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Dissolution properties of CO₂ in the high pressure environment equivalent to 3500m deep sea

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Abstract

The purpose of the present study is to investigate the influence of CO₂ hydrate formation and dissociation on the dissolution properties of liquid CO₂. In order to clarify the influence of CO₂ hydrate formation and dissociation, pressure and temperature are measured under both conditions of hydrate region and non-hydrate region. Hysteresis is obtained in the formation and dissociation of CO₂ hydrate as a function of temperature. It is confirmed that there is hysteresis in the case of hydrate region, however, virtually no hysteresis in the case of non-hydrate region. As the result, it is confirmed that hysteresis is caused by CO₂ hydrate and all hysteresis loop obtained in this study are all different, though experiment conditions is almost same. In other words, it is suggested that the amount of CO₂ hydrate is constant change

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Keywords: CO₂ storage, CO₂ hydrate, Hysteresis ;

1. Introduction

Carbon dioxide is considered to be greenhouse gas which most contributes to global warming of the earth. Various concepts of CO₂ storage in the deep sea have been proposed. (1) Deep ocean storage method, (2) Deep ocean dissolution method. Under the condition of pressure higher than 4.5 MPa and temperature lower than 283.4 K, the CO₂ clathrate hydrate is formed. The hydrate can form at the interface between CO₂ and sea water. In the sea around Japan, there is the area where is sufficient environment of CO₂ hydrate formation. However, it has been reported frequently that CO₂ hydrate has been generated a small amount or has not been generated, though under the

condition of hydrate region. This problem hinders the realization of CO₂ storage in the deep sea. And there is little knowledge about CO₂ hydrate formation and dissociation under the deep sea condition.

In the previous study of CO₂ hydrate, Takagi et al. [1] shows that the amount of CO₂ hydrate in the porous media increases with decrease of the initial temperature. This phenomenon suggests the factor of CO₂ hydrate formation. And, Komai et al. [2] shows that conditions for hydrate formation are greatly affected by the number of runs and the restarting temperature.

The purpose of the present study is to investigate the influence of CO₂ hydrate formation and dissociation on the dissolution properties of liquid CO₂. In order to clarify the influence of CO₂ hydrate formation and dissociation, pressure and temperature were measured under both condition of the hydrate region and non-hydrate region. And, Hysteresis is obtained in the formation and dissociation of CO₂ hydrate as a function of temperature. In this paper we present the experimental results on the hysteresis loop and discuss the amount of CO₂ hydrate influence on dissolution of liquid CO₂.

2. Experimental sections

2.1. Experimental apparatus

Figure 1 shows a schematic diagram of experimental apparatus. The apparatus is mainly composed of a test section, a plunge pump, a compressor, a vacuum pump, a CO₂ bombs. The test section and pipe arrangement are made by stainless steel for withstand high pressure (the length is 227 mm, the inner diameter is 46 mm), here, direction of CO₂ injection is showed as green line in Figure 1. Platinum resistance thermometer sensor installed at the bottom of the chamber and pressure gauges are installed at the top of the chamber. And all experimental apparatus is set in the constant-temperature bath.

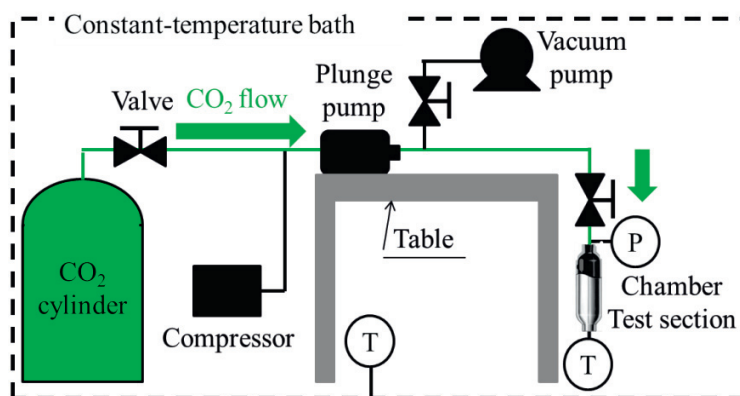
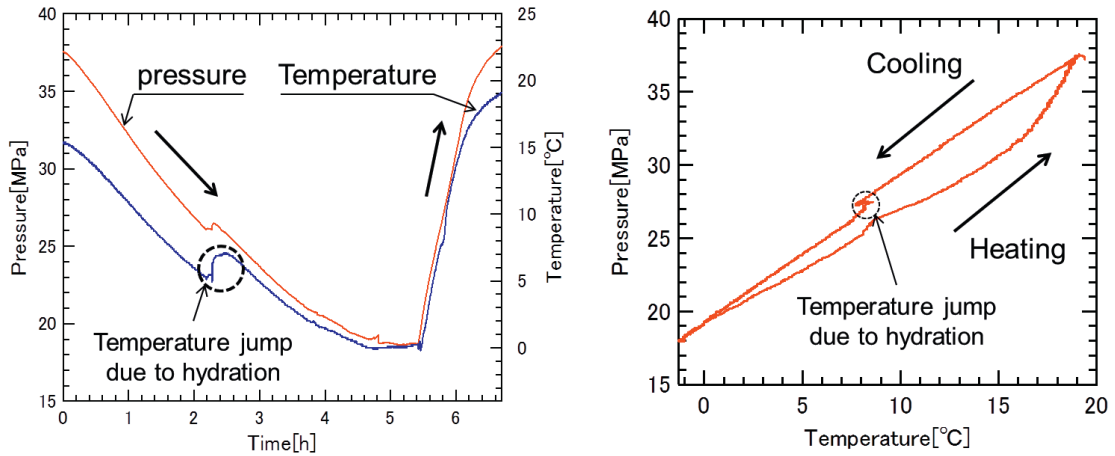


