Hydrate Nucleation in Quiescent and Dynamic Conditions

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Abstract. Gas hydrate nucleation is the spontaneous formation of an ordered crystalline lattice from a disordered phase. This inherently random process often involves long induction times particularly in quiescent conditions. An experimental study was conducted to explore the kinetics of hydrate formation in the presence of mineral grains and when subjected to mechanical agitation. Results show that tetrahydrofuran THF hydrate nucleation is facilitated in the presence of most minerals, and induction times are a function of mineralogy and surface characteristics. While mechanical vibration does not suppress the inherent stochastic nature of nucleation, mechanical agitation triggers nucleation when the imposed acceleration exceeds $\sim 10\text{m/s}^2$.

Keywords: hydrate, nucleation, mechanical agitation, interfacial tension

1. Introduction

The nucleation of a new phase is the initial step in water freezing and hydrate formation. The spontaneous formation of an ordered crystalline lattice from a disordered phase is a random process [Mullin, 2001]. In fact, a liquid can be “supercooled” beyond the solid phase equilibrium conditions without experiencing phase transformation. During this metastable state, small crystallites nucleate and immediately break apart. The induction time for decisive crystal growth can vary significantly and may extend for days when gas hydrate forms in quiescent conditions [Sloan and Fleyfel, 1991].

Continued crystal growth starts when nuclei exceed a critical size [Mullin, 2001]. During phase transformation, the equilibrium temperature can be depressed by ionic concentration or capillary effects, due to the decrease in water activity [Englezo and Hall, 1994]. Supercooling, induction time, and equilibrium temperature depression are graphically defined on Figure 1 where the temperature signature corresponds to a fluid that undergoes exothermic phase transition during cooling.

While thermodynamic equilibrium conditions can be accurately predicted [Skovborg *et al.*, 1993; Sloan and Koh, 2008], the kinetics of hydrate formation depend on inherently stochastic nuclei formation [Bishnoi and Natarajan, 1996; Natarajan *et al.*, 1994; Lee *et al.*, 2013]. Kinetics affects laboratory protocols, flow assurance [Sloan *et al.*, 2009], hydrogen storage [Koh *et al.*, 2009], some forms of CO₂ sequestration and CO₂-CH₄ replacement [Tohidi *et al.*, 2010; Jung *et al.*, 2010]. The effects of sediment characteristics and externally imposed vibrations on hydrate nucleation are experimentally investigated in this study. A review of previous studies is presented first.

2. Previous Studies

Nucleation is affected by thermal history, the type of solution, the presence and type of impurities, and agitation.

(1) Thermal history of the solution: The molecular structure of water that was previously part of hydrate may not be completely disordered when the PT conditions remain near the stability field. This memory effect reduces induction times for hydrate re-formation [Vysniauskas and Bishnoi, 1983]. An order of magnitude increase in the cooling rate lowers the mean nucleation temperature by 0.6 to 2°C [Hobbs, 1974].

(2) Physical properties of the solution: Viscosity and the amount of available mass affect nucleation and crystal growth [Young and Cross, 1911]. Dissolved salts lower the activity of water through strong coulombic attraction as compared to the weaker hydrogen or Van der Waals bonds in hydrate structures; lower activity requires lower temperature and higher pressure for phase equilibrium [Englezos and Hall, 1994; Sloan and Koh, 2008]. Other biological and polymeric inhibitors effectively hinder nucleation [Al-Adel et al., 2008; Lin et al., 2004].

(3) Impurities: The presence of impurities favors heterogeneous nucleation, and reduces both the induction time and the degree of supercooling as a function of particle surface characteristics [Cha et al., 1988; Englezos and Hall, 1994; Riestenberg et al., 2003; Ting and McCabe, 1934]. On the contrary, small pore sizes shift the stability field to higher pressure or lower temperature [Clennell et al., 1999; Fletcher, 1958; Handa and Stupin, 1992; Husowitz and Talanquer, 2004; Kwon et al., 2008; Østergaard et al., 2002; Restagno et al., 2000].

(4) Mechanical agitation: Experiments show that stirring, shaking, or shocking can

trigger nucleation in a supersaturated fluid [Mullin, 2001; Mullin and Raven, 1962; Skovborg *et al.*, 1993; Young, 1911; Young and Cross, 1911]. Similarly, mechanical stimulation facilitates ice nucleation and gas hydrate formation [Barrer and Edge, 1967; Skovborg *et al.*, 1993; Sloan and Fleyfel, 1991; Tajima *et al.*, 2004]. Experimental results for other systems show that the nucleation rate and the morphology of precipitates are affected by stirring conditions and rate [Akkermans *et al.*, 2006; Liang *et al.*, 2004; Ting and McCabe, 1934].

