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## MODELING THE INFLUENCE OF HEAT TRANSFER ON GAS HYDRATE FORMATION

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### ABSTRACT

Gas hydrates are crystalline structures of water and gas which form at high pressures and low temperatures. Hydrates have important applications in carbon sequestration, desalination, gas separation, gas transportation and influence flow assurance in oil-gas production. Formation of gas hydrates involves mass diffusion, chemical kinetics and phase change (which necessitates removal of the heat of hydrate formation). When hydrates are synthesized artificially inside reactors, the heat released raises the temperature of the water inside the reactor and reduces the rate of hydrate formation (since the driving force is reduced). An examination of literature shows that there is inadequate understanding of the coupling between heat and mass transfer during hydrate formation. Current models treat heat and mass transfer separately during hydrate formation. In this study, we develop a first principles-based mathematical framework to couple heat and mass transfer during hydrate formation. Our model explores the difference between “actual subcooling” and “apparent subcooling” in the hydrate forming system. The apparent subcooling depends on the targeted reactor temperature and is supposedly, the driving force for hydrate growth. However, due to the increase in temperature of the reactor, the actual subcooling is lower than the apparent subcooling. All these effects are modeled for a 1-D hydrate forming reactor. Results of our simulations are compared with some experimental observations from literature. We also present mathematical scaling to determine the temperature rise in a hydrate-forming reactor. In addition to artificial synthesis

of hydrates, the mathematical framework developed can also be applied to other hydrate forming systems (flow assurance, hydrate formation in nature).

Keywords: hydrates, heat transfer, reactor cooling, metal foams

### NOMENCLATURE

$\rho$	Density of water (kg/m <sup>3</sup> )
$c_p$	Specific Heat Capacity of water (J/Kg K)
$\lambda$	Thermal conductivity of water (W/m K)
$h$	Heat transfer coefficient (W/m <sup>2</sup> K)
$p$	Perimeter of reactor cross-section (m)
$A_c$	Cross-sectional area of reactor (m <sup>2</sup> )
$k$	Mass transfer coefficient (m/s)
$\Delta H$	Enthalpy of hydrate formation (J/mol)
$c$	Gas concentration (mol/m <sup>3</sup> )
$c_{eq}$	Equilibrium Gas Concentration (mol/m <sup>3</sup> )
$L$	Length of water column in reactor (m)
$T_\infty$	Coolant Temperature (K)
$Z$	Compressibility factor
$R$	Universal Gas Constant (J/mol K)
$P_{eq}$	Equilibrium Pressure of hydrate (Pa)
$A_s$	Side area of the reactor (m <sup>2</sup> )
$\Delta T_r$	Temperature rise above initial (K)
$\Delta T_{sub}$	Actual subcooling (K)
$Z_{eq}$	Compressibility factor at equilibrium pressure
$A_{eq}$	Slope of equilibrium curve of hydrate formation, $\ln P$ vs $1/T$ (K)
$n_h$	Moles of hydrates formed

## 1. INTRODUCTION

Clathrate hydrates are ice-like crystalline compounds formed from water and another component at high pressures (usually) and low temperatures. Gas hydrates are clathrate hydrates which form from water and another gas like methane, carbon dioxide, etc. Natural gas hydrates are well-known in the oil & gas industry and are notorious for clogging subsea pipelines. However, in the 21<sup>st</sup> century, hydrates have been recognized for their potential energy-related applications like carbon capture & sequestration, desalination, gas storage and transportation [1, 2, 3]. All of these applications require fast, efficient hydrate formation for economic feasibility reasons.

Hydrate formation is similar to crystallization process and hence its formation kinetics is determined by hydrate nucleation and growth. Whilst the nucleation kinetics is strongly dependent on the surface chemistry and the thermodynamic conditions [4–6], hydrate growth is based on a strong interplay of heat and mass transfer in the hydrate forming system. Hydrate formation being akin to a crystallization process, is accompanied by a large heat of formation. This heat of formation can be detrimental to hydrate growth in applications where fast hydrate formation is required. Although there exists a plethora of hydrate growth models across literature for various applications [7,8], the coupled effect of heat and mass transfer is not well understood in literature. Most models tend to treat heat and mass transfer separately [9–11]; this article is an attempt to bridge this gap by developing a novel method of coupling hydrate growth kinetics and heat transfer.

