Auxiliary Material for

Thermodynamic and hydrodynamic constraints on overpressure caused by hydrate dissociation: a pore-scale model

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Assumption of isothermal dissociation

Here, we justify the simplifying assumption of isothermal hydrate dissociation. We show that the effect of the latent heat of hydrate dissociation on the dissociation rate and hence on the pressure evolution is, for our model system, secondary to that of multiphase flow.

Our model represents the following scenario: a small sample is subjected to rapid heating (raising the temperature from T_0 to $T_0 + \Delta T$), for instance by advection of warm fluids within the sediment pores or due to the nearby presence of a hot wellbore. We make two major assumptions related to heat transfer: (a) the initial conditions in our simulations are uniform temperature ($T_0 + \Delta T$) within the sample, such that the entire sample is brought out of equilibrium at $t = 0$; and (b) throughout the simulations, we neglect the inhibiting effect of the latent heat of dissociation on the dissociation rate. Endothermic hydrate dissociation absorbs heat and thus reduces the dissociation rate, which in turn will affect the pressure evolution. However, as we demonstrate here, the small effect of the latent heat on the temperature and hence on the reaction rate relative to that of an external thermal stimulation justifies these assumptions.

To quantify the effect of the latent heat on the temperature distribution we compare the following two characteristic timescales: (1) timescale for heat propagation across the sample, t_{heat}; and (2) timescale for dissociation to cause a sufficiently large perturbation in the temperature field, t_{diss}. We use the conventional assumption that heat transport in fine sediments and relatively low temperatures is dominated by conduction (*Cortes et al.*, 2004). The time required for the dissipation of a temperature perturbation within the sample is

$$t_{\text{heat}} \sim L^2/\kappa, \tag{1}$$

where L is the sample size and κ is its composite (effective) thermal diffusivity.

To evaluate the time required to perturb the temperature by dissociating a sufficient mass of hydrate, t_{diss}, we compute the temperature drop (effective value, uniform throughout the sample) due to the dissociation,

$$\Delta T_{\text{diss}} = Q_{\text{diss}}^e/(c_b \rho_b), \tag{2}$$

where $Q_{\text{diss}}^e = \Delta H_{\text{diss}} m_{\text{diss}}/V_b$ is the evolved heat per unit volume of bulk sediment, c_b and ρ_b are the specific heat and density of the bulk sediment, ΔH_{diss} is the latent heat of dissociation, and V_b is the total (bulk) sample volume. The cumulative dissociated hydrate mass at time $t = t_{\text{diss}}$ (since the application of ΔT at $t = 0$) is $m_{\text{diss}} = (dm_h/dt)t_{\text{diss}}N_c$, where N_c is the number of hydrate crystals
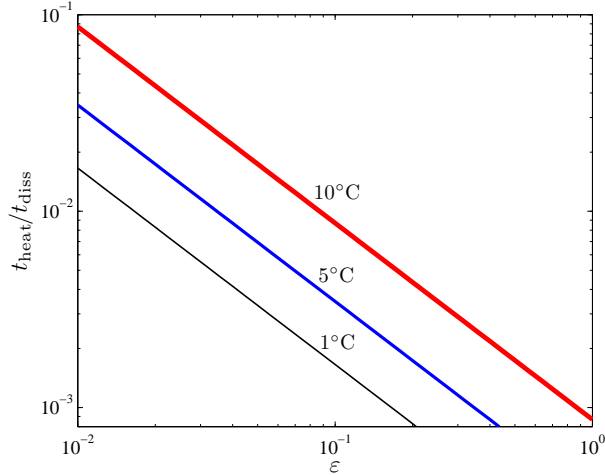
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Figure 1: Comparison between the timescale of heat propagation, t_{heat}, and that required for dissociation to perturb the temperature (by $\varepsilon\Delta T$), t_{diss}. Each line corresponds to a different thermal stimulation (initial temperature rise at the boundaries, ΔT). Due to the low kinetic rate of hydrate dissociation, the perturbation caused by latent heat of dissociation during t_{heat} is small; for instance, the time required to dissociate sufficient hydrate mass to perturb the temperature by $0.1°C$ ($1/100$ of a temperature rise of $\Delta T = 10°C$) is ~ 10 times larger than t_{heat}. The effect of the latent heat of dissociation decreases with decreasing thermal stimulation (ΔT). The small inhibiting effect of the latent heat on the dissociation rate allows us to assume an initially uniform temperature and simulate isothermal dissociation, excluding heat transfer effects.

