

KINETICS OF HYDRATES FORMATION

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Abstract. *In the oil industry there is a great interest in understanding the kinetics of gas hydrates formation. Hydrates can cause a lot of damages, mainly in drilling operations, since they can form and grow into the annular, BOP or into kill and choke lines, causing serious security problems and productivity loss. In contrast to the advances observed in the thermodynamics of hydrates, the kinetics is less understood. A good knowledge on the kinetics of the hydrate formation would allow the exploitation of the kinetics mechanism favourably to depress the hydrate formation rate. Although hydrate formation may be unavoidable (drilling operations in deep and ultra deep waters), the rate of formation could be slowed. To date, after the work from Sugaya and Mori (1996), there is a consensus that hydrates initial grow occurs through a thin film at the interface between the liquid water and the hydrate forming substance. The rate of lateral grow of hydrate films have been extensively investigated in last ten years, and different modeling have been developed. The focus of this work is to present the state of art in predicting hydrates lateral growth rate, and describe and discuss three models of hydrates lateral growing: Uchida et al. (1999), Freer (2000) and Mori (2001).*

Keywords: *Hydrates, kinetics, lateral growth rate, interface.*

1. INTRODUCTION

Gas hydrates are crystalline compounds that are formed when water contacts certain non polar substances (gases or liquids) under favorable pressure and temperature conditions. In the hydrate's crystalline structure, water molecules are hydrogen-bonded and configured into cages, each enclosing at most one molecule of some non polar substance called "guest substance".

The guest molecules capable to stabilize the structure of hydrate have sizes of $3,8 \text{ \AA}$ to 9 \AA . Depending on the size of the guest molecule, hydrates could conform in three different structures: I, II and H. In oil industry applications, the most common structure is II, since the molecules that constitute natural gases generally have molecular sizes that stabilize this structure.

The industrial interest in gas hydrates began with the discovery that hydrate formation could plug natural gas pipelines (Hammersmidt, 1934). Before this discovery, the studies about hydrates formations had been focused in the development of methods to predict hydrate formation conditions. As a result of extensive thermodynamic studies, considerable hydrate phase equilibrium data and methods to predict hydrate formation conditions are available (Parrish and Prausnitz, 1972; Munck et al., 1988; Ballard and Sloan, 2002; Jager et al., 2003).

One of the ways to prevent the hydrate formation is adding thermodynamic inhibitor, such as salts (e.g. NaCl , KCl and CaCl_2) and alcohols (e.g. methanol and ethylene-glicol). This inhibitors shift the conditions of hydrate formation to lower temperatures and greater pressures. There are available a plenty of mathematical models to predict, with good precision, the equilibrium temperatures and pressures of hydrates with inhibitors (Anderson and Prausnitz, 1986; Munck et al., 1988; Englezos and Bishnoi, 1988; Zuo and Stenby, 1997).

With the advances of drilling operations in deeper waters, the amount of inhibitors necessary to avoid hydrates formation became prohibitive. This fact brought the need to know precisely the kinetics mechanisms of hydrates formation, to develop techniques that allow the exploitation of the kinetics mechanism favorably to depress the hydrate formation rate.

Englezos et al. (1987a,b) developed the first reasonable model for the kinetics of hydrate formation to engineering application. In that work were performed kinetic measurements of methane and ethane hydrates in a high stirred reactor. In these experiments the hydrate formation rate was determined by measuring the moles of gas consumed as a function of time. The model views hydrate formation as a three-step process:

1. Transport of the gas from the bulk of the gas phase to the liquid bulk phase;
2. Diffusion of the gas from the bulk of the water phase and the liquid film to the hydrate crystal–liquid interface through a laminar diffusion layer around the hydrate particle;
3. “Reaction” at the interface, which is an adsorption process describing the incorporation of gas molecules into the cavities of the water structures and the subsequent stabilization of the framework of the structured water.

Englezos *et al.* (1987a,b) assumed the driving force for crystallization as the difference in the fugacity of the dissolved gas and the three phase equilibrium fugacity at the experimental temperature, which was substantiated by assuming negligible heat transfer resistance. The model was comprised of five differential equations and boundary conditions, combined both hydrate kinetics and mass transfer.

