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Simultaneous mass and heat transfer to/from the edge of a clathrate-hydrate film causing its growth along a water/guest-fluid phase boundary

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HIGHLIGHTS

- Presents analytic model for hydrate-film growth along water/guest-fluid interface.
- Simultaneous mass and heat transfer to/from film front is formulated and solved.
- Methane-hydrate-film growth is found to be rate-controlled by the mass transfer.
- The obtained predictions of film growth are compared to existing observations.

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ABSTRACT

This paper deals with the unidirectional growth of a clathrate-hydrate film along a planar interface between liquid water and a hydrate-guest substance in the gas or liquid state, such as methane gas. The paper first discusses the physical or logical flaws of previous hydrate-film growth models, then describes a new model in which the diffusive mass transfer of the guest substance to the front edge of a hydrate film and the conductive heat transfer from the edge are simultaneously solved to yield a solution for the film growth. The solution procedure is so formulated as to adhere to the balance, on the rate basis, between the film growth relevant to the mass flow of the guest substance to the film-front edge and the heat release from the edge resulting from the exothermic hydrate-crystal formation. The paper finally describes the predictions for the hydrate-film growth along the water/methane interface for comparison with the literature data of relevant experimental observations.

1. Introduction

Clathrate hydrates (abbreviated as hydrates) are crystalline compounds composed of hydrogen-bonded water molecules configured into collective *cages*, each generally enclosing at most one *guest* molecule of some apolar substance which we call a "guest substance" or a "hydrate former". Light hydrocarbons, such as methane and ethane, acid gases, such as hydrogen sulfide and carbon dioxide, and fluorocarbon refrigerants, such as difluoromethane and 1,1,1,2-tetrafluoroethane, are typical examples of such guest substances having potential importance in the development of hydrate-based technologies for, as examples, natural-gas storage and transport (Horiguchi et al., 2011; Kondo et al., 2014), the separation of toxic or greenhouse species from low-quality natural gas or industrial flue gases (Akatsu et al., 2013; Ma et al., 2016), and refrigeration utilizing the heat of hydrate dissociation (Ogawa et al., 2006). With few exceptions, such substances are poorly soluble in water in the liquid state. Thus, when a macroscopic phase of some guest substance in either the gas or liquid state (abbreviated "guest fluid" hereafter) is brought into contact with that of liquid water, a hydrate preferentially forms and grows at the interface between the two phases, taking the form of a thin, polycrystalline film. Experimental observations of such growth of hydrate films along liquid-water/guest-fluid interfaces have been reported in many previously published papers (Sugaya and Mori, 1996; Ohmura et al., 1999; Uchida et al., 1999; Hirai et al., 1999; Freer et al., 2001; Mochizuki, 2003; Sun et al., 2007; Peng et al., 2007; Taylor et al., 2007; Tanaka et al., 2009; Beltrán and Servio, 2010; Saito et al., 2011; Kishimoto et al., 2012; Li et al., 2013,

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Nomenclature

A_f surface area of hydrate-film front
a, b, c dimensionless parameters used in Eq. (29)
C_{gw}, C_w molar densities of water/hydrate-guest-substance mixture and pure water, respectively
$c_p, c_{p,gw}$ specific heat capacity at constant pressure, and that of water/guest-substance mixture having the same composition as that of the hydrate crystals, respectively
D_{gw} binary diffusion coefficient of guest substance in liquid-water phase
h_f, k_f area-averaged coefficients for heat transfer from, and mole-based mass transfer to, hydrate-film front, respectively
L_δ χ-axial location of a hydrate-film segment used to measure δ_{init}
M_g, M_w molar masses of guest substance and water, respectively
$\dot{N}_{g,f}$ molar flow rate of guest substance to hydrate-film front via liquid–water phase
n hydration number
p system pressure
$\dot{Q}_f$ rate of the heat discharge from hydrate-film front to surroundings
$\dot{S}$ rate of heat release due to hydrate formation per unit area of hydrate-film front surface
T temperature
T_{eq} three-phase (gas/liquid/hydrate) equilibrium temperature
$T_f, \overline{T_f}$ local temperature at hydrate-film-front surface and its surface-area-averaged value, respectively
T_{gw}, T_{hw} local temperatures at water/guest-fluid interface and water/hydrate-film interface parallel to the former interface, respectively
$T_{xf,j}$ temperature at the nodal point in a control volume located at hydrate-film front
T_∞ undisturbed system temperature
t, t_1 time as a variable and its value at a specified instant, respectively
V_w molar volume of water
v_f instantaneous axial velocity of hydrate-film front along water/guest-fluid interface
v_f^* asymptotic value of v_f
X, Y variables used in Eq. (29); $X \equiv ln[1/(\Delta/\mathrm{m})]$, $Y \equiv ln[v_f^*/(\mathrm{mm/s})]$
x, y, z Cartesian coordinates
$x_f, x_{f,init}$ x-axial position of hydrate-film front as a time-dependent variable and its initial value, respectively
x_g concentration (mole-fraction) of guest substance dissolved in liquid-water phase
$x_{gs}, x_{gs,h}$ guest-in-water solubility (mole-fraction) in water/guest-fluid two-phase equilibrium and that in water/hydrate two-phase equilibrium, respectively
$x_{ws,h}$ mole fraction of water in water/guest-substance mixture in contact with hydrate-film front

