Numerical study of CO_2 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_2 hydrate dissolution rates in the ocean. Mass transfer equations and CO_2 solubility data were used to estimate the CO_2 hydrate dissolution rates. The higher pressure and lower temperature significantly reduced the CO_2 hydrate dissolution rates due to the increase of CO_2 particle density. In the high salinity condition, the rates of CO_2 hydrate dissolution were decreased compared to pure water control. This is due to decrease of CO_2 solubility in surrounding water, thus reducing the mass transfer of CO_2 from the hydrate particle to CO_2 under-saturated water. The results obtained from this study could provide fundamental knowledge to slow down or prevent the CO_2 hydrate dissolution for long-term stable CO_2 storage in the ocean as a form of CO_2 hydrate.

Keywords: CO_2 hydrate dissolution; mass transfer; ocean conditions; CO_2 storage

1. Introduction

The CO_2 concentration in atmosphere has been rapidly increased for decades by anthropogenic activities using fossil fuels (Lamorena and Lee 2008, 2009). Environmental disasters such as global warming and climate change were accompanied by increase of CO_2 concentration. To reduce huge amount of CO_2, sequestration of CO_2 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_2 sequestration, CO_2 storage in marine sediments have been received attention because it can guarantee massive CO_2 storage capacity as well as have advantages for application (Lamorena *et al*. 2011, Lee *et al*. 2013). Formation of CO_2 hydrate layer in the vicinity of the storage site could avoid the buoyant liquid CO_2 leakage without impermeable cap-rock structures in marine sediments (House *et al*. 2006).

CO_2 hydrates are ice-like crystalline structures which enclose CO_2 as guest molecule inside the hydrogen-bonded water cages (Slaon 2003). The structure of CO_2 hydrate can be stably maintained at high pressure, low temperature, moderate salinities, and CO_2 saturated condition. CO_2 hydrate structure can be decomposed in either of two ways: one is dissociation and the other

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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_2 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_2 hydrate decomposes into gaseous CO_2 and liquid water. However, during the dissolution process, CO_2 hydrate dissolves into aqueous CO_2 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_2 concentration dissolved in ocean ($\approx$ 2 mM) is much smaller than its solubility at certain environmental condition, CO_2 hydrate can be easily decomposed by dissolution when it is exposed to CO_2-undersaturated seawater.

Therefore, CO_2 hydrate dissolution should be fully understood in advance to suggest proper tactics for CO_2 storage in marine sediments. Several studies have reported that dissolution rates of CO_2 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_2 between the hydrate and seawater can be significantly varied by marine environmental factors (pressure, temperature, and salinity), thus changing the reaction mechanism of CO_2 hydrate dissolution. However, no adequate studies have been conducted to investigate the effect of such factors on CO_2 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_2 hydrate dissolution rates was investigated numerically using the mass transfer equations (liquid CO_2 droplet and CO_2 hydrate) and CO_2 solubility data. This study can provide basic knowledge to predict the CO_2 hydrate lifetime in marine sediments, which is directly related successful CO_2 storage in marine sediments.

2. Methodology

CO_2 entrapped in the hydrate particle can be dissolved to the CO_2-undersaturated seawater by mass transfer, due to non-equilibrium between the particle and the seawater. Decomposition of CO_2 hydrate by the dissolution process can be expressed as following equation

$$CO_2 \cdot nH_2O(s) \rightarrow CO_2 + nH_2O(l) \tag{1}$$
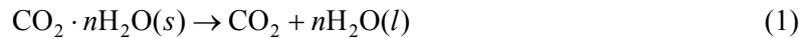
Where, n indicates the hydration number (HN) of CO_2 hydrate and it can be calculated by using Eq. (2). Assuming that mole fraction of CO_2 in the hydrate ($x^H_{CO_2,cr}$) is approximately 0.141, HN of 6.1 can be obtained. The total mass of CO_2 hydrate particle ($m^H_{CO_2}$) can be calculated based on the volume and density of the particle (Eq. (3)).