Figure 1 Schematic diagram of experimental apparatus.

2.1. Experimental procedure and conditions

CO₂ hydrate formation and dissociation processes were measured. The experimental procedure is showed below. Test section and all pipe arrangements were deaerated sufficiently before experiments. Pure water is supplied to the test section. The temperature of the test section is set a according to conditions. After the temperature reaches a constant value, liquid CO₂ is injected. The test section is pressurized to a pressure of prescribed value and the valve above the test section is closed. When liquid CO₂ is injected, the temperature in the test section is cooled rapidly until the CO₂ hydrate formation. The pressure in the test section decreases because liquid CO₂ dissolute in pure water. That is, the densities of pure water and liquid CO₂ and/or CO₂ hydrate formation increase. CO₂ hydrate formation usually brings an abrupt temperature increase. After the CO₂ hydrate formation, the temperature in the test section is heated rapidly to dissociate CO₂ hydrate. Figure 2 shows an example of typical trend curves of

temperature and pressure in the test section: (a) time variation of temperature and pressure, (b) hysteresis loop of pressure and temperature.



(a) Time variation of temperature and pressure

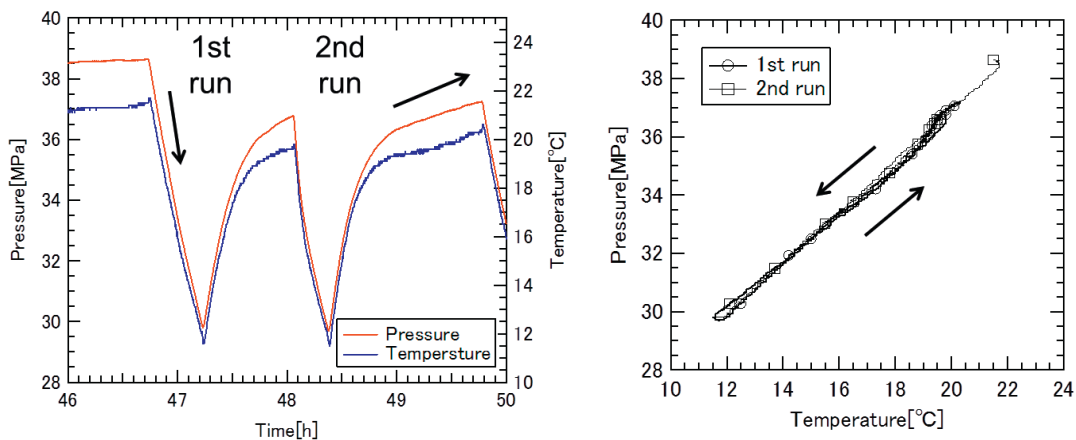
(b) Hysteresis loop of pressure and temperature

Figure 2 an example of typical trend curves of temperature and pressure in the test section: (a) time variation of temperature and pressure, (b) hysteresis loop of pressure and temperature

3. Results and discussions

3.1. Hysteresis in the non- hydrate region

Figure 3 shows the curves of temperature and pressure in the test section under the non-hydrate region: (a) time variation of temperature and pressure, (b) hysteresis loop of pressure and temperature. In this experiment, two continuous experimental runs were conducted. To prevent CO₂ hydrate formation, the temperature in the test section varied between about 12°C and 24°C. As the result, it was confirmed that there is virtually no hysteresis.