3. Experimental Study

Two experimental studies are conducted to investigate the effect of minerals on THF (tetrahydrofuran) hydrate nucleation under quiescent conditions, and to identify the characteristics of mechanical agitation that favor ice and THF hydrate formation. THF provides accurate control on hydrate saturation, overcomes the long diffusion-controlled formation time from aqueous phase, and nucleates at atmospheric pressure; thus THF has been a popular proxy for methane in laboratory studies of hydrate-bearing sediment properties [Lee *et al.*, 2007; Yun *et al.*, 2007]. Devices and test procedures are described first.

3.1 Experimental devices and configurations

Figure 2 illustrates the experimental configurations used for the two studies. Temperature is controlled using a high-precision cooler and measured using a smooth bar K-type thermocouple (precision of $\sim 0.1^{\circ}\text{C}$) for both static and dynamic tests. The temperature is measured at the tip of the thermocouple. In dynamic tests (Figure 2b),

external vibrations are supplied through a stainless steel rod (3.175mm in diameter 100mm in length) coupled to a piezoelectric actuator (Model 712A01, PCB Piezotronics, Inc.). Vibration frequency and amplitude are controlled through the power supply and the rod vibration is measured using a collinearly mounted accelerometer (Model 350B04, PCB Piezotronics, Inc.). The vibration frequency explored in this study ranges from 800Hz to 7000Hz , and the amplitude ranges from 1nm to 1 μ m.

3.2 Materials - Specimen preparation

Specimens for static tests consist of 20ml 81H₂O:19THF solution (stoichiometric solution – 100% hydrate) and 5g of soils. Table 1 summarizes the main properties of the selected soils. The randomly-shaped RP2 kaolinite is smaller than the hexagonal shaped SA1. Crushed silt is angular, low specific surface silt. Precipitated silt consists of silt-size aggregations with extensive inter-particle pore networks which result in high specific surfaces. The irregularly shaped GCC particles are bulkier than the very uniform, rice-shaped PCC particles.

The selected soil is added to the solution, shaken vigorously, and left to rest in the sealed cylinder for 1~2 hours to allow for sedimentation. A thin layer of oil is added to cover THF solution specimens immediately after mixing to prevent THF evaporation during testing. Each test starts with a freshly prepared specimen to avoid contamination or memory effects.

Dynamic tests involve either 10ml deionized water (ice formation) or 10ml 19H₂O:81THF stoichiometric solution (100% hydrate formation).

3.3 Experimental procedures

Prepared specimens in test cylinders are sealed and immersed into a cooling bath with a constant temperature of -5°C . In dynamic tests, the oscillatory vibration with preselected frequency and amplitude is applied immediately after the cylinder is submerged in the cooler. Bath and specimen temperatures are monitored to detect phase transformation.

3.4 Typical temperature signatures

The equilibrium temperature at the THF hydrate boundary depends on the volume fraction of water and THF (Figure 3a). At atmospheric pressure, the equilibrium temperature of $81\text{H}_2\text{O}:19\text{THF}$ solution is $\sim 4.5^{\circ}\text{C}$. Typical temperature-time signatures of deionized water, excess water THF solution ($90\text{H}_2\text{O}:10\text{THF}$), stoichiometric mixture ($81\text{H}_2\text{O}:19\text{THF}$), and excess THF solution ($40\text{H}_2\text{O}:60\text{THF}$) are shown in Figure 3b. The induction time in these signatures varies from 3000s (water) to more than 6000s (excess water solution). Supercooling reaches -7.5°C (stoichiometric solution). The exothermic peak readily seen in all cases marks the beginning of the transformation. All reactions reach the equilibrium temperature. The excess water solution exhibits the exothermic peak for hydrate formation followed by the peak for ice formation.

4. Results and Analyses

4.1 Heterogeneous hydrate nucleation – Static tests

A total of 40 static tests were completed as part of this study. Results are summarized in Figure 4. Measured induction times are log-normally distributed (Note: a

log-normal distribution of induction times was also observed in CO₂ hydrate nucleation in Na-montmorillonite suspensions [Lee *et al.*, 2013]). The presence of minerals facilitates nucleation, except in the case of precipitated calcium carbonate PCC. Industrial precipitated mineral (PCC and PS) are less effective at nucleating hydrates than their crushed counterparts (GCC and CS); industrial minerals also exhibit higher water-mineral contact angle.