Like other crystallization processes, the driving force for hydrate formation is a strong function of the subcooling present in the setup. Subcooling in hydrate formation is defined as the difference between the equilibrium temperature of hydrate formation and the experimentally set operating temperature. It is well-known that a higher subcooling provides a higher driving force for hydrate formation. Kar et. al. and other authors have shown that such dependence can be exponential in nature and hence, a variation in temperature of the system can alter hydrate kinetics significantly. In this work, we define apparent subcooling as the difference between equilibrium temperature of hydrate formation and the experimentally set temperature for operation. The actual subcooling of the system is the difference between the equilibrium temperature of hydrate formation and the actual temperature of the system during hydrate formation. The actual temperature of the system increases during hydrate formation due to the exothermic heat release. Hence the actual subcooling is always less than the apparent subcooling, which reduces the hydrate formation rate.

In this work, we develop a fundamentals-based model to couple heat transfer and hydrate kinetics and explore the consequences on hydrate growth. It should be noted that the analysis pertains to the early stage of hydrate formation when the hydrate deposition on the gas-water interface is not too significant. With increasing hydrate formation, mass transfer resistances through the hydrate layer have to be accounted for.

## 2. MATERIALS AND METHODS

Fig 1 shows a schematic of the simulation domain wherein a pressure vessel containing gas and water is subjected to hydrate forming conditions. The pressure vessel is cooled using a coolant flowing around the vessel; hydrates start forming at the gas-water interface. Our simulations capture the initial temperature response of the system and the corresponding amount of hydrate formation. Diffusional limitations of the gas through the hydrate layer have not been considered in the current model since the model only captures initial hydrate formation. The one-dimensional transient fin equation is used to model the transient temperature distribution in the water phase (Equation 1). The heat generation due to hydrate reaction is incorporated as a boundary condition at the gas-water interface. A Robin boundary condition with the total convective heat transfer coefficient is implemented on sides of the vessel and an adiabatic boundary condition at the bottom of the vessel. Hydrate phase-change rate is modeled as gas diffusion-limited, as shown in our previous work. The formulation draws similarities with “surface-attachment” kinetics in the phase-change process of ice [12]. Equation (2) represents the total amount of hydrate formed over time.

$$\rho c_p \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} - \frac{h p}{A_c} (T - T_\infty)$$

$$\text{BCs, } -\lambda \frac{\partial T}{\partial x}(0, t) = k \Delta H (c - c_{eq}), \quad \frac{\partial T}{\partial x}(L, t) = 0 \quad (1)$$

$$\text{IC, } T(x, 0) = T_\infty$$

$$c = \frac{P}{ZRT}, \quad c_{eq} = \frac{P_{eq}}{Z_{eq}RT}, \quad Z = Z(P, T), \quad Z_{eq} = Z_{eq}(P_{eq}, T)$$

$$n_h = \int_0^t k A_c (c - c_{eq}) dt \quad (2)$$

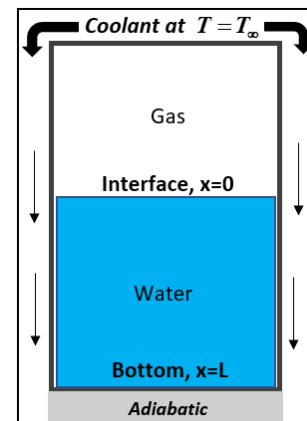


Fig 1: Schematic of the domain for simulation of methane hydrate formation.

Since the system is solved as a 1-D problem, variations in the radial distribution of temperature are not captured and the radial geometry of the reactor does not play any role in the

simulations. The compressibility factor,  $Z$ , is calculated using the Peng-Robinson equation of state [13] and the equilibrium curve is obtained from Sloan [14] to compute the equilibrium pressure and temperature. The equations are solved in MATLAB using an ode15s solver by converting the PDE in (1) to a system of ODEs. The ode15s solver employs the method of lines to solve a system of odes. All simulations in this study are conducted for methane hydrates; however, this framework is applicable for other gas hydrates as well.