(a) Time variation of temperature and pressure

(b) Hysteresis loop of pressure and temperature

Figure 3 the curves of temperature and pressure in the test section under the non-hydrate region: (a) time variation of temperature and pressure, (b) hysteresis loop of pressure and temperature

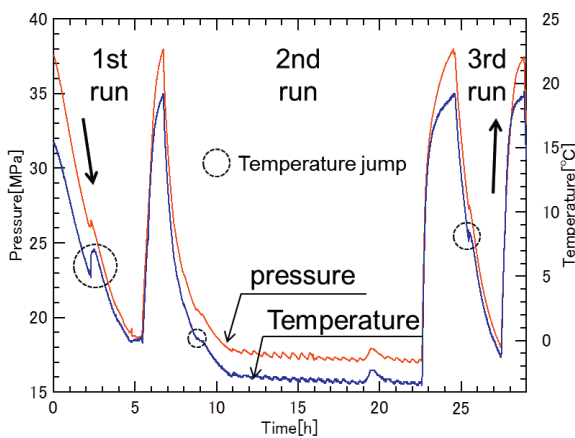
3.2. Hysteresis in the hydrate region

Figure 4 shows the curves of temperature and pressure in the test section under the hydrate region: (a) time variation of temperature and pressure, (b) hysteresis loop of pressure and temperature. Table 1 gives the hysteresis date of initial temperature, pressure and cool gradient obtained from three continuous runs. In this experiment, three continuous experimental runs were conducted. The starting point for each run was about 19.1°C and 37.7MPa. It is clear that there is the hysteresis of pressure and temperature in the test section compared with the hysteresis in the non-hydrate region. It was confirmed that CO₂ hydrate formation brings the hysteresis. From this result, It is suggested these hysteresis that the difference in the pressure between cooling process and heating process indicate the amount of CO₂ hydrate. It is assumed that it has the largest amount of CO₂ hydrate in 1st run and the amount of CO₂ hydrate in 2nd and 3rd run are almost equal. However, It appear that these hysteresis have a linear tendency though a few hysteresis date. Also, the differences of the amount of CO₂ hydrate are usually regarded to be due to cooling gradient, Lekvam et al. [3]. Cooling gradient in each hysteresis, the largest was 8.0 K/h (3rd run), followed in order by 6.3K/h (2nd run) and 4.4 K/h (1st run). However, there were no correlation between cooling gradient and the amount of CO₂ hydrate.

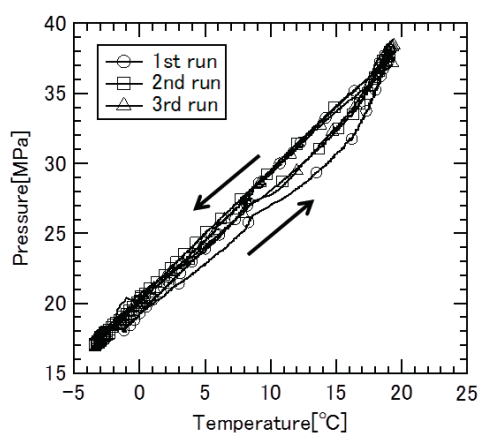
Figure 5 shows the temperature jumps caused by CO₂ hydrate formation: (a) temperature jump in 1st run, (b) temperature jump in 2nd run, (c) temperature jump in 3rd run. Aya et al. [4] shows that the difference of the temperature jump classified by types of CO₂ hydrate formation and they proposed that Dynamic formation require large temperature jump, on the other hand, static formation require slightly temperature jump. In the case of this experiment, it was suggested that temperature jump in 1st run classified in dynamic formation, 2st and 3rd run classified in static formation.

