

Dissolution Characteristics of Liquid Carbon Dioxide Injected at the Intermediate Depth of the Ocean

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The solubility, the surface concentration and the dissolution behavior of carbon dioxide in deep sea were numerically investigated. Base on the calculations the relations between the surface concentration of liquid carbon dioxide droplet with the hydrate film and the solubility and those between the ambient carbon dioxide concentration in the plume and the dissolution rate were obtained. The results show that a carbon dioxide droplet is released both at 1000 m in depth with the initial droplet diameter of 0.011 m or less and at 1500 m in depth with a diameter of 0.015 m or less, and the droplet is completely dissolved below 500 m in depth. The hydrate film acts as a resistant layer for the dissolution of liquid carbon dioxide, and the effect of the hydrate film on the dissolution of liquid carbon dioxide depended upon the depth.

Key Words : Carbon Dioxide, Global Warming, Sequestration, Dissolution, Hydrate Film

Nomenclature

A : Surface area of a carbon dioxide droplet (m^2)	$M_{s,w}$: Molecular weight of seawater (carbon dioxide free) (kg/kmole)
C_D : Drag coefficient	n_{CO_2} : Number of moles of carbon dioxide dissolved in seawater
C_o : Surface concentration of a carbon dioxide droplet (kg/m^3)	P : Pressure (MPa)
C_s : Solubility of carbon dioxide in seawater (kg/m^3 and $kmol/m^3$)	S : Salinity (‰)
$C_{p,s}$: Solubility of carbon dioxide in pure water (kg/m^3 and $kmol/m^3$)	T : Temperature (K)
C_∞ : Concentration at infinity (kg/m^3)	U : Rising velocity of a carbon dioxide droplet (m/sec)
d_{CO_2} : Diameter of a carbon dioxide droplet (m)	U_s : Velocity of the surrounding seawater (m/sec)
D : Diffusion coefficient (m^2/s)	V : Volume of a carbon dioxide droplet (m^3)
f_{CO_2} : Fugacity of carbon dioxide (MPa)	$V_{s,w}$: Volume of seawater (carbon dioxide free) (m^3)
g : Gravitational acceleration (m/sec^2)	V_{CO_2} : Molar volume of carbon dioxide at its normal boiling temperature ($m^3/kmol$)
k : Mass transfer coefficient (m/sec)	x_{CO_2} : Solubility of carbon dioxide in seawater in mole fraction
K_H : Henry's law constant (MPa)	x_{CO_2} : Solubility of carbon dioxide in pure water in mole fraction
	α : Salting-out coefficient
	β : Effect factor of the hydrate film
	γ : Effect factor of the ambient concentration

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in the plume

- Φ : Dimensionless association factor of seawater
- $\mu_{s,w}$: Viscosity of seawater (kg/m · s)
- $\nu_{s,w}$: Kinematic viscosity of seawater (m²/sec)
- ρ_{CO_2} : Density of carbon dioxide (kg/m³)
- $\rho_{s,w}$: Density of seawater (carbon dioxide free) (kg/m³)

1. Introduction

The use of fossil fuels like coal, oil and natural gases around the world causes an increase of the carbon dioxide content in the atmosphere (Choi, 1992). In order to reduce the concentration of the greenhouse gas, the idea of carbon dioxide sequestration in the ocean is proposed to be an effective mitigation strategy to counteract potential global warming due to the "greenhouse effect" (Marchetti, 1977 and Steinberg et al. 1984). Carbon dioxide sequestration in the ocean can be classified into two categories. One is the dissolution and the diffusion of carbon dioxide at an intermediate depth (500 m ~ 1,500 m), where released liquid carbon dioxide droplets dissolve in seawater during the process of rising due to buoyancy (Fig. 1). The other is the deep-sea disposal and storage of carbon dioxide in a seabed deeper than 3,000 m, where the liquid carbon dioxide density becomes larger than that of ambient seawater. Liquid carbon dioxide stored in a deep seabed would dissolve in the undercurrent flows (Fig. 2).

