

# FORMATION AND GROWTH OF CO<sub>2</sub> CLATHRATE HYDRATE SHELLS AROUND GAS BUBBLES OR LIQUID DROPS.

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## INTRODUCTION

Deep ocean disposal of CO<sub>2</sub> may be required to mitigate rises in its atmospheric levels if other measures are ineffective and the worst global warming scenarios begin to occur. Work at PETC is directed at evaluating the technical feasibility of this option for long-term disposal.

At the pressures and temperatures associated with the depths required for effective sequestration of CO<sub>2</sub> (> 500 m), the crystalline CO<sub>2</sub> clathrate hydrate (CO<sub>2</sub> · nH<sub>2</sub>O, 6 < n < 8) can form (1). Clathrate hydrates are a special type of inclusion compound in which small molecules, such as CO<sub>2</sub>, are held in cavities formed by hydrogen-bonded H<sub>2</sub>O molecules by van der Waals forces (1,2). The formation of the CO<sub>2</sub> clathrate hydrate can either facilitate or complicate the sequestration of CO<sub>2</sub> in the ocean (3). Sequestration would be facilitated if the clathrate hydrates form as solid crystals dense enough to sink and thus increase the residence time of the CO<sub>2</sub> in the ocean. The formation can complicate sequestration if a thin coating of the hydrate forms on the surface of injected bubbles or drops of CO<sub>2</sub>. This complication would hinder dissolution of the CO<sub>2</sub> and permit its rise to unacceptably shallower depths and thus its premature return to the atmosphere. Being able to predict the fate of CO<sub>2</sub> hinges on our understanding of these phenomena and their likely occurrence in ocean disposal scenarios.

In this report, experimental and theoretical results concerning the formation of hydrate shells on gas bubbles and liquid drops of CO<sub>2</sub> are presented. The experimental observations show that, in the presence of hydrate crystals, a thin hydrate shell forms from a nucleus at one point on the surface of the bubble or drop and then rapidly spreads out along this surface. A model was developed to estimate both the thickness of the initially formed shell and bounds on the ultimate thicknesses of shells in saturated and unsaturated environments. The model assumes that the ultimate thickness of the shell is governed by the diffusion of the CO<sub>2</sub> through the hydrate shell and diffusion or convection of dissolved CO<sub>2</sub> away from the hydrate-covered particle.

## EXPERIMENTAL

All of the experimental observations were made in a high-pressure, variable-volume view cell of 10 to 40 cm<sup>3</sup> capacity. The view cell was enclosed in a chamber where the temperature could be maintained in the region of interest (0 to 10°C). The formation of hydrates was observed by injecting CO<sub>2</sub> (99+ % purity) into water treated by reverse osmosis. More complete descriptions of the view cell and the basic experimental procedures have been published (3,4).

## RESULTS AND DISCUSSION

Much of the research on the impact of hydrate formation on ocean disposal of CO<sub>2</sub> has focused on the rates of hydrate formation and growth around a gaseous bubble or liquid drop of CO<sub>2</sub> injected into a large body of water (5,6,7). Teng, et al. have assumed that the CO<sub>2</sub> hydrate shell grows uniformly from 'hydrate clusters' that exist in the water around an initially hydrate-free drop (5). They also assume that the growth of hydrates is limited by the kinetics of the process and that the hydrate clusters can exist in water with local CO<sub>2</sub> concentrations lower than would exist if in equilibrium with hydrates. The values they get for hydrate formation time and thickness depend on the value they use for their rate constant, but there is no rational way of estimating its value.

Experiments have been performed at PETC in a high-pressure, variable-volume view cell in which the formation, dissolution, and relative densities of CO<sub>2</sub> hydrates have been studied (7). In the course of these experiments, several observations have been made of hydrate shells forming on either freshly injected gaseous bubbles or liquid drops of CO<sub>2</sub> in water already containing hydrate crystals. In all such cases, the hydrate shell grew from a nuclei at the point on the surface in contact with crystalline hydrate and then rapidly spread out along the drop or bubble surface. Others have also reported similar phenomenon (8). These observations do not support the view that a hydrate shell forms gradually from a uniform dispersion of nascent hydrate clusters on the surface of the drop. Two specific examples from our experimental work are described below.

In one experiment, four individual drops of liquid CO<sub>2</sub> were sequentially injected into the view cell that contained water and hydrate crystals which had earlier formed in the experiment around the injection port. The fate of each individual drop was monitored before the next drop was introduced. The temperature in the cell was 8.3°C and the pressure in the cell ranged from 16.0 to 18.0 MPa during the injection sequence. The drops were approximately 0.5 to 1.0 cm in diameter. Immediately upon injection, a thin hydrate coating began to form at the point of contact between the drop and the hydrate mass on the injection port. The hydrate shell grew from this point and completely enveloped the drop in 1 to 2 s.