This model was far more sophisticated than any previous model, because it incorporated phenomena such as crystallization and primary nucleation. Both data and model provided a foundation for future advances in hydrate kinetics.

Years later, Skovborg and Rasmussen (1994) simplified the Englezos’s model. This simplified model considers the transport of the gas from the bulk of the gas phase to the liquid bulk phase the governing step of hydrate formation, neglecting the crystallization step. Therefore, the new model considers only the mass transfer process.

Although the advances obtained in hydrate kinetic studies, some hypothesis of the models of Englezos *et al.* (1987a, b) and Skovborg e Rasmussen (1994) had been placed in check by posterior studies. The driving force was considered as the difference in the fugacity of the dissolved gas and the three phase equilibrium fugacity at the experimental temperature. However, as discussed by Sloan (1998) this assumption cannot represent physical reality because there would be a pressure gradient in the system, which imposes a mechanical impossibility. Neglecting the heat transfer effects is considered a second critique about these models.

The models of Englezos *et al.* (1987a, b) and Skovborg e Rasmussen (1994) considered that hydrate formation occurs in the liquid bulk phase. This assumption isn’t reasonable, because the guest molecules have a small solubility in water (much less than 15%, which is the hydrate composition). So, the more likely place for hydrate formation is in the interface between the hydrate former phase and the water phase. This idea was confirmed by optical experiments performed by Sugaya and Mori (1996), which revealed that initial hydrate growth occurs as a thin film propagating across the guest–water interface.

After the results obtained by Sugaya and Mori (1996), several studies of interfacial hydrate formation have recently appeared in the literature. The rate of lateral grow of the hydrate film is a parameter extensively studied by several authors. In this work the focus is to present the state of art in predicting hydrates lateral growth rate. Three models of hydrates lateral growing will be described and discussed: Uchida *et al.* (1999), Freer (2000) and Mori (2001).

2. PREDICTION MODELS OF HYDRATE FILM LATERAL GROWTH

2.1 Uchida *et al.* (1999)

Uchida *et al.* (1999), experimentally observed hydrate-film growth on a water droplet surface submerged in liquid CO_2 . The resulting images allowed them to determine the rate of lateral growth as a function of the difference between the equilibrium temperature at the experimental pressure and the experimental temperature.

This work also presents a model correlating the linear growth rate of the hydrate film along the interface (v_f), to the hydrate film thickness (δ) and the degree of system subcooling ($\Delta T = T_{eq} - T_{exp}$). The model was developed over the following assumptions:

- a) Hydrate crystals successively form only at the film front where the temperature remains constant at the equilibrium temperature corresponding to the system pressure p ;
- b) The front of the hydrate film has a semicircular geometry;
- c) The film thickness (δ) is approximated by $2r_c$ (r_c is the nucleation critical radius);
- d) The heat release by the hydrate-crystal formation at the film front is removed by thermal conduction;
- e) The temperature gradient in the film front had been assumed as $(\partial T / \partial r)_{r_c} \cong (T_{eq} - T_{exp}) / r_c$;

The above assumptions are illustrated in Fig. 1.

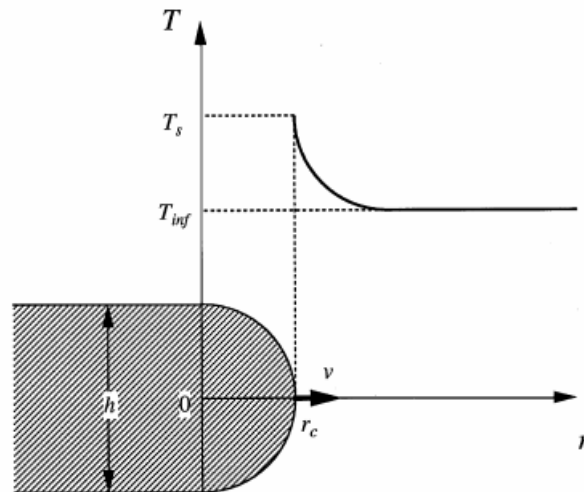


Figure 1 – Hypothesis assumed by Uchida *et al.* (1999).