In order to evaluate these two strategies, the

dissolution rate of liquid carbon dioxide is important because pH decreases as carbon dioxide dissolves in seawater. Sam (1997) reported on the safety of the underground disposal of carbon dioxide. Herzog et al. (1996) observed the environmental impacts of the ocean disposal of carbon dioxide. Aya et al. (1992) and Shindo et al. (1995) investigated the shrinkage of hydrate-coated and hydrate-free carbon dioxide drops resting on a solid plate or a wire grid immersed in quiescent water or seawater. Nishikawa et al. (1995) and Hirai et al. (1996 and 1997) performed similar observations with carbon dioxide drops at 3,000 m in depth, each held stationary by a basket or wire ring in steady, nearly parallel flow of seawater or pure water. Teng et al. (1996) attempted to assess the effect of the variation of solubility along depth (0 m ~ 1,000 m) on the dissolution of carbon dioxide effluent, and Teng and Yamasaki (1998) reported on the solubility of liquid carbon dioxide in synthetic seawater at temperatures from 278 K to 293 K and pressures from 6.44 MPa to 29.49 MPa. Loken and Austvik (1993) obtained experimentally the hydrate equilibrium line and the carbon dioxide gas/liquid equilibrium line.

However, most of the researchers attempted to predict the carbon dioxide dissolution behavior with the physical and chemical properties of pure water or neglecting the effect of hydrate film that is ice-like inclusion compounds formed at the interface between a carbon dioxide droplet and seawater. Also they calculated the dissolution behavior by assuming that the solubility and the salinity are constant along depth. In order to

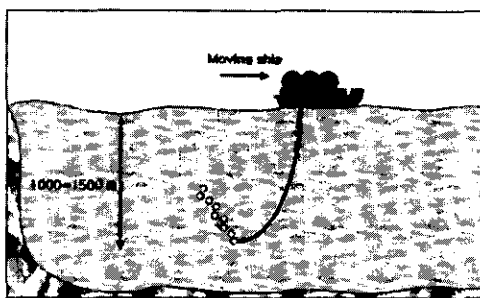


Fig. 1 Dissolution of CO₂ droplets released from pipe outlet hanged from a moving ship at intermediate depth of ocean

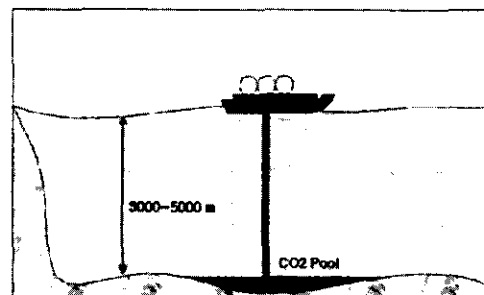


Fig. 2 Deep ocean storage of liquid CO₂ at a seabed deeper than 3000m

make carbon dioxide dissolve completely, it is important to predict the carbon dioxide dissolution behavior along depth accurately. However, these unrealistic property data used for the previous research could give inaccurate predictions.

For a more realistic study, therefore, a point in Clipperton-clarion which was assigned to the Republic of Korea by the United Nations for seabed mining was chosen as the carbon dioxide sequestration spot. This spot is located at 125.5° W and 20.5° N. The solubility, the surface concentration and the dissolution behavior of carbon dioxide at ocean depths are investigated using the real properties data of Clipperton-clarion. In addition, the relations between the surface concentration of a liquid carbon dioxide droplet with hydrate film and the solubility and those between the ambient carbon dioxide concentration in the plume and the dissolution rate are predicted in this study.

2. Governing Equations

2.1 Solubility of liquid carbon dioxide

Carbon dioxide and seawater have very different physical characteristics. Carbon dioxide is a nonpolar substance, while seawater has strong polarity. Therefore, the solubility of liquid carbon dioxide in seawater is much larger than that of water in liquid carbon dioxide. For the present study, the liquid carbon dioxide-seawater system is treated as a one-sided solubility system assuming that liquid carbon dioxide is the solute and seawater is the solvent. The carbon dioxide solubility, C_s , may be defined as

$$C_s \equiv \frac{n_{CO_2}}{V_{s,w}} \quad (1)$$

The solubility may be expressed alternatively in mole fraction as

$$x_{CO_2} = \frac{C_s}{(C_s + \rho_{s,w}/M_{s,w})} \quad (2)$$

or

$$C_s = \frac{x_{CO_2} \rho_{s,w}}{(1 - x_{CO_2}) M_{s,w}} \quad (3)$$

The solubility of carbon dioxide in pure water may be expressed by the modified Henry's law

