$ m and T_{ini} is the initial temperature of test section. From Equations 7 and 8, the volume of the hydrate formation is obtained by following equation:

$$V_{Hydrate} = \frac{Q}{\Delta h} \cdot \frac{1}{\rho_{Hydrate}} \tag{9}$$

where Δh is reaction heat, $\rho_{Hydrate}$ is the density of the hydrate. The value of Δh is proposed by Bozzo et al., (1975) and Aya et al., (1997). In this study, the volume of the hydrate formation is estimated using each value, and the difference of each value is shown as an error bar.

3.2.3 Relation between Flow Rate and Volume of CO_2 Hydrate Formation

Figure 6 show the relation between the flow rate of water and the volume ratio of the hydrate formation. The vertical axis represents the volume ratio of CO_2 hydrate formation in the test section. It is confirmed the

tendency that the volume ratio of the hydrate formation increased as the initial temperature of the test section is lowers. It is considered that it is influenced the phenomena that the propagation rate of CO_2 hydrate on the interface is greater as the temperature lowers. And, the amount of the hydrate in the test section is estimated at about 0.5 to 3.0 % in this experimental condition.

Figure 6. Relation between the flow rate and volume ratio of CO_2 hydrate formation in the test section

3.3 Friction Factor

The relation between Reynolds number and friction factor are shown in Figures 7-9. The horizontal axis represents Reynolds number. The vertical axis represents the friction factor. Reynolds number and friction factor are defined as follows:

$$Re = \frac{d_p \rho u}{\mu(1-\varepsilon)} \tag{10}$$

$$u = \frac{Q_w}{\rho A} \tag{11}$$

$$f = \frac{\Delta P}{L} \cdot \frac{d_p}{\rho u^2} \cdot \frac{\varepsilon^3}{1-\varepsilon} \tag{12}$$

where d_p is the particle diameter of glass beads, u is superficial velocity, μ is viscosity, Q_w is the mass flow rate of water, A is cross-sectional area of the empty column, ΔP is differential pressure and L is the length of the measurement section. In these figures, physical properties of water are used. And, the solid line shows the Ergun's equation proposed for single-phase flow in the packed bed in these figures. Ergun's equation is expressed as follows (Ergun, 1952):

$$f = \frac{150}{Re} + 1.75 \tag{13}$$

Figure 7 shows the result in $z = 0.7$-1.3 m when the front of liquid CO_2 flow in the $z = 0.1$-0.7 m. That is, it is the case that only water phase flows through the measurement section. It is confirmed that experimental results are well correlated with Ergun's equation in all experimental conditions.

Figure 8 shows the result in $z = 1.3$-1.9 m when the front of liquid CO_2 reach at $z = 1.9$ m. The solid and open plots indicate the condition of CO_2 hydrate-formation and no-formation, respectively. Under the both conditions, the measured friction factor was larger than the value estimated from Ergun's equation. It is considered that this result is influenced by the flow resistance of water and liquid CO_2 two-phase flow in the packed bed. And, the difference of the friction factor between the hydrate formation and no-formation condition is small. In addition, the difference of the friction factor between the conditions of the hydrate formation (278.2, 280.2 and 282.2 K) is also small. This result indicates that the influence of CO_2 hydrate on the flow of liquid CO_2 is small in the middle part of the packed bed.

Figure 9 shows the result in z = 0.1-0.7 m when the front of liquid CO_2 reach at z = 0.7 m. Under the both conditions of the hydrate formation and no-formation, the measured friction factor was larger than the value estimated from Ergun's equation as is the case in Figure 8. The friction factor under the condition of CO_2 hydrate formation is about 1.4 times higher than that under the condition of no-formation when the Reynolds number is about 8. Similarly, the friction factor under the condition of CO_2 hydrate formation is higher than that under the condition of no-formation when the Reynolds number is about 11. These results suggest that the hydrate becomes the factor of flow resistance of liquid CO_2 under the condition that Reynolds number is low. However, with increase of Reynolds number, the difference of the friction factor between the hydrate formation and no-formation condition become small. This result indicates that the influence of CO_2 hydrate on the flow of liquid CO_2 becomes small as Reynolds number increases. In addition, the difference of the friction factor between the conditions of the hydrate formation is small as is the case in middle part. It is considered that the amount of the hydrate formation is not so change by initial temperature as shown in Figure 6. And, the relation between the differential pressure and the influence of the phenomenon that the strength of CO_2 hydrate membrane is very strong just below the dissociation temperature was not observed in this study.

Figure 7. Relation between Reynolds number and friction factor
(Measurement section: z = 0.7-1.3 m, CO_2 front at z = 0.1-0.7 m)

Figure 8. Relation between Reynolds number and friction factor
(Measurement section: z = 0.7-1.3 m, CO_2 front at z = 1.3 m)

Figure 9. Relation between Reynolds number and friction factor

(Measurement section: z = 0.1-0.7 m, CO_2 front at z = 0.7 m)

4. Conclusion

In order to investigate the influence of CO_2 hydrate on the flow of liquid CO_2 when liquid CO_2 injected in the packed bed, differential pressure and temperature are measured under both condition of CO_2 hydrate formation and no-formation. As the result, the following concluding remarks were obtained.

1) Under the condition of no-formation, differential pressure in each section increased. And, temperature of the test section did not change.

2) Under the condition of CO_2 hydrate formation, the value of the differential pressure at the inlet of the packed bed became large compared with the value of middle and downstream part of the test section. And, temperature of the test section rose. In addition, there were correlation between the time when differential pressure rise and temperature rise.

3) From the measurement of time variation of temperature, it is suggested that not only the front of liquid CO_2 but also after passing the front, remained water and liquid CO_2 reacts to form the hydrate.

4) It was suggested that the volume ratio of the hydrate formation increased as the initial temperature of the test section is lowers.

5) Experimental results were well correlated with Ergun's equation under the condition that only water phase flows through the measurement section. However, under the both conditions of CO_2 hydrate formation and no-formation, the measured friction factor was larger than the value estimated from Ergun's equation.

6) The difference of the friction factor between the hydrate formation and no-formation condition was small in the middle part of the packed bed. On the other hand, in the upstream part, the difference of the friction factor between the hydrate formation and no-formation condition became small with increase of Reynolds number. In addition, the difference of the friction factor between the conditions of the hydrate formation was small.

7) These results suggest that the influence of the CO_2 hydrate formation is not so dominant for liquid CO_2 injection in CCS at high Reynolds number within the present experimental conditions.

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