Assuming the balance between the heat transfer away from the film front and the heat released by the hydrate-crystal formation at the front, Uchida *et al.* (1999) presented the following equation:

$$v_f \Delta h_H \rho_H = -k \left(\frac{\partial T}{\partial r} \right)_{r_c} = -k \frac{(T_s - T_{inf})}{r_c} = -k \frac{2(T_s - T_{inf})}{\delta} \quad (1)$$

where v_f is the lateral growth rate, Δh_H is the latent heat of the hydrate formation (in J/mol), ρ_H is the mole density of the hydrate (in mol/mm^3) and k is the thermal conductivity of the surrounding phases (in $W.m^{-1}.K^{-1}$).

In equation (1), the film thickness is the only unknown parameter. Then, this parameter is adjusted to best fit the experimental data. Figure 2 shows the model (dashed lines) with the experimental data (points), adjusted for a film thickness of $0.13 \mu m$.

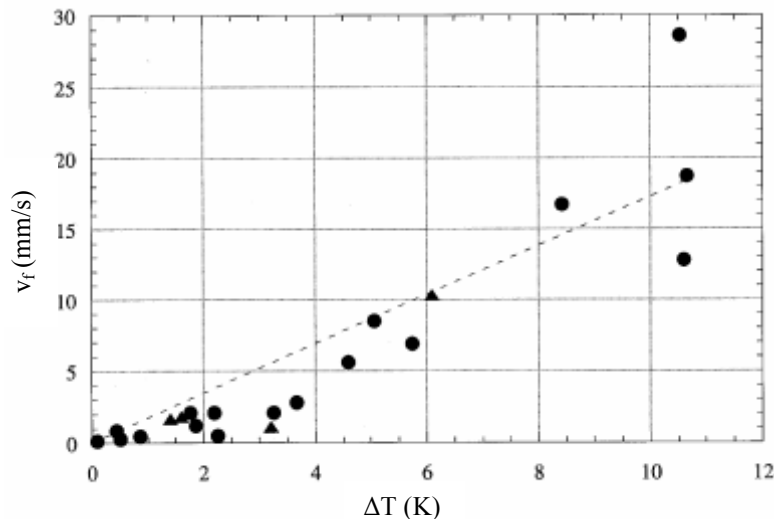


Figure 2 - Propagation rate of CO_2 hydrate versus temperature difference ($\Delta T = T_{eq} - T_{exp}$). (Uchida *et al.*, 1999).

In Figure 2 it's clear that the model developed by Uchida *et al.* (1999) didn't fit well to the experimental data. Some probable causes of this shift are:

- a) The thermal conductivity of the surrounding phases was estimated accounting only for the water, neglecting the thermal conductivity of CO_2 . However, the difference of thermal conductivity is approximately five times in a liquid CO_2 water system. This may result in some decrease in accuracy (Uchida *et al.*, 1999).

- b) According with Mori (2001), the temperature gradient at the hydrate film front assumed has little physical reasoning;
- c) The model correlates the data of v_f versus ΔT with a linear regression. In Fig. 2, it's clear that this is a poor approximation.

2.2 Mori (2001)

Mori (2001) presented a convective heat transfer model to correlate the linear growth rate of the hydrate film along the interface (v_f), to the hydrate film thickness (δ) and the degree of system sub cooling ($\Delta T = T_{eq} - T_{exp}$). The model results have been compared with two experimental databases, from the works of Uchida *et al.* (1999) and Hirai *et al.* (1999). In both cases the hydrate film thickness has been estimated.

This model is based on the idea that the front of a hydrate film lateral growth on the interface between stagnant water and a guest fluid should see an oncoming countercurrent flow at a velocity which is opposite in direction but equal in magnitude to v_f , the velocity of the film front relative to the stationary coordinates laid on the undisturbed interface.

The heat released at the film front is assumed to be removed away from it to the fluid phases by steady convective heat transfer. The film front is semicircular in shape, and is held at the three-phase equilibrium temperature. The backward conductive heat transfer through the film is ignored as in the model of Uchida *et al.* (1999).

