

Lawrence Berkeley National Laboratory

Recent Work

Title

Simulation of Gas Production from Multilayered Hydrate-Bearing Media with Fully Coupled Flow, Thermal, Chemical and Geomechanical Processes Using TOUGH + Millstone. Part 1: Numerical Modeling of Hydrates

Permalink

<https://escholarship.org/uc/item/7dh967zn>

Journal

Transport in Porous Media, 128(2)

ISSN

0169-3913

Authors

Moridis, GJ
Queiruga, AF
Reagan, MT

Publication Date

2019-06-15

DOI

10.1007/s11242-019-01254-6

Peer reviewed

Simulation of Gas Production from Multilayered Hydrate Bearing Media with Fully Coupled Flow, Thermal, Chemical, and Geomechanical Processes using TOUGH+Millstone: Part 1: Numerical Modeling of Hydrates

George J. Moridis · Alejandro F. Queiruga · Matthew T. Reagan

the date of receipt and acceptance should be inserted later

Abstract TOUGH+Millstone has been developed for the analysis of coupled flow, thermal and geomechanical processes associated with the formation and/or dissociation of CH₄-hydrates in geological media. It is composed of two constituent codes: (a) a significantly enhanced version of the TOUGH+HYDRATE simulator, v2.0, that accounts for all known flow, physical, thermodynamic and chemical processes associated with the behavior of hydrate-bearing systems undergoing changes and includes the most recent advances in the description of the system properties, coupled seamlessly with (b) Millstone v1.0, a new code that addresses the conceptual, computational and mathematical shortcomings of earlier codes used to describe the geomechanical response of these systems. The capabilities of TOUGH+Millstone are demonstrated in the simulation and analysis of the system flow, thermal and geomechanical behavior during gas production from a realistic complex offshore hydrate deposit.

In the first paper of this series, we discuss the physics underlying the T+H hydrate simulator, the constitutive relationships describing the physical, chemical (equilibrium and kinetic) and thermal processes, the states of the CH₄+H₂O system and the sources of critically important data, as well as the mathematical approaches used for the development of the of mass and energy balance equations and their solution. Additionally, we provide verification examples of the hydrate code against numerical results from the simulation of laboratory and field experiments.

Keywords Methane hydrates · Reservoir Simulation · Geomechanics · Coupled processes

1 Introduction

Gas hydrates are solid crystalline compounds of water and gaseous substances described by the formula $G \cdot N_H H_2O$, in which the molecules of gas G (guests) occupy voids within the lattices of

G. Moridis
Petroleum Engineering Department, Texas A&M University, United States
Energy Geosciences Division, Lawrence Berkeley National Laboratory, California, United States
E-mail: moridis@tamu.edu; GJMoridis@lbl.gov

A. Queiruga
Energy Geosciences Division, Lawrence Berkeley National Laboratory, California, United States
E-mail: afqueiruga@lbl.gov

M. Reagan
Energy Geosciences Division, Lawrence Berkeley National Laboratory, California, United States
E-mail: mtreagan@lbl.gov

ice-like crystal structures with N_H (the hydration number) water molecules per gas molecule. The formation and dissociation of hydrates is described by the general equation:



where ΔH_0 is the enthalpy of formation/dissociation. Note that hydrate formation is an exothermic process.

Gas hydrate (GH) deposits occur in two different geographic settings where the necessary conditions of low temperature T and high pressure P exist for their formation and stability: in the Arctic (typically in association with permafrost) and in deep ocean sediments (Kvenvolden, 1988). The majority of naturally-occurring hydrocarbon GH contain primarily CH_4 . Pure CH_4 -hydrates contain a factor of 164 more concentrated methane compared to standard P and T conditions (STP). Natural CH_4 -hydrates crystallize mostly in the structure I form, which has a hydration number N_H ranging from 5.77 to 7.4, with an average of $N_H = 6$ and complete hydration at $N_H = 5.75$ (Sloan and Koh, 2008). Natural GH can also contain other hydrocarbons (alkanes C_nH_{2n+2} , $n = 2$ to 4) and trace amounts of other gases (mainly CO_2 , H_2S or N_2).

This series presents a comprehensive description of the physical equations, material relations, and numerical algorithms required to simulate oceanic hydrate reservoirs with characteristics observed in real formulations. Due to the scope of this problem, the presentation is separated into three parts. The first two parts each detail the formulation and algorithms of the two computational simulators developed for these problems and are meant to serve as an exhaustive guide to replicate the analysis and inform future algorithmic developments. The third part of this describes a representative system of methane production from a realistic oceanic hydrate system.

In this paper we describe TOUGH+HYDRATE v2.0 (T+H), the first of the two constituent codes of the TOUGH+Millstone simulator, developed for the analysis of coupled flow, thermal and geomechanical processes associated with the formation and dissociation of hydrates in geological media. The TOUGH+HYDRATE simulator accounts for all known flow, physical, thermodynamic and chemical processes associated with the behavior of hydrate-bearing systems. The second constituent code is the Millstone v1.0 geomechanical simulator, which is the subject of the second paper of this series. In the absence of strong geomechanical effects, TOUGH+HYDRATE can be used as a stand-alone code, uncoupled from Millstone.

2 Background

The TOUGH+HYDRATE code (T+H) (Moridis et al., 2008) has been continually developed at Lawrence Berkeley National Laboratory (LBNL) to model non-isothermal CH_4 release, phase behavior and flow under conditions of both naturally-occurring and laboratory-made CH_4 -hydrate deposits by solving the coupled equations of fluid flow and heat balance. T+H is a successor to earlier simulators from LBNL first released in 1998 (Moridis et al., 1998; Moridis, 2003; Moridis and Collett, 2004; Moridis et al., 2004, 2005) for application to large-scale simulations of hydrate behavior.

The current version (V2.0) is the third update of the 2008 T+H code (Moridis et al., 2008). It models all known processes involved in natural CH_4 -hydrates in complex geologic media using either an equilibrium or a kinetic model (Kim et al., 1987; Clarke and Bishnoi, 2001; Moridis et al., 2008). It includes fluid and heat transport, the thermophysical properties of reservoir fluids, thermodynamic changes and phase behavior, and the non-isothermal chemical reaction of CH_4 -hydrate formation and dissociation. T+H is a fully implicit compositional simulator that accounts for heat and up to four mass components (i.e., H_2O , CH_4 , CH_4 -hydrate, and water-soluble inhibitors such as salts or alcohols) that are partitioned among four possible phases: gas, aqueous liquid, ice, and hydrate. The T+H code can describe all 15 possible thermodynamic states of the CH_4+H_2O system and any combination of the three main dissociation methods: depressurization, thermal

stimulation, and the effect of inhibitors. As will be demonstrated in this series, T+H was designed to handle the phase changes, state transitions, and strong nonlinearities that are typical of hydrate dissociation problems.

This paper presents significant features have been added to this latest version to enable simulation of observed hydrate reservoir characteristics, in the scope of a complete description of the entire physical formulation.

Hydrate reservoirs are often characterized by very low permeability, necessitating consideration of Klinkenberg diffusion and Knudsen flow. Conversely, in regions near the well, the gas-dominated regions exhibit extremely fast flow requiring Forchheimer flow. Very long term studies to which T+H has been applied exhibit diffusion-dominated transport of methane through the aqueous phase.

Numerous architectural improvements have been made to the code, described 5

The coupling to the Millstone geomechanical code is another significant alteration to the T+H code itself, which will be described in Part 2. The periodically updated manual to T+H (Moridis and Pruess, 2014) contains more in-depth descriptions of every capability that was not required for the hydrate reservoir simulation presented in Part 3. T+H V2.0 incorporates a series of important new capabilities. These include:

- Consideration of Klinkenberg (1941) flow (non-Darcian, gas slippage effects) for hydrate-bearing media with low effective permeability (e.g., usually associated with medium to high hydrate saturations)
- Knudsen flow (non-Darcian) for hydrate-bearing media with extremely effective permeability (e.g., usually associated with high to very high hydrate saturations), and ability to seamlessly move from the Knudsen flow regime to the Klinkenberg regime
- Forchheimer (1901) flow (non-Darcian) for high-velocity flow regimes in the vicinity of wells in high-permeability media
- Multi-component diffusion capabilities, which are important in long-term (geologic time) simulations focusing on hydrate formation (especially associated with super-saturation in oceanic environments)
- Advanced viscosity computation options, including the friction theory of Quinones et al. (2000)
- New option for the estimation of the departure enthalpy equation using the Lee-Kessler (1975) method for mixtures of polar and non-polar materials (water and CH₄)
- Expansion of the phase diagram and properties of H₂O by including Region III (IAPWS, 2007; 2009) describing properties in the vicinity of the critical point, thus making possible consideration of thermal dissociation of hydrates at high pressures and temperatures
- Addition of an option for the ab initio computation of hydrate properties using the Ballard (2002) method
- Addition of the LIS package (Nishida, 2010) for significantly faster solution of the matrix equations in T+H v2.0

Various versions of T+H have been used for a wide range of investigations of gas production from hydrates in both oceanic deposits and in accumulations associated with the permafrost that cover the entire spectrum of hydrate types, e.g., Class 1 (Moridis et al., 2008), Class 2 (Moridis and Reagan, 2007, 2010a,b; Moridis et al., 2013; Reagan et al., 2014), Class 3 (Moridis and Reagan, 2007; Moridis et al., 2011), and Class 4 (Moridis and Sloan, 2007; Li et al., 2010; Moridis et al., 2011).

3 Model Description

3.1 Fundamental equations - Mass accumulation terms

Following the approach in Moridis (2014); Pruess et al. (1999, 2012), the components of the pore-filling media are broken into components labeled by κ . Let M^κ denote a mass density for component

97 κ . The balance of mass and heat dictates that, for every subdivided element or gridblock of the
 98 simulation domain, the following holds for each component κ :

$$\frac{d}{dt} \int_{V_n} M^\kappa dV = \int_{\Gamma_n} \mathbf{F}^\kappa \cdot \mathbf{n} dA + \int_{V_n} q^\kappa dV, \quad (2)$$

99 where V_n is the volume of the subdomain n with differential dV [m^3]; M^κ is the mass accumulation
 100 of component κ [$\text{kg} \cdot \text{m}^{-3}$]; Γ_n is the surface of subdomain n with differential dA [m^2]; \mathbf{F}^κ is the flux
 101 vector of component κ [$\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-1}$]; \mathbf{n} is the inward unit normal vector; and q^κ is the source/sink
 102 term of component κ [$\text{kg} \cdot \text{m}^3 \cdot \text{s}^{-1}$].

103 The non-isothermal hydrate system can be fully described by the appropriate mass and energy
 104 balance equations. The following components κ are considered: $\kappa = h$ for hydrate (for kinetic for-
 105 mation/dissociation only); w for H_2O ; m for CH_4 ; i for a water-soluble inhibitor (salt or organic
 106 substance); and θ for heat. Heat is included in this list as a pseudo-component as it is tracked sim-
 107 ilarly to the mass balance equations. Note that hydrate behavior cannot be described isothermally.
 108 Thus, the maximum number of mass components is 4 for kinetic hydrate formation/dissociation
 109 corresponding to 5 equations. For equilibrium hydrate formation/dissociation, hydrate is a state
 110 of the $\text{H}_2\text{O}+\text{CH}_4$ system instead of a separate species, reducing the number of components and
 111 equations to 3 and 4, respectively.