in the sample. Using the kinetic model of *Kim et al.* (1987) (Eq. 1 in the manuscript) to compute the rate of dissociation dm_h/dt, we get $Q_{\text{diss}}^e = \Delta H_{\text{diss}} K_h \exp\left[-E/(RT)\right] F_A A_h \left(f_{eq} - f\right) t_{\text{diss}} N_c/V_b$. By substituting $N_c/V_b = \phi S_h/V$ (where ϕ is the porosity, S_h is the hydrate saturation and V is a typical volume of a pore), and noting that $F_A A_h/V \sim a^{-1}$, where a is the pore size, we obtain

$$Q_{\text{diss}}^e \sim \Delta H_{\text{diss}} K_h \exp\left(\frac{-E}{RT}\right) \left(f_{eq} - f\right) t_{\text{diss}} \phi S_h a^{-1}. \tag{3}$$

Inserting this into Eq. (2) provides the following scaling:

$$t_{\text{diss}} \sim \frac{\Delta T_{\text{diss}} c_b \rho_b}{\Delta H_{\text{diss}} K_h \exp\left[-E/(RT)\right] \left(f_{eq} - f\right) \phi S_h a^{-1}}. \tag{4}$$

The two timescales, t_{heat} and t_{diss}, are computed using the following parameter values (similar to those in the simulations presented in the manuscript): $a = 1\,\mu\text{m}$, $L = 100a$, $p_0 = 2.58$ MPa, $T_0 = 0.5°C$, $\phi = 0.4$, $S_h = 0.04$, $R = 8.314$ J mol^{-1} K^{-1}, $E = 8.1 \times 10^4$ J mol^{-1}, $K_h = 3.6 \times 10^4$ kg m^{-2} Pa^{-1} s^{-1} (*Clark and Bishnoi*, 2001), $\kappa = 5.3 \times 10^{-7}$ m^2 s^{-1}, $c_b = 2083$ J kg^{-1} K^{-1}, $\rho_b = 1800$ kg m^{-3} (*Kwon et al.*, 2010), and $\Delta H_{\text{diss}} = 450$ kJ/kg (*Waite et al.*, 2009). In evaluating t_{diss} we use fixed p-T conditions everywhere in the sample such that the fugacity difference remains constant, $f_{eq} - f = p_{eq}(T_0 + \Delta T) - p_0$. We note that this assumption is conservative since it provides the maximum possible driving force for dissociation, while in reality pressure increase and latent heat of dissociation will act to reduce the dissociation rate and hence will lower the amount of withdrawn heat.

This simple analysis clearly shows that, due to the low kinetic rate of hydrate dissociation, the timescale for heat dissipation is much smaller than that required for latent heat of dissociation to

significantly perturb the temperature (and hence the dissociation rate) [Fig. 1]. In conclusion, the small inhibiting effect of the latent heat on the dissociation rate justifies our assumptions of initially uniform temperature and isothermal dissociation under fixed, uniform temperature, allowing us to exclude heat transfer from our simulations.

Effective compressibility of the system

The gas generated by hydrate dissociation invades the porous medium, displacing water. During this drainage process, the pressure of the defending phase (water) is controlled by an *effective* compressibility of the system, c_t, that is independent of its bulk fluid compressibility. Water viscosity introduces spatial non-locality due to redistribution of water along the invasion front. Slow drainage in disordered media occurs in the form of bursts ["Haines jumps" (*Haines*, 1930)], which lead to sudden changes in water pressure. When one or more pores are invaded during a burst, the interface menisci at neighboring pores readjust, receding along throats or even leading to a backfilling of previously drained pores (*Måløy et al.*, 1992; *Xu et al.*, 2008). The short timescales associated with water pressure build-up relative to that of drainage out of the system makes fluid redistribution along the front a crucial mechanism (*Måløy et al.*, 1992; *Furuberg et al.*, 1996; *Xu et al.*, 2008). This mechanism reduces the capillary pressure (the local curvature decreases as the meniscus recedes) and suppresses further invasion until the excess water pressure is dissipated, thus limiting the burst size.

Incorporating meniscus readjustments in a dynamic pore-network model (*Aker et al.*, 1998; *Lam*, 2004) is computationally intensive. For instance, *Lam* (2004) used the concept of volume capacitance that describes the liquid volume extracted from the porous medium locally per unit decrease in pressure (*Furuberg et al.*, 1996) within a pore-network model. In *Holtzman and Juanes* (2010) we take a simpler approach, introducing the main effect of front interface dynamics through an effective compressibility of the system, even though water is nearly incompressible.