In another experiment, several individual gaseous bubbles of CO<sub>2</sub> formed from a hydrate mass in the view cell when the pressure was decreased below the CO<sub>2</sub> vapor/liquid equilibrium point. The cell was at 5.6°C. The vapor/liquid equilibrium point at this temperature is near 3.5 MPa. The gaseous bubbles were between 0.3 and 0.5 cm in diameter. A hydrate coating immediately began to form, again starting at the point of contact between the bubble and the hydrate mass. The bubbles were completely covered in about 1 s.

Based upon the experimental observations, we propose a model assuming that a hydrate shell rapidly forms around the bubble of gas or drop of liquid CO<sub>2</sub>. Instead of depending on the kinetics of the hydrate formation process to determine the thickness of the hydrate shell, we assume that the rate of thickening or thinning of the shell is determined by the diffusion of CO<sub>2</sub> through the shell and diffusion or convection of the dissolved CO<sub>2</sub> away from the hydrate-covered bubble or drop. Based on this assumption, we are able to put bounds on the thickness of the initially formed shell and on the thicknesses of shells in environments saturated and unsaturated with respect to CO<sub>2</sub>. The specific case discussed below in presenting the model refers to liquid CO<sub>2</sub> drops in water, although the technique would be applicable to any gaseous or liquid molecule capable of forming hydrates.

#### Initial Shell Thickness

If a spherical drop of CO<sub>2</sub> is introduced into a large body of water, the CO<sub>2</sub> will dissolve in the water at the interface and diffuse away. Hydrates can only form if the pressure of the drop,  $P$ , is greater than the pressure required for hydrate formation at the temperature of the system,  $P_H$ . For steady-state diffusion from the drop into an infinite reservoir, the concentration profile is given by

$$C = C_0 + \frac{R_0}{r} \quad (1)$$

where  $C_0$  is the concentration of the CO<sub>2</sub> at the interface of the drop of radius  $R_0$  and  $C$  is the CO<sub>2</sub> concentration at any position  $r > R_0$ .

Our observations and the observations of others (8) indicate that drops of CO<sub>2</sub> or other molecules capable of forming hydrates can exist in water for long periods of time (hours to days) without the formation of hydrates even though their formation is thermodynamically possible. This delay is thought to be due to the absence of primary nucleation events that must occur prior to crystallization of the hydrate (8). Under such conditions,  $C_0$  can exceed the concentration of CO<sub>2</sub> that would be possible with hydrates present, which is the saturated concentration,  $C_H$ , at  $P_H$ .

Figure 1 illustrates the basic premise of the model by showing possible concentration profiles around a CO<sub>2</sub> drop both in the absence and presence of a hydrate shell. The saturation concentration at the hydrate equilibrium pressure is 0.01 g/ml. The saturation concentration at the system pressure in the absence of hydrates is 0.02 g/ml. The conditions which lead to these concentrations are not unique, but such concentrations might pertain, for example, if the CO<sub>2</sub> were injected into the ocean at 2000 meters and hydrates were stable at 1000 meters. If no hydrates formed for a period of time, the upper concentration profile would develop. Once hydrates formed, all the CO<sub>2</sub> in excess of 0.01 g/cc could contribute to the formation of the hydrate shell. This excess would all be in the first 0.5 cm of water surrounding the bubble. It is also assumed that none of the gas in the drop can diffuse through the hydrate fast enough to be incorporated into the initial hydrate shell. As soon as a molecularly thick hydrate shell forms, the only CO<sub>2</sub> available for initial hydrate formation is the excess dissolved CO<sub>2</sub>.

If the concentration difference is integrated from  $R_0$  to the value of  $r = r_H$  (radius where the CO<sub>2</sub> concentration in the absence of hydrates is equal to the CO<sub>2</sub> concentration in the presence of hydrates at the edge of the shell, i.e., 1.0 cm in Figure 1), the amount of CO<sub>2</sub> available for initially forming a hydrate shell can be determined as shown below.

$$\begin{aligned} \text{Excess hydrate former} = m_{ex} &= \int_{R_0}^{r_H} (C_0 - C_H) 4\pi r^2 dr \\ &= 4\pi R_0^3 C_H [(C_0/C_H)/2 + ((C_0/C_H)^2 - 1) - .333 * ((C_0/C_H)^3 - 1)] \end{aligned} \quad (2)$$