(King, 1969) as

$$x_{CO_2}^w = \frac{f_{CO_2}}{K_H} \quad (4)$$

The solubility of carbon dioxide in seawater also depends on the salinity. The effect of salinity on the solubility may be examined by considering the Setchenow equation (King, 1969)

$$x_{CO_2} = x_{CO_2}^w e^{\alpha S\%} \quad (5)$$

From Eq. (4) and (5), the solubility of carbon dioxide in seawater can be derived as

$$x_{CO_2} = \left(\frac{f_{CO_2}}{K_H} \right) e^{\alpha S\%} \quad (6)$$

The Henry's law constant (K_H) and the salting-out coefficient (α) are expressed by Teng and Yamasaki (1998) as follows,

$$K_H = \alpha + b + P + c \times P^2 \quad (7)$$

with

$$\begin{aligned} \alpha &= 5.20 \times 10^3 - 39.2 \times T + 0.075 \times T^2 \\ b &= -103 + 0.708 \times T - 1.20 \times 10^{-3} \times T^2 \\ c &= 0.022 \end{aligned}$$

and

$$\alpha = 0.543 - 3.54 \times 10^{-3} \times T + 5.69 \times 10^{-6} \times T^2 \quad (8)$$

2.2 Dissolution behavior of carbon dioxide droplet

The dissolution behavior of liquid carbon dioxide droplet is described as

$$\frac{d(\rho_{CO_2} V)}{dt} = -kA(C_o - C_\infty) \quad (9)$$

According to Hirai (1996 and 1997) and Mori (1998), the carbon dioxide droplet behaves like a rigid sphere because of the hydrate film formed at the interface between a carbon dioxide droplet and seawater. Therefore, the mass transfer coefficient k is described from (Clift et al., 1978)

$$Sh = 1 + (S_c + 1/Re)^{1/3} 0.752 Re^{0.472} \quad (10)$$

Because S_c is much greater than $1/Re$ generally,

$$Sh = 1 + 0.752 Re^{0.472} S_c^{1/3} \quad (11)$$

The second term on the right-hand side of Eq. (11) is greater than unity. Hence Eq. (11) becomes

$$Sh = 0.752 Re^{0.472} S_c^{1/3} \quad (12)$$

Substituting $Sh = kd_{CO_2}/D$, $Re = Ud_{CO_2}/\nu_{s,w}$ and $S_c = \nu_{s,w}/D$ into Eq. (12), the equation can be expressed as follows :

$$\frac{kd_{CO_2}}{D} = 0.752 \left(\frac{Ud_{CO_2}}{\nu_{s,w}} \right)^{0.472} \left(\frac{\nu_{s,w}}{D} \right)^{1/3} \quad (13)$$

From Eq. (13), the mass transfer coefficient k turns out to be as follows:

$$k = 0.752 \frac{U^{0.472} D^{2/3}}{d_{CO_2}^{0.528} \nu_{s,w}^{0.139}} \quad (14)$$

And, the rising velocity U in Eq. (14) is estimated as follows (Clift et al., 1978):

$$U = \sqrt{\frac{4d_{CO_2}(\rho_{s,w} - \rho_{CO_2})g}{3C_D\rho_{s,w}}} \quad (15)$$

Also, the diffusion coefficient D in Eq. (14) is evaluated from the Wilke-Chang equation. (Wilke and Chang, 1955)

$$D = \frac{7.4 \times 10^{-8} (\Phi M_{s,w})^{0.5} T}{\mu_{s,w} V_{CO_2}^{0.6}} \quad (16)$$

A carbon dioxide droplet rises upward due to buoyancy when it is released at the intermediate depth of the ocean. Eq. (9) can be described as

$$\frac{d}{dt} \left(\frac{4}{3} \pi r^3 \rho_{CO_2} \right) = -4\pi r^2 k (C_0 - C_\infty) \quad (17)$$

$$\frac{d}{dt} (d_{CO_2}) = -\frac{2k(C_0 - C_\infty)}{\rho_{CO_2}} - \frac{d_{CO_2}(d\rho_{CO_2}/dt)}{3\rho_{CO_2}} \quad (18)$$

where

$$\frac{d}{dt} (d_{CO_2}) = \frac{dd_{CO_2}}{dz} \cdot \frac{dz}{dt} = \frac{dd_{CO_2}}{dz} (U - U_s) \quad (19)$$

$$\frac{d}{dt} (\rho_{CO_2}) = \frac{d\rho_{CO_2}}{dz} \cdot \frac{dz}{dt} = \frac{d\rho_{CO_2}}{dz} (U - U_s) \quad (20)$$

If $C_0 \gg C_\infty$, Eq. (18) can be simplified to calculate the change in diameter of carbon dioxide droplet as a function of depth (z)

$$\frac{d(d_{CO_2})}{dz} = -\frac{2kC_0}{(U - U_s)\rho_{CO_2}} - \frac{d_{CO_2}}{3\rho_{CO_2}} \frac{d(\rho_{CO_2})}{dz} \quad (21)$$

In a pure single droplet model, U_s is equal to zero.