The effective compressibility c_t can be obtained by the following argument. The capillary number is a ratio of viscous forces over capillary forces at the pore scale, $Ca = \Delta p_{visc}/\Delta p_{cap}$. Assuming Poiseuille flow, the viscous pressure drop over a pore length is $\Delta p_{visc} \sim \mu v a/k$, with $k \sim a^2$, and v the average flow velocity evaluated from the cumulative values of the drained volume, time, and cross-sectional area along the boundaries (*Furuberg et al.*, 1996). Together with the Young–Laplace equation, $\Delta p_{cap} \sim \gamma/a$, this leads to the classical definition $Ca = \mu v/\gamma$. An alternative definition is the ratio of time scales for pressure dissipation and pore filling (*Furuberg et al.*, 1996), $Ca^* = \Delta t_{press}/\Delta t_{fill}$. Unlike *Furuberg et al.* (1996), we invoke pore-scale quantities only. The time scale for pressure dissipation is $\Delta t_{press} \sim a^2/D$, where $D = (k/\mu)/c_t$ is the hydraulic diffusivity. The pore filling time scale is simply $\Delta t_{fill} \sim a/v$, leading to $Ca^* = (\mu v/\gamma)(c_t\gamma/a)$. Equating the two definitions of the capillary number provides the effective compressibility of slow drainage in a disordered medium: $c_t = a/\gamma$.

References

Aker, E., K. J. Måløy, and A. Hansen (1998), Simulating temporal evolution of pressure in two-phase flow in porous media, *Phys. Rev. E*, *58*(2), 2217–2226, doi:10.1103/PhysRevE.58.2217.

Clark, M., and P. R. Bishnoi (2001), Determination of activation energy and intrinsic rate constant of methane gas hydrate decomposition, *Can. J. Chem. Eng.*, *79*(1), 143–147, doi:10.1002/cjce.5450790122.

Cortes, D. D., A. I. Martin, T. S. Yun, F. M. Francisca, J. C. Santamarina, and C. Ruppel (2004), Thermal conductivity of hydrate-bearing sediments, *J. Geophys. Res.*, *114*, B11,103, doi:10.1029/2008JB006235.

Furuberg, L., K. J. Måløy, and J. Feder (1996), Intermittent behavior in slow drainage, *Phys. Rev. E*, *53*(1), 966–977, doi:10.1103/PhysRevE.53.966.

Haines, W. B. (1930), Studies in the physical properties of soils. V. The hysteresis effect in capillary properties, and the modes of moisture redistribution associated therewith, *J. Agr. Sci.*, *20*, 97–116, doi:10.1017/S002185960008864X.

Holtzman, R., and R. Juanes (2010), Crossover from fingering to fracturing in deformable disordered media, *Phys. Rev. E*, *82*(4), 046,305, doi:10.1103/PhysRevE.82.046305.

Kim, H. C., P. R. Bishnoi, R. A. Heideman, and S. S. H. Rizvi (1987), Kinetics of methane hydrate decomposition, *Chem. Eng. Sci.*, *42*(7), 1645–1653, doi:10.1016/0009-2509(87)80169-0.

Kwon, T.-H., K.-I. Song, and G.-C. Cho (2010), Destabilization of marine gas hydrate-bearing sediments induced by a hot wellbore: A numerical approach, *Energ. Fuel.*, *24*(10), 5493–5507, doi:10.1021/ef100596x.

Lam, C.-H. (2004), Fluid invasion in porous media: viscous gradient percolation, *Phys. Rev. Lett.*, *92*(25), 254,503, doi:10.1103/PhysRevLett.92.254503.

Måløy, K. J., L. Furuberg, J. Feder, and T. Jøssang (1992), Dynamics of slow drainage in porous media, *Phys. Rev. Lett.*, *68*(14), 2161–2164, doi:10.1103/PhysRevLett.68.2161.

Waite, W. F., et al. (2009), Physical properties of hydrate-bearing sediments, *Rev. Geophys.*, *47*(4), RG4003, doi:10.1029/2008RG000279.

Xu, L., S. Davies, A. B. Schofield, and D. A. Weitz (2008), Dynamics of drying in 3D porous media, *Phys. Rev. Lett.*, *101*, 094,502, doi:10.1103/PhysRevLett.101.094502.