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Direct numerical simulation of CO_2 hydrate dissociation in pore-scale flow by applying CFD method

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ABSTRACT

The objective of this work is to establish a new pore-scale($m \sim \mu m$) model for estimating the dissociation rate of CO_2 hydrate(CO2H) synthesized in laboratory-scale sediment samples. Finite Volume Method (FVM) with unstructured mesh were constructed in a representative regular face-centered cubic unit. At the surface of CO2H, the model reported by Fukumoto et al. (2015) has been employed. Surface mass transfer of CO2H and the heat transfer between hydrate and water are also considered. In the bulk flow, concentration and temperature of liquid CO_2 in water flow was analyzed by Computational Fluid Dynamics (CFD) method without considering ice or gas phase under high pressure state. In this study, tentative cases with porosity 0.74, 0.66, and 0.49 are individually considered in sediment samples. The initial temperature 253.15 K of CO2H pellets inside the cubic unit dissociated due to the driving force of fugacity variation, ex. 2.01 and 1.23 MPa while warm water of 276.15 and 282.15 K flow in. In the calculation, periodic conditions are imposed at each surfaces of inlet/right/front sides updated every time step. In addition, the flux of CO2H's surfaces are all regarded as being dissolved into the water, and compared to Clarke and Bishnoi (2004) and Nihous and Masutani's (2006) correlations at Reynolds number of about 50. In conclusion, the overall distribution of dissociation flux in this study is affected by porosity in both two cases of water temperature. Higher water temperature induces higher dissociation flux at the surface of hydrate. Numerical results of this work show good agreement with Nihous' model, which is modified from Clarke's model in considering real conditions. The trend of flux becomes saturated if the slow surface dissociation rate dominated the process at Reynolds number over 100.

1. Introduction

To lower the CO_2 concentration in the atmosphere, carbon dioxide capture and storage (CCS) is thought to be effective. One scheme of CCS is to store CO_2 in the form of gas hydrate in subseabed geological formation, as was proposed by Inui and Sato [17]. In addition, much research about the formation and dissociation of CO_2 hydrate (CO2H) during sequestration in the deep ocean or geologic sediment has been discussed. Particularly, flow and transport in porous media is relevant to many areas of engineering and science including groundwater hydrology, the recovery of oil, and CO_2 sequestration. Rehder et al. (2004) reported measurements of the dissolution rate of well-characterized, laboratory-synthesized carbon-dioxide hydrates in an open-ocean seafloor setting. Uchida et al. [19] indicated that the pore effect on the phase equilibrium was mainly due to the water activity change. Molins et al. [4] simulated reactive transport at the pore scale to provide estimates of realistic reaction rates in natural sediments. This approach can be used to inform continuum scale models, and understand the processes that lead to rate discrepancies in field applications. Davison et al.'s [10] pore-scale modeling results suggest that the newly-developed pore-scale model can be used to examine engineered fluids with adaptable properties including density. For the numerical techniques for analyzing pore-scale flow, unstructured meshes can be considered well suited to pore-scale modeling for two reasons: an ability to handle complicated geometries and an adaptive sizing of target unit with high mesh resolution [32,33]. Additionally, unstructured meshes can be used with Computational Fluid Dynamics (CFD) techniques based on methods of Finite Element Method (FEM) or Finite Volume Method (FVM) and so on. Pore-scale numerical simulations based on FEM by using unstructured tetrahedral mesh has been used to define the pore structure by Nathan [37]. A numerical simulations of laminar flow based on FVM with unstructured meshes was used to