Greek letters

Δ reference length scale for characterizing the control-volume grids used in numerical heat- and mass-transfer calculations
$\Delta H_{h/lg}, \Delta h_{h/lg}$ molar enthalpy change and mass-based specific enthalpy change, respectively, accompanying hydrate dissociation
$\Delta \dot{m}_h$ mass-based rate of hydrate formation in each control volume located at the hydrate-film front
$\Delta \dot{m}_t, \Delta \dot{m}_m$ value of $\Delta \dot{m}_h$ matching with the rate of heat transfer from the control volume and that matching with the rate of mass transfer of the guest substance to the area that the control volume occupies on the hydrate-film front
$\Delta \dot{S}$ rate of heat generation in each control volume due to hydrate formation
$\Delta T_{eq}, \Delta T_{eq\text{-}f}, \Delta T_f, \Delta \overline{T_f}$ temperature differences defined as $T_{eq}-T_\infty$, $T_{eq}-\overline{T}_f$, $T_f - T_\infty$, and $\overline{T_f} - T_\infty$, respectively
Δt step size used in executing time-step calculation
$\Delta x, \Delta y, \Delta z$ x-, y- and z-axial spans, respectively, of each control volume laid in the grid for heat- or mass-transfer computation
$\Delta x_f, \Delta y_j$ x- and y-axial spans, respectively, of each control volume located at hydrate-film front
$\Delta(x_f)$ x-axial displacement of hydrate-film front during time increment Δt, $\equiv x_f|_{t=t} - x_f|_{t=t-\Delta t}$
$\Delta x_{g,f}, \Delta \bar{x}_{g,f}$ difference between x_{gs} at $T = T_\infty$ and $x_{gs,h}$ at $T = T_f$ and that between x_{gs} at $T = T_\infty$ and $x_{gs,h}$ at $T = \overline{T_f}$, respectively
$\Delta x_{g,eq}, \Delta x_{g,\infty}$ difference between x_{gs} at $T = T_\infty$ and $x_{gs,h}$ at $T = T_{eq}$ and that between x_{gs} and $x_{gs,h}$ at $T = T_\infty$, respectively
δ thickness of hydrate film
δ_{init} initial hydrate-film thickness experimentally measured
λ thermal conductivity
ξ_{gs} magnitude of the gradient of x_{gs} with T averaged over a finite T range
Π_f dimensionless parameter defined in Eq. (5)
ρ density
τ age of a hydrate-film segment at the instant of its thickness measurement
ϕ fractional disagreement between hydrate-formation rate deduced from the rate of heat removal from hydrate-film front and that deduced from the rate of guest-substance supply to the hydrate-film front, defined in Eq. (30)
χ coordinate indicating the x-axial distance measured from hydrate-film front in the direction of decreasing x

Subscripts

g hydrate-guest substance
h hydrate
i, j ordinal numbers (=1, 2, 3, ...) assigned to each control volume
$j+, j-$ y-axial directions from the control volume at $y = y_j$ to those at $y = y_{j+1}$ and $y = y_{j-1}$, respectively
w water
xf+, xf− x-axial directions from the control volume at hydrate-film front to liquid-water phase and to the inside of hydrate film, respectively

2014; Kitamura and Mori, 2013). Some of these papers provided quantitative data about the axial motion (in a macroscopic sense) of the hydrate-film front in terms of v_f, the axial velocity of the film front in the direction normal to a tangent to the film front at each instant (Uchida et al., 1999; Hirai et al., 1999; Freer et al., 2001; Peng et al., 2007; Taylor et al., 2007; Tanaka et al., 2009; Saito et al., 2011; Kishimoto et al., 2012; Kitamura and Mori, 2013; Li et al., 2014). In addition, some efforts have also been devoted to