$$n = \left(\frac{1 - x^H_{CO_2,cr}}{x^H_{CO_2,cr}} \right) \tag{2}$$

$$m^H_{CO_2} = \frac{4}{3} \pi r_p^3 \rho^H_{CO_2} \tag{3}$$

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_2 hydrate is hardly influenced by mass transfer on the hydrate surface, change in density over time can be neglected ($d\rho_{CO_2}^H/dt \to 0$). Then, the particle-shrinkage rate ($dr_p/dt \to 0$) can be represented by the overall mass-transfer coefficient (K_f), fugacity of CO_2 in the hydrate particle ($f_{CO_2}^H$) and CO_2-undersaturated water ($f_{CO_2}^W$), and density of bulk CO_2 hydrate (Eq. (6)).

$$\frac{dm_{CO_2}^H}{dt} = 4\pi\, r_p^2 \frac{dr_p}{dt} \rho_{CO_2}^H + \frac{4}{3}\pi\, r_p^3 \frac{d\rho_{CO_2}^H}{dt} \tag{4}$$

$$\frac{-dm_{CO_2}^H}{dt} = 4\pi\, r_p^2 K_f \left(f_{CO_2}^H - f_{CO_2}^W \right) \tag{5}$$

$$\left| \frac{dr_p}{dt} \right| = \frac{K_f \left(f_{CO_2}^H - f_{CO_2}^W \right)}{\rho_{CO_2}^H} \tag{6}$$

Due to large variations of particle-shrinkage rate (1.5E-06~1.1E-05 m/s), use of liquid CO_2 droplet data was considered to estimate CO_2 hydrate dissolution rates more correctly (Teng *et al.* 1999). Liquid CO_2 droplet injected into CO_2-undersaturated water can be surrounded by hydrate interphase. Therefore, mass transfer of CO_2 from the droplet to the water can be described as Eq. (7).

$$-\frac{d}{dt}\left(\frac{4}{3}\pi\, r_{drop}^2 \rho_0 \right) = 4\pi\, r_{drop}^2 K_f \left(f_{CO_2}^H - f_{CO_2}^W \right) \tag{7}$$

Where, ρ_0 and r_{drop} is the initial density of liquid CO_2 and radius of the droplet, respectively. Because change in the molar density of liquid CO_2 is negligible during the dissolution process, Eq. (7) can be simplified to Eq. (8).

$$\left| \frac{dr_{drop}}{dt} \right| = \frac{K_f \left(f_{CO_2}^H - f_{CO_2}^W \right)}{\rho_0} \tag{8}$$

New equation (Eq. (9)) estimating the dissolution rate of CO_2 hydrate particle can be yielded by combining of Eqs. (6) and (8).

$$\left| \frac{dr_p}{dt} \right| = \left| \frac{dr_{drop}}{dt} \right| \frac{\rho_0}{\rho_{CO_2}^H} \tag{9}$$

3. Results and discussion

Shrinkage rates of CO_2 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_2 hydrate dissolution rates. Liquid CO_2 density at different pressure and temperature were obtained by using peace software to calculate thermodynamic state variables of CO_2 (Fig. 1). In this study, 1,100 kg/m^3 of CO_2 hydrate particle density was assumed to calculate the dissolution rates of CO_2 hydrate. The unit of CO_2 hydrate dissolution rates was converted from μmol/m$^2\cdot$s to cm/yr, using

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

$$\mathrm{DR\ (m/s)} = 2 \times \mathrm{DR\ (\mu mol/m^2 \cdot s)} \times \frac{M_{CO_2}}{\rho_{CO_2}^{H}} \times \left(\frac{M_{CO_2} + HN \cdot M_{H_2O}}{M_{CO_2}} \right) \times 10^{-6}\ \mathrm{mol/\mu mol} \qquad (10)$$