112 Under equilibrium conditions, the mass accumulation terms M^κ for each component κ in Eq. 2
 113 are given by

$$M^\kappa = \sum_{\beta=A,G,I,H} \phi S_\beta \rho_\beta X_\beta^\kappa \quad \kappa = w, m, i \quad (3)$$

114 where ϕ is the porosity, ρ is the density [$\text{kg} \cdot \text{m}^{-3}$]; S_β is the saturation of the phase; X_β^κ is the mass
 115 fraction of component κ in phase β . In hydrates, the mass components are partitioned among four
 116 possible phases β : H , denoting the solid-hydrate phase (components: m, w for equilibrium or h for
 117 kinetic); A for the aqueous phase (components: mainly w , but also containing dissolved m and/or
 118 dissolved i); G for the gaseous phase (components: mainly m , and vapor w); and I denoting the
 119 solid ice (component: w).

120 In the equilibrium model, each phase has the following constraints:

$$\beta = G : X_G^i = 0 \quad (4)$$

$$\beta = H : X_H^w = \frac{W^m}{W^h}, \quad X_H^m = 1 - X_H^w, \quad X_H^i = 0 \quad (5)$$

$$\beta = I : X_I^m = X_I^i = 0, \quad X_I^w = 1 \quad (6)$$

121 The terms W^m and W^h denote the molecular weights of the CH_4 and of the hydrate, respectively,
 122 reflecting the stoichiometry in Eq. 1. Under kinetic conditions, the mass accumulation terms M_κ
 123 in Eq. 2 are given by

$$M^\kappa = \sum_{\beta=A,G,H,I} \phi S_\beta \rho_\beta X_\beta^\kappa, \quad \kappa = w, m, h, i \quad (7)$$

124 In the kinetic model, the constraints for each phase are:

$$\beta = A : X_A^h = 0 \quad (8)$$

$$\beta = G : X_G^h = X_G^i = 0 \quad (9)$$

$$\beta = H : X_H^w = X_H^m = X_H^i = 0, \quad X_H^h = 1 \quad (10)$$

$$\beta = I : X_I^m = X_I^h = X_I^i = 0, \quad X_I^w = 1 \quad (11)$$

125 The model of Kim et. al (Kim et al., 1987; Clarke and Bishnoi, 2001) is used to describe the
 126 kinetic behavior of the hydrate mass component and phase (where $\kappa = m$ indexes into the methane
 127 component):

$$Q^m = \frac{\partial M^m}{\partial t} = -K_0 \exp\left(\frac{\Delta E_a}{RT}\right) F_A A (f_{eq} - f_v) \quad (12)$$

128 where K_0 is the intrinsic hydration reaction constant [$\text{kg m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$]; ΔE_a is the hydration
 129 activation energy [J mol^{-1}]; R is the universal gas constant [$8.314 \text{ J mol}^{-1} \text{ K}^{-1}$]; F_A is an area
 130 adjustment factor [dimensionless]; A is the surface area participating in the reaction [m^2]; f_{eq} and
 131 f_v are the fugacities [Pa] at the equilibrium temperature T_{eq} and at temperature T , respectively.

132 The surface area is computed by assigning the hydrate saturation uniformly to the interstitial
 133 spaces of the porous medium. The original solid grain volume (assuming spherical grain) is deter-
 134 mined as $V_p = 4\phi r_p^3/3$, where r_p is the grain radius [m]. Then, the number of voids N_V is assumed
 135 to be equal to the number of solid grains, and the corresponding void volume V_V is computed from

$$N_V = \frac{1 - \phi}{V_p}, \quad V_V = \frac{\phi}{N_V}. \quad (13)$$

136 At the interface of pores and voids, the grain surface area is computed as $A_p = 4\pi r_p^2$, resulting in
 137 a total area (per unit volume) of $A_{TV} = N_V A_p$. Then, the void volume is assumed to vary linearly
 138 with r_V^3 where $r_V = 0.1547 r_p$ is a representative radius of a sphere inscribed in the interstitial space
 139 between the grains. A representative hydrate particle radius r_H and volume V_H are computed by

$$V_H = \frac{\phi S_H}{N_V}, \quad r_h = r_V \left(\frac{V_H}{V_V}\right)^{1/3} = r_V S_H^{1/3} \quad (14)$$

140 and the reactive area is computed by

$$A = f_A A_{TV} \left(\frac{r_H}{r_V}\right)^2 = f_A N_V \left(4\phi r_p^2\right)^{1/3} S_H^{2/3}. \quad (15)$$

141 The area adjustment factor f_A accounts for the deviation of the interstitial volume from the as-
 142 sumption of grain sphericity, and can incorporate heterogeneity related to the hydrate ‘‘particle’’
 143 size, shape, and saturation distribution. An estimate of r_p can be obtained from sieve analysis.
 144 Alternatively, given the intrinsic permeability k , the Kozeny-Carman equation estimates r_p by

$$r_p = \left[45k \frac{(1 - \phi)^2}{\phi^3}\right]^{1/2}. \quad (16)$$

145 3.2 Fundamental equations - Heat accumulation terms

146 The heat accumulation term includes contributions from the rock matrix and all phases, and, in
 147 the kinetic model, is given by the equation

$$M_\theta = \int_{T_0}^T (1 - \phi) \rho_R C_R dT + \sum_{\beta=A,G,H,I} \phi S_\beta \rho_\beta X_\beta U_\beta + Q_{diss}, \quad (17)$$

148 where

$$Q_{diss} = \begin{cases} \Delta(\phi \rho_H S_H \Delta H^0) & \text{for equilibrium dissociation} \\ Q_H \Delta H^0 & \text{for kinetic dissociation} \end{cases} \quad (18)$$

149 In the above equation, ρ_R is the rock density [kg m^{-3}]; C_R is the heat capacity of the dry rock
 150 [$\text{J kg}^{-1} \text{ K}^{-1}$]; U_β is the specific internal energy of phase β [J kg^{-1}]; $\Delta()$ denotes a change; and ΔH^0

151 is the specific enthalpy of hydrate dissociation/formation [J kg^{-1}]. The specific internal energy of
 152 the gaseous phase is a very strong function of composition, related to the specific enthalpy of the
 153 gas phase H_G by

$$U_G = \sum_{k=w,m} X_G^\kappa u_G^\kappa + U_{dep} = \left(H_G - \frac{P}{\rho_G} \right), \quad (19)$$

154 where W_G^κ is the specific internal energy of component κ in the gaseous phase, and U_{dep} is the
 155 specific internal energy departure of the gas mixture [J kg^{-1}]. The internal energy of the aqueous
 156 phase accounts for the effects of gas and inhibitor solution with

$$U_A = X_A^w u_A^w + X_A^m (u_A^m + u_{sol}^m) + X_A^i (u_A^i + u_{sol}^i) \quad (20)$$

157 where u_A^w , u_A^m , and u_A^i are the specific internal energies of H_2O , CH_4 , and the inhibitor at the
 158 conditions in the aqueous phase, respectively; and u_{sol}^m and u_{sol}^i are the specific internal energies
 159 corresponding to the dissolution of CH_4 and of the inhibitor in water, respectively. The terms u_A^i
 160 and U_H are determined from

$$u_A^i = h_A^i - \frac{P}{\rho_i} = \int_{T_0}^T C_i dT - \frac{P}{\rho_i} \quad (21)$$

$$U_H = H_H - \frac{P}{\rho_H} = \int_{T_0}^T C_H dT - \frac{P}{\rho_H} \quad (22)$$

161 where T_0 is a reference temperature; h_A^i and H_H are the specific enthalpies of H_2O and hydrate
 162 (phase or component), respectively; and C_i and C_H are the temperature-dependent heat capacities
 163 of the inhibitor and the gas hydrate, respectively [$\text{J kg}^{-1}\text{K}^{-1}$].

164 3.3 Fundamental equations - Flux terms

165 The mass fluxes of water, CH_4 and inhibitor include contributions from the aqueous and gaseous
 166 phases:

$$\mathbf{F}^\kappa = \sum_{\beta=A,G} \mathbf{F}_\beta^\kappa, \quad \kappa = w, m, i \quad (23)$$

167 The contributions of the two immobile solid phases ($\beta = H, I$) to the fluid fluxes are zero. In the
 168 kinetic model, the mass flux of the hydrate component is zero as well.

169 For the aqueous phase ($\beta = A$), the phase flux F_A is described by Darcy's law:

$$\mathbf{F}_A = \rho_A \mathbf{v}_\beta = \rho_A \left[-\frac{k k_{rA}}{\mu_A} \nabla \phi_A \right], \quad \nabla \phi_A = \nabla P_A - \rho_A \mathbf{g} \quad (24)$$

170 where k is the rock intrinsic permeability [m^2]; k_{rA} is the relative permeability of the aqueous phase
 171 A [dimensionless]; μ_A is the phase viscosity [Pa s]; P_A is the phase pressure [Pa]; \mathbf{v}_A is the velocity
 172 of the aqueous phase; and \mathbf{g} is the gravitational acceleration vector [m s^{-2}]. The aqueous pressure
 173 P_A is related to the gas pressure P_G by

$$P_A = P_G - P_{cGW} \quad (25)$$

174 where P_{cGW} is the gas-water capillary pressure [Pa]. The gas pressure is equal to $P_G = P_G^m + P_G^w$
 175 where P_G^m and P_G^w are the CH_4 and water vapor partial pressures [Pa] in the gas phase, respectively.

176 The CH_4 solubility in the aqueous phase is related through Henry's law,

$$P_G^m = H^m(T) Y_A^m, \quad (26)$$

177 where $H^m(T)$ [Pa] is the temperature- and salinity-dependent Henry's coefficient. As an option,
 178 the CH_4 solubility may also be determined from the equality of fugacities in the aqueous and the
 179 gas phase Moridis and Freeman (2014).

180 The mass flux of the gaseous phase ($\beta = G$) incorporates advection and diffusion contributions
 181 with

$$\mathbf{F}_G^\kappa = -k_0 \left(1 + \frac{b}{p_G}\right) \frac{k_{rG} \rho_G}{\mu_G} X_G^\kappa (\nabla p_G - \rho_G \mathbf{g}) + \mathbf{J}_G^\kappa, \quad \kappa = w, m \quad (27)$$

182 where k_0 [m^2] is the absolute permeability at large gas pressures; and b [Pa] is the Klinken-
 183 berg (Klinkenberg, 1941) b -factor (appropriately expanded to account for Knudsen flow effects,
 184 as needed) accounting for gas slippage effects. The Klinkenberg b -factor is either provided as an
 185 input or computed using relations such as the correlation proposed by Jones (1972):

$$\frac{b}{b_r} = \left(\frac{k}{k_r}\right)^{-0.36} \quad (28)$$

186 where the subscript r denotes a reference medium with a known b -factor and k (e.g., see Wu et al.
 187 (1988)). Additional relations implemented in T+H are described by Moridis and Freeman (2014).
 188 The use of a Klinkenberg-type b -factor to describe Knudsen flow is discussed later in this section.