This model assumes that the hemi circular front of the film is bisected by the water/hydrate-former interface such that one quadrant is in contact with water and the other with the hydrate former (see Fig. 3)

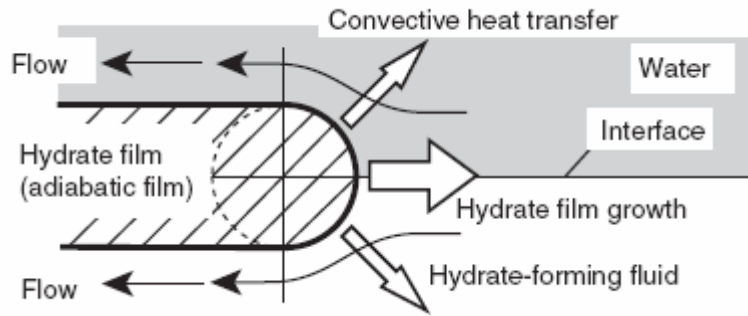


Figure 3 – Hydrate film model of Mori (2001) (modified from Mochizuki and Mori, 2006).

Denoting the average heat transfer coefficient in the quadrant in contact with the water and the hydrate former (or “guest”) phase by $\bar{\alpha}_w$ and $\bar{\alpha}_g$, respectively, there is the following equation for the energy balance over the hydrate film hemi circular front.

$$v_f \delta \rho_h \Delta h_h = \frac{1}{4} \pi \delta (\bar{\alpha}_w + \bar{\alpha}_g) \Delta T \quad (2)$$

where v_f is the lateral growth rate, δ is the hydrate film thickness, Δh_h is the latent heat of the hydrate formation (in J/kg), ρ_h is the mole density of the hydrate (in kg/m^3) and ΔT is the degree of system sub cooling ($T_{eq} - T_{exp}$).

Mori (2001) assumed that the heat transfer coefficients, $\bar{\alpha}_w$ and $\bar{\alpha}_g$, are given by a simple type of convective heat-transfer correlation in a dimensionless form.

$$\overline{Nu} = A Re^m Pr^n \quad (3)$$

Where Nu , Re and Pr are, respectively, the Nusselt, the Reynolds and the Prandtl numbers, and m , n and A are characteristics constants for equation (3) and they have positive values.

Thus, assuming that the heat transfer from the film front may be evaluated by regarding it as the front half of the cylinder, considering a creeping flow ($Re \ll 1$), Mori (2001) proposed the following equation:

$$v_f \delta = C \Delta T^{3/2} \quad (4)$$

where:

$$C = \left[\frac{\pi A}{4} \frac{1}{\rho_h \Delta h_h} \left(\frac{\lambda_w}{\kappa_w^{1/3}} + \frac{\lambda_g}{\kappa_g^{1/3}} \right) \right]^{3/2} \quad (5)$$

and k_w k_g are the thermal diffusivity of water and the hydrate former, respectively. The film thickness could be estimated in such a way to best fit the model to the experimental data. A comparison between the model and the experimental data from Uchida *et al.* (1999) is showed in the Fig. 4.

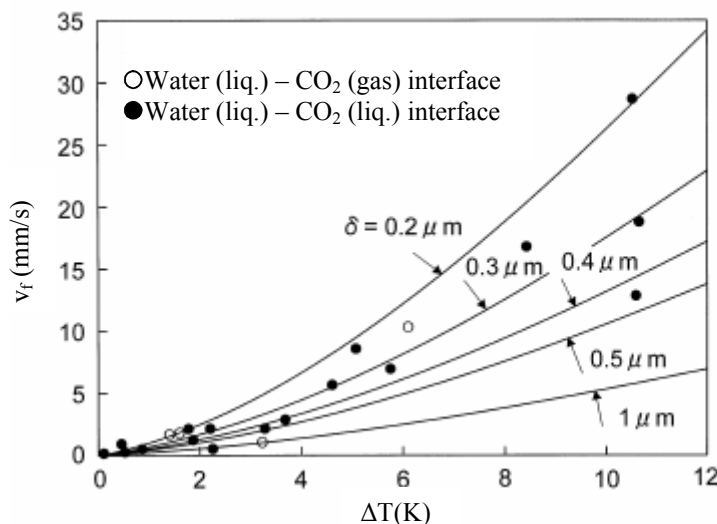


Figure 4 – Model of Mori (2001) compared with the experimental data from Uchida *et al.* (Modified from Mori (2001)).