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

Where, DR stands for dissolution rate and M_{CO_2} (0.044 kg/mol) and M_{H_2O} (0.018 kg/mol) is molar weight of CO_2 and H_2O, respectively. CO_2 hydrate dissolution rates calculated at different pressure and temperature are summarized in Table 1 and illustrated in Fig. 2. CO_2 hydrate dissolution rates were decreased by pressure increase and temperature decrease. This indicates that desorption layer of 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 CO_2 can be reduced, resulting in decrease of CO_2 hydrate dissolution rates. Decrease of water velocity required to stabilize the CO_2 hydrate particle could be another potential reason for reduced CO_2 hydrate dissolution rates. The density of CO_2 increases at higher pressure and lower temperature; thus, the rise velocity of CO_2 hydrate particle driven by buoyancy can be decreased at certain environments. Due to correlation between dissolution on the surface of 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 CO_2 hydrate dissolution rates. This indicates that dissolution rates of CO_2 hydrate are significantly influenced by thermodynamic and hydrodynamic conditions. 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 CO_2 storage in
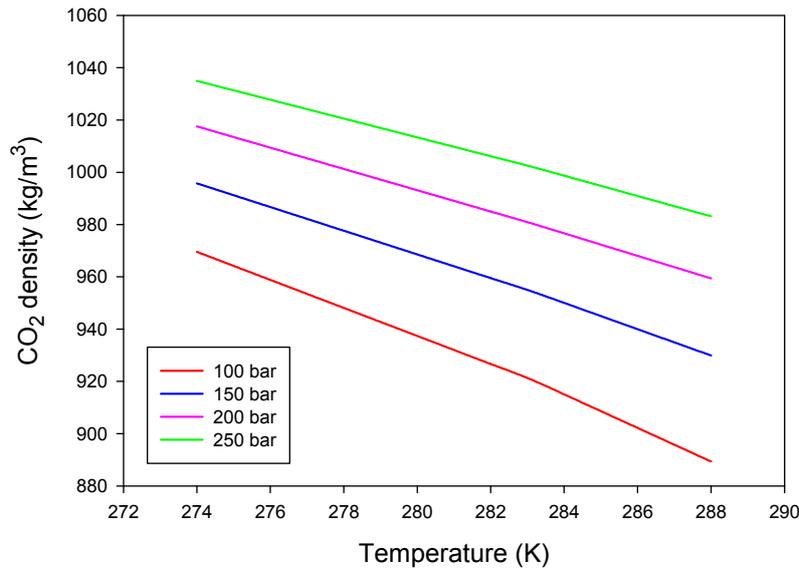

Fig. 1 Density of liquid CO_2 at different pressure and temperature

Table 1 Dissolution rates of CO_2 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: $\mu mol/m^2 \cdot s$ and right column: cm/yr

marine sediments should be implemented at depth more than 2,500 m to prevent or minimize the environmental risks caused by CO_2 hydrate dissolution.

CO_2 hydrate dissolution rates were simulated in pure water and seawater at 150 bar and 274-288 K conditions (Fig. 3 and Table 2). CO_2 hydrate dissolution rates in seawater were lower than those in pure water, indicating that salinity condition could help prevent the CO_2 hydrate dissolution. This is due to different CO_2 solubility in pure water and seawater. It has been known that less amount of CO_2 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_2 hydrate occurs until surrounding conditions are reestablished by CO_2
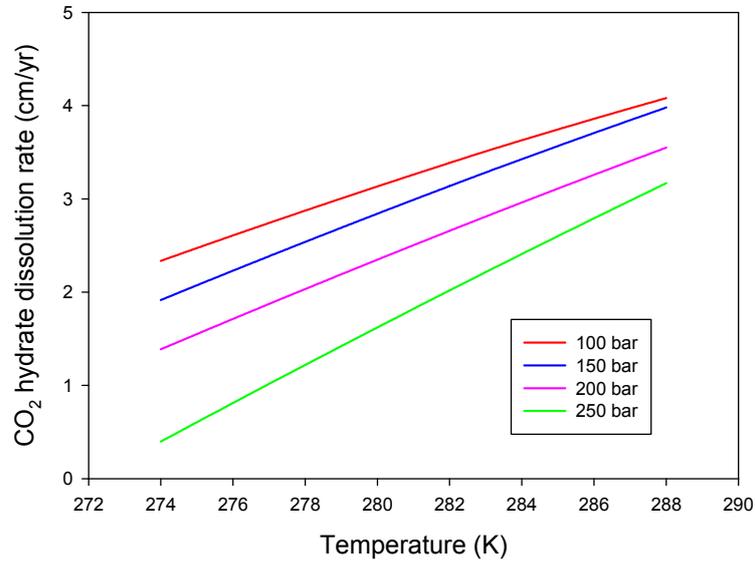
Fig. 2 Dissolution rate of CO_2 hydrate at different pressure and temperature