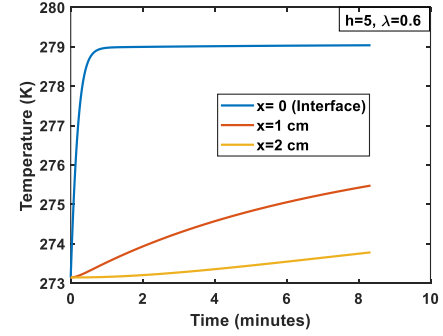
### 3. RESULTS AND DISCUSSION

We simulate methane hydrate formation in a cylindrical reactor 1 m tall, with 0.2 m diameter. The reactor is half filled with water; hydrates start forming on the gas-liquid interface. A list of all the parameters used in the simulations is provided in Table 1. As shown in our previous work [15], hydrate formation is limited by molecular diffusion of the gas. The mass transfer coefficient associated with gas diffusion to the hydrate interfaces was obtained as  $k = 10^{-3}$  m/s during the stage of film growth. Since we are investigating hydrate growth after the film growth stage, mass transfer coefficients are expected to be lower due to the diffusion barrier created by the forming hydrate on the gas-water interface. While this mass transfer resistance is a function of time and increases with hydrate formation, we assume a constant mass transfer coefficient of  $k = 10^{-4}$  m/s in our simulations.

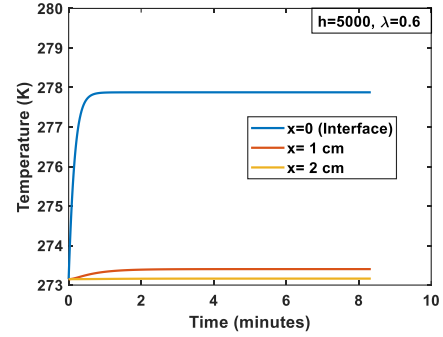
The simulations conducted in this paper explore the coupling between heat transfer and hydrate kinetics. The heat generated during hydrate formation, tends to increase the temperature in the vicinity of hydrate formation and thereby reduces the subcooling available for hydrate formation. This reduction in subcooling reduces the hydrate formation rate and the total amount of hydrates formed. As discussed previously, this effect reduces the apparent subcooling which is the difference between the equilibrium temperature and the initial temperature of water. The actual subcooling is lesser than the apparent subcooling due to the temperature rise in the vicinity of hydrate formation.

**Table 1: Parameters for the simulation in Fig. 2a.**

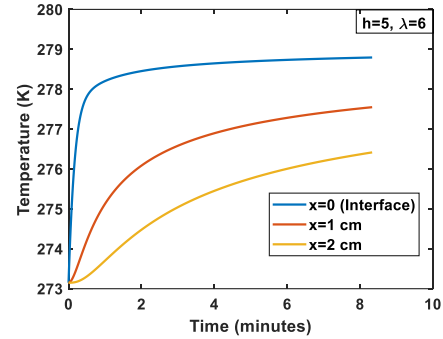
Height of reactor	1 m	P	6 MPa
L	0.5 m	$T_{\infty}$	273.15 K
$\lambda$	0.6 W/mK	R	8.314 J/mol K
Diameter of reactor (D)	0.2 m	Hydrate formula	$\text{CH}_4 \cdot 5.75\text{H}_2\text{O}$
$k$	1E-04 m/s	$h$	5 W/m <sup>2</sup> K
$\Delta H$	54 kJ/mol	$A_{eq}$	9733 K
$\rho$	1000 kg/m <sup>3</sup>	$Z(P, T_{\infty})$	0.93
$c_p$	4.18 J/gK	$P = \pi D$	0.628 m



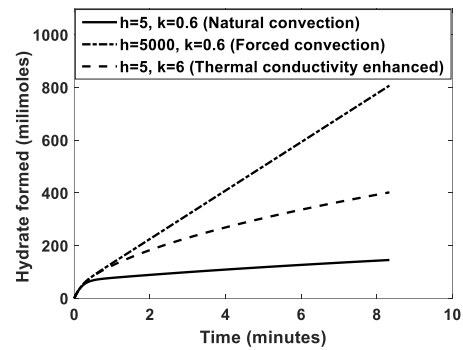
(a)



(b)



(c)



(d)

Fig 2: (a) Temperature response of system with natural convection for heat removal (b) Temperature response of system with forced convection for heat removal (c) Temperature response of system with thermal conductivity enhancement of 10X. (d) Amount of hydrate formed over time.  $h$  has units of W/m<sup>2</sup>K and  $\lambda$  has units of W/mK.  $x$  is the distance from the interface in cm.

