

## Numerical study of CO<sub>2</sub> hydrate dissolution rates in the ocean: Effect of pressure, temperature, and salinity

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**Abstract.** In this study, we numerically investigated the effect of pressure (100-250 bar), temperature (274-288 K), and salinity (3.5% w/w electrolytes) on CO<sub>2</sub> hydrate dissolution rates in the ocean. Mass transfer equations and CO<sub>2</sub> solubility data were used to estimate the CO<sub>2</sub> hydrate dissolution rates. The higher pressure and lower temperature significantly reduced the CO<sub>2</sub> hydrate dissolution rates due to the increase of CO<sub>2</sub> particle density. In the high salinity condition, the rates of CO<sub>2</sub> hydrate dissolution were decreased compared to pure water control. This is due to decrease of CO<sub>2</sub> solubility in surrounding water, thus reducing the mass transfer of CO<sub>2</sub> from the hydrate particle to CO<sub>2</sub> under-saturated water. The results obtained from this study could provide fundamental knowledge to slow down or prevent the CO<sub>2</sub> hydrate dissolution for long-term stable CO<sub>2</sub> storage in the ocean as a form of CO<sub>2</sub> hydrate.

**Keywords:** CO<sub>2</sub> hydrate dissolution; mass transfer; ocean conditions; CO<sub>2</sub> storage

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### 1. Introduction

The CO<sub>2</sub> concentration in atmosphere has been rapidly increased for decades by anthropogenic activities using fossil fuels (Lamarena and Lee 2008, 2009). Environmental disasters such as global warming and climate change were accompanied by increase of CO<sub>2</sub> concentration. To reduce huge amount of CO<sub>2</sub>, sequestration of CO<sub>2</sub> in terrestrial (depleted oil and gas reservoirs, coal beds, and saline aquifers) and ocean (marine sediments) area has been highlighted as one of promising strategies (Kyung *et al.* 2014, 2015, Park *et al.* 2014). Among the several options for CO<sub>2</sub> sequestration, CO<sub>2</sub> storage in marine sediments have been received attention because it can guarantee massive CO<sub>2</sub> storage capacity as well as have advantages for application (Lamarena *et al.* 2011, Lee *et al.* 2013). Formation of CO<sub>2</sub> hydrate layer in the vicinity of the storage site could avoid the buoyant liquid CO<sub>2</sub> leakage without impermeable cap-rock structures in marine sediments (House *et al.* 2006).

CO<sub>2</sub> hydrates are ice-like crystalline structures which enclose CO<sub>2</sub> as guest molecule inside the hydrogen-bonded water cages (Slaon 2003). The structure of CO<sub>2</sub> hydrate can be stably maintained at high pressure, low temperature, moderate salinities, and CO<sub>2</sub> saturated condition. CO<sub>2</sub> hydrate structure can be decomposed in either of two ways: one is dissociation and the other

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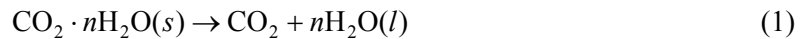
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is dissolution (Rehder *et al.* 2004, Lapham *et al.* 2014). Dissociation process takes place when surrounding environment cannot meet the equilibrium pressure (P) and temperature (T) for stable hydrate. On the other hand, dissolution process occurs when the chemical potentials of CO<sub>2</sub> between the dissolved phase and the hydrate phase are not in equilibrium, although the equilibrium conditions (P and T) are satisfied for stable hydrate. During the dissociation process, CO<sub>2</sub> hydrate decomposes into gaseous CO<sub>2</sub> and liquid water. However, during the dissolution process, CO<sub>2</sub> hydrate dissolves into aqueous CO<sub>2</sub> and liquid water until either saturation conditions in the surroundings are equilibrated or all of the hydrate is disappeared (Lapham *et al.* 2014). Since CO<sub>2</sub> concentration dissolved in ocean ( $\approx 2$  mM) is much smaller than its solubility at certain environmental condition, CO<sub>2</sub> hydrate can be easily decomposed by dissolution when it is exposed to CO<sub>2</sub>-undersaturated seawater.