189 The term \mathbf{J}_G^κ in Eq. 27 is the diffusive mass flux of component κ in the gas phase [$\text{kg}/(\text{m}^2\text{s})$].
 190 Diffusive flux is an important term for long term studies due to the ultra-low permeability typically
 191 found in HBS, and thus Knudsen diffusion is included. The term \mathbf{J}_G^κ in Eq. 27 is the diffusive mass
 192 flux of component κ in the gas phase [$\text{kg}/(\text{m}^2\text{s})$] given by

$$\mathbf{J}_G^\kappa = -\phi S_G \underbrace{\left(\phi^{1/3} S_G^{7/3}\right)}_{\tau_G} D_G^\kappa \rho_G \nabla X_G^\kappa = -\phi S_G \tau_G D_G^\kappa \rho_G \nabla X_G^\kappa, \quad \kappa = w, m \quad (29)$$

193 where D_G^κ is the multicomponent molecular diffusion coefficient of component κ in the gas phase
 194 in the absence of a porous medium [m^2s^{-1}], and τ_G is the gas tortuosity [dimensionless]. The
 195 Millington and Quirk model (Millington and Quirk, 1961) was used to compute τ_G in Equation
 196 29; additional models are discussed in Moridis and Pruess (2014). The diffusive mass fluxes of the
 197 water vapor and CH_4 gas are related through the relationship of Bird et al. (1960)

$$\mathbf{J}_G^w + \mathbf{J}_G^m = 0, \quad (30)$$

198 which ensures that the total diffusive mass flux of the gas phase is zero with respect to the mass
 199 average velocity. The total gas mass flux is the product of the Darcy velocity and density of the
 200 gas phase.

201 In the case of Knudsen flow, a Klinkenberg-type b -factor that is computed by the method
 202 of Florence et al. (2007)] and Freeman et al. (2011) is used to allow the gas flow computations
 203 described by Eq. 27:

$$\frac{b}{p_G} = (1 + \alpha_\kappa K_n) \left(1 + \frac{4K_n}{1 + K_n}\right) - 1, \quad (31)$$

204 where K_n is the Knudsen diffusion number [dimensionless] characterizing the deviation from con-
 205 tinuum flow and accounting for the effect of the mean free path of gas molecules $\bar{\lambda}$ being comparable
 206 to the pore dimensions, computed by (Freeman et al., 2011)

$$K_n = \frac{\bar{\lambda}}{r_{pore}} = \frac{\mu_G}{2.81708 \rho_G} \sqrt{\frac{\pi R T \phi}{2 k W^m}}. \quad (32)$$

207 The term α_κ in Eq. 31 is determined from Karniadakis and Beskok (2002) by

$$\alpha_\kappa = \frac{128}{15 \pi^2} \tan^{-1}(4 K_n^{0.4}). \quad (33)$$

208 The Knudsen diffusion is important in media with pores smaller than few micrometers and at low
 209 pressures. The Knudsen diffusivity D_K [m^2/s] can be computed by (Freeman et al., 2011; Civan,
 210 2008)

$$D_K = \frac{4\sqrt{k}\bar{\phi}}{2.81708} \sqrt{\frac{\pi RT}{2M}} \quad \text{or} \quad D_K = \frac{kb}{\mu_G}. \quad (34)$$

211 In hydrate-free regions near the well, the methane gas phase usually exhibits flow that is tur-
 212 bulent. In this regime, turbulent flow is accounted for using the Forchheimer equation (Forchheimer,
 213 1901; Wattenbarger and Ramey, 1968). The velocity \mathbf{v}_G is computed from the solution of the
 214 quadratic equation

$$\nabla\Phi_G = - \left(\frac{\mu_G}{k k_{rG}} \mathbf{v}_\beta + F_T \rho_\beta \mathbf{v}_\beta |\mathbf{v}_\beta| \right), \quad (35)$$

215 in which F_T is the ‘‘turbulence correction factor’’ (Katz, 1959). The solution

$$\mathbf{v}_\beta = \frac{2\nabla\Phi_\beta}{\frac{\mu_\beta}{k k_{r\beta}} + \sqrt{\left(\frac{\mu_\beta}{k k_{r\beta}}\right)^2 + 4 F_T \rho_\beta |\nabla\Phi_\beta|}} \quad (36)$$

216 is used in the equations of flow (24 and 27). There are various options to compute F_T (Moridis and
 217 Freeman, 2014).

218 The flux of components $\kappa = w, m, i$ in the aqueous phase is described by

$$\mathbf{F}_A^\kappa = X_A^\kappa \mathbf{F}_A + \mathbf{J}_A^\kappa, \quad (37)$$

219 where the diffusion term \mathbf{J}_A^κ is

$$\mathbf{J}_A^\kappa = -\phi S_A \underbrace{\left(\phi^{1/3} S_A^{7/3} \right)}_{\tau_A} D_A^\kappa \rho_A \nabla X_A^\kappa = -\phi S_A (\tau_A) D_A^\kappa \rho_A \nabla X_A^\kappa, \quad (38)$$

220 where D_A^κ is the molecular diffusion coefficient of component κ in H_2O , and τ_A is the aqueous phase
 221 tortuosity.

222 The heat flux accounts for conduction, advection, and radiative heat transfer:

$$\mathbf{F}^\theta = -\bar{k}_\theta \nabla T + \sum_{\beta=A,G} h_\beta \mathbf{F}_\beta \quad (39)$$

223 where \bar{k}_θ is the composite thermal conductivity of the medium/fluid ensemble [$\text{W}/(\text{m K})$] and h_β
 224 is the specific enthalpy of phase $\beta = A, G$ [J kg^{-1}]. Of the possible options to estimate \bar{k}_θ , the
 225 following equation (based on the laboratory studies of Kneafsey et al. (2005)) is recommended for
 226 hydrated-bearing media:

$$\bar{k}_\theta = k_{\theta d} + \left(\sqrt{S_A} + \sqrt{S_H} \right) (k_{\theta w} - k_{\theta d}) + \phi S_I k_{\theta I}. \quad (40)$$

227 Here, $k_{\theta I}$, $k_{\theta w}$, and $k_{\theta d}$ are the thermal conductivities of the ice, the water-saturated, and the dry
 228 porous medium, respectively.

229 The specific enthalpy of the gas phase is computed as

$$H_G = \sum_{\kappa=w,m} X_G^\kappa h_G^\kappa + H_{dep}, \quad (41)$$

230 where h_G^κ is the specific enthalpy of component κ in the gaseous phase and H_{dep} is the specific
 231 enthalpy departure of the gas mixture [J kg^{-1}]. The specific enthalpy of the aqueous phase is
 232 estimated from

$$H_A = X_A^w h_A^w + X_A^m (h_A^m + H_{sol}^m) + X_A^i (h_A^i + H_{sol}^i), \quad (42)$$

233 where h_A^w , h_A^m , and h_A^i are the specific enthalpies of H_2O , CH_4 , and the inhibitor at the aqueous
 234 phase conditions, respectively; and H_{sol}^m and H_{sol}^i are the specific enthalpy of dissolution [J kg^{-1}]
 235 of CH_4 and the inhibitor in the aqueous phase, respectively.

236 3.4 Fundamental equations - Sinks and sources

237 In sinks with specified mass production rate, withdrawal of the mass component κ is described by

$$\hat{q}^\kappa = \sum_{\kappa=A,G} X_\beta^\kappa q_\beta, \quad \beta = w, m \quad (43)$$

238 where q_β is the production rate of phase β [kg m^{-3}]. For source terms (well injection), the addition
 239 of a mass component κ occurs at desired rates \hat{q}^κ ($\kappa = w, m$). Inhibitor injection can occur either
 240 as a rate as an individual mass component, \hat{q}^i , or as a fraction of the aqueous phase injection rate,
 241 i.e. $\hat{q}^i = X_A^i \hat{q}_A$ where X_A^i is the injected inhibitor mass fraction.

242 In the kinetic model, the additional sink/source terms corresponding to hydrate dissociation
 243 and release of CH_4 and H_2O in each element must be accounted for. The source term for CH_4 is
 244 $\hat{q}^m = Q^m$, where the production rate Q^m [$\text{kg m}^{-3} \text{s}^{-1}$] is computed from Eq. 12 as

$$Q^m = -\frac{W^m}{W^h} Q^h. \quad (44)$$

245 Similarly, the source term for water (liquid or ice) is $\hat{q}^w + Q^w$, where the release of water Q^w is
 246 determined from the stoichiometry of Eq. 1:

$$Q^w = -\frac{N_H W^w}{W^h} Q^h. \quad (45)$$

247 Under equilibrium conditions, the rate of heat removal or addition includes contributions of
 248 fluid removal or addition as well as direct heat inputs or withdrawals q_d (e.g., microwave heating):

$$\hat{q}^\theta = q_d + \sum_{\beta=A,G} h_\beta q_\beta. \quad (46)$$

249 Under kinetic conditions, the rate of heat removal or addition is determined from

$$\hat{q}^\theta = q_d + \sum_{\beta=A,G} h_\beta q_\beta + Q^h \Delta H^0. \quad (47)$$

250 3.5 Thermophysical properties

251 Since the last published version of T+H, the thermophysical relations for methane gas hydrate
 252 have been improved by the additions described in Section 2. The thermophysical properties and
 253 parameters of the various states of water (i.e., state boundaries, density, enthalpy, viscosity, and
 254 thermal conductivity), including the transition Region II in the vicinity of the critical point, are
 255 provided by the correlations proposed by Wagner et al. (2000); International Association for the
 256 Properties of Water and Steam (IAPWS) (2012, 2011a,b, 2009, 2008, 2007). The thermal conduc-
 257 tivity of ice is computed using the heat capacity polynomial equation with the coefficients reported
 258 in Yaws (1999). The properties of the gas phase are provided by one of three cubic equations of
 259 state: (a) the Peng-Robinson equation Peng and Robinson (1976), (b) the Soave-Redlich-Kwong
 260 equation (Soave, 1972), and (c) the standard Redlich-Kwong equation (Redlich and Kwong, 1949).
 261 The Lee-Kesler method (Lee and Kesler, 1975) is used to compute the enthalpy of hydrocarbons.
 262 The gas viscosity and thermal conductivity using the high-pressure method of Chung et al. (1988)
 263 or the Friction Theory of Quiñones-Cisneros et al. (2000). Binary diffusivities are computed by the
 264 method of Fuller et al. (1969) and Riazi and Whitson (1993).