Analyzing the results presented in Fig. 4, one can see that the film thickness that best fit the experimental data is $\delta = 0.3 \mu m$. This model better adjusts to the experimental data, when compared with the model developed by Uchida *et al.* (1999). These better results are due to the fact that the power of 3/2 correlation between v_f and ΔT is more reasonable than the linear correlation assumed by Uchida *et al.* (1999). It's important to note that this better correlation power is a consequence of the convective heat transfer assumption.

However, the model of Mori (2001) has some limitations because it doesn't account for the kinetics of crystallization. These limitations will be clarified in the next section

2.3 Freer (2000)

Freer (2000) experimentally studied CH_4 hydrate film growth on a water/ CH_4 interface. His work also presented a mathematical model to correlate the rate of hydrate film lateral growth with the temperature difference driving force ($T_{eq} - T_{exp}$).

In his work, Freer measured the rate of hydrate film lateral growth in two different ways: as a function of the bulk aqueous phase temperature (T_b) and as a function of the equilibrium temperature in the experimental pressure. Fig. 5 shows methane hydrate growth rates as a function of the bulk temperature for different hydrate equilibrium temperatures, and, Fig. 6 shows methane hydrate growth rates as a function of the equilibrium temperature for different bulk temperatures.

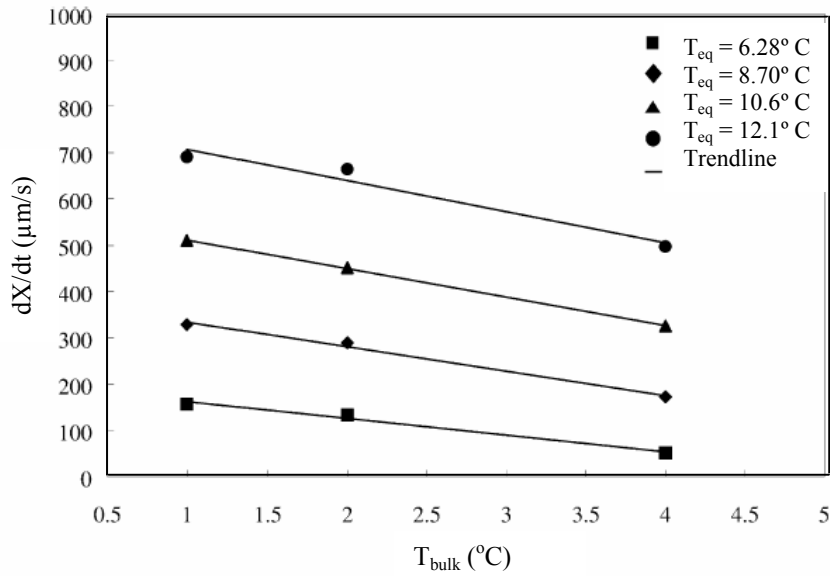


Figure 5 – Methane hydrate growth rates with bulk temperature perturbations (modified from Freer, 2000).

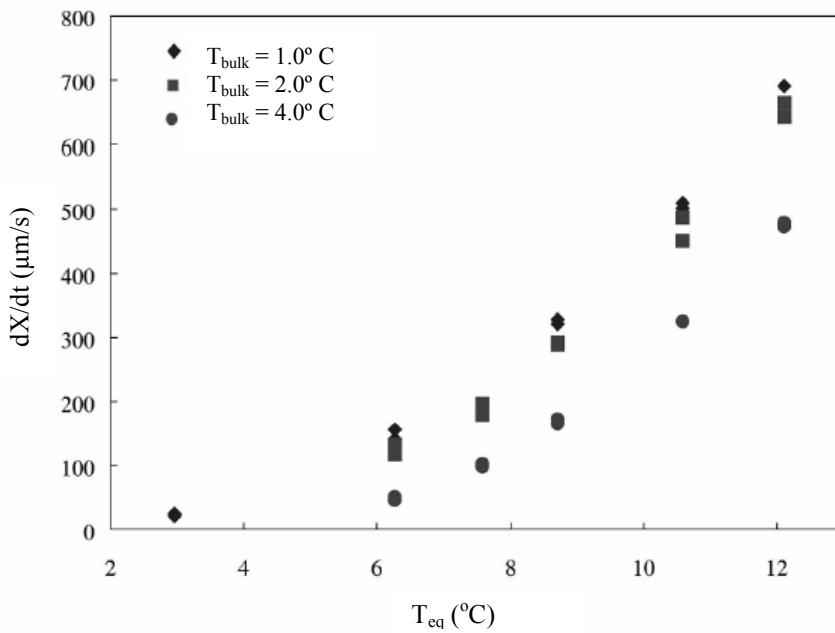


Figure 6 - Methane hydrate growth rates with equilibrium temperature perturbations (Modified from Freer, 2000).

