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DEVELOPMENT OF KINETIC MODEL FOR THF-HYDRATE GROWTH

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Abstract. *This paper aims to develop a kinetic model for hydrate growth in order to study the radial growth of hydrate. For that, a cylindrical vessel has been constructed to perform experiments involving macroscopically formation of THF-hydrate varying the sub-cooling from -3.0 up to 1.0 °C. Besides, computational simulations using the commercial software ANSYS Fluent® based on heat transfer, mass transfer, kinetic and porosity have been done in order to propose a new model for this phenomenon.*

Keywords: *Hydrate Growing, Kinetic Model, CFD, ANSYS/FLUENT--Student®.*

1. INTRODUCTION

The understanding of hydrate growth mechanism plays a key role in developing hydrate formation risk management in oil and gas flowlines, primarily in shutdown and restart operations. Several research centers have been studying the possible mechanisms that could control the hydrate growth in several scenarios. These mechanisms base their studies in models concerned with heat transfer, mass transfer or intrinsic kinetics, all of them treated independently. Hence, they do not present a model that includes all the related phenomena.

This work presents a numerical simulation, using Computational Fluid Dynamics (CFD) that propose a new kinetic model for hydrate formation taking into account the relation among the heat transfer and mass transfer, considering for the hydrate a transient porosity. The kinetic model have been implement by User Defined Functions (UDF). The verification was performed by experimental data using tetrahydrofuran (THF) as hydrate former. It because, THF is unique in that is liquid in atmospheric pressure, unlimitedly soluble in liquid water, and it forms a hydrate under atmospheric pressure (IIDA et al.; 2001). Unlike hydrophobic hydrate compounds, THF-water solution allows hydrate crystals to form and grow anywhere. Considering the mixture is composed at a molar ratio of 1:17, that is the stoichiometric ratio of THF in structure II hydrate, it guarantees the completely transformation of the THF-water solution in THF hydrate.

2. KINETIC MODEL

The first's kinetic studies of gas hydrate growth related the adsorption of the hydrate forming molecules (HFM) into the crystal-liquid interface (ENGLEZOS et al., 1987) with a simultaneous transport of the HFM from the solution to the crystal-liquid interface, taking into account an equilibrium between the HFM flux and the adsorption rate.

In the sequence studies related with mass transfer in water dominate systems, reported the (SKOVBOG e RASMUSSEM, 1994; KHOSHRSRAY et al., 2015) gas hydrate growth mainly in regions near of gas-liquid interface due to high gas concentrations which can be the order of 0.15 molar fraction; requiring in many cases of high pressures to diluted the gas and foster training conditions of hydrate formation. On the other hand; in order to simplifying the experimental procedure many studies use THF liquid such as hydrate former, representing a great alternative principally by the affinity of THF with water an ambient pressure. Besides, the crystalline structure of THF (sII) is

common in the majority of the hydrocarbons of oil and gas production. Hence, the present proposal believe that the study of THF hydrate formation could be apply in future works involved hydrocarbons in oil and gas production.

Considering a water dominate system with THF liquid diluted in the molar fraction of 1/18; the present kinetic model concentrate the analyses in the adsorption process of THF molecules for the crystal-liquid interface into domain called control volume, where the hydrate growth is considered such as porous media with the porosity varying along the time, Figure 1.

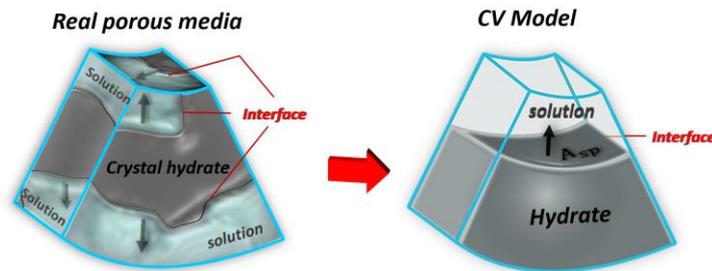


Figure 1. Control volume model representation.

Of the molecular dynamics study for THF hydrate growth (1:17) realized by Wu et al. 2014; was observed for the crystal-liquid interface a drop concentration due the adsorption process, which can be related with an located mass transfer without the formation of the viscous film where the solution molar fraction remains constant (1/18 ~ 0.055), Figure 2.

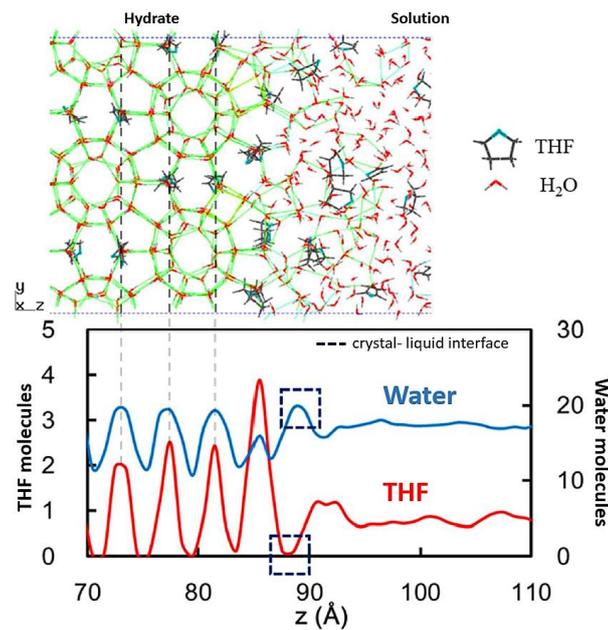


Figure 2. Molar relation of molecules of THF and Water in hydrate growth direction (WU et al. 2014 – Adapted).