Therefore, CO<sub>2</sub> hydrate dissolution should be fully understood in advance to suggest proper tactics for CO<sub>2</sub> storage in marine sediments. Several studies have reported that dissolution rates of CO<sub>2</sub> hydrate are mainly controlled by diffusion (mass transfer), not by strength of the hydrogen-bonded water cages (Teng *et al.* 1997, 1999, Rehder *et al.* 2004, Lapham *et al.* 2014). Interfacial mass transfer of CO<sub>2</sub> between the hydrate and seawater can be significantly varied by marine environmental factors (pressure, temperature, and salinity), thus changing the reaction mechanism of CO<sub>2</sub> hydrate dissolution. However, no adequate studies have been conducted to investigate the effect of such factors on CO<sub>2</sub> hydrate dissolution to date. In this study, the effect of pressure (100-250 bar), temperature (274-288 K), and salinity (3.5% w/w electrolytes) on CO<sub>2</sub> hydrate dissolution rates was investigated numerically using the mass transfer equations (liquid CO<sub>2</sub> droplet and CO<sub>2</sub> hydrate) and CO<sub>2</sub> solubility data. This study can provide basic knowledge to predict the CO<sub>2</sub> hydrate lifetime in marine sediments, which is directly related successful CO<sub>2</sub> storage in marine sediments.

## 2. Methodology

CO<sub>2</sub> entrapped in the hydrate particle can be dissolved to the CO<sub>2</sub>-undersaturated seawater by mass transfer, due to non-equilibrium between the particle and the seawater. Decomposition of CO<sub>2</sub> hydrate by the dissolution process can be expressed as following equation



Where, n indicates the hydration number (HN) of CO<sub>2</sub> hydrate and it can be calculated by using Eq. (2). Assuming that mole fraction of CO<sub>2</sub> in the hydrate ( $x_{\text{CO}_2,cr}^H$ ) is approximately 0.141, HN of 6.1 can be obtained. The total mass of CO<sub>2</sub> hydrate particle ( $m_{\text{CO}_2}^H$ ) can be calculated based on the volume and density of the particle (Eq. (3)).

$$n = \left( \frac{1 - x_{\text{CO}_2,cr}^H}{x_{\text{CO}_2,cr}^H} \right) \quad (2)$$

$$m_{\text{CO}_2}^H = \frac{4}{3} \pi r_p^3 \rho_{\text{CO}_2}^H \quad (3)$$

The rate of change in total mass of the particle over time by mass transfer can be

expressed by Eq. (4). Since the density of bulk CO<sub>2</sub> hydrate is hardly influenced by mass transfer on the hydrate surface, change in density over time can be neglected ( $d\rho_{\text{CO}_2}^{\text{H}}/dt \rightarrow 0$ ). Then, the particle-shrinkage rate ( $dr_p/dt \rightarrow 0$ ) can be represented by the overall mass-transfer coefficient ( $K_f$ ), fugacity of CO<sub>2</sub> in the hydrate particle ( $f_{\text{CO}_2}^{\text{H}}$ ) and CO<sub>2</sub>-undersaturated water ( $f_{\text{CO}_2}^{\text{W}}$ ), and density of bulk CO<sub>2</sub> hydrate (Eq. (6)).

$$\frac{dm_{\text{CO}_2}^{\text{H}}}{dt} = 4\pi r_p^2 \frac{dr_p}{dt} \rho_{\text{CO}_2}^{\text{H}} + \frac{4}{3}\pi r_p^3 \frac{d\rho_{\text{CO}_2}^{\text{H}}}{dt} \quad (4)$$

$$-\frac{dm_{\text{CO}_2}^{\text{H}}}{dt} = 4\pi r_p^2 K_f (f_{\text{CO}_2}^{\text{H}} - f_{\text{CO}_2}^{\text{W}}) \quad (5)$$

$$\left| \frac{dr_p}{dt} \right| = \frac{K_f (f_{\text{CO}_2}^{\text{H}} - f_{\text{CO}_2}^{\text{W}})}{\rho_{\text{CO}_2}^{\text{H}}} \quad (6)$$