265 The hydration number N_H and the thermal properties of the CH_4 -hydrate are input functions
 266 of temperature. The hydrate density ρ_H is computed from the Ballard equation:

$$\rho_H = \left[v_0 \exp \left(\alpha_1 \Delta T + \alpha_2 \Delta T^2 + \alpha_3 \Delta T^3 + \alpha_4 \Delta P \right) \right]^{-1} \quad (48)$$

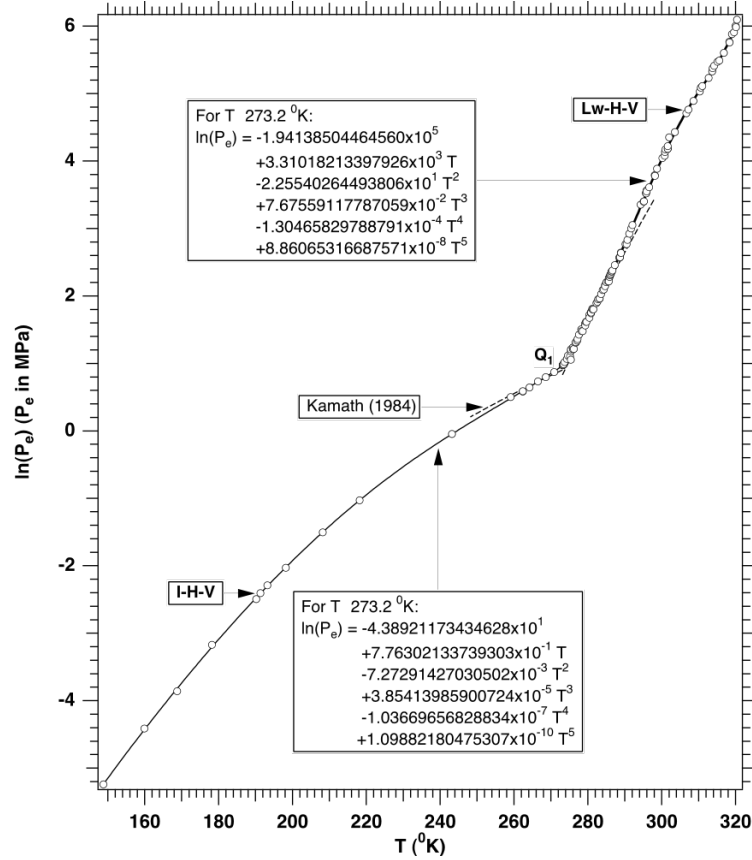


Fig. 1 CH₄-hydrate: relationship of the equilibrium hydration pressure P_e to the temperature T (Moridis, 2003)

267 (Ballard, 2002) in which the temperature change is $\Delta T = T - T_0$, the pressure change is $\Delta P =$
 268 $P - P_0$, with reference temperature $T_0 = 298.15\text{K}$, and pressure $P_0 = 10^5$ Pa; the coefficients are
 269 given by $\alpha_1 = 3.38496 \times 10^{-4} \text{K}^{-1}$, $\alpha_2 = 5.40099 \times 10^{-7} \text{K}^{-2}$, $\alpha_3 = -4.76946 \times 10^{-11} \text{K}^{-3}$, $\alpha_4 =$
 270 $1 \times 10^{-10} \text{Pa}^{-1}$, and the specific volume is $v_0 = 1000 W^m / (22.712 N_H)$ (Ballard, 2002). The specific
 271 enthalpy of the solid hydrate H_H [J/kg] is estimated from the general equation $H_H = \int_{T_{0H}}^T C_H dT$,
 272 where $T_{0H} = 273.15 \text{K}$ and $C_H = 2,100 \text{J/kg/K}$ (Ballard, 2002).

273 Of particular interest are the pressures and temperatures of the Lw-H-V and I-H-V three-
 274 phase lines in the H₂O-CH₄ diagram which delineate the limits to hydrate formation/dissociation.
 275 The relationship between the equilibrium hydration pressure P_e and the equilibrium hydration
 276 temperature T_e can be obtained from two sources. The first involves the parametric equation
 277 (Moridis, 2003) in Figure 1 which delineates the spectrum of hydrate formation/dissociation over
 278 both three-phase lines. The second is the regression equation of Kamath that is only applicable to
 279 the Lw-H-V line (Kamath, 1984).

280 There are no specific measurements of the equilibrium P - T relationship along the I-H-Lw and
 281 the I-V-Lw phase lines (see Figure 1) of a H₂O-CH₄ system, but it is considered to follow the
 282 solidus line of the water-ice system (International Association for the Properties of Water and
 283 Steam (IAPWS), 2007):

$$P = P_Q - 6.26 \times 10^5 \left(1.0 - T_d^{-3}\right) + 1.97135 \times 10^5 \left(1.0 - T_d^{21}\right) \quad (49)$$

284 where P is in Pa, $T_d = T/273.16$ [K], P_Q [Pa] is the pressure at the hydrate quadruple point (Fig.
285 1). Finally, $T = 273.16$ K and is constant along the I-V-Lw line.

286 3.6 Geomechanical dependence on ϕ and k

287 In some cases, the full solution of the geomechanics using Millstone is not necessary, and T+H
288 can use simplified relationships to adjust the porosity. As it is significantly cheaper computation-
289 ally, a scoping simulation using this simplified approach is typically run as a first pass. Multiple
290 approaches have been used. For hydrate bearing sediments, the most applicable relation describes
291 the ϕ -dependence on P in unconsolidated media that gain significant mechanical strength from the
292 presence of solid phases such as ice or hydrates (Moridis, 2014), in which

$$\phi = \phi_0 F_{PT}, \quad \text{where} \quad F_{PT} = \exp(\alpha_p \Delta P + \alpha_T \Delta T), \quad (50)$$

293 where α_T is the thermal expansivity of the porous medium [K^{-1}] and α_p is the pore compressibility
294 [Pa^{-1}], which can be either a fixed number or a function of pressure (Moridis et al., 2008, 2009,
295 2012). The factor α_p can also account for solid phases as function of $S_S = S_H + S_I$ with the
296 empirical model:

$$\alpha_p = \exp \left\{ \log \alpha_{PL} + (\log \alpha_{PU} - \log \alpha_{PL}) \left[1 - B_x(2.25, 2.25, S_S^t) \right] \right\}, \quad (51)$$

297 where

$$S_S^t = \frac{S_S - S_{min} + \delta}{S_{Smax} - S_{Smin} + 2\delta}, \quad (52)$$

298 α_{PL} is the lower limit of the medium compressibility (corresponding to the full strengthening effect
299 of cementing solid phases), α_{PU} is the upper limit of the medium compressibility (corresponding
300 to the absence of cementing phases), B_x is the incomplete beta function, S_{Smin} is the largest solid
301 saturation at which $\alpha_p = \alpha_{PU}$, S_{Smax} is the lowest solid saturation at which $\alpha_p = \alpha_{PL}$, and δ is a
302 smoothing factor. Eq. 51 is based on geomechanical and geophysical data derived from laboratory
303 and field observations. For example, this approach may be adequate in shallow stiff permafrosts.
304 In Part 2 of this series, the complete geomechanics treatment will be described, in which ϕ is
305 incrementally updated using the mechanical strain. In Part 3, T+H is run without Millstone using
306 this simplified approach to compare with the fully detailed TOUGH+Millstone simulation.

307 The ϕ - k relationship in the matrix is described by the empirical equation (Rutqvist and Tsang,
308 2002):

$$\frac{k}{k_0} = \exp \left[\gamma \left(\frac{\phi}{\phi_0} - 1 \right) \right], \quad (53)$$

309 where γ is an empirical reduction factor that ranges between 5 (for soft unconsolidated media) and
310 29 (for highly consolidated media). Note that the equations described apply to ϕ and k changes
311 when the P and T changes are small; large changes necessitate coupling with a geomechanical
312 solver, which is responsible for computing changes to ϕ as well as the geometry of the gridblock.
313 The change to the gridblock volume V_n is the dominant source for geomechanical effects.

314 3.7 Effects of solid phases and wettability

315 Hydrate behavior includes the evolution of solid phases yielding significant effects on ϕ and k . The
316 simplest model conceptualizes porous media as bundles of capillary tubes which implies a power
317 law dependence of permeability on porosity,

$$\frac{k}{k_0} = F_{\phi S} = \left(\frac{\phi}{\phi_0} \right)^n \quad (54)$$

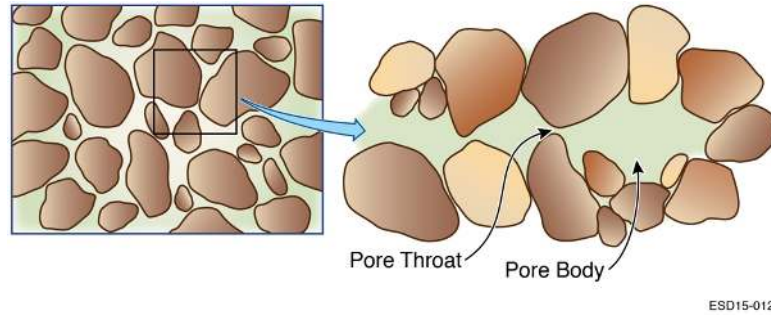


Fig. 2 Schematic of pore channels showing convergent-divergent geometry with a succession of pore throats and pore bodies

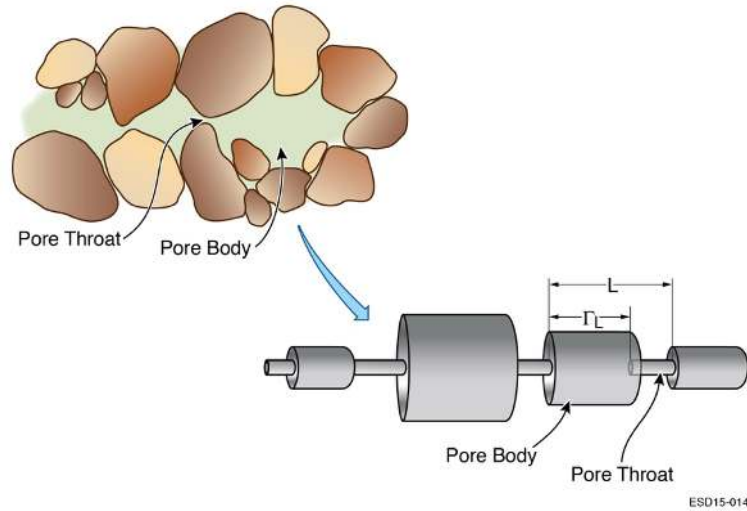


Fig. 3 Tubes-in-series model of pore channels.

318 where $F_{\phi S}$ is a *permeability adjustment factor* that describes the effects of the presence of solid
 319 phases other than the medium grains and changes in porosity on permeability, and the subscript
 320 “0” denotes properties at a solid-free reference state. Note that the effect of P and T is a separate
 321 issue. The exponent n has been reported in the range from 2 to 3 (Phillips, 1991), describing a
 322 mild dependence of k on ϕ that suggests solid phases forming at the center of the pores.

323 In media with inter-granular porosity, pore channels generally have a convergent-divergent geom-
 324 etry, as illustrated in Figure 2. If solids are deposited the pore walls or in the throats, small
 325 depositions can give rise to a dramatic decrease in k and even $k = 0$ with throat clogging (Pape
 326 et al., 1999; Xu et al., 2004; Morrow et al., 1981; Vaughan, 1987). This can be understood by the
 327 ‘tubes-in-series’ model shown in Figure 3. A non-zero ‘critical porosity’ ϕ_c is introduced resulting
 328 in the following $k - \phi$ relationship (Xu et al., 2004; Verma and Pruess, 1988):

$$\frac{k}{k_0} = F_{\phi S} = \left(\frac{\phi - \phi_c}{\phi_0 - \phi_c} \right)^n \quad (55)$$

329 This relation indicates a very strong dependence of k on ϕ , with exponents as large as $n = 10$ or
 330 more (Pape et al., 1999). The solid-phase effect on the k - ϕ relationship merits further fundamental
 331 research.