Mineral surfaces lower the thermal agitation of water molecules, and prompt their alignment; hence, mineral surfaces that more closely mimic the hydrate crystal structure are more efficient nucleators [Blackwell, 1999; Park and Sposito, 2003; Turnbull and Vonnegut, 1952]. The number of water molecules per unit volume next to mineral surfaces n_w (1/m³) can be estimated in terms of porosity n and specific surface S_s (m²/g):

$$n_w = \frac{S_s (1 - n) G_s \rho_w}{(l_{\text{water}})^2} \quad (1)$$

where G_s is specific gravity of minerals, ρ_w is water density, and l_{water} is the characteristic length of a water molecule (estimated n_w for each specimen based on the above equation are SA1: 180/m³, RP2: 145/m³, PS: 600/m³, CS: 0.565/m³, GCC:9/m³, and PCC: 49.5/m³). Experimental results in Figure 4 do not show clear benefits from specific surface (highest for the two kaolinite clays), implying that specific surface is less important than other mineral surface characteristics including roughness. In fact, the rate of nucleation has been linked to the Gibbs free energy ΔG^* , which can be linked to contact and interfacial tension [Hobbs, 1974].

Sediment pores can also affect nucleation kinetics in various ways, particularly as pore sizes become smaller than 10nm [Clennell *et al.*, 1999; Handa and Stupin, 1992; Kwon *et al.*, 2008; Østergaard *et al.*, 2002]: nanometer-sized pores restrict embryo size,

water activity is reduced, and capillary suction hinders nucleation (multiphase fluids).
Pore sizes in this study are 100nm or larger and exert minimal effects on nucleation.

4.2 The effect of mechanical vibration on nucleation

The effect of mechanical vibration on nucleation is explored by plotting the data on tripartite plots so that imposed sinusoidal vibration frequency, displacement, velocity, and acceleration are shown at once (Figure 5). The measured data were sorted from short to long induction times, and the boundary between short induction times (crosses) and long induction times (circles) was gradually displaced to attain maximum data discrimination. Results obtained with both water-to-ice and THF solution-to-hydrate transformations show that the boundary from short-to-long induction times is parallel to iso-acceleration lines; thus, acceleration is the best predictor of reduced induction time.

A characteristic acceleration threshold is apparent in Figure 5. This is further explored in Figure 6 where induction times are plotted versus peak acceleration. The solid line represents the mean induction time $\mu(t_{ind})$ and dashed lines represent the one standard deviation $\pm\sigma(t_{ind})$ band in induction times measured for specimens without vibration as the control group. The induction time decreases when the peak acceleration exceeds $\sim 10\text{m/s}^2$. Histograms of short and long induction times for high and low accelerations show that mechanical vibration does not suppress induction time variability. Hydrate nucleation under quiescent conditions shows decreased induction times and variability (in linear scale) when the system is driven further into stability conditions [Lee *et al.*, 2013].

Several hypotheses have been advanced to explain the role of agitation on

nucleation. Some suggest that mechanical agitation enhances nucleation by altering incipient nuclei to favor crystallization sites [Melia and Moffitt, 1964; Mullin and Raven, 1962]. Others consider that mechanical agitation causes transient inhomogeneous energy distribution and high energy regions favor nucleation [Mullin, 2001].

At the molecular scale, agitation must cause enough relative displacement among neighboring molecules to facilitate nucleation and the formation of a new structure. Let's idealize molecular scale interactions as a damped, single degree of freedom with a linear spring k , mass m , and dashpot η . The motion that the second molecular layer experiences $y_{m(t)}$ is related to the motion imposed on the first layer $y_{b(t)} = A\cos(\omega t)$ as

$$y_{m(t)} = H * y_{b(t)}, \quad (2)$$

Where the transfer function H represents the intermolecular response function. The equation of motion follows Newton's second law:

$$m \frac{\partial^2 y_{m(t)}}{\partial t^2} + \eta \frac{\partial (y_{m(t)} - y_{b(t)})}{\partial t} + k (y_{m(t)} - y_{b(t)}) = 0. \quad (3)$$

The combination of Equations 2 and 3 renders:

$$H = \frac{\omega\eta - k}{\omega^2 m + \omega\eta - k}. \quad (4)$$

Thus, the maximum relative displacement δ become

$$\delta = |y_{m(t)} - y_{b(t)}|_{\max} = |(H - 1)y_{b(t)}|_{\max} = \frac{A}{1 + \frac{\eta}{\omega m} - \left(\frac{\omega_r}{\omega}\right)^2}. \quad (5)$$

where the resonant frequency $\omega_r^2 = k/m$. The excitation frequencies in this study are much lower than molecular resonance/relaxation frequencies, $\omega/\omega_r \ll 1$. In this regime, the relative displacement between contiguous molecular layers δ/A scales with ω^2 . This is in agreement with experimental results in Figure 5 that show acceleration $a = A\omega^2$ as the

key vibration characteristic that affects induction time.