Due to large variations of particle-shrinkage rate (1.5E-06~1.1E-05 m/s), use of liquid CO<sub>2</sub> droplet data was considered to estimate CO<sub>2</sub> hydrate dissolution rates more correctly (Teng *et al.* 1999). Liquid CO<sub>2</sub> droplet injected into CO<sub>2</sub>-undersaturated water can be surrounded by hydrate interphase. Therefore, mass transfer of CO<sub>2</sub> from the droplet to the water can be described as Eq. (7).

$$-\frac{d}{dt} \left( \frac{4}{3} \pi r_{\text{drop}}^2 \rho_0 \right) = 4\pi r_{\text{drop}}^2 K_f (f_{\text{CO}_2}^{\text{H}} - f_{\text{CO}_2}^{\text{W}}) \quad (7)$$

Where,  $\rho_0$  and  $r_{\text{drop}}$  is the initial density of liquid CO<sub>2</sub> and radius of the droplet, respectively. Because change in the molar density of liquid CO<sub>2</sub> is negligible during the dissolution process, Eq. (7) can be simplified to Eq. (8).

$$\left| \frac{dr_{\text{drop}}}{dt} \right| = \frac{K_f (f_{\text{CO}_2}^{\text{H}} - f_{\text{CO}_2}^{\text{W}})}{\rho_0} \quad (8)$$

New equation (Eq. (9)) estimating the dissolution rate of CO<sub>2</sub> hydrate particle can be yielded by combining of Eqs. (6) and (8).

$$\left| \frac{dr_p}{dt} \right| = \left| \frac{dr_{\text{drop}}}{dt} \right| \frac{\rho_0}{\rho_{\text{CO}_2}^{\text{H}}} \quad (9)$$

### 3. Results and discussion

Shrinkage rates of CO<sub>2</sub> droplets previously reported by Warzinski *et al.* (2004) was used to investigate the effect of pressure (100-250 bar) and temperature (274-288 K) on CO<sub>2</sub> hydrate dissolution rates. Liquid CO<sub>2</sub> density at different pressure and temperature were obtained by using peace software to calculate thermodynamic state variables of CO<sub>2</sub> (Fig. 1). In this study, 1,100 kg/m<sup>3</sup> of CO<sub>2</sub> hydrate particle density was assumed to calculate the dissolution rates of CO<sub>2</sub> hydrate. The unit of CO<sub>2</sub> hydrate dissolution rates was converted from  $\mu\text{mol}/\text{m}^2\cdot\text{s}$  to cm/yr, using

following equations previously reported by Rehder *et al.* (2004).

$$DR \text{ (m/s)} = 2 \times DR \text{ (\mu mol/m}^2 \cdot \text{s)} \times \frac{M_{\text{CO}_2}}{\rho_{\text{CO}_2}^{\text{H}}} \times \left( \frac{M_{\text{CO}_2} + HN \cdot M_{\text{H}_2\text{O}}}{M_{\text{CO}_2}} \right) \times 10^{-6} \text{ mol/\mu mol} \quad (10)$$

$$DR \text{ (cm/yr)} = DR \text{ (m/s)} \times 10^2 \text{ cm/m} \times 3.1536 \times 10^7 \text{ s/yr} \quad (11)$$