3. Results and Discussions

In the calculations, it is assumed that 10 m difference depth corresponds to 0.1 MPa pressure

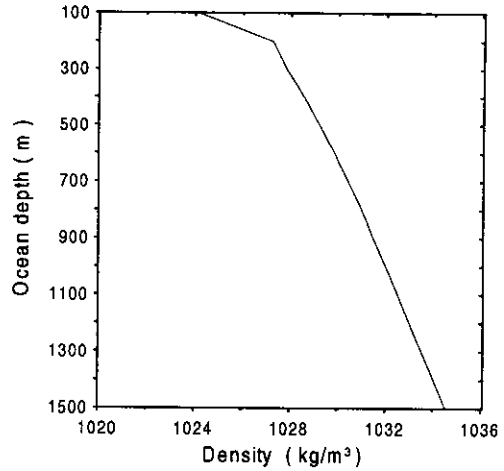


Fig. 3 Density distributions of seawater along depth

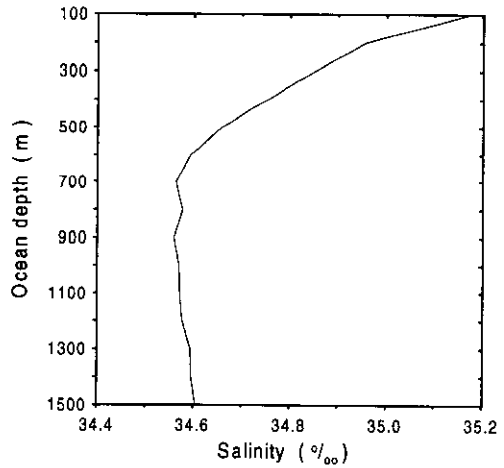


Fig. 4 Salinity distributions of seawater along depth

difference. The density of pure liquid carbon dioxide (ρ_{CO_2}) and the fugacity (f_{CO_2}) are obtained from the National Institute of Standards and Technology Database 23 : REFPROP 6.01 (1998). On the other hand, the density, the kinematic viscosity, the temperature and the salinity along depth at Clipperton-clarion are available at the IRI/LDEO Climate Data Library (Columbia univ., 1999). Figures 3 and 4 show the density and the salinity along depth at the release point. Figure 5 shows the temperature of the seawater along depth at the release point and the equilibrium line of carbon dioxide reported by Loken and Austvik (1993). The density of pure liquid carbon dioxide applied at the temperature