Table 1. Initial temperature, pressure and cool gradient for hysteresis experiments

| | P(initial) (MPa) | T(initial) (°C) | Cooling gradient (K/h) |
|-----|---------------------|--------------------|---------------------------|
| 1st | 37.6 | 19.2 | 4.4 |
| 2nd | 38 | 19.1 | 6.3 |
| 3rd | 37.5 | 19.1 | 8.0 |



(a) Time variation of temperature and pressure



(b) Hysteresis loop of pressure and temperature

Figure 4 the curves of temperature and pressure in the test section under the hydrate region: (a) time variation of temperature and pressure, (b) hysteresis loop of pressure and temperature

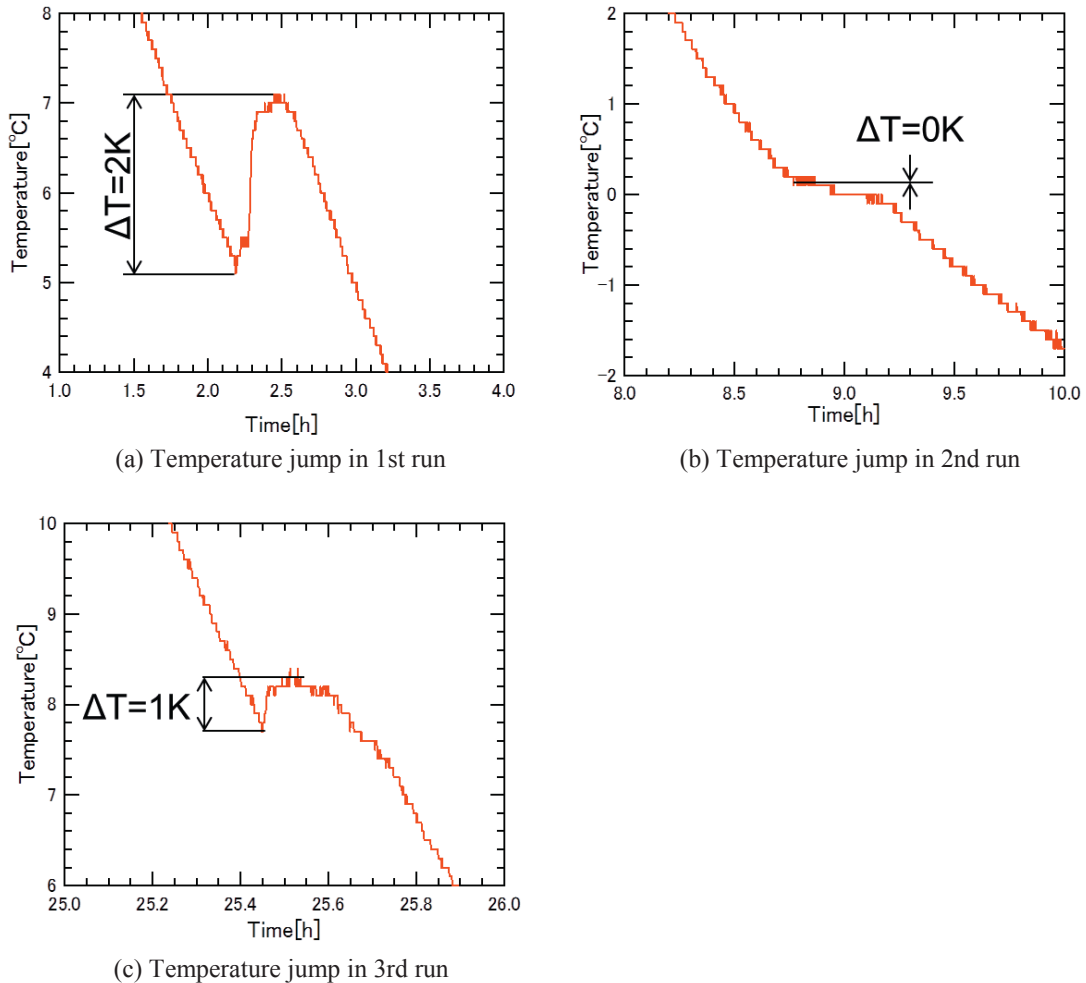


Figure 5 the temperature jumps caused by CO₂ hydrate formation: (a) temperature jump in 1st run, (b) temperature jump in 2nd run, (c) temperature jump in 3rd run