Where, DR stands for dissolution rate and  $M_{\text{CO}_2}$  (0.044 kg/mol) and  $M_{\text{H}_2\text{O}}$  (0.018 kg/mol) is molar weight of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , respectively.  $\text{CO}_2$  hydrate dissolution rates calculated at different pressure and temperature are summarized in Table 1 and illustrated in Fig. 2.  $\text{CO}_2$  hydrate dissolution rates were decreased by pressure increase and temperature decrease. This indicates that desorption layer of  $\text{CO}_2$  hydrate would be more stable at higher pressure and lower temperature conditions, due to stronger hydrogen bonds between water molecules consisting of the crystal structure (Kyung *et al.* 2015). Therefore, interface reaction breaking up the crystal lattice that liberates the enclosed  $\text{CO}_2$  can be reduced, resulting in decrease of  $\text{CO}_2$  hydrate dissolution rates. Decrease of water velocity required to stabilize the  $\text{CO}_2$  hydrate particle could be another potential reason for reduced  $\text{CO}_2$  hydrate dissolution rates. The density of  $\text{CO}_2$  increases at higher pressure and lower temperature; thus, the rise velocity of  $\text{CO}_2$  hydrate particle driven by buoyancy can be decreased at certain environments. Due to correlation between dissolution on the surface of  $\text{CO}_2$  hydrate and the velocity of the water contacting with the hydrate (Bigalke *et al.* 2009), higher pressure and lower temperature can lead lower  $\text{CO}_2$  hydrate dissolution rates. This indicates that dissolution rates of  $\text{CO}_2$  hydrate are significantly influenced by thermodynamic and hydrodynamic conditions.  $\text{CO}_2$  hydrates formed at depth 2,500 meters (i.e., 250 bar) initially rose and dissolved slowly; however, the further it rose, the faster it dissolved. This suggests that  $\text{CO}_2$  storage in

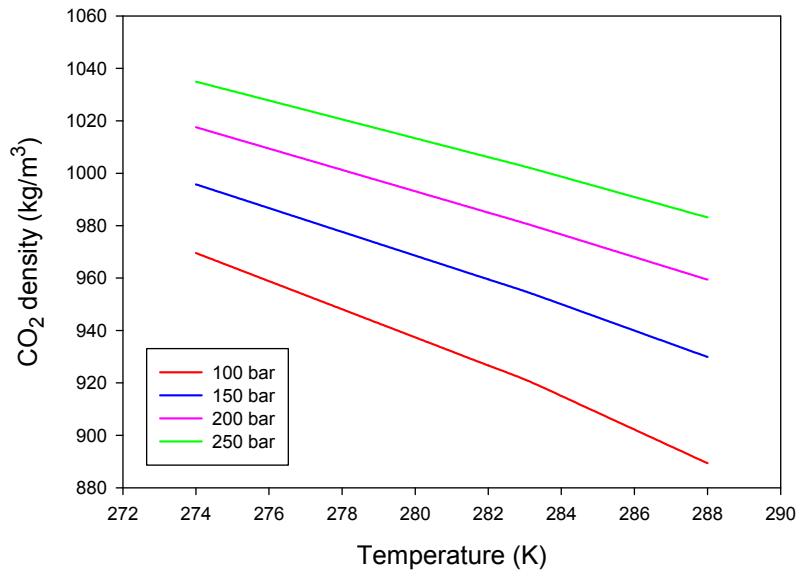


Fig. 1 Density of liquid  $\text{CO}_2$  at different pressure and temperature

Table 1 Dissolution rates of CO<sub>2</sub> hydrate at different pressure and temperature

Pressure (100 bar)									
274 K		275 K		276 K		277 K		278 K	
2.648	2.336	2.804	2.473	2.958	2.608	3.110	2.742	3.259	2.874
279 K		280 K		281 K		282 K		283 K	
3.407	3.005	3.554	3.134	3.698	3.261	3.840	3.386	3.981	3.510
284 K		285 K		286 K		287 K		288 K	
4.115	3.629	4.247	3.745	4.376	3.859	4.503	3.971	4.628	4.081
Pressure (150 bar)									
274 K		275 K		276 K		277 K		278 K	
2.172	1.916	2.352	2.074	2.529	2.230	2.705	2.385	2.879	2.539
279 K		280 K		281 K		282 K		283 K	
3.051	2.691	3.222	2.841	3.391	2.990	3.558	3.138	3.723	3.284
284 K		285 K		286 K		287 K		288 K	
3.885	3.426	4.045	3.567	4.203	3.706	4.359	3.844	4.513	3.980
Pressure (200 bar)									
274 K		275 K		276 K		277 K		278 K	
1.573	1.387	1.758	1.551	1.942	1.713	2.125	1.874	2.306	2.033
279 K		280 K		281 K		282 K		283 K	
2.485	2.192	2.663	2.348	2.839	2.504	3.014	2.658	3.187	2.811
284 K		285 K		286 K		287 K		288 K	
3.358	2.961	3.527	3.111	3.695	3.258	3.861	3.405	4.025	3.550
Pressure (250 bar)									
274 K		275 K		276 K		277 K		278 K	
0.451	0.398	0.686	0.605	0.920	0.812	1.153	1.016	1.383	1.220
279 K		280 K		281 K		282 K		283 K	
1.612	1.422	1.839	1.622	2.065	1.821	2.289	2.019	2.511	2.215
284 K		285 K		286 K		287 K		288 K	
2.731	2.409	2.950	2.601	3.166	2.792	3.380	2.981	3.593	3.168