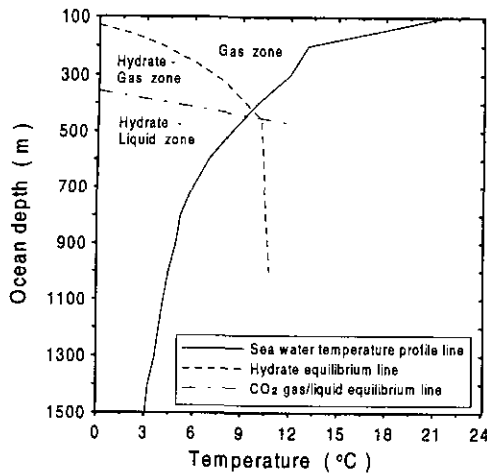


Fig. 5 Temperature distributions of seawater along depth

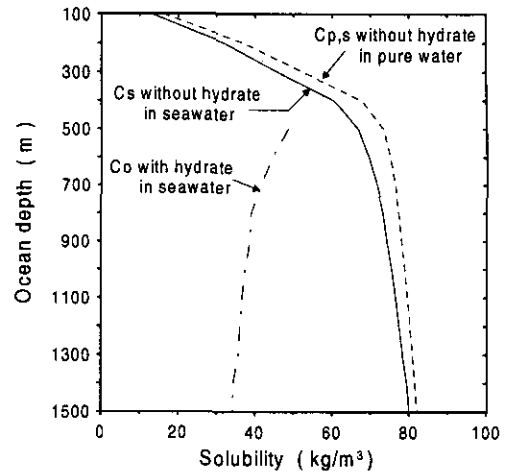


Fig. 7 Solubility distributions of liquid carbon dioxide along depth

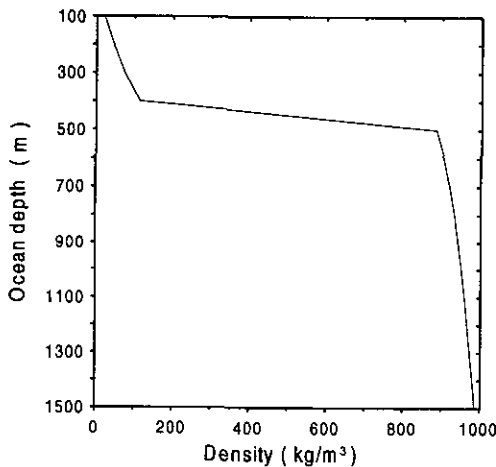


Fig. 6 Density distributions of liquid carbon dioxide along depth

and the pressure along depth at Clipperton-clarion is shown in Fig. 6 where the sudden change in the density of liquid carbon dioxide is observed from 400 m to 500 m in depth.

3.1 Solubility of carbon dioxide

Figure 7 shows the solubility of liquid carbon dioxide in pure water and seawater calculated by Eq. (4) and Eq. (6). From the figure, it is found that the solubility of carbon dioxide in seawater is lower than that in pure water. The solubility without hydrate in seawater is 81%~98% of that in pure water depending upon the depth. If the

difference is averaged in the range of the depth from 100 m to 1500 m, the relation between the solubility in seawater and pure water becomes as follows :

$$C_s = 0.93 C_{p,s} \tag{18}$$

When the carbon dioxide dissolution behaviors were studied in the previous researches, the solubility in pure water was used instead of that in seawater (Hirai et al., 1996 and 1997). Therefore, it is difficult to get an accurate prediction on the dissolution behavior. However, if the researchers use Eq. (18) with the carbon dioxide solubility in pure water, the dissolution behavior of a liquid carbon dioxide droplet in seawater could be predicted more accurately than that of the previous studies.

The sudden change in the gradient of the solubility of liquid carbon dioxide is observed around 500 m in depth from Fig. 7. The solubility of liquid carbon dioxide increases at the average rate of 0.1349 kg/m³ per meter from 100 m to 500 m in depth. On the other hand, the increasing rate of the solubility from 500 m to 1500 m significantly decreases to 0.0132 kg/m³ per meter, which is only one tenth of the former. In addition, it is known from Figs. 5~7 that a liquid carbon dioxide droplet changes to a carbon dioxide bubble in gas phase around 500 m in depth. And, carbon dioxide quickly escapes to the atmosphere

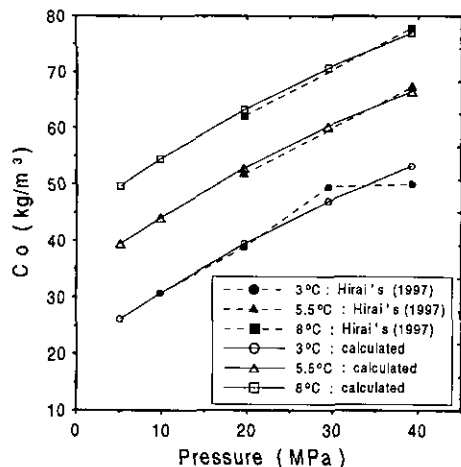


Fig. 8 Comparison of the experimental and calculated surface concentration

if a liquid carbon dioxide droplet does not completely dissolve in seawater below 500 m, because its density in gas phase is much lower than that of seawater. Therefore, in order to prevent carbon dioxide from escaping into the atmosphere, it is important to make carbon dioxide dissolve completely below 500 m in sea water.