332 In multiphase flow, the effect of the interference of any phase on the flow of any other phase is
 333 represented by the phase relative permeabilities. The effective permeability k_β for phase β is given
 334 by

$$k_\beta = k k_{r\beta} \quad \text{where} \quad k = k_0 F_{\phi S} = k_{00} k_{rr} F_{\beta S} \quad (56)$$

335 and k_{rr} is the relative magnitude that relates the permeability k_0 of a given medium to k_{00} of
 336 the reference medium at the same P and T . The term k_{rr} is introduced when insufficient data
 337 is available and an analogue reference medium is needed. With the same medium as reference,
 338 $k_{rr} = 1$, and, with a different reference, $k_{rr} = k_0/k_{00}$. The factor $F_{\phi S}$ describes the effect of solid
 339 phases: $F_{\phi S} = 1$ if $S_S = 0$. Surface tension effects between phases yield capillary pressures P_{cap}
 340 which describe the difference between the wetting (aqueous) and the non-wetting (gas) phase and
 341 are dependent upon the pore size distribution (Moridis and Pruess, 2014). The models of van
 342 Genuchten (1980); Corey (1954); Stone (1970); Parker et al. (1987); Brooks and Corey (1966) are
 343 used to compute relative permeability and capillary pressure.

344 The relations between porosity, permeability, and the formation of solid phases are difficult to
 345 characterize. Multiple relations are included in T+H and selected depending on how much data
 346 is available for a given system. Formation of solid phases will alter the pore size distribution,
 347 generally reducing pore sizes and increasing capillary pressures. Without detailed information on
 348 these effects, T+H involves a phenomenological approach that relates P_{cap} to ϕ and k through the
 349 Leverett J-function (Leverett, 1941):

$$P_{cap}(S_A) = \sqrt{\frac{k_{00} \phi}{k \phi_{00}}} P_{cap,00} \quad (57)$$

350 where $P_{cap,00}$ is the capillary pressure corresponding to a reference medium at the reference con-
 351 ditions with permeability and porosity k_{00} and ϕ_{00} , respectively; and $S_S = S_H + S_I = 0$. When
 352 $S_S > 0$, the fraction of pore space available to fluid phases is $S_A + S_G$, with the constraint

$$S_A + S_G = 1 - S_S. \quad (58)$$

353 The total current porosity ϕ and the active porosity ϕ_a available to fluids are then defined as

$$\phi_a = \underbrace{(F_{pt} \phi_{rr} \phi_{00})}_{\phi} (S_A + S_G) \Rightarrow \frac{\phi_a}{\phi_{00}} = F_{pt} \phi_{rr} (S_A + S_G) = F_{pt} \phi_{rr} (1 - S_S) \quad (59)$$

354 where the term F_{pt} is the porosity adjustment factor that accounts for the effects of P and T on
 355 ϕ (obtained either from Eq. 50 or from a geomechanical model). The argument in the capillary
 356 pressure function $P_{cap,0}$ on the righthand side of Eq. 57 is the aqueous saturation S_A ; in a medium
 357 with $S_S > 0$, S_A is adjusted to the *scaled* saturation

$$S_A^* = \frac{S_A}{S_A + S_G} \quad (60)$$

358 From Eq. 56, the partitioning of k_β of phase β into separate dependencies on porosity, solid satura-
 359 tion, and fluid saturation leads to a conceptual ambiguity in the representation of k -reduction from
 360 solid deposition. Hydrate and ice formation must begin to form in the water-filled portion of the
 361 pore space, but solid crystals may grow into primarily gas-filled pores. Without further information,
 362 it is not possible to ascertain the applicability of Eqs. 55 or 56, and appropriate parameters are
 363 lacking.

364 T+H includes two proposed alternative models to describe the wettability processes ($k_{r\beta}$ and
 365 P_{cap}) in hydrate- and/or ice-bearing media (Moridis and Pruess, 2014; Moridis, 2003; Moridis et al.,
 366 2009, 2012). The ‘‘Original Porous Medium’’ (OPM) model, is based on the treatment of (a) ϕ as
 367 independent from the emergence of hydrates or ice but still dependent on P and T , (b) k_0 as
 368 independent to the evolution of the solid phases, and (c) the relative permeability for fluid flow

369 controlled by the phase saturations. The ‘‘Evolving Porous Medium’’ (EPM) models, considers the
 370 evolution of the solid phases (hydrate and ice) as creation of a new porous medium with continuously
 371 changing ϕ_0 and k_0 , whose pore space is only occupied by the aqueous and gas phases.

372 The permeability adjustment factor (Eq. 56) is computed using

$$F_{\phi_S} = k_{r\phi} k_{rS}, \quad (61)$$

373 where $k_{r\phi}$ is the permeability ϕ -factor that describes the dependence of ϕ and k_{rS} is the permeability
 374 S-factor that relates reduction in the k_0 to the presence of solid phases. In the OPM model, $k_{rS} = 1$
 375 for small changes in P , T and S_S . When ϕ changes are accounted for,

$$k_{r\phi} = \exp[\gamma(F_{PT} - 1)], \quad (62)$$

376 otherwise, $k_{r\phi} = 1$. γ and F_{PT} are as discussed in Eqs. 50 and 55. In the OPM model P_{cap} is
 377 estimated from Eq. 57, in which:

- 378 – $\phi/\phi_{00} = \phi_{rr} F_{PT}$ is computed from Eq. 50,
- 379 – $k_{00}/k = 1/k_{rr} k_{r\phi}$ is computed from Eqs. 56 and 62, and
- 380 – $P_{cap,00}$ is computed with S_A^* from Eq. 60

381 For large changes in P , T and S_S , the needed properties are calculated from the geomechanical
 382 model. The final expression for estimating the capillary pressure in the OPM model is:

$$P_{cap} = \sqrt{\frac{\phi_{rr} F_{PT}}{k_{rr} k_{r\phi}}} P_{cap,00}(S^*). \quad (63)$$

383 While there are two different EPM models in T+H, the authors recognize that a better model
 384 needs to be developed for hydrate systems using further theoretical, laboratory, and field studies.
 385 The evolving intrinsic permeability in EPM #1 Model is estimated by using (Moridis, 2014; Moridis
 386 and Pruess, 2014)

$$k_{rS} = \frac{1}{2} [k_{rA}(S_A = 1 - S_S) + k_{rG}(S_G = 1 - S_S)] \quad (64)$$

387 in Eq. 61, thus providing a simple estimate of the permeability ϕ -factor. The phase effective per-
 388 meabilities are computed using Eq. 56, in which:

- 389 – $k_{r\beta}$ is computed based on the scaled saturations from Eq. 60,
- 390 – F_{ϕ_S} is computed from Eq. 60,
- 391 – $k_{r\phi}$ is computed from Eq. 62, and k_{rS} is computed from Eq. 64.

392 The capillary pressure in the EPM #1 model is estimated using Eq. 57 using:

- 393 – ϕ_a/ϕ_{00} , computed from Eq. 59, is used instead of ϕ/ϕ_{00} ,
- 394 – $k_{00}/k = 1/k_{rr} F_{\phi_S}$ is computed from Eqs. 59 and 60,
- 395 – $k_{r\phi}$ is computed from Eq. 62, and k_{rS} is computed from Eq. 64.

396 The final expression for estimating the capillary pressure in the EPM #1 model is

$$P_{cap} = \sqrt{\frac{\phi_{rr} F_{PT} (1 - S_S)}{k_{rr} k_{r\phi} k_{rS}}} P_{cap,00}(S^*). \quad (65)$$

397 The difference between the EPM #2 and EPM #1 models is the k_{rS} estimate. In the EPM #2
 398 model, the quantity $F_{\phi_S} = k_{r\phi} k_{rS}$ in Eq. 60 is provided by Eq. 56, leading to

$$k_{rS} = \left[\frac{\phi_0(1 - S_S) - \phi_C}{\phi_0 - \phi_C} \right]^n. \quad (66)$$

399 As in the OPM case, the EPM equations are applicable to small P , T , and S_S changes, requiring
 400 the geomechanical model for large changes.

Table 1 Primary Variables in Equilibrium Hydrate Simulations without Inhibitor

| Phase | State Identifier | Primary Variable 1 | Primary Variable 2 | Primary Variable 3 |
|----------------------------|------------------|--------------------|--------------------|--------------------|
| 1- Phase: G | Gas | P_G | Y_G^m | T |
| 1- Phase: A | Aqu | P | X_A^m | T |
| 2- Phase: A+G | AqG | P_G | S_A | T |
| 2- Phase: I+G | IcG | P_G | S_I | T |
| 2- Phase: H+G | GsH | P_G | S_G | T |
| 2- Phase: A+H | AqH | P | S_A | T |
| 2- Phase: A+I | AqI | P | S_A | X_A^m |
| 2- Phase: I+H | IcH | P | S_I | T |
| 3- Phase: A+H+G | AGH | S_G | S_A | T |
| 3- Phase: A+I+G | AIG | P_G | S_A | S_G |
| 3- Phase: A+I+H | AIH | P | S_A | S_G |
| 3- Phase: I+G+H | IGH | S_G | S_I | T |
| Quadruple Point I+H+A+G | QuP | S_G | S_A | S_I |

(Note: If an inhibitor is present, X_A^i becomes the 3rd primary variable, and the 3rd becomes the 4th.)

401 4 T+H Numerical Formulation and Code Capabilities

402 4.1 States and primary variables

403 The previous section details the system of equations that define the dynamics for the multiphase,
 404 multicomponent system. Up until this point, it has not been stated *which* variables are being solved
 405 more. Due to the complex nature of these equations, it is difficult to pick good variables to describe
 406 the state of the system, especially for the many different phase combinations. Thus, we are left
 407 with a set of difficult to solve differential algebraic equations,

$$\frac{d}{dt} \int_{V_n} M^\kappa(x_n) dV = \int_{\Gamma_n} \mathbf{F}^\kappa(x_n) \cdot \mathbf{n} dA + \int_{V_n} q^\kappa(x_n) dV, \quad (67)$$

408 where x_n is the vector of primary variables for the gridblock n . It is necessary to change which
 409 system values are the primary variables in different phase combinations, as certain values that are
 410 useful in one phase cannot uniquely describe the system in another phase. The physical properties
 411 enumerated above cannot M cannot be solved for any choice of primary variables. There is no
 412 natural correspondence between any of the equations and any single one of the primary variables.

413 A total of 26 states (phase combinations) covering the entire phase diagram in Figure 1 are
 414 described in T+H. Of those, 13 correspond to the equilibrium hydration reaction option, and 13 to
 415 the kinetic hydration reaction option. The primary variables (i.e. the variables that are necessary
 416 and sufficient to uniquely define each state of the system) used for the various phase states without
 417 inhibitor are listed in Tables 1 and 2. For systems with an inhibitor, mass fraction of the inhibitor
 418 in the aqueous phase, X_A^i is an additional primary variable. The option set for both equilibrium or
 419 kinetic hydration reactions is complete, although some of the phase states are only feasible under
 420 laboratory conditions and difficult to reach during gas production from natural hydrate deposits.