The ratio,  $C_0/C_H$ , can be approximated by the ratio  $P/P_H$  even though solubilities (concentrations at equilibrium) are not necessarily linear with pressure. Using the composition of hydrates (6.15 mol water/mol  $\text{CO}_2$ ) and the specific volume of hydrate (22.4 mL/mol  $\text{H}_2\text{O}$ ) allows the thickness of the hydrate shell,  $\Delta r$ , to be calculated as follows (9).

$$\Delta r = \frac{\frac{m_{ex}}{44.01} * 6.15 * 22.4}{4\pi R_0^2} \quad (3)$$

Table 1 shows typical shell thicknesses for  $\text{CO}_2$  hydrate shells formed at oceanic temperatures for drops of various size at different  $\text{CO}_2$  concentrations. The values in the first three columns were selected to illustrate the effects of drop size ( $R_0$ ), hydrate equilibrium concentration ( $C_H$ , which is a function of temperature and pressure), and the amount of excess  $\text{CO}_2$  over that required for hydrate formation ( $C_0/C_H$ ). The fourth column was calculated using Equation 2 and assumes that all of the excess  $\text{CO}_2$  ( $m_{ex}$ ) forms hydrates of uniform thickness. The fifth column represents the maximum hydrate thickness under these scenarios and was calculated using Equation 3. The final column represents the ratio of hydrate shell thickness to the size of the initial hydrate-free drop.

**Table 1. Thickness of Initial Hydrate Shells formed from  $\text{CO}_2$  Droplets injected into the Ocean at 0-15 C and Depths of 0-3000 meters.**

$R_0$ , cm	$C_H$ g/mL	$C_0/C_H$	Mass of $\text{CO}_2$ in Hydrate, g	$\Delta r$ , cm	$(\Delta r)/R_0$
0.1	0.01	1.5	0.000018	0.00045	0.0045
0.5	0.01	1.5	0.002291	0.00224	0.0045
1.0	0.01	1.5	0.018326	0.00448	0.0045
1.0	0.02	1.5	0.036652	0.00897	0.0090
1.0	0.03	1.5	0.054978	0.01345	0.0134
1.0	0.03	2.0	0.251327	0.06150	0.0615
1.0	0.02	2.0	0.167551	0.04100	0.0410
0.5	0.06	1.2	0.002011	0.00197	0.0039
0.5	0.06	2.0	0.062832	0.06150	0.1230

Note that in the cases shown in Table 1 the shell is always less than 0.1 cm in thickness. Thicker shells could result if the value of  $C_0/C_H$  were higher, but such values are unlikely unless the injection depth was very great (i.e., 3000 meters). In cases where the equilibrium concentrations greatly exceed the hydrate equilibrium concentrations (large  $C_0/C_H$ ), it is less likely that steady-state, diffusion-controlled concentration profiles would be developed for the liquid  $\text{CO}_2$  prior to hydrate formation. The maximum excess  $\text{CO}_2$  is dissolved when this steady state is reached, so the formation of the hydrate shell from excess dissolved  $\text{CO}_2$ , which is less than the maximum, will result in a thinner hydrate shell. Also, in cases where the  $\text{CO}_2$  is dispersed more quickly than occurs with steady diffusion, there would be less excess  $\text{CO}_2$  and the shell would be thinner than given in these estimates. Thus, this analysis gives an estimate of the upper limit of the initial hydrate shell thickness which would be less than 0.1 cm.

#### Steady-State Shell Model

Once the hydrate shell forms around a body of  $\text{CO}_2$ , its thickness can either increase or decrease. If the drop is in a reservoir which is unsaturated with  $\text{CO}_2$ , then the shell thickness will reach some steady-state value. The shell remains at constant thickness and the  $\text{CO}_2$  diffuses through the shell, causing the drop to shrink. For this to occur, the flux away from the drop must equal the flux through the shell. This is expressed in the equation below.

$$D_H \frac{C_0 - C_H}{\Delta r} 4\pi R_i^2 = -D_w \left( \frac{\partial C}{\partial r} \right)_0 4\pi R_0^2 \quad (4)$$

In this equation,  $D_H$  and  $D_w$  are the diffusivities of  $\text{CO}_2$  in the hydrate and water, respectively,  $C_0$  and  $C_H$  are the equilibrium concentrations of  $\text{CO}_2$  in water at the system pressure and the hydrate equilibrium pressure, respectively, and  $R_0$  and  $R_i$  are the outer and inner radius of the shell, respectively.  $(\partial C/\partial r)_0$  is the concentration gradient of  $\text{CO}_2$  in the water phase at the outside of the hydrate shell. Note that the inside of the hydrate shell is pure  $\text{CO}_2$ , but  $C_0$  represents the true driving force since at this concentration in water the chemical potential is equal to the chemical potential of the pure  $\text{CO}_2$ .