3.2 Surface concentration

The most important characteristic nature of carbon dioxide sequestration into the ocean is the formation of a hydrate film at the interface between seawater and a liquid carbon dioxide droplet so that the surface concentration of a liquid carbon dioxide droplet with hydrate film is different from the solubility of pure liquid carbon dioxide. The hydrate film disturbs liquid carbon dioxide dissolution. However, the formation of hydrate film was neglected in the most previous studies because of the simplicity (Teng et al., 1996). To take account of this matter, the experimental data of surface concentration are obtained from the Research Center for Carbon Recycling and Utilization at Tokyo Institute of Technology in Japan. Using the experimental data and Engineering Equation Solver, Version 4.734 (1998), the prediction formula in error of 2.0 % at temperature and pressure of common engineering applications is prepared. The calculated results in this study and experimental data in pure water by

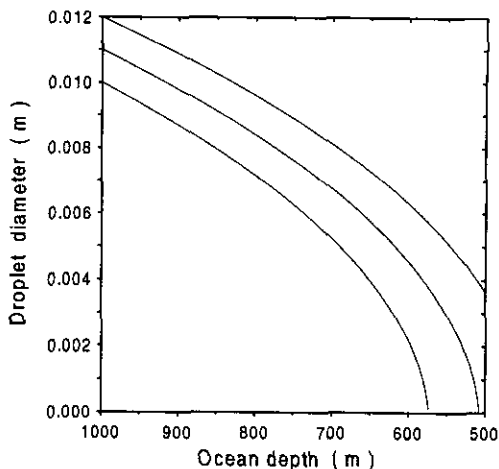


Fig. 9 Dissolution behavior of a carbon dioxide droplet with the hydrate film released a 1000 m in depth

the Tokyo Institute of Technology are shown in Fig. 8. Using the calculated data from the Tokyo Institute of Technology and Eq. (18), the surface concentration (C_o) of carbon dioxide droplet is calculated and presented in Fig. 7. In Fig. 8, the calculated results agree well with the experimental results. If the prediction formula is used for estimating carbon dioxide dissolution behavior, it is easy to predict the surface concentration of carbon dioxide with the hydrate film without doing an experiment.

3.3 Dissolution Behavior

Figure 9 shows the dissolution behavior of carbon dioxide when the droplet is released at 1,000 m in depth and rises up to 500 m in depth. When the initial diameter of carbon dioxide droplet is 0.011 m or less, the droplet is completely dissolved in seawater. However, if the diameter of the droplet is bigger than 0.011 m, dissolution is not completed before the carbon dioxide droplet reaches 500 m in depth.

Hirai et al. (1997) showed the droplet released at 1000 m was completely dissolved when the initial diameter of carbon dioxide droplet is 0.01 m or less. The difference between the result of Hirai's and that of this study's is because the conditions of released spot and Hirai et al. calculated the dissolution behavior with the surface

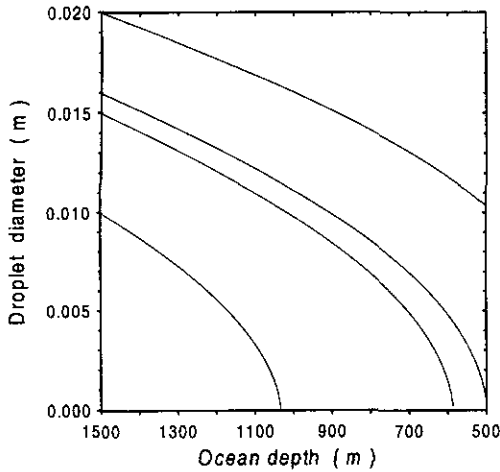


Fig. 10 Dissolution behavior of a carbon dioxide droplet with the hydrate film released a 1500 m in depth

concentration in pure water. This comparison means sea water disturbs the dissolution of liquid carbon dioxide.

Also, the dissolution behavior is shown in Fig. 10 for a carbon dioxide droplet released at 1,500 m in depth. A carbon dioxide droplet of diameter 0.015 m or less is completely dissolved below 500 m in depth, but the droplet bigger than 0.015 m is not completely dissolved. Therefore, the initial diameter of the released droplet is a key parameter for the dissolution in the intermediate depth of the ocean.

3.4 Relation between surface concentration and solubility

The relation between surface concentration and solubility is given as the following equation

$$C_o = \beta C_s \quad (19)$$

Using the data of surface concentration (C_o) from Fig. 7, the dissolution behaviors of liquid carbon dioxide released at 1,000 m and 1,500 m in depth are calculated and shown in Fig. 11 and Fig. 12. According to the results of Hirai et al. (1996), β is about 0.5 at 10~40 MPa with constant temperature of 276 K. However, it is found from Fig. 11 and Fig. 12 that β becomes 0.6, not 0.5 if the droplet is released at 1,000 m in depth.