421 4.2 Numerical Discretization

422 The continuum Eq. 2 is discretized in space using the integral finite difference method (IFDM) (Ed-
 423 wards, 1972; Narasimhan and Witherspoon, 1976; Narasimhan et al., 1978). The volume averages
 424 are defined by

$$\int_{V_n} M dV = V_n M_n, \quad (68)$$

Table 2 Primary Variables in Kinetic Hydrate Simulations without Inhibitor

| Phase | State Identifier | Primary Variable 1 | Primary Variable 2 | Primary Variable 3 | Primary Variable 4 |
|----------------------------|------------------|--------------------|--------------------|--------------------|--------------------|
| 1- Phase: G | Gas | P_G | Y_G^m | S_H | T |
| 1- Phase: A | Aqu | P | X_A^m | S_H | T |
| 2- Phase: A+G | AqG | P_G | S_A | S_H | T |
| 2- Phase: I+G | IcG | P_G | S_I | S_H | T |
| 2- Phase: H+G | GsH | P_G | S_A | S_I | T |
| 2- Phase: A+H | AqH | P | S_A | X_A^m | T |
| 2- Phase: A+I | AqI | P | S_A | X_A^m | T |
| 2- Phase: I+H | IcH | P | S_I | S_G | T |
| 3- Phase: A+H+G | AGH | P_G | S_A | S_G | T |
| 3- Phase: A+I+G | AIG | P_G | S_A | S_H | S_G |
| 3- Phase: A+I+H | AIH | P | S_A | S_I | T |
| 3- Phase: I+G+H | IGH | P_G | S_G | S_I | T |
| Quadruple Point I+H+A+G | QuP | P_G | S_A | S_G | S_I |

(Note: If an inhibitor is present, X_A^i becomes the 4th primary variable, and the 4th primary variable (listed in this table) becomes the 5th primary variable.)

425 where M is a volume-normalized extensive quantity, and M_n is the average value of M over a
 426 volume V_n . Surface integrals are approximated as a discrete sum of averages over surface segments
 427 A_{nm} :

$$\int_{\Gamma_n} \mathbf{F}^k \cdot \mathbf{nd}\Gamma = \sum_m A_{nm} F_{nm}. \quad (69)$$

428 Here F_{nm} is the average value of the (inward) normal component of \mathbf{F} over the surface segment
 429 A_{nm} between volumes V_n and V_m . The discretization is illustrated in Figure 4. The discretized flux
 430 is expressed in terms of (a) the upstream mobility λ_{nm} evaluated at the facets of the elements and
 431 (b) the pressures at the center of the elements V_n and V_m . The mobile values are upstream-weighted
 432 where necessary. For the basic Darcy flux term in Eq. 24, we have

$$F_{\beta,nm} = - \underbrace{k_{nm} \left[\frac{k_{r\beta} \rho_\beta}{\mu_\beta} \right]}_{\lambda_{nm}} \left[\frac{P_{\beta,n} - P_{\beta,m}}{D_{nm}} - (\rho_\beta g)_{nm} \right] \quad (70)$$

433 where the subscripts (nm) denote a suitable averaging at the interface between grid blocks n and m
 434 (e.g. interpolation, harmonic weighting, or upstream weighting). $D_{nm} = D_n + D_m$ is the distance
 435 between the nodal points n and m , and g_{nm} is the component of gravitational acceleration in the
 436 direction from m to n . The term in the underbrace λ_{nm} is upstream weighted to be evaluated at
 437 the center of the facet.

438 Substitution of the discrete surface and volume integrals into the formulation yields a set of
 439 first-order ordinary differential equations describing the mass balance of component κ and the heat
 440 balance (θ) in time:

$$\frac{dM_n^\eta}{dt} = \frac{1}{V_n} \sum_m A_{nm} F_{nm}^\eta + q_m^\eta; \quad \eta = \kappa, \theta. \quad (71)$$

441 The time derivatives are approximated using the backward Euler method that is first-order accurate
 442 and L-stable. The following set of coupled non-linear, algebraic equations for residuals R_n^η result
 443 from including the temporal discretization:

$$R_n^{\kappa,k+1} = M_n^{\kappa,k+1} - M_n^{\kappa,k} - \frac{\Delta t}{V_n} \left(\sum_m A_{nm} F_{nm}^{\kappa,k+1} + V_n q_n^{\kappa,k+1} \right) = 0. \quad (72)$$

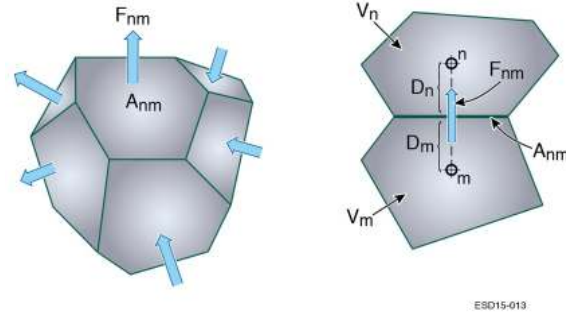


Fig. 4 Illustration of the connected volumes mesh for the IFDM.

444 For each volume V_n , there are N_η equations, so that for a system discretized into N_E grid blocks
 445 there are $N_\eta \times N_E$ coupled non-linear equations. Eq. 72 is solved fully implicitly for each gridblock's
 446 primary variables x_n , with all parameters, fluxes, and sink and source terms evaluated at t_{k+1} .

447 4.3 Solution of Discretized Equations

448 The unknowns are the $N_\eta \times N_E$ independent primary variables $\{x_i; i = 1, \dots, N_\eta N_E\}$ which com-
 449 pletely define the state of the flow system at t_{k+1} . These equations are solved by the Newton-
 450 Raphson method, the iterations of which are indexed by p . Expanding Eq. 72 at iteration step $p+1$
 451 in a Taylor series in terms of the properties and conditions at index p yields

$$R_n^{\eta, k+1}(x_{i, p+1}) = R_n^{\eta, k+1}(x_{i, p}) + \sum_i \left[\frac{\partial R_n^{\eta, k+1}}{\partial x_i} \right]_p (x_{i, p+1} - x_{i, p}) \quad (73)$$

452 In T+H, all terms $\partial R_n / \partial x_i$ in the Jacobian matrix of Eq. 65 are evaluated by numerical differen-
 453 tiation. Iteration is continued until the residuals are reduced below a preset convergence tolerance:

$$\left| \frac{R_{n, p+1}^{\eta, k+1}}{M_{n, p+1}^{\eta, k+1}} \right| \leq \epsilon_1. \quad (74)$$

454 The default relative convergence criterion is $\epsilon_1 = 10^{-5}$. When the accumulation terms are smaller
 455 than ϵ_1 , the following absolute convergence criterion (with a default value of $\epsilon_2 = 1$) is imposed:

$$\left| R_{n, p+1}^{\eta, k+1} \right| \leq \epsilon_1 \epsilon_2. \quad (75)$$

456 5 Implementation

457 T+H (Moridis, 2014; Moridis and Pruess, 2014) is written in object oriented FORTRAN 2003 with
 458 cross-platform portability. The solution of the Jacobian matrix has been improved by including the
 459 the LIS (Nishida, 2010) and PETSc (Balay et al., 2014) matrix solvers. The simulations described
 460 in this series were primarily solved using LIS's stabilized Biconjugate gradient Krylov solver with an
 461 incomplete LU decomposition preconditioner, which has been determined to be the best option for
 462 the non-symmetric, non-positive-definite Jacobian matrices that arise from the numerical methods
 463 described.

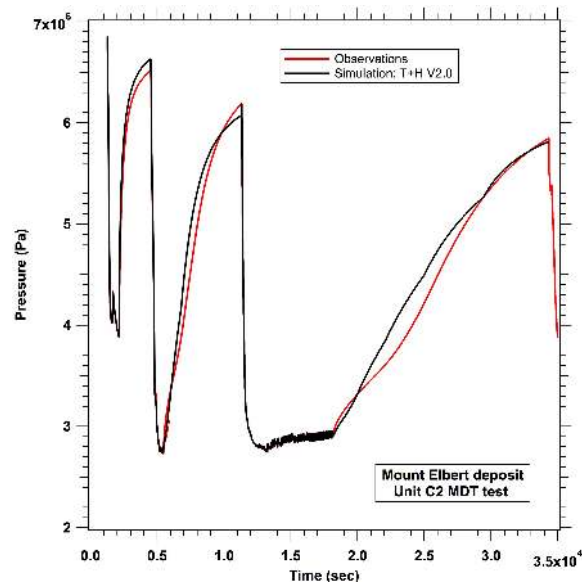


Fig. 5 Experimental results duplicated from Anderson et al. (2008)

464 6 Validation and Verification

465 Because the hydration reaction in porous media is complex, involving several coupled (physical,
 466 chemical and thermodynamic) strongly non-linear processes, there are no analytical solutions of
 467 benchmark problems. Validation and verification is thus achieved through comparisons to labora-
 468 tory and field studies and to results obtained by previously validated simulators.

469 The previously validated T+H V1.0 was used for comparison. The first verification problem
 470 involved the analysis of a short-term field test of depressurization-induced hydrate dissociation
 471 that had been conducted in February of 2007 at the the Mount Elbert location in North Slope,
 472 Alaska. The collected data from the well were used in a code comparison study that was conducted
 473 by several different teams and involved T+H V1.0 and other hydrate codes. The reservoir properties
 474 and conditions and specifics of the code comparison study are documented in Anderson et al. (2008,
 475 2011). Figure 5 shows a comparison between measurements and optimized numerical predictions
 476 that involve optimized parameters determined through the history matching process that had been
 477 followed in Anderson et al. (2008). The simulated pressure response using T+H V2.0 is very close
 478 to the field observations, and practically identical to the T+H V1.0 results (Anderson et al. (2008),
 479 Figure A5), from which they differ only in the 4th decimal place and beyond, with the newest
 480 simulation executed about twice as fast.

481 The second verification problem involves the description of lab-scale gas production tests using
 482 natural cores of hydrate-bearing media undergoing depressurization-inducing dissociation. These
 483 laboratory tests were conducted by Kneafsey and Moridis (2014) under tightly controlled conditions
 484 that included independent testing of the core media properties and X-ray computed tomography
 485 (CT) to examine the gas hydrate-bearing sediment structure and the spatial distribution of the
 486 hydrate saturation. In the original study, the simulations were conducted using T+H V1.0 and V1.2,
 487 and led to the determination of the porosity and hydrate saturation in the two core subdomains
 488 identified through analysis of the CT scans. Figure 6 shows a comparison of the amount of the
 489 released gas measured to both the older (T+H v1.0 and v1.2) and the newer (T+H v2.0) results
 490 obtained with the optimized parameters. The numerical predictions are practically identical, with
 491 T+H v2.0 executing about twice as fast.

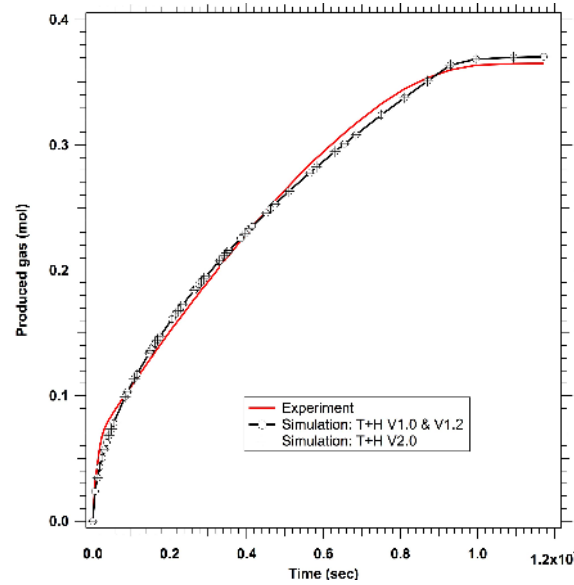


Fig. 6 Experimental results from Kneafsey and Moridis (2014).

