



# A rigorous mechanistic model for predicting gas hydrate formation kinetics: The case of CO<sub>2</sub> recovery and sequestration

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## ARTICLE INFO

### Article history:

Received 1 August 2010

Received in revised form 29 August 2011

Accepted 31 August 2011

Available online 19 October 2011

### Keywords:

Gas hydrate  
CO<sub>2</sub> recovery  
Energy storage  
Simulation  
Nucleation  
Growth  
Kinetics

## ABSTRACT

A rigorous mechanistic model for predicting gas hydrate formation crystallization kinetics is presented and the special case of CO<sub>2</sub> gas hydrate formation regarding CO<sub>2</sub> recovery and sequestration processes has been investigated by using the proposed model. A physical model for prediction of secondary nucleation rate is proposed for the first time and the formation rates of secondary nuclei by crystal–crystal collisions and crystal–impeller collisions are formulated. The objective functions for simultaneous determination of nucleation and growth kinetics are presented and a theoretical framework for predicting the dynamic behavior of gas hydrate formation is presented. Predicted time variations of CO<sub>2</sub> content, total number and surface area of produced hydrate crystals are in good agreement with the available experimental data. The proposed approach can have considerable application for design of gas hydrate converters regarding energy storage and CO<sub>2</sub> recovery processes.

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## 1. Introduction

Natural gas hydrate (NGH) has drawn much attention as one of the new gas storage and transportation media for small and middle gas fields. The gas can be stored in NGH under milder conditions, for example, at much higher temperature than LNG and at lower temperature than pressure cylinders. Carbon dioxide recovery and sequestration via gas hydrate formation is also of particular interest [1]. A major source of CO<sub>2</sub> is the combustion of fossil fuels in power plants, gas and oil refineries and other industrial processes. While CO<sub>2</sub> has the lowest Global Warming Potential, it has the largest impact on climate change because of the quantity emitted [2].

It has been estimated that, the cost of separation and disposal of CO<sub>2</sub> from existing coal fired, air blown boilers would increase the cost of electricity by about 75%. The cost of separation of CO<sub>2</sub> alone reduces the power generation efficiency from 38% to 26%. A thorough review on the processes for CO<sub>2</sub> separation is available in the literature [3,4].

Marine carbon dioxide sequestration via CO<sub>2</sub> hydrate formation has been suggested as a less energy intensive technique for mitigating CO<sub>2</sub> emissions [5]. In this process, CO<sub>2</sub> generated from a thermal power plant will be collected, liquefied, and injected to a submerged

hydrate crystallizer where the CO<sub>2</sub> hydrate particles are produced at a proper pressure and temperature. The working fluid is water, which is non-toxic, non-volatile and inexpensive, compared to other solvents. Disposal of CO<sub>2</sub> in the ocean or in deep saline aquifers in the form of CO<sub>2</sub> hydrate requires a thorough understanding of phase equilibria and kinetics of hydrate conversion.

Since accurate determination of hydrate formation kinetic is an important task regarding optimum design of gas hydrate converters, a rigorous mechanistic model for predicting gas hydrate formation crystallization kinetics is proposed and its application to the special case of CO<sub>2</sub> gas hydrate formation process has been presented.

## 2. Experimental procedure

In the current study, CO<sub>2</sub> hydrates are formed in a batch stirred tank reactor and the particle size distribution is measured in situ with a focused beam reflectance method (FBRM) probe [6]. The FBRM probe can measure chord lengths as small as 0.5 μm and as large as 1000 μm. During gas dissolution and hydrate particle growth, the pressure in the reactor is maintained at a value above the three-phase equilibrium pressure. Prior to beginning the experiment, the reactor is cleaned several times with ultra-pure water and the entire apparatus is flushed with the experimental gas. After the reservoirs and the reactor have been filled, the particle size analyzer and the data acquisition program are started and the temperatures are closely monitored. The data acquisition