Observing the results presented one can note that the rate of hydrate film growth has a linear dependence with the bulk water phase temperature, while has a nonlinear dependence with the equilibrium temperature. These results were unexpected, and imply that there isn't a unique growth rate for the same driving force ($T_{\text{eq}} - T_{\text{exp}}$) and that both the bulk and equilibrium temperatures must be specified to define adequately molecular attachment at the hydrate interface.

Freer (2000) initially tried to reproduce the experimental data with a simplified transient conductive heat-transfer model. In such model one-dimensional heat transfer from a planar moving film front to a stationary semi-infinite water phase extending beyond the front was assumed. The results obtained with this model didn't correspond to the experimental data, as shown in Fig. 7.

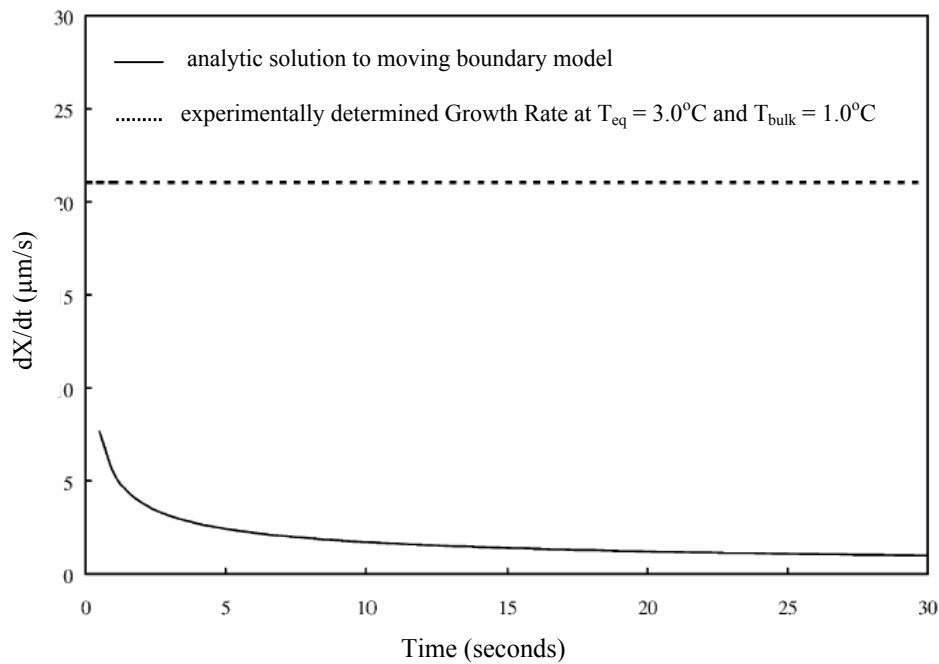


Figure 7 – Hydrate film growth rate as a function of time (Modified from Freer, 2000).

The results given by the model proposed by Freer were much lower than the corresponding experimental data. Thus, Freer (2000) denied the validity of his conductive heat transfer model, and proposed an alternative model that combined convective heat transfer away from the film front and the kinetics of crystallization over the film surface.

Considering this, an overall rate constant was defined accounting for both kinetic and heat transfer resistance, and is given as:

$$\Delta h_H \rho_H \frac{dX}{dT} = K (T_{eq} - T_{bulk}) \quad (6)$$

where:

$$K = \frac{1}{h} + \frac{1}{k} \quad (7)$$

In equation (7), K is the total resistance, h is the heat transfer coefficient, and k is the methane hydrate kinetic rate coefficient. In equation (6), Δh_H is the heat of hydrate dissociation, ρ_H is the hydrate density and dX/dT is the rate of the film lateral growth.