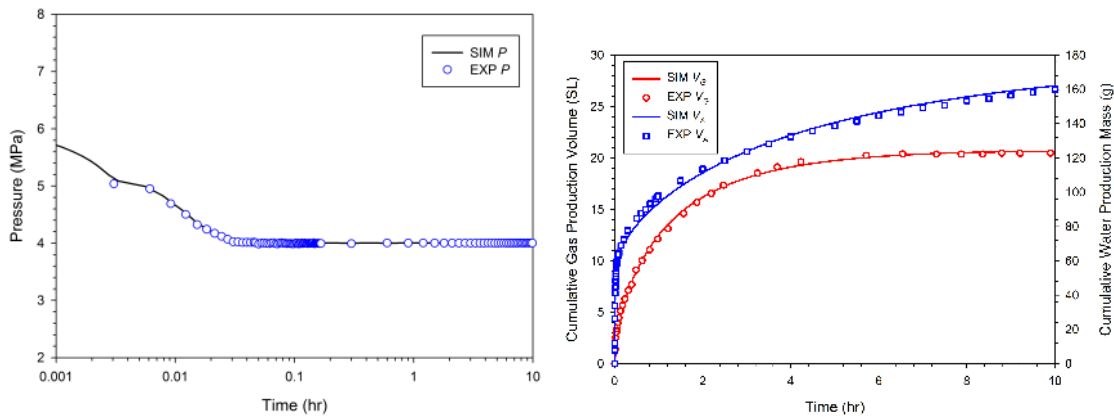


Fig. 7 Experimental results from Yin et al. (2018a,b).

492 The third verification problem describes the dissociation of a laboratory-created hydrate-bearing
 493 sand core. The formation is performed by the multi-step process described in detail by Yin et al.
 494 (2018a). The ensuing dissociation test was depressurization-driven, and is described in minute detail
 495 in Yin et al. (2018b). The dissociation process was reproduced numerically and fully analyzed
 496 using T+H v2.0 in a process involving inverse modeling (via history-matching) to determine the
 497 optimal values of key properties and parameters. The right of Figure 7 shows an excellent agreement
 498 between the measurements and the predictions of the produced volumes of gas and water during
 499 the dissociation experiments. The same excellent agreement between measurements and numerical
 500 predictions is observed in the evolution of pressure in the left of Figure 7. Note that because of the
 501 limited duration of the laboratory experiments (Kowalsky and Moridis, 2007), the simulations in
 502 the second and third verification problem were conducted using kinetic (as opposed to equilibrium)
 503 dissociation conditions.

504 7 Summary

505 In this series, we document the development and use of the TOUGH+Millstone simulator, which
506 involves a coupling of the fully implicit TOUGH+HYDRATE v2.0 (T+H) simulator, describing
507 flow, thermal, and chemical processes in hydrate-bearing media, with the Millstone v1.0 geome-
508 chanical model to describe the corresponding geomechanical response. In the first paper of this
509 series, we discuss the T+H V2.0 simulator, a numerical simulator designed to describe the flow and
510 thermal behavior of hydrate-bearing geologic media and a significant expansion of earlier versions.
511 In the absence of analytical solutions for hydrate systems, the verification process of the T+H
512 V2.0 code involves comparisons to numerical results from older versions of the code that had been
513 used in code comparison studies (against other codes) and in the analysis of laboratory studies
514 under tightly controlled conditions. In the second part of this series we describe Millstone v1.0, a
515 new geomechanical framework that is the second component of the TOUGH+Millstone simulator.
516 The combined simulator is applied to a real-world production analysis of a multilayered hydrate
517 reservoir in the third and final part of the series.

518 Acknowledgments

519 This work was supported by the Assistant Secretary for Fossil Energy, Office of Natural Gas and
520 Petroleum Technology, through the National Energy Technology Laboratory, under the U.S. De-
521 partment of Energy, Contract No. DE-AC03-76SF00098, and also through a funded collaboration
522 with Chevron.

523 References

- 524 K. A. Kvenvolden, Methane hydrate—a major reservoir of carbon in the shallow geosphere, *Geo*
525 *Chem* 71 (1988) 41–51.
- 526 E. D. Sloan, C. Koh, *Clathrate Hydrates of Natural Gases*, Taylor and Francis, Inc., Boca Raton,
527 FL, 3rd edition edition, 2008.
- 528 G. J. Moridis, M. B. Kowalsky, K. Pruess, TOUGH+HYDRATE v1.0 User’s Manual: A Code
529 for the Simulation of System Behavior in Hydrate-Bearing Geologic Media, Technical Report
530 LBNL-0149E, Lawrence Berkeley National Laboratory, 2008.
- 531 G. J. Moridis, J. A. Apps, K. Pruess, L. Myer, EOSHYDR: A TOUGH2 Module for CH₄-Hydrate
532 Release and Flow in the Subsurface, Technical Report LBNL-42386, Lawrence Berkeley National
533 Laboratory, 1998.
- 534 G. J. Moridis, Numerical studies of gas production from methane hydrates, *SPE Journal* 32 (2003)
535 359–370.
- 536 G. J. Moridis, T. Collett, Gas production from class 1 hydrate accumulations (section i, chapter
537 6), in: C. Taylor, J. Qwan (Eds.), *Recent Advances in the Study of Gas Hydrates*, Kluwer
538 Academic/Plenum Publishers, 2004, pp. 75–88.
- 539 G. J. Moridis, T. Collett, S. Dallimore, T. Satoh, S. Hancock, B. Weatherhill, Numerical studies of
540 gas production from several methane hydrate zones at the mallik site, mackenzie delta, canada,
541 *Journal of Petroleum Science and Engineering* 43 (2004) 219–239.
- 542 G. J. Moridis, M. B. Kowalsky, K. Pruess, TOUGH-Fx/HYDRATE v1.1 User’s Manual: A Code
543 for the Simulation of System Behavior in Hydrate-Bearing Geologic Media, Technical Report
544 LBNL-58950, Lawrence Berkeley National Laboratory, 2005.
- 545 H. C. Kim, P. R. Bishnoi, R. A. Heideman, S. S. H. Rizvi, Kinetics of methane hydrate decompo-
546 sition, *Chem Eng. Sci* 42 (1987) 1645–1653.
- 547 M. Clarke, P. R. Bishnoi, Determination of activation energy and intrinsic rate constant of methane
548 gas hydrate decomposition, *Can. J. of Chem. Eng.* 79 (2001) 143–147.

- 549 G. J. Moridis, M. Kowalsky, K. Pruess, Depressurization-induced gas production from class 1
550 hydrate deposits, *SPE Reservoir Evaluation and Engineering* 10 (2008) 458–488.
- 551 G. J. Moridis, K. Pruess, User’s Manual of the TOUGH+ v1.5 Core Code: A General Purpose Sim-
552 ulator of Non-Isothermal Flow and Transport Through Porous and Fractured Media, Technical
553 Report LBNL-6869E, Lawrence Berkeley National Laboratory, 2014.
- 554 A. Nishida, Experience in developing an open source scalable software infrastructure in japan, in:
555 Computational Science and Its Applications - ICCSA 2010. Lecture Notes in Computer Science
556 6017.
- 557 G. J. Moridis, M. B. Kowalsky, K. Pruess, Depressurization-induced gas production from class 1
558 hydrate deposits, *SPE Reservoir Evaluation and Engineering* 10 (2008) 458–488.
- 559 G. J. Moridis, M. T. Reagan, Gas production from oceanic class 2 hydrate accumulations, in:
560 Offshore Technology Conference, Houston, Texas.
- 561 G. J. Moridis, M. T. Reagan, Estimating the upper limit of gas production from class 2 hydrate
562 accumulations in the permafrost, 1: Concepts, system description and the production base case,
563 *J. Petr. Sci. Eng.* (2010a) 194–201.
- 564 G. J. Moridis, M. T. Reagan, Estimating the upper limit of gas production from class 2 hydrate
565 accumulations in the permafrost, 2: Alternative well designs and sensitivity analysis, *J. Petr.*
566 *Sci. Eng.* 76 (2010b) 124–137.
- 567 G. J. Moridis, J. Kim, M. T. Reagan, S. j. Kim, Feasibility of gas production from a gas hydrate
568 accumulation at the ubgh2-6 site of the ulleung basin in the korean east sea, *Journal of Petroleum*
569 *Science and Engineering* 108 (2013) 180–210.
- 570 M. T. Reagan, G. J. Moridis, J. N. Johnson, L. Pan, C. M. Freeman, K. L. Boyle, N. D. Keen,
571 J. Husebo, Field-Scale Simulation of Production from Oceanic Gas Hydrate Deposits, *Transport*
572 *In Porous Media*, In Press, 2014.
- 573 G. J. Moridis, M. T. Reagan, Strategies for gas production from oceanic class 3 hydrate accumu-
574 lations, in: Offshore Technology Conference, Houston, Texas.
- 575 G. J. Moridis, S. Silpngarmert, M. T. Reagan, T. Collett, K. Zhang, Gas production from a cold,
576 stratigraphically bounded hydrate deposit at the mount elbert site, north slope, alaska, *J. Marine*
577 *Petr. Geol.* 28 (2011) 517–534.
- 578 G. J. Moridis, E. D. Sloan, Gas production potential of disperse low-saturation hydrate accumula-
579 tions in oceanic sediments, *J. of Energy Conversion and Management* 48 (2007) 1834–1849.
- 580 G. Li, G. J. Moridis, K. Zhang, X. s. Li, Evaluation of gas production potential from marine gas
581 hydrate deposits in shenhu area of the south china sea, *Energy & Fuels* 24 (2010) 6018–6033.
- 582 G. J. Moridis, M. T. Reagan, K. L. Boyle, K. Zhang, Evaluation of the gas production potential
583 of challenging hydrate deposits, *Transport in Porous Media* 90 (2011) 269–299.
- 584 G. J. Moridis, User’s Manual for the HYDRATE v1.5 option of TOUGH+ v1.5: A Code for the
585 Simulation of System Behavior in Hydrate-Bearing Geologic Media, Technical Report LBNL-
586 6871E, Lawrence Berkeley National Laboratory, 2014.
- 587 K. Pruess, C. Oldenburg, G. Moridis, TOUGH2 User’s Guide, Version 2.0, Technical Report LBNL-
588 43134, Lawrence Berkeley National Laboratory, 1999.
- 589 K. Pruess, C. Oldenburg, G. Moridis, TOUGH2 User’s Guide, Version 2.1, Technical Report LBNL-
590 43134, Lawrence Berkeley National Laboratory, 2012.
- 591 G. J. Moridis, C. M. Freeman, User’s Manual for the REALGASBRINE v1.0 option of TOUGH+:
592 A Code for the Simulation of System Behavior in Gas-Bearing Geologic Media, Technical Report
593 LBNL-6870E, Lawrence Berkeley National Laboratory, 2014.
- 594 L. J. Klinkenberg, The permeability of porous media to liquids and gases, in: *Api Drilling and*
595 *Production Practice*, 1941, pp. 200–213.
- 596 S. C. Jones, A rapid accurate unsteady-state klinkenberg parameter, *SPE Journal* (1972) 383–397.
- 597 Y. Wu, K. Pruess, P. Persoff, Gas flow in porous media with klinkenberg effects, *Transp. Porous*
598 *Media* 32 (1988) 117–137.