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**Nomenclature**

$a$	interfacial area per unit of liquid volume, $\text{m}^2/\text{m}^3$	$t$	time, s
$A_{g-l}$	gas–liquid interfacial area, $\text{m}^2$	$T$	temperature, K
$A_p$	surface area of the particle, $\text{m}^2$	$V_a$	abraded volume, $\text{m}^3$
$B$	nucleation rate, $\text{no}/\text{sm}^3$	$V_L$	liquid volume, $\text{m}^3$
$c$	concentration of the $\text{CO}_2$ in the liquid water, $\text{mol}/\text{m}^3$	$v_w$	molar volume of water, $\text{m}^3/\text{mol}$
$c_{w0}$	initial concentration of water molecules, $\text{mol}/\text{m}^3$	$v_m$	molar volume of hydrate, $\text{m}^3/\text{mol}$
$D^*$	corrected diffusivity of the gas, $\text{m}^2/\text{s}$	$y_L$	film thickness, m
$f$	fugacity of the gas, MPa	$y$	distance from the gas–liquid interface, m
$G$	linear growth rate, m/s	$v$	impact velocity, m/s
$H$	Henry's constant, MPa		
$k_d$	mass-transfer coefficient around the particle, $\text{mol}/\text{m}^2 \text{MPa s}$	<b>Greek letters</b>	
$k_L$	liquid side mass transfer coefficient, m/s	$\alpha$	nucleation rate constant in Eq. (33), $\text{no}/\text{m}^2 \text{s}$
$k_r$	intrinsic rate constant, $\text{mol}/\text{m}^2 \text{MPa s}$	$\alpha_s$	nucleation rate constant in Eqs. (29) and (32), $\text{no}/\text{m}^2 \text{s}$
$k_j$	parameters in Eqs. (24)–(31) where $j = 1-6$	$\beta$	exponent in Eq. (26)
$K^*$	overall rate constant, $\text{mol}/\text{m}^2 \text{MPa s}$	$\gamma$	Hatta number
$L_c$	mean crystal size, m	$\Delta f$	driving force, MPa
$L$	distance between the gas–liquid interface and the bottom of the reactor, m	$\Delta G$	free energy, J
$M_H$	molecular weight of the hydrate, $\text{kg}/\text{kmol}$	$\Delta g$	free energy change per unit volume of product, $\text{J}/\text{m}^3$
$n_H$	moles of gas in the hydrate phase during formation, mol	$\mu_n$	$n$ th moment of the crystal size distribution, $\text{no m}^n/\text{m}^3$
$n_{eq}$	moles of gas dissolved at three-phase equilibrium	$\sigma$	surface energy of hydrate-water, $\text{J}/\text{m}^2$
$n_B$	number of moles of gas dissolved in the bulk liquid phase	$\varphi$	crystal size distribution, $\text{m}^{-1}$
$n_{tb}$	number of gas molecules dissolved at the turbidity time	$\Psi$	exponent in Eq. (31)
$n_w$	number of water molecules per gas molecule	$\rho_H$	hydrate density, $\text{kg}/\text{m}^3$
$n_c$	number of parent crystals per unit volume, $\text{no}/\text{m}^3$	$\lambda$	number of moles of $\text{CO}_2$ gas per mole of hydrate
$N_p$	number of particles in liquid phase at the turbidity time	$\eta$	collision efficiency
$NT$	total number of data points	$\varepsilon$	power input per unit mass, $\text{J}/\text{kg s}$
$N$	impeller speed, $\text{s}^{-1}$		
$P$	pressure, MPa	<b>Subscripts</b>	
$R$	universal gas constant, $\text{MPa m}^3/\text{mol K}$	$b$	bulk
$R_y(t)$	global reaction rate, $\text{mol}/\text{m}^3 \text{s}$	$exp$	experimental
$r$	radial distance, m	$calc$	calculated
$r_{cr}$	critical radius, m	$g$	gas
		$eq$	equilibrium
		$i$	data point $i$

program reads temperatures and pressure once every 30 s and calculates the moles of free gas in the system and the FBRM reads chord length distributions every 10 s. Once the temperatures have stabilized, the stirrer is started and the reactor is put on automatic control. As the gas in the reactor is consumed, the control valve automatically opens to supply additional gas from the supply reservoir, and thus, maintain isobaric conditions. The reactor is monitored for the appearance of hydrates, which are marked by the solution becoming translucent and by a sharp change in slope of the total number of particles on the FBRM display. Experiments are carried out at temperatures ranging from 274 to 279 K and pressure ranging from 1.6 to 3.0 MPa [6].

**3. Theory**

Hydrate formation is a crystallization process that occurs in a supersaturated environment. Englezos et al. [7] have considered the growth of a hydrate particle as a two-step process. The first step is diffusion of dissolved gas from the bulk to the crystal–liquid interface and second step is the integration of gas molecules into the structured water framework. By assuming that the rates of two steps are equal, the rate of growth per particle in spherical coordinates is given by following equation:

$$\left(\frac{dn_H}{dt}\right)_p = K^* A_p (f - f_{eq}) \quad (1)$$

where  $1/K^* = 1/K_r + 1/K_d$  such that  $K_d$  is the bulk mass transfer coefficient and  $K_r$  is the reaction (integration) rate constant. Therefore the integration of Eq. (1) for all particles of any size yields:

$$R_y(t) = \pi K^* (f - f_{eq}) \int_0^\infty r^2 \varphi(r, t) dr \quad (2)$$

where  $R_y(t)$  is the global rate of reaction for all particles and  $\varphi(r, t)$  is the crystal size distribution. The integral in the above equation is equal to second moment of the particle size distribution such that we have:

$$R_y(t) = \pi K^* \mu_2 (f - f_{eq}) \quad (3)$$

Using the two film theory and assuming quasi-steady-state conditions, the mass balance for the gas in the film in a slice of thickness  $dy$  and unit cross sectional area yields:

$$D^* \frac{d^2 Y}{dy^2} = \pi K^* \mu_2 Y \quad (4)$$

where

$$Y = (f - f_{eq}) \quad (5)$$

$$D^* = \frac{D(c_{w0} + c_{eq})}{(H - f_{eq})} \quad (6)$$

and the boundary conditions are:

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