Based on a thin wire approximation for the heat transfer, Freer (2000) considered the heat transfer coefficient constant. The kinetic rate coefficient was proposed to follow an Arrhenius type expression, given by:

$$k = k_o \exp\left(-\frac{E_a}{RT_{eq}}\right) \quad (8)$$

where k_o is the pre-exponential factor and E_a is the activation energy.

The proposed model has three unknown parameters (h , k and E_a), which were fitted from the data using a least-squares method. The parameters obtained are showed in Table 1.

Table 1 - Regressed parameters (according to Freer (2000)).

Parameter	k_o (W/m ² K)	E_a (kJ/mol)	h (W/m ² K)
Regressed value	1.60567×10^{36}	20599	42326

According to Freer (2000), the heat transfer coefficient agrees well with values calculated using the thin wire approximation for a film thickness ranging from 2 to 5 μm and with Reynolds number ranging from 10^{-5} to 10^{-2} . The film thickness range compares well with the value of 5 μm reported by Makogon et al (1998; *apud* Freer, 2000) for methane hydrate films. The activation energy was found to be larger than values reported by Mullin (1993; *apud* Freer, 2000) for diffusion (10–20 kJ/mol) and surface integration (40–60 kJ/mol). Freer (2000) believes that the order of magnitude discrepancy between the regressed and diffusion values suggests that hydrate formation is surface integration controlled. The large regressed activation energy may result from complexity of the ordering process at the interface, which becomes more favorable at higher temperatures. At the solidification interface, both methane and water molecules must combine to form the stable hydrate lattice.

In Figure 8 is showed the results given by the model proposed by Freer, with the experimental data.

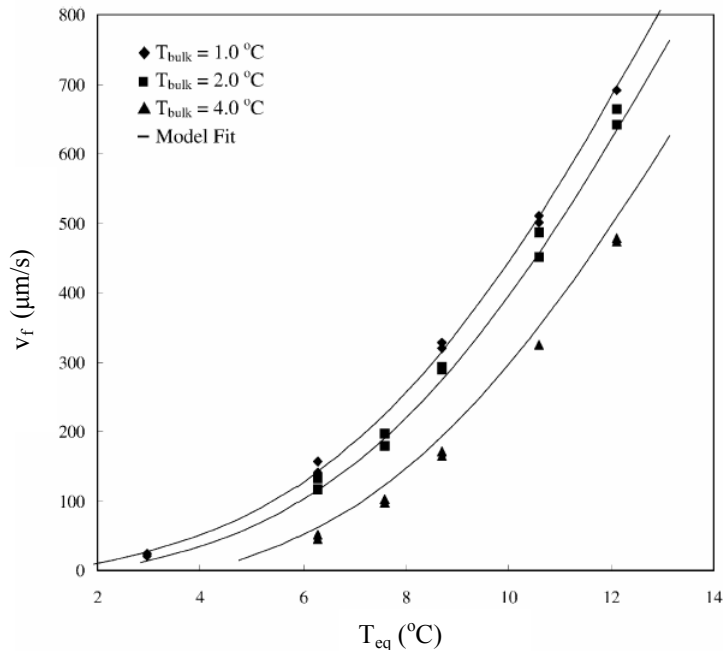


Figure 8 – Model of Freer (2000) versus experimental data (modified from Freer, 2000).

It could be noted that the model fitted well the experimental data, and deviations were attributed to the heat transfer approximation.

3. CONCLUSIONS

This work presented three different studies about hydrate formation, two of them for CO_2 hydrates (Uchida *et al.*, 1999 and de Mori, 2001) and one for hydrates of CH_4 . The models presented can be extended to other hydrate formers.

The three models considered different phenomena in modeling hydrate formation. Uchida *et al.* (1999) accounted only for heat conduction from the film front to the aqueous phase. The model gives a poor correlation with the experimental data mainly due to the linear correlation between v_f and ΔT . The film thickness estimated by Uchida *et al.* (1999) is $\delta = 0.13\mu\text{m} \pm 0.01\mu\text{m}$. One has very difficulties to find in the literature any experimental data that allow affirming if the model of Mori (2001) gives more realistic hydrate film thickness than the model of Uchida *et al.* (1999).