5. Conclusions

Solid phase hydrate formation exhibits induction time, supercooling, and transformation temperature depression. Nucleation is inherently stochastic and experimental results should be expressed in statistical form.

The induction time of THF hydrate formation in various types of mineral suspensions follows a log-normal distribution. Nucleation is favored in the presence of most minerals. Mineral surface properties affect the induction time and the degree of supercooling, but do not change the equilibrium temperature during phase transformation. Mineralogy and fluid-mineral interaction (i.e., contact angle and interfacial tension) are more important than particle size and sediment porosity..

Mechanical vibration facilitates nucleation but it does not suppress the inherent stochastic nature of nucleation.

The tripartite analysis of experimental results reveals that acceleration is a better discriminator between short and long induction times than vibration frequency, amplitude, or velocity. Experimental results suggest that nucleation is prompted when the imposed acceleration exceeds $\sim 10\text{m/s}^2$. Relative molecular displacement emerges as the underlying mechanism. Thus, boundary layer shear and pore-scale turbulence in steady state flow conditions should favor nucleation.

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Young, S. W., and R. J. Cross (1911), The mechanical stimulus to crystallization, *Journal of the American Chemical Society*, 33(8), 1375-1388.

345 Table 1. Physical properties of selected sediments

	Kaolinite (SA1)	Kaolinite (RP2)	Precipitated silt (PS)	Crushed silt (CS)	Ground CaCO ₃ (GCC)	Precipitated CaCO ₃ (PCC)
Specific gravity, G_s	2.6	2.6	2.08	2.65	2.71	2.71
Mean grain size, d_{50} [μm]	1.1	0.36	20	20	12	1
pH	6.5	4.66	7	7	8.76	9.87
Specific surface, S_s [m^2/g]	36	29	120	0.113	1.8	9.9
Liquid limit, LL	43	78	-	-	28	52
Sphericity, S	0.7	0.7	0.9	0.9	0.8	0.2
Roundness, R	0.1	0.3	0.7	0.1	0.5	0.9

346

Figure Captions

Figure 1. Schematic temperature-time signature corresponding to an exothermic phase transformation during cooling – Labels denote supercooling, induction time, freezing point depression, and equilibrium temperature.

Figure 2. Experimental configuration: (a) static test and (b) vibration test. Components: 1. Piezoelectric actuator (Model 712A01, PCB Piezotronics, Inc.). 2. Accelerometer (Model 350B04, PCB Piezotronics, Inc.). 3. Nylon coupler. 4. Thermocouple (K-type, precision = 0.1°C). 5. Heat-insulation foam cover. 6. Stainless steel rod.

Figure 3. Phase transformation. (a) Stability temperature for THF-water mixtures at atmospheric pressure. (b) Typical temperature-time signatures for tap water, THF solution with excess water (90H₂O:10THF), stoichiometric mixture 100% hydrate (81H₂O:19THF), and THF solution with excess THF (40H₂O:60THF).

Figure 4. Effect of mineral grain characteristics on induction time. kaolinite (SA1), kaolinite (RP2), precipitated silt (PS), crushed silt (CS), ground CaCO₃ (GCC), precipitated CaCO₃ (PCC)

Figure 5. Experimental results in tripartite: (a) water to ice and (b) stoichiometric THF-water to hydrate transition. Induction times are represented by symbols: in (a) crosses are results of $t_{ind} < 2500s$ and circles are results of $t_{ind} > 2500s$; in (b) crosses are results of $t_{ind} < 5000s$ and circles are results of $t_{ind} > 5000s$.

Figure 6. Experimental results: Induction time t_{ind} versus peak acceleration a . Cases: (a) tap water and (b) stoichiometric mixture (81H₂O:19THF) 100% hydrate. Discrete points are experimental results obtained with mechanical vibrations. As a reference, the mean and standard deviation values of 16 specimens without vibration are shown as solid and dashed lines.

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(a)

(b)

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(a)

(b)

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(a) Water to ice

(b) Stoichiometric H₂O-THF mixture to THF hydrate

Figure 6. Experimental results: Induction time t_{ind} versus peak acceleration a . Cases: (a) tap water and (b) stoichiometric mixture (81H₂O:19THF) 100% hydrate. Discrete points are experimental results obtained with mechanical vibrations. As a reference, the mean and standard deviation values of 16 specimens without vibration are shown as solid and dashed lines.