\* unit of left column:  $\mu\text{mol}/\text{m}^2\cdot\text{s}$  and right column:  $\text{cm}/\text{yr}$

marine sediments should be implemented at depth more than 2,500 m to prevent or minimize the environmental risks caused by CO<sub>2</sub> hydrate dissolution.

CO<sub>2</sub> hydrate dissolution rates were simulated in pure water and seawater at 150 bar and 274-288 K conditions (Fig. 3 and Table 2). CO<sub>2</sub> hydrate dissolution rates in seawater were lower than those in pure water, indicating that salinity condition could help prevent the CO<sub>2</sub> hydrate dissolution. This is due to different CO<sub>2</sub> solubility in pure water and seawater. It has been known that less amount of CO<sub>2</sub> can be dissolved in seawater (or synthetic seawater) compared with pure water (Stewart and Munjal 1970) due to the high concentration of electrolytes (3.5% w/w). Since the dissolution of CO<sub>2</sub> hydrate occurs until surrounding conditions are reestablished by CO<sub>2</sub>

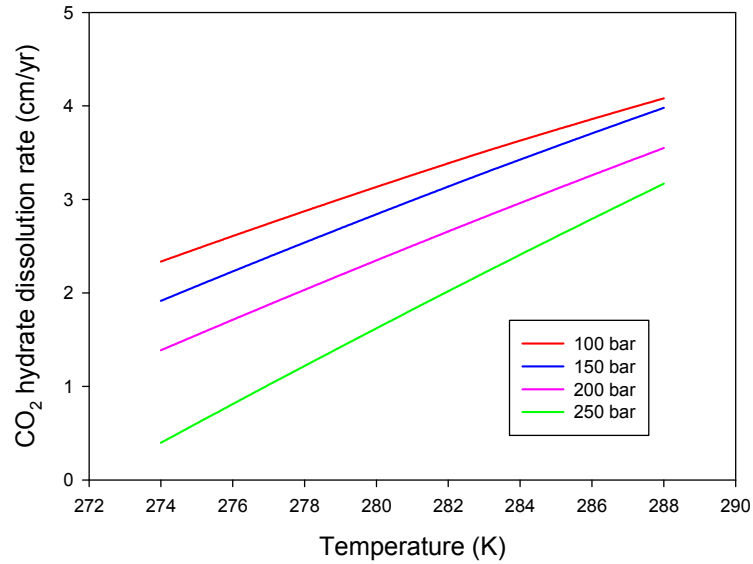


Fig. 2 Dissolution rate of CO<sub>2</sub> hydrate at different pressure and temperature

saturation (Lapham *et al.* 2014), seawater which have lower CO<sub>2</sub> solubility than pure water can meet the conditions more easily. Additionally, highly dissolved ions in seawater can interrupt CO<sub>2</sub> mass transfer from the CO<sub>2</sub> hydrate surface to surrounding seawater. The difference of CO<sub>2</sub> hydrate dissolution rates between pure water and seawater was larger at higher temperature than at lower temperature. This indicates that the CO<sub>2</sub> hydrate dissolution rates are less sensitive in seawater than pure water with respect to temperature fluctuation.