saturation (Lapham *et al*. 2014), seawater which have lower CO_2 solubility than pure water can meet the conditions more easily. Additionally, highly dissolved ions in seawater can interrupt CO_2 mass transfer from the CO_2 hydrate surface to surrounding seawater. The difference of CO_2 hydrate dissolution rates between pure water and seawater was larger at higher temperature than at lower temperature. This indicates that the CO_2 hydrate dissolution rates are less sensitive in seawater than pure water with respect to temperature fluctuation.
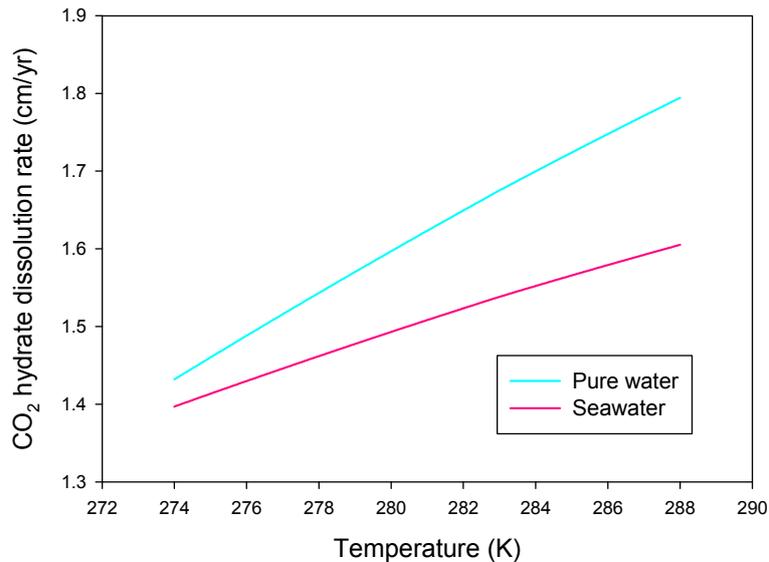

Fig. 3 Dissolution rates of CO_2 hydrate in pure water and seawater at 150 bar

Table 2 Dissolution rates of CO_2 hydrate in pure water and seawater at 150 bar

CO_2 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_2 hydrate dissolution rates was investigated. Numerical analysis was carried out to evaluate the effect of pressure, temperature, and salinity on CO_2 hydrate dissolution rates using the data of liquid CO_2 droplet dissolution rates in seawater. CO_2 hydrate dissolution in marine environment has been emerged as an important issue on CO_2 storage in marine sediments. Nevertheless, only few studies have dealt with CO_2 hydrate dissolution in the ocean. Therefore, CO_2 hydrate dissolution in the ocean should be properly understood with the pivotal environmental factors to select proper sites for CO_2 storage and to predict the behavior and fate of sequestered CO_2 under the marine sediment environments.

CO_2 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_2 hydrate. Dissolution of CO_2 hydrate in the ocean is inevitable phenomena due to different chemical potential between CO_2 hydrate and CO_2-undersaturated seawater. However, based on the results obtained from the study, we could suggest proper tactics for the CO_2 storage in the marine sediments without serious environmental risks. Prevention of direct CO_2 hydrate exposure to seawater with hydrocarbon films, surfactants, microbial or sediment layers might significantly reduce the dissolution rates of CO_2 hydrate. CO_2 injection in some CO_2-rich fluid area such as Okinawa trough could be another effective way to minimize CO_2 hydrate dissolution.

Acknowledgments

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