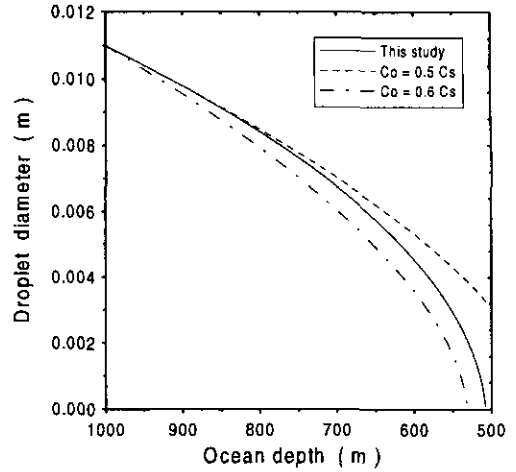


Fig. 11 Effect of the hydrate film on the dissolution behavior released at 1000 m in depth

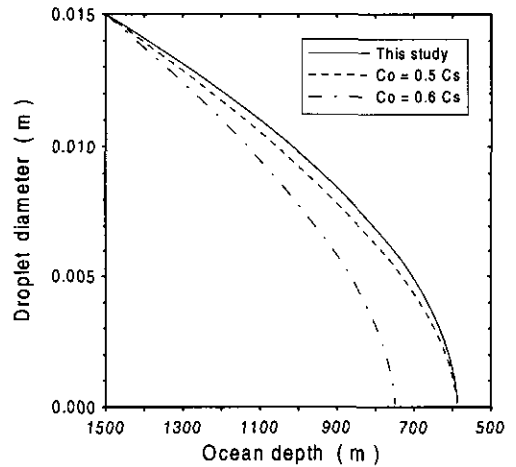


Fig. 12 Effect of the hydrate film on the dissolution behavior released at 1500 m in depth

And, if it is released at 1,500 m in depth β corresponds with 0.5 as the results of Hirai et al. (1996). Therefore, the different values of β should be applied for accurate prediction depending upon the releasing depth.

The dissolution behavior of carbon dioxide droplet with ($\beta=0.5$ and 0.6) and without ($\beta=1$) the hydrate film is shown in Fig. 13 and Fig. 14. The figures show that the hydrate film acts as an obstacle for the dissolution into seawater. Therefore, if the hydrate film formation is neglected, it gives very poor prediction for the carbon dioxide dissolution behavior.

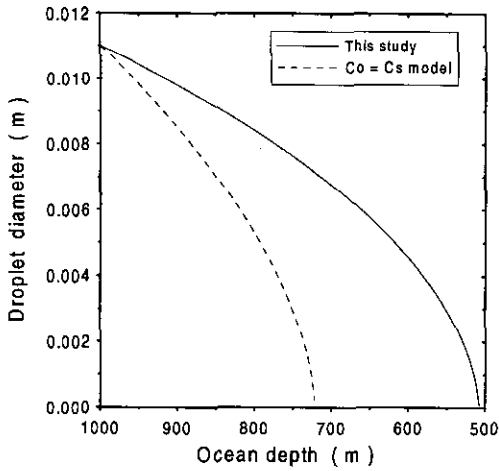


Fig. 13 Effect of the hydrate film on carbon dioxide dissolution behavior released at 1000 m in depth

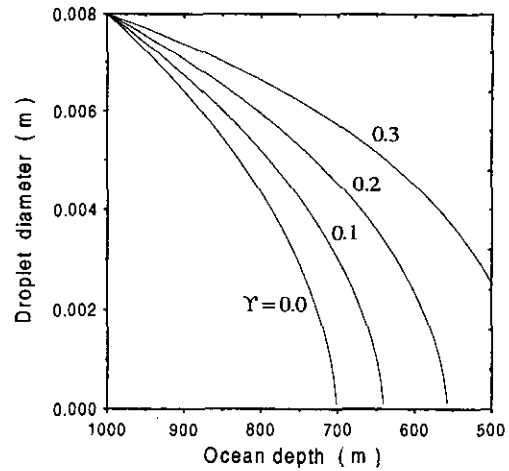


Fig. 15 Effect of the ambient carbon dioxide concentration on the dissolution behavior of carbon dioxide released at 100 m in depth