- 599 R. J. Millington, J. P. Quirk, Permeability of porous solids, *Trans. Faraday Soc.* 57 (1961) 1200–
600 1207.
- 601 R. B. Bird, W. E. Stewart, E. N. Lightfoot, *Transport Phenomena*, John Wiley & Sons, Inc, New
602 York, 1960.
- 603 F. A. Florence, J. A. Rushing, K. E. Newsham, T. A. Blasingame, Improved permeability pre-
604 diction relations for low-permeability sands, in: *SPE Rocky Mountain Oil and Gas Technology*
605 *Symposium*, Denver, Colorado.
- 606 C. M. Freeman, G. J. Moridis, T. A. Blasingame, A numerical study of microscale flow behavior
607 in tight gas and shale gas reservoir systems, *Transp. in Porous Media* 90 (2011) 253–268.
- 608 G. E. M. Karniadakis, A. Beskok, *Micro Flows: Fundamentals and Simulation*, Springer, New York,
609 London, 2002.
- 610 F. Civan, Effective correlation of apparent gas permeability in tight porous media, *Transp. in*
611 *Porous Med* 83 (2008) 375–384.
- 612 P. Forchheimer, *Wasserbewegung durch boden*, *ZVDI* 45 (1901) 1781.
- 613 R. A. Wattenbarger, H. J. Ramey, Gas well testing with turbulence, damage and wellbore storage,
614 *SPE* 1835, *J. Pet. Tech.* (1968) 877–884.
- 615 D. L. e. a. Katz, *Handbook of Natural Gas Engineering*, McGraw-Hill, New York, 1959.
- 616 T. Kneafsey, L. Tomutsa, G. J. Moridis, Y. Seol, B. Freifeld, C. E. Taylor, A. Gupta, Methane
617 hydrate formation and dissociation in partially saturated sand – measurements and observations,
618 in: *5th International Conference on Gas Hydrates*, Trondheim, Norway, pp. 213–220.
- 619 W. Wagner, J. R. Cooper, A. Dittmann, J. Kijima, H. j. Kretzschmar, A. Kruse, R. Mareš,
620 K. Oguchi, H. Sato, I. Stöcker, O. Šifner, Y. Takaishi, I. Tanishita, J. Trübenbach, T. Willkom-
621 men, The iapws industrial formulation 1997 for the thermodynamic properties of water and
622 steam, *ASME J. Eng. Gas Turbines and Power* 122 (2000) 150–182.
- 623 International Association for the Properties of Water and Steam (IAPWS), *Guideline on a Low-*
624 *Temperature Extension of the IAPWS-95 Formulation for Water Vapor*, Boulder, Colorado, 2012.
- 625 International Association for the Properties of Water and Steam (IAPWS), *Revised Release on the*
626 *Pressure along the Melting and Sublimation Curves of Ordinary Water Substance*, Plzeň, Czech
627 Republic, 2011a.
- 628 International Association for the Properties of Water and Steam (IAPWS), *Release on the IAPWS*
629 *Formulation 2011 for the Thermal Conductivity of Ordinary Water Substance*, Plzeň, Czech
630 Republic, 2011b.
- 631 International Association for the Properties of Water and Steam (IAPWS), *Revised Release on the*
632 *Equation of State 2006 for H₂O Ice Ih*, Doorwerth, The Netherlands, 2009.
- 633 International Association for the Properties of Water and Steam (IAPWS), *Release on the IAPWS*
634 *Formulation 2008 for the Viscosity of Ordinary Water Substance*, Berlin, Germany, 2008.
- 635 International Association for the Properties of Water and Steam (IAPWS), *Revised Release on the*
636 *IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam*,
637 Lucerne, Switzerland, 2007.
- 638 C. Yaws, *Chemical Properties Handbook*, McGraw-Hill Education, 1999.
- 639 D. Y. Peng, D. B. Robinson, A new two-constant equation of state, *Indust. and Engr. Chemistry:*
640 *Fundamentals* 15 (1976) 59–64.
- 641 G. Soave, Equilibrium constants from a modified redlich–kwong equation of state, *Chem. Eng. Sci.*
642 27 (1972) 1197–1203.
- 643 O. Redlich, J. N. S. Kwong, On the thermodynamics of solutions, *Chem. Rev.* 44 (1949) 1.
- 644 B. L. Lee, M. G. Kesler, A generalized thermodynamic correlation based on three-parameter
645 corresponding states, *AIChE Journal* 21 (1975) 510–527.
- 646 T. H. Chung, M. Ajlan, L. L. Lee, K. E. Starling, Generalized multiparameter correlation for
647 nonpolar and polar fluid transport properties, *Ind. Eng. Chem. Res.* 27 (1988) 671–679.
- 648 S. E. Quiñones-Cisneros, C. K. Zéberg-Mikkelsen, E. H. Stenby, The friction theory (f-theory) for
649 viscosity modeling, *Fluid Phase Equilib.* 169 (2000) 249–276.

- 650 E. N. Fuller, K. Ensley, J. C. Giddings, Diffusion of halogenated hydrocarbons in helium: The
651 effect of structure on collision cross sections, *J. Phys. Chem.* 73 (1969) 3679–3685.
- 652 M. R. Riazi, C. H. Whitson, Estimating diffusion coefficients of dense fluids, *Ind. Eng. Chem. Res.*
653 32 (1993) 3081–3088.
- 654 A. L. Ballard, A Non-Ideal Hydrate Solid Solution Model for a Multi-Phase Equilibria Program,
655 Ph.D. thesis, Colorado School of Mines, 2002.
- 656 V. A. Kamath, Study of heat transfer characteristics during dissociation of gas hydrates in porous
657 media, Ph.D. thesis, Univ. of Pittsburgh, 1984.
- 658 G. J. Moridis, M. B. Kowalsky, K. Pruess, tough+hydrate v1.1 User’s Manual: A Code for the
659 Simulation of System Behavior in Hydrate-Bearing Geologic Media, Technical Report LBNL-
660 0149E, Lawrence Berkeley National Laboratory, 2009.
- 661 G. J. Moridis, M. B. Kowalsky, K. Pruess, Tough+hydrate v1.2 User’s Manual: A Code for the
662 Simulation of System Behavior in Hydrate-Bearing Geologic Media, Technical Report LBNL-
663 0149E, Lawrence Berkeley National Laboratory, 2012.
- 664 J. Rutqvist, C. Tsang, A study of caprock hydromechanical changes associated with co2 injection
665 into a brine aquifer, *Environmental Geology* 42 (2002) 296–305.
- 666 O. M. Phillips, *Flow and Reactions in Permeable Rocks*, Cambridge University Press, Cambridge,
667 New York, Melbourne, 1991.
- 668 H. Pape, C. Clauser, J. Iffland, Permeability prediction based on fractal pore-space geometry,
669 *Geophysics* 64 (1999) 1447–1460.
- 670 T. Xu, Y. Ontoy, P. Molling, N. Spycher, M. Parini, K. Pruess, Reactive transport modeling of
671 injection well scaling and acidizing at tiwi field, philippines, *Geothermics* 33 (2004) 477–491.
- 672 C. Morrow, D. Lockner, D. Moore, J. Byerlee, Permeability of granite in a temperature gradient,
673 *Journal of Geophysical Research* 86 (1981) 3002–3008.
- 674 P. J. Vaughan, Analysis of permeability reduction during flow of heated, aqueous fluid through
675 westerly granite, in: C. F. Tsang (Ed.), *Coupled Processes Associated with Nuclear Waste*
676 *Repositories*, Academic Press, New York, 1987, pp. 529–539.
- 677 A. Verma, K. Pruess, Thermohydrologic conditions and silica redistribution near high-level nuclear
678 wastes emplaced in saturated geological formations, *J. of Geophys. Res.* 93 (1988) 1159–1173.
- 679 M. van Genuchten, A closed-form equation for predicting the hydraulic conductivity of unsaturated
680 soils, *Soil Sci. Soc.* (1980) 892 – 898.
- 681 A. T. Corey, The interrelation between gas and oil relative permeabilities, *Producers Monthly*
682 (1954) 38–41.
- 683 H. L. Stone, Probability model for estimating three-phase relative permeability, *Trans. SPE of*
684 *AIME* 249 (1970) 214–218.
- 685 J. C. Parker, R. J. Lenhard, T. Kuppusamy, A parametric model for constitutive properties gov-
686 erning multiphase flow in porous media, *Water Resour. Res.* 23 (1987) 618–624.
- 687 R. H. Brooks, A. T. Corey, Properties of porous media affecting fluid flow, *ASCE J. Irrig. Drain*
688 *Div.* 6 (1966) 61.
- 689 M. C. Leverett, Capillary behavior in porous solids, *Trans. Soc. Pet. Eng. AIME* 142 (1941)
690 152–169.
- 691 A. L. Edwards, TRUMP: A Computer Program for Transient and Steady State Temperature Distri-
692 butions in Multidimensional Systems,, Technical Report, National Technical Information Service,
693 National Bureau of Standards, Springfield, VA, 1972.
- 694 T. N. Narasimhan, P. A. Witherspoon, An integrated finite difference method for analyzing fluid
695 flow in porous media, *Water Resour. Res.* 12 (1976) 57 – 64.
- 696 T. N. Narasimhan, P. A. Witherspoon, A. L. Edwards, Numerical model for saturated-unsaturated
697 flow in deformable porous media, part 2: The algorithm, *Water Resour. Res.* 14 (1978) 255–261.
- 698 S. Balay, S. Abhyankar, M. F. Adams, J. Brown, P. Brune, K. Buschelman, V. Eijkhout, W. D.
699 Gropp, D. Kaushik, M. G. Knepley, L. C. McInnes, K. Rupp, B. F. Smith, H. Zhang, PETSc
700 Web page, <http://www.mcs.anl.gov/petsc>, 2014.

- 701 B. J. Anderson, J. W. Wilder, M. Kurihara, M. D. White, G. J. Moridis, S. J. Wilson, M. Pooladi-
702 Darvish, Y. Masuda, T. S. Collett, R. Hunter, et al., Analysis of modular dynamic formation test
703 results from the mount elbert 01 stratigraphic test well, milne point unit, north slope, alaska,
704 British Columbia, Canada (2008).
- 705 B. J. Anderson, M. Kurihara, M. D. White, G. J. Moridis, S. J. Wilson, M. Pooladi-Darvish,
706 M. Gaddipati, Y. Masuda, T. S. Collett, R. B. Hunter, et al., Regional long-term production
707 modeling from a single well test, mount elbert gas hydrate stratigraphic test well, alaska north
708 slope, *Marine and petroleum geology* 28 (2011) 493–501.
- 709 T. J. Kneafsey, G. J. Moridis, X-ray computed tomography examination and comparison of gas
710 hydrate dissociation in nghp-01 expedition (india) and mount elbert (alaska) sediment cores:
711 Experimental observations and numerical modeling, *Marine and Petroleum Geology* 58 (2014)
712 526–539.
- 713 Z. Yin, G. Moridis, H. K. Tan, P. Linga, Numerical analysis of experimental studies of methane
714 hydrate formation in a sandy porous medium, *Applied Energy* 220 (2018a) 681–704.
- 715 Z. Yin, G. Moridis, Z. R. Chong, H. K. Tan, P. Linga, Numerical analysis of experimental studies
716 of methane hydrate dissociation induced by depressurization in a sandy porous medium, *Applied*
717 *Energy* 230 (2018b) 444–459.
- 718 M. B. Kowalsky, G. J. Moridis, Comparison of kinetic and equilibrium reactions in simulating the
719 behavior of gas hydrates, *Energy Conversion and Management* 48 (2007) 1850. (LBNL-63357).