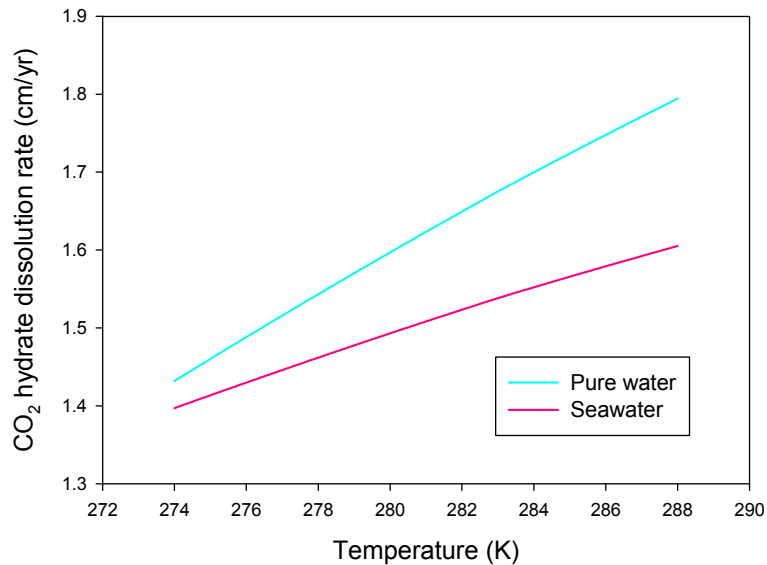


Fig. 3 Dissolution rates of CO<sub>2</sub> hydrate in pure water and seawater at 150 bar

Table 2 Dissolution rates of CO<sub>2</sub> hydrate in pure water and seawater at 150 bar

CO <sub>2</sub> hydrate dissolution rate at 150 bar (cm/yr)									
274 K		275 K		276 K		277 K		278 K	
PW*	SW*	PW	SW	PW	SW	PW	SW	PW	SW
1.432	1.397	1.460	1.414	1.488	1.430	1.516	1.446	1.543	1.462
279 K		280 K		281 K		282 K		283 K	
PW	SW	PW	SW	PW	SW	PW	SW	PW	SW
1.570	1.478	1.597	1.493	1.623	1.508	1.649	1.523	1.675	1.538
284 K		285 K		286 K		287 K		288 K	
PW	SW	PW	SW	PW	SW	PW	SW	PW	SW
1.700	1.552	1.724	1.566	1.748	1.579	1.771	1.592	1.794	1.605

\* PW: pure water; SW: seawater

#### 4. Conclusions

In this study, effect of various environmental factors on the change of CO<sub>2</sub> hydrate dissolution rates was investigated. Numerical analysis was carried out to evaluate the effect of pressure, temperature, and salinity on CO<sub>2</sub> hydrate dissolution rates using the data of liquid CO<sub>2</sub> droplet dissolution rates in seawater. CO<sub>2</sub> hydrate dissolution in marine environment has been emerged as an important issue on CO<sub>2</sub> storage in marine sediments. Nevertheless, only few studies have dealt with CO<sub>2</sub> hydrate dissolution in the ocean. Therefore, CO<sub>2</sub> hydrate dissolution in the ocean should be properly understood with the pivotal environmental factors to select proper sites for CO<sub>2</sub> storage and to predict the behavior and fate of sequestered CO<sub>2</sub> under the marine sediment environments.

CO<sub>2</sub> hydrate dissolution rates can be significantly reduced at higher pressure and lower temperature conditions. Seawater containing high concentration of electrolytes considerably slowed down the dissolution rates of CO<sub>2</sub> hydrate. Dissolution of CO<sub>2</sub> hydrate in the ocean is inevitable phenomena due to different chemical potential between CO<sub>2</sub> hydrate and CO<sub>2</sub>-undersaturated seawater. However, based on the results obtained from the study, we could suggest proper tactics for the CO<sub>2</sub> storage in the marine sediments without serious environmental risks. Prevention of direct CO<sub>2</sub> hydrate exposure to seawater with hydrocarbon films, surfactants, microbial or sediment layers might significantly reduce the dissolution rates of CO<sub>2</sub> hydrate. CO<sub>2</sub> injection in some CO<sub>2</sub>-rich fluid area such as Okinawa trough could be another effective way to minimize CO<sub>2</sub> hydrate dissolution.

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