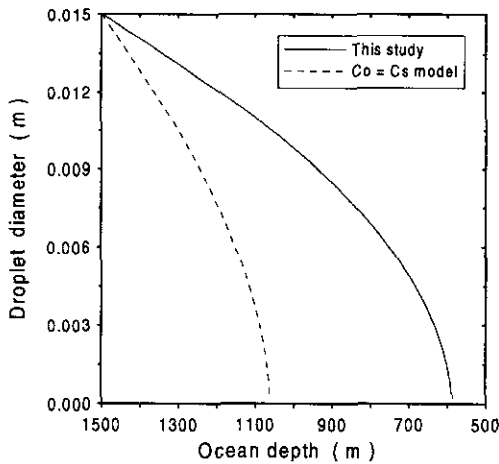


Fig. 14 Effect of the hydrate film on carbon dioxide dissolution behavior released at 1500 m in depth

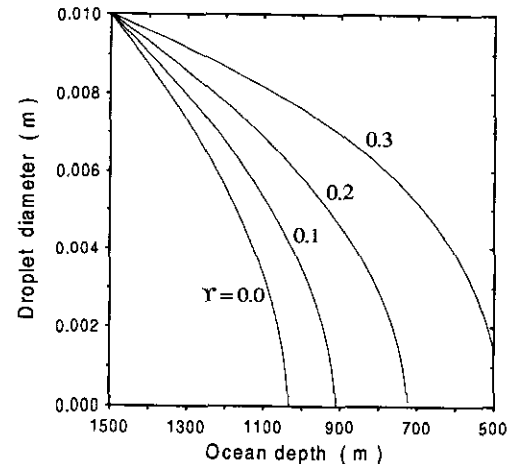


Fig. 16 Effect of the ambient carbon dioxide concentration on the dissolution behavior of carbon dioxide released at 150 m in depth

3.5 Relation between dissolution behavior and ambient carbon dioxide concentration

Once liquid carbon dioxide is injected from a nozzle, a number of small carbon dioxide droplets are created. A large group of small droplets is called a plume. Because the concentration of carbon dioxide in the plume is much higher than that of plain seawater, the dissolution rate of liquid carbon dioxide in the plume rapidly decreases. It is because the dissolution rate is

proportional to the concentration gradient around the droplet. In order to increase the dissolution rate of carbon dioxide, it is necessary to restrain the formation of a large plume and to decrease the ambient concentration of carbon dioxide droplet around the releasing point.

The effect of the ambient concentration of carbon dioxide on the dissolution rate is shown in Fig. 15 and Fig. 16 using Eq. (20).

$$C_{\infty} = \gamma C_s \tag{20}$$

It may be seen from Fig. 15 and Fig. 16 that an increase of the ambient carbon dioxide concentration induces a suppressing effect of dissolution retardation. This means that the ambient carbon dioxide concentration is another crucial parameter for the complete dissolution at the intermediate ocean depth. Therefore, in order to reduce the ambient carbon dioxide concentration, the injection of liquid carbon dioxide from a moving ship is much more effective than that from a fixed point.

4. Conclusions

The conclusions from the present study are as follows :

(1) Liquid carbon dioxide changes to carbon dioxide bubbles around 500 m in depth. Therefore, liquid carbon dioxide should be completely dissolved below 500 m in depth.

(2) The prediction formula in error of 2.0 % at temperatures and pressures used in common engineering applications is suggested. Thus, the surface concentration of carbon dioxide with the hydrate film could be predicted without doing an experiment.

(3) The droplet is completely dissolved below 500 m in depth if the carbon dioxide droplet is released both at 1,000 m in depth with the initial droplet diameter of 0.011 m or less and at 1,500 m in depth with the diameter of 0.015 or less. Therefore, the initial diameter of the released droplet is a key parameter for the dissolution in the intermediate depth of the ocean.

(4) Surface concentration of carbon dioxide droplet with the hydrate film is about 50% of carbon dioxide solubility at 1,500 m in depth and about 60% of carbon dioxide solubility at 1,000 m in depth. Therefore, the effect of the hydrate film has to be considered differently depending upon the depth.

(5) The hydrate film acts as a barrier for the dissolution of liquid carbon dioxide.

(6) The ambient carbon dioxide concentration in the plume is another crucial parameter for complete dissolution at the intermediate ocean depth. Therefore, the injection of liquid carbon

dioxide from a moving ship is more effective than that from a fixed pipeline.

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