The thickness of the hydrate shell,  $\Delta r$ , can be determined using the following equation obtained by rearrangement of Equation 4.

$$\Delta r = \frac{-\frac{D_H}{D_w}(C_0 - C_H)}{(\partial C/\partial r)_0 (R_0^2/R_i^2)} \quad (5)$$

At pseudo-steady state, the thickness is constant as determined by the above equation. For a thin shell, the ratio of radii will be nearly 1.0 and can be eliminated. The concentration gradient at the surface of the hydrate can be determined by a steady- or unsteady-state diffusion model.

#### Steady-State Infinite Reservoir

Further approximation can be made by assuming that  $\text{CO}_2$  is diffusing away from the drop at steady state into a water phase that is very large in extent. The only mathematical requirement is that diffusion be radially symmetric and that the concentration decreases to zero far from the drop. In this case, the concentration gradient at  $R_0$  is represented by  $-C_H/R_0$ . Replacing the concentration gradient term in Equation 4 with this latter term and rearranging gives the following equation.

$$\frac{\Delta r}{R_i} = \frac{\frac{D_H}{D_w} \left[ \frac{C_0}{C_H} - 1 \right]}{\left( \frac{R_0}{R_i} \right)} \quad (6)$$

As before, the ratio of the inside and outside radii will be near unity in most cases. Since the ratio of concentrations of  $\text{CO}_2$  will range between 1 and 2 for typical ocean injections, the relative thickness of the hydrate is determined by the ratio of diffusivities in the hydrate and water phases.

It might be useful to compare diffusivities in polymers versus melts to estimate relative values. Diffusivities in liquids are about  $10^{-4}$  to  $10^{-5}$   $\text{cm}^2/\text{sec}$  and diffusivities in solids are about  $10^{-10}$   $\text{cm}^2/\text{sec}$  (10). Using Equation 6, the estimated relative thickness would be in the range of  $10^{-6}$  to  $10^{-5}$  cm. This indicates that the thin layer of hydrates that initially forms on the outside of the drop should get thinner, although the absolute thickness of the hydrate depends on the drop radius.

Because of changing drop size as the  $\text{CO}_2$  dissolves, tiny fissures or cracks may develop in the hydrate shell that may increase the effective diffusivity in the hydrate layer allowing a thicker hydrate shell. However, hydrate formation should be accelerated in these fissures because of the better contact between  $\text{CO}_2$  and water. Such fissures would rapidly heal which means that the overall model should be reasonable. This has been observed in our laboratory.

If no hydrates are present, the gradient at the edge of the drop will increase by the factor  $C_0/C_H$ , assuming that diffusion is limiting. The absence of a shell will increase the dissolution rate by this same factor. For example, at  $7.7^\circ\text{C}$ , the equilibrium hydrate pressure is approximately 3.3 MPa. If solubility is linearly proportional to pressure (Henry's Law),  $\text{CO}_2$  injected at 10 MPa (approximately 1000 m depth) would dissolve three times slower with the hydrate shell than without it. The time required will depend on the extent to which the equilibrium concentration of  $\text{CO}_2$  at the system pressure exceeds the equilibrium  $\text{CO}_2$  concentration in the presence of hydrates (the solubility of  $\text{CO}_2$  in water at the hydrate equilibrium pressure). Simply put, the  $\text{CO}_2$  dissolution rate will decrease by a factor of  $C_0/C_H$  due to hydrate formation.

The thickness of the shell is such a small fraction of the drop diameter that the buoyancy of the drop will not be affected by the hydrate, although the drag coefficient may be affected since the hydrate-covered drop may be somewhat more rigid.

### Steady-State Saturated Reservoir

The main assumption in the steady-state infinite reservoir model is that the  $\text{CO}_2$  concentration decreases with distance from the drop. A drop injected into  $\text{CO}_2$ -saturated water cannot dissolve but can form a layer of hydrates. Since hydrates are present, the water would be saturated at the hydrate equilibrium pressure and the  $\text{CO}_2$ , which is at a higher (hydrostatic) pressure, would still diffuse through the hydrate shell. However, the net flux would have to contribute entirely to the growth of the hydrate shell thickness at the hydrate-water interface. The growth of the hydrate caused by this flux can be determined from the following equation.

$$\frac{d\Delta r}{dt} = D_H \frac{C_0 - C_H}{\rho_H \Delta r} \quad (7)$$

where  $\rho_H$  is the density of the hydrate phase in moles of  $\text{CO}_2$  hydrate per unit volume.