Between the three models presented, the most realistic is the proposed by Freer (2000). That model accounts not only for heat transfer, but also for the kinetic of crystallization. The model of Freer (2000) is capable to predict the correlation between the rate of hydrate film growth and both temperatures (equilibrium and bulk phase temperature), while the other two models can't. This model requires knowing both the equilibrium and the bulk phase temperature, not only the difference between this temperatures as the in the other two models presented.

4. ACKNOWLEDGEMENTS

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5. REFERENCES

- Anderson, F. E., Prausnitz, J.M., 1986, "Inhibition of gas hydrates by methanol", *AIChE Journal*, Vol. 32, pp. 1321-1333.
- Ballard, A. L., Sloan, E. D., 2002, "The Next Generation of Hydrate Prediction: An Overview", *Journal of Supramolecular Chemistry*, Vol. 216, pp. 257-270
- Englezos, P., Bishnoi, P. R., 1988, "Prediction of gas hydrate formation conditions in aqueous electrolyte solutions", *AIChE Journal*, Vol. 34, pp 1718-1721.
- Englezos, P., Kalogerakis, N., Dholabhai, P. D., Bishnoi, P. R. , 1987a, "Kinetics of formation of methane and ethane gas hydrates, *Chemical Engineering Science*, Vol. 42, pp. 2647-2658;
- Englezos, P., Kalogerakis, N., Dholabhai, P. D., Bishnoi, P. R., 1987b, "Kinetics of Gas Hydrates Formation from Mixtures of Methane and Ethane", *Chemical Engineering Science*, Vol. 42, pp. 2647-2658;
- Freer, E. M. , 2000, "Methane Hydrate Formation Kinetics", M.S. Thesis, Colorado School of Mines;
- Hammerschmidt, E.G., 1934, "Formation of Gas Hydrates in Natural Gas Transmission Lines", *Ind. Eng. Chem., Unites States*, Vol. 26, pp. 851-855.
- Hirai, S., Tabe, Y., Kamijo, S., Okazaki, K., Eliasson, B., Riemer, P., Wokaun, E., 1999, *Greenhouse Gas Control Technologies*, Pergamon, Amsterdam, pp. 1049±1051;
- Jager, M. D., Ballard, A. L., Sloan, E. D., 2003, "The next generation of hydrate prediction: II. Dedicated aqueous phase fugacity model for hydrate prediction", *Fluid Phase Equilibria*, Vol. 211, pp. 85-107.
- Mochizukia, T., Mori, Y. H., 2006, "Clathrate-hydrate film growth along water/hydrate-former phase boundaries - numerical heat-transfer study", *Journal of Crystal Growth* Vol. 290, pp. 642–652;
- Mori, Y. H., 2001, "Estimating the thickness of hydrate films from their lateral growth rates: application of a simplified heat transfer model", *Journal of Crystal Growth*, Vol. 223, pp. 206-212;
- Munck, J.; Skjold – Jorgensen, S., Rasmussen, P., 1988, "Computations of the Formation of Gas Hydrates", *Chem. Eng. Sci., Great Britain*, Vol. 43, pp. 2661-2672.
- Skovborg, P., Rasmussen, P., 1994, "A mass transport limited model for the growth of methane and ethane gas hydrates", *Chemical Engineering Science*, Vol. 49, pp. 1131-1143;
- Sloan, E. D. Jr., 1998, "Clathrate Hydrates of Natural Gases", 2nd ed., Marcel Dekker, New York, USA;
- Sugaya, M., Mori, Y. H., 1996, "Behavior of Clathrate Hydrate Formation at the Boundary of Liquid Water and a Fluorocarbon in Liquid or Vapor State", *Chem. Eng. Sci.*, Vol. 51, pp. 3505-3517.
- Uchida, T., Ebinuma, T., Kawabata, J., Narita, H., 1999, "Microscopic Observations of Formation Processes of Clathrate-Hydrate Films at an Interface Between Water and Carbon Dioxide", *Journal of Crystal Growth*, Vol. 204, pp. 348-356.
- Zuo, Y., Stenby, E. H., 1997, "Prediction of Gas Hydrate Formation Conditions in Aqueous Solutions of Single and Mixed Electrolytes", *SPE Journal*, Vol. 2, pp. 406-416.