3.3. Hysteresis in the dissociation temperature

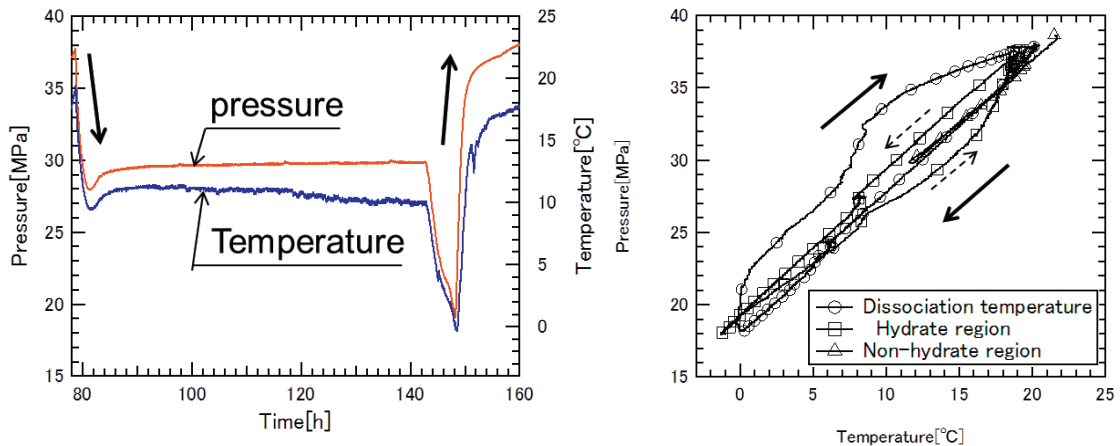
Figure 6 shows the curves of temperature and pressure in the test section under dissociation temperature: (a) time variation of temperature and pressure, (b) hysteresis loop of pressure and temperature compared with the hysteresis in hydrate and non-hydrate region. In this experiment, test section was kept at the dissociation temperature for 60 hours. It could be explained the dissociation temperature by CO₂ solubility. CO₂ solubility in the hydrate region decreases linearly with decreasing temperature, whereas it increases in the non-hydrate region. The dissociation temperature is defined as the temperature where these two solubilities coincide. In this experiment, the dissociation temperature is about 12°C. And, it has been reported that the strength of CO₂ hydrate membrane is very strong just below the dissociation temperature, Yamane et al. [5]. It is considered that the dissociation temperature is poorly understood, although several mechanisms have been suggested.

It should be pointed out that the direction of hysteresis loop is opposite the hysteresis loop in the hydrate region. It indicates the pressure in heating process is larger than heating process. If CO₂ hydrate formed or CO₂ hydrate dissolution in water, the density in the test section increases. Namely, the pressure in heating process should be

smaller than the temperature in cooling process. Moreover, It was also confirmed by the hysteresis in the hydrate region and non-hydrate region.

Next remarkable point is the variation of temperature and pressure during test section kept in the dissociation temperature from 82-142 hour. The temperature decreases though pressure is constant. It indicates apparent density in the test section does not change. However, temperature and pressure changes except during dissociation temperature behave similar with the hysteresis in hydrate and non-hydrate region. It is clear that the dissociation temperature affects this phenomenon.

Theses phenomenon might be key to verify the mystery of the dissociation temperature. Unfortunately, above phenomenon seen only in the dissociation temperature is not well understood at this time.



(a) Time variation of temperature and pressure (b) Hysteresis compared with hydrate and non-hydrate region

Figure 6 the curves of temperature and pressure in the test section under the dissociation temperature: (a) time variation of temperature and pressure, (b) hysteresis loop pressure and temperature compared with the hysteresis in hydrate and non-hydrate region

4. Conclusions

In order to investigate the influence of CO₂ hydrate formation and dissociation on the dissolution properties of liquid CO₂, time series changing of temperature, pressure and hysteresis were measured under the hydrate, non-hydrate region and the dissociation temperature conditions.

In the case of the non-hydrate region, two continuous experimental runs were conducted and it was confirmed that there is virtually no hysteresis.

In the case of the hydrate region, three continuous experimental runs were conducted and it was confirmed CO₂ hydrate formation brings the hysteresis. Also, it was suggested these hysteresis that the difference in the pressure between cooling process and heating process indicate the amount of CO₂ hydrate. Therefore It could be assumed that it has the largest amount of CO₂ hydrate in 1st run and the amount of CO₂ hydrate in 2nd and 3rd run are almost equal. However, these hysteresis appear to have a linear tendency though a few hysteresis data. It is considered that the amount of CO₂ hydrate decreases as the cooling gradient increases. However, there were no correlation between cooling gradient and the amount of CO₂ hydrate in these experiments.

Temperature jump classified by types of CO₂ hydrate formation. In the case of this experiment, it was suggested that temperature jump in 1st run classified in dynamic formation, 2st and 3rd run classified in static formation.

In the case of the dissociation temperature, test section was kept at the dissociation temperature for 60 hours. It was confirmed the direction of hysteresis loop was opposite the hysteresis loop in the hydrate region. It indicates the pressure in heating process is larger than heating process. The temperature decreases though pressure is constant. It

suggests apparent density in the test section does not change from 82-142 hour. Those phenomenon seen only in the dissociation temperature.

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