Based upon a solid-phase diffusivity of  $10^{10}$   $\text{cm}^2/\text{sec}$ , and a hydrate thickness of  $10^{-4}$  cm, the hydrate would thicken at the rate of  $10^3$  to  $10^4$   $\text{cm}/\text{hr}$ . This equation can be integrated to give the thickness as a function of time as shown below.

$$\Delta r = \left[ \Delta r_0^2 + D_H \frac{C_P - C_H t}{\rho_H} \right]^{1/2} \quad (8)$$

In this equation,  $t$  is the time and  $\Delta r_0$  is the initial hydrate thickness which is not known but is likely to be small. As the shell thickens, the hydrate growth rate will decrease, but for typical rise times for  $\text{CO}_2$  injected into the ocean (10-100 hrs), a hydrate thickness of greater than  $10^2$  to  $10^1$  cm would not be expected. Since the thickness has a square root dependency on the solid-state diffusivity of  $\text{CO}_2$ , uncertainties in this value are less critical in estimating the thickness of the hydrate shell.

No definitive experiments have been performed to demonstrate that the hydrate layer continues to thicken in  $\text{CO}_2$  saturated water as predicted by Equation 8. It is difficult to perform such experiments because saturated water will form multiple hydrate nucleation sites. However, one could inject a  $\text{CO}_2$  drop into saturated water and see if it is completely converted to hydrate.

### CONCLUSION

It has been demonstrated that a very thin hydrate shell should form around drops of injected  $\text{CO}_2$ . If injected into unsaturated water, a stable hydrate thickness on the order of  $10^2$  to  $10^4$  times the radius of the drop will form. The hydrates can significantly retard the dissolution of the  $\text{CO}_2$ .

If injected into saturated water, the hydrate will form a thicker shell, possibly approaching  $10^1$  cm in thickness for growth periods in excess of 100 hours. Since the water is saturated with respect to hydrate-forming conditions, the hydrate shell serves only to slow the diffusion of  $\text{CO}_2$  and thus prevent the formation of additional hydrate from the injected  $\text{CO}_2$ . Saturated conditions could occur in the vicinity of the injection. Under this scenario, additional hydrates could form on the hydrate-covered drop from the  $\text{CO}_2$  dissolved in the water. This was the subject of an earlier paper (7).

In summary, in all cases addressed in this paper, the modeling results predict that a hydrate shell on a  $\text{CO}_2$  drop will remain thin and the drop will disappear more slowly than predicted by conventional models that do not consider hydrate formation. The stabilization of the drop by the thin shell will make it more likely that the injected  $\text{CO}_2$  will rise to unacceptably shallower depths before dissolution. Injection strategies that avoid or limit this phenomena will be required for effective sequestration. Such options have been previously discussed (7).

In salt water, a further complication exists. As hydrates form, dissolved salts are excluded from the solid and their concentration in the water builds up. Since the salinity of the water affects the hydrate equilibrium pressure and the solubility of  $\text{CO}_2$ , this effect should be accounted for. At steady state, there is no net hydrate formation and this effect can be neglected. However, if the shell is changing in thickness, the effect of salinity could be important.

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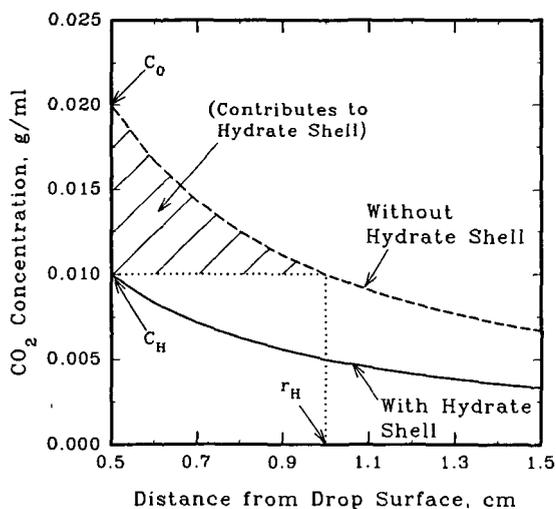


Figure 1. Concentration profiles around a  $\text{CO}_2$  drop (0.5-cm radius) in the presence and absence of a hydrate shell in an infinite reservoir (arbitrary example).