Fig 2 shows the results of the simulation in a typical methane hydrate forming reactor. Fig 2a shows the transient temperature distribution for a heat transfer coefficient (around the reactor) of  $h=5 \text{ W/m}^2\text{K}$ , corresponding to natural convection. The thermal conductivity  $\lambda$  is  $0.6 \text{ W/mK}$ , corresponding to the value of water. Our model captures the temperature rise at the interface of gas-water where hydrates are forming and the temperature distribution inside the water column. As the equilibrium temperature of methane hydrate formation at 6 MPa is about 280 K, the temperature near the interface rises close to 280 K and reaches steady state. The difference between the equilibrium temperature and the steady state temperature represents the actual subcooling and drives hydrate formation. It should be noted that the apparent subcooling is much higher than the actual subcooling.

To sustain hydrate formation with a strong driving force (via high subcooling), the system has to be cooled effectively. Fig. 2b shows the influence of forced convective liquid cooling around the reactor, with a heat transfer coefficient of  $h = 5000 \text{ W/m}^2\text{K}$ . There is lesser temperature rise (higher actual subcooling) in the water column as a consequence of faster heat removal from the sides. Fig. 2c shows the effect of enhancing thermal conductivity of the water medium by 10X ( $\lambda = 6 \text{ W/mK}$ ), which can be achieved using metal foams, metal nanoparticles etc [16,17]. Fig 2d shows the total amount of hydrate formed at the gas-water interface over time, calculated using equation (2). As is evident from the plots, increasing the heat transfer coefficient or thermal conductivity significantly increases the total amount of hydrate formed.

It should be noted that such temperature responses have been reported in literature, especially for cases where the hydrate former is miscible with water [18,19]. For methane or carbon dioxide hydrate systems, the mass transfer coefficient of the gas to the hydrate formation sites decreases over time due to increased resistance from the hydrate film [20, 21]. Therefore, the temperature starts decreasing due to a reduction in the rate of hydrate formation, instead of maintaining a steady state as in our simulations. This is a limitation of our simulation, which considers a constant mass transfer coefficient. Simulations can be further improved by including the influence of mass transfer resistance resulting from the hydrate film.

#### 4. EXPERIMENTAL VALIDATION OF THE MODEL

We have validated the presently developed model against the work of Fan et. al. [22], which reported an enhancement in hydrate growth resulting from the use of metal foams that increased the effective thermal conductivity of the water medium. The steady state growth rate of hydrates can be modeled with and without the presence of metal foams in the water phase. The thermal conductivity enhancement due to metal foams was reported to be 100X by Fan et. al. [22]. Presently, we conducted simulations for two cases with thermal conductivity values of  $0.6 \text{ W/mK}$  and  $60 \text{ W/mK}$ , and for a mass transfer coefficient of  $k = 7.4 \times 10^{-5} \text{ m/s}$ . Fig 3 shows the

match between experimentally reported data on hydrate formation and the simulations. Excellent agreement is seen for both values of thermal conductivity. We note that the mass transfer coefficient is an order of magnitude lesser than the corresponding values during film growth. This is expected since the accumulated hydrate film provides additional mass transfer resistance. Overall, our model captures the benefits of heat transfer enhancement during gas hydrate formation very well.