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Nomenclature

C	volumetric molar concentration of CO_2 in the ambient water [$mol{\cdot}m^{-3}$]
C_H	volumetric molar concentration of CO_2 in the aqueous solution equilibrated with the stable hydrate phase [$mol{\cdot}m^{-3}$]
C_K	volumetric molar concentration of CO_2 in water at the centroid of a cell attaching to the hydrate surface [$mol{\cdot}m^{-3}$]
C_I	volumetric molar concentration of CO_2 in the ambient aqueous solution at the surface of the hydrate ball [$mol{\cdot}m^{-3}$]
C_X	average molar volumetric concentration of CO_2 in the ambient water flow for a given cross section of water flow [$m{\cdot}s^{-2}$]
d	diameter of the CO_2 hydrate ball [m]
D	diffusion coefficient of CO_2 in water [$mol{\cdot}m^{-3}$]
E	activation energy [$J\ mol^{-1}$]
F	dissociation rate flux [$mol\ s^{-1}\ m^{-2}$]
f_{eq}	fugacity of the quadruple equilibrium [Pa]
f_g	fugacity of gaseous CO_2 [Pa]
G	molar Gibbs free energy [$J\ mol^{-1}$]
H_L	latent heat of hydrate dissociation [$J\ mol^{-1}$]
h_L	length of the water layer attached on the hydrate surface [m]
k_{D0}	intrinsic dissociate rate constant based on Clarke-Bishnoi model [$mol\ Pa^{-1}\ s^{-1}\ m^{-2}$]
k_{bl}	dissociation rate constant based on new model [$mol^2\ J^{-1}\ s^{-1}\ m^{-2}$]
L	thickness of computational cell [m]
M_B	molecular weight of water [$g\ mol^{-1}$]
P	thermodynamic pressure [Pa]
P_{eq}	quadruple equilibrium pressure for CO_2 hydrate as a function of T [Pa]
Q	volumetric flow rate of the ambient water [$m^3\ s^{-1}$]
$\dot{Q}_H$	the rate at which the latent heat is transferred to the CO_2 hydrate by dissociation [$J\ m^{-2}\ s^{-1}$]
R	gas constant, 8.314 [$J\ K^{-1}\ mol^{-1}$]
T	absolute temperature [K]
T_L	temperature at the centroids of a cell in the solid hydrate [K]
T_H	temperature at the centroids of a cell in the aqueous phase [K]
x	mole fraction of CO_2 [–]
x_{eq}	solubility of CO_2 in the aqueous solution in equilibrium with the stable hydrate phase [–]
x_I	mole fraction of CO_2 in the aqueous phase at the surface of the hydrate ball [–]
α_L	thermal diffusivity in the aqueous phase [$m\ s^{-2}$]
α_H	thermal diffusivity in the hydrate ball [$m\ s^{-2}$]
Δr	thickness of the computational cell [m]
δ	thickness of the boundary layer [m]
$\Delta\mu$	chemical potential difference [$J\ mol^{-1}$]
ρ	density of the ambient water [$kg\ m^{-3}$]
φ	the association parameter for the solvent water
η_L	is the viscosity of water [$mPa{\cdot}s$]
V_A	is the molar volume of CO_2 [$m^3\ mol^{-1}$]
ν_L	kinematic viscosity of water [$m\ s^{-2}$]
λ_L	heat conductivity of water [$W\ K^{-1}\ m^{-1}$]
λ_H and λ_L	the heat conductivities in the hydrate and water [$W\ K^{-1}\ m^{-1}$]

solve the incompressible, steady Navier-Stokes equations through a cluster of metal idealized pores by Boomsma et al. [38].

The objective of this work is to establish a new pore-scale model for estimating the dissociation rate of CO2H in homogeneous porous media. In this work, CO_2 dissociated at the surface is assumed to be dissolved into liquid water totally without considering the gas nucleated. Major assumptions in this study are listed as below:

1. Homogeneous face-centered packing of multi-CO2H pellets.
2. Only dissociation occurred at the surface, no any formation occurred together with dissociation.
3. The surface structure will not collapse with the dissociation of CO2H at the surface of pellets.
4. This study is considered as a single-phase flow cooperated with mass, heat and momentum transfers.

The features of our work are summarized as:

1. By using unstructured cubic unit mesh with periodic boundary conditions imposed at inlet/right/front surfaces of regular face-centered cubic unit, and FVM, to accomplish high-accuracy simulation of kinetic dissociation phenomena in laboratory-scale sediment samples.
2. To cooperate with molecular simulation, and field-scale simulators, we aim at establishing pore-scale modeling to analyze the simultaneous kinematic process of CO2H dissociation due to non-equilibrium states.
3. To embed kinetic surface dissociation model and VTL method [20] in CFD code to analyze momentum, mass, and heat transfer simultaneously is a simple way of estimating the dissociation rate in CO2H synthesized core.

2. Surface dissociation modeling

In this study, it is assumed that the dissociation flux (F_1) is proportional to the driving force, the free energy difference($\Delta\mu$) introduced by Sean et al. [18], expressed as

$$F_1 = k_{bl} RT \ln\left(\frac{C_{Hsol}}{C_I}\right) \tag{1}$$

where k_{bl} is the rate constant [$mol^2\ J^{-1}\ s^{-1}\ m^{-2}$]. According to the work by Fukumoto et al. [39], k_{bl} is listed below:

$$k_{bl} = \exp\left(-\frac{11,729}{T} + 26.398\right) \tag{2}$$

where C_{Hsol} mole fraction of CO_2 in the aqueous solution at equilibrium with hydrate, to that in the ambient aqueous solution at the surface of the hydrate C_I.

3. Basic transport equations

Incompressible flow around CO2H's surface is governed by the continuity and the Navier-Stokes equations. The advection-diffusion equations of non-conservative type for mass concentration C and temperature T are also solved.

$$\nabla \cdot \mathbf{u} = 0 \tag{3}$$

$$\frac{\partial \mathbf{u}}{\partial t} + \nabla \cdot (\mathbf{uu}) = -\nabla P + \frac{1}{\mathrm{Re}} \nabla \cdot [\nabla \mathbf{u} + (\nabla \mathbf{u})^T] + \frac{\rho_w}{\mathrm{Fn}^2} g \tag{4}$$

$$\frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C = \frac{1}{\mathrm{ReSc}} \nabla^2 C \tag{5}$$