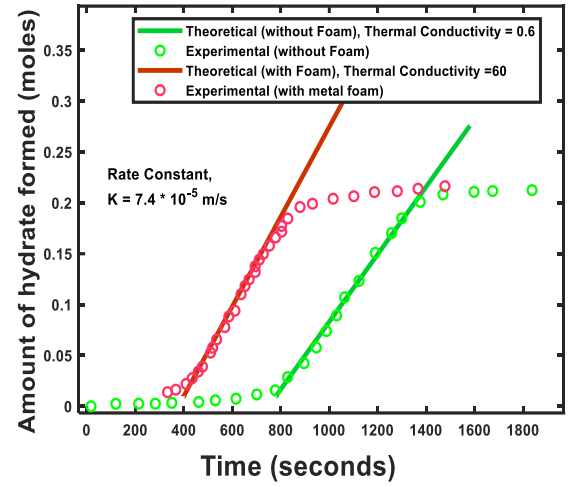


Fig 3: Validation of presently developed model with the experimental data of Fan et. al. [22].

#### 5. SCALING ANALYSIS OF TEMPERATURE RISE DURING HYDRATE FORMATION

The mathematical framework developed in this article can be used to derive the scaling of steady-state temperature rise in the reactor. From equations (1), the scale of temperature rise in the reactor,  $\Delta T_r = T - T_\infty$  can be obtained as:

$$\Delta T_r \sim \frac{kA_c \Delta H}{hA_s} (c - c_{eq}) \quad (3)$$

where  $A_c$  is the cross-sectional area of the reactor and  $A_s$  is the side area of the reactor through which the heat is dissipated. The concentrations can be approximately converted in terms of temperatures using methods developed in Kar et. al.[15], resulting in:

$$\frac{\Delta T_r}{\Delta T_{sub}} \sim \frac{kA_c \Delta H}{hA_s} \frac{PA_{eq}}{ZRT_\infty^3} \quad (4)$$

where  $\Delta T_{sub} = T_{eq} - T$  is the actual subcooling in the system,  $P$  is the pressure,  $Z$  is the compressibility factor of the gas at conditions of  $(P, T_\infty)$ ,  $R$  is the universal gas constant,  $A_{eq}$  is the slope of the equilibrium curve of hydrate formation from a plot of  $\ln P$  vs  $1/T$ . The values of  $A_{eq}$  are outlined in Kar et. al. [14,15]. If the ratio,  $\Delta T_r / \Delta T_{sub} \ll 1$ , then the heat generated due to hydrate formation is dissipated effectively, and does not

adversely affect the hydrate formation rate. However, if  $\Delta T_r / \Delta T_{sub} \gg 1$  then hydrate formation is heat transfer-limited, and there is a need for more effective heat dissipation for increasing hydrate formation rate.

The scaling presented in equation (4) can be utilized to derive important conclusions about any hydrate formation process. We examine the system analyzed in the previous section, which involves methane hydrates forming inside a cylindrical reactor (parameters are provided in Table 1). For the case in Fig. 2a, the ratio of the temperature differences in (4),  $\Delta T_r / \Delta T_{sub} \sim 46$ , which signifies heat-transfer controlled hydrate formation. Consequently, the temperature spikes very close to the equilibrium temperature of hydrate formation. For the case in Fig. 2b, with  $h = 5000 \text{ W/m}^2\text{K}$ ,  $\Delta T_r / \Delta T_{sub} \sim 0.05$ , which is in the transition region and results in lower temperature spikes. This analysis shows that to achieve even better heat dissipation, i.e.  $\Delta T_r / \Delta T_{sub} < 0.01$ , a heat transfer coefficient  $h > 25 \text{ kW/m}^2\text{K}$  will be required. It should be noted that the scaling in equation (4) does not contain the thermal conductivity of the liquid phase, since the scaling is based on the steady state temperature at the interface. A high thermal conductivity delays the transition to steady state as can be seen from Fig. 3c, but does little to affect the steady-state rise in temperature.

## 6. CONCLUSIONS

The rate at which hydrates form strongly depends on the temperature distribution inside the reactor. Our modeling shows that inadequate removal of the heat associated with hydrate formation can significantly raise the temperature of the system and reduce the formation rate. Improve the heat dissipation by cooling the reactor, increasing the thermal conductivity of the liquid phase, etc. are essential tools to enhance hydrate growth. This work develops a fundamentals-based framework to couple the chemical kinetics of hydrate formation with the heat transfer in the system. Mathematical scaling arguments are also developed to identify hydrate formation systems that would be heat transfer-limited.

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