Thus, of the Figure 1, the hydrate rate growth can be understand as rate adsorption process describe by the Equation (1).

$$R_H = K \frac{A_{sp}}{V} (C_s - C_{eq}) \quad (1)$$

where, R_H is the hydrate rate growth ($\text{mol}/\text{m}^3\text{-s}$), K is the kinetic parameter of the model (m/s); A_{sp} is the superficial area crystal-liquid interface (m^2/s); V is the control volume (m^3); C_s is the THF molar concentration (mol/m^3) and C_{eq} is the equilibrium concentration (mol/m^3).

Moreover, the equilibrium concentration in the crystal-liquid interface was associated with the temperature effect in the adsorption process of the HFM. In order to understand it, the relation between the kinetic C_{eq} and the thermodynamic ΔG^0 parameters of the adsorption process was considered, Equation (2).

$$C_{eq} = C_s e^{\frac{\Delta G^0}{RT}} \quad (2)$$

where, ΔG^0 is the changes of Gibbs free energy (J/mol); R is the universal gas constant (8.314 J/K-mol) and T is the local temperature (K).

And for the changes of Gibbs free energy ΔG^0 , was employed the next thermodynamics relations (MILLIN, 2001):

$$\Delta G^0 = \Delta H_F^0 - \Delta S^0 T \quad (3)$$

$$\Delta S^0 = \frac{\Delta H_F^0}{T_{eq}} \quad (4)$$

where, ΔH_F^0 is the hydrate formation enthalpy (J/mol); ΔS^0 is the changes of entropy(J/K-mol) and T_{eq} is the equilibrium temperature of hydrate dissociation.

Hence kinetic of the THF hydrate growth process (1:17) is governed by the kinetic adsorption process directly influenced by temperature, Equation (5).

$$R_H = KC_s \frac{A_{sp}}{V} \left(1 - e^{\frac{\Delta H_F^0 (T_{eq} - T)}{RT_{eq} T}} \right) \quad (5)$$

3. EXPERIMENTAL PROCEDURE

This work applied an experimental methodology to observe the radial growth of hydrate using image and temperature record. The cell, schematically shown in Fig. 3 (a), is an acrylic cylinder with 12.6 cm height, 0.5 cm thickness and 14.0 cm diameter. The cell is submerged in a 50 wt. % monoethylene glycol thermal bath that could be set to different sub-cooling levels. It was used THF-water solution and the temperatures into the cell are monitored by five thermocouples (one HSTC-TT-K-24S-72 and four TJ60-CASS-116U-4, OMEGA) which are submerged until half height of the liquid solution, distributed along the radius, Fig. 3 (b). The thermocouples are placed inside of the cylinder equidistant (17.5 mm) from wall to center in order to determine the temperature distribution of the hydrate film and the others are outside into thermal bath taking into account the temperatures on the external wall and bath. A camera (Logitech C920) is fixed at the top of the thermal box.

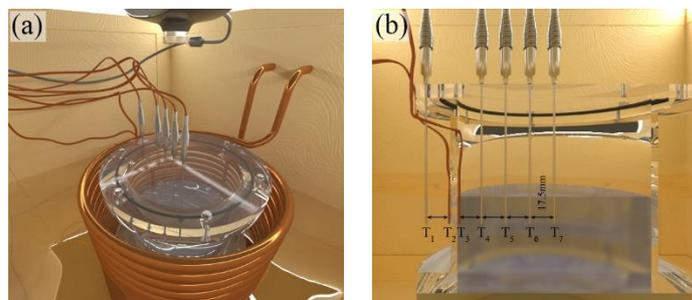


Figure 3. (a) Schematic of the experimental set-up. (b) Thermocouples array detail.

The experiments used a solution of THF and deionized water with 1:17 molar ratio colored with blue dye, which was used in order to facilitate the porous visualization because the dye molecules are bigger than the sII hydrate cavities, thus the hydrate remains crystalline. After pouring the solution into the experimental cell, it is hermetically

closed. Every experimental run initiates by set bath (boundary) temperature and start the temperature and image acquisition. These data are recorded every minute, throughout the experiment. The tests have taken up to three days

4. NUMERICAL PROCEDURE

For the numerically study this work employ the CFD software ANSYS/FLUENT-Student®, where was enabled the Energy Equation including a source term, via user defined function (UDF), due to heat release on hydrate growth describe in the Equation (6.a).

$$\frac{\partial}{\partial t} [\varphi \rho_s E_s + (1-\varphi) \rho_H E_H] = \nabla \cdot (k_{eff} \nabla T) + \bar{L} R_H \quad (6.a)$$

$$k_{eff} = \varphi k_s + (1-\varphi) k_H \quad (6.b)$$

where, φ is the hydrate porosity; ρ is the density (kg/m^3); E is the specific energy (kJ/kg); \bar{L} is the latent heat of formation (J/mol); R_H is the hydrate rate growth ($\text{mol/m}^3\text{-s}$), k_{eff} is the effective thermal conductivity (kW/K-m) and each subscript s , H is referred to solution and hydrate respectively.

Besides, for the hydrate was necessary implement an equation for the hydrate conservation mass implemented via user defined scalar (UDS) with a new variable called porosity φ , Equation (7).

$$\frac{\partial}{\partial t} [(1-\varphi) \rho_H] = R_H M_H \quad (7)$$

where, M_H is the hydrate molar mass (kg/mol).

For the hydrate rate growth of the Equations (6.a) and (7); was implement a sub-routine via UDF considering the Equation (5) and geometric parameters of the control volume to represent the THF hydrate porosity. The control volume was obtained from a 2D uniform geometry interpreted such as axisymmetric domain by ANSYS/FLUENT-Student® which taking into account a sweep of 1 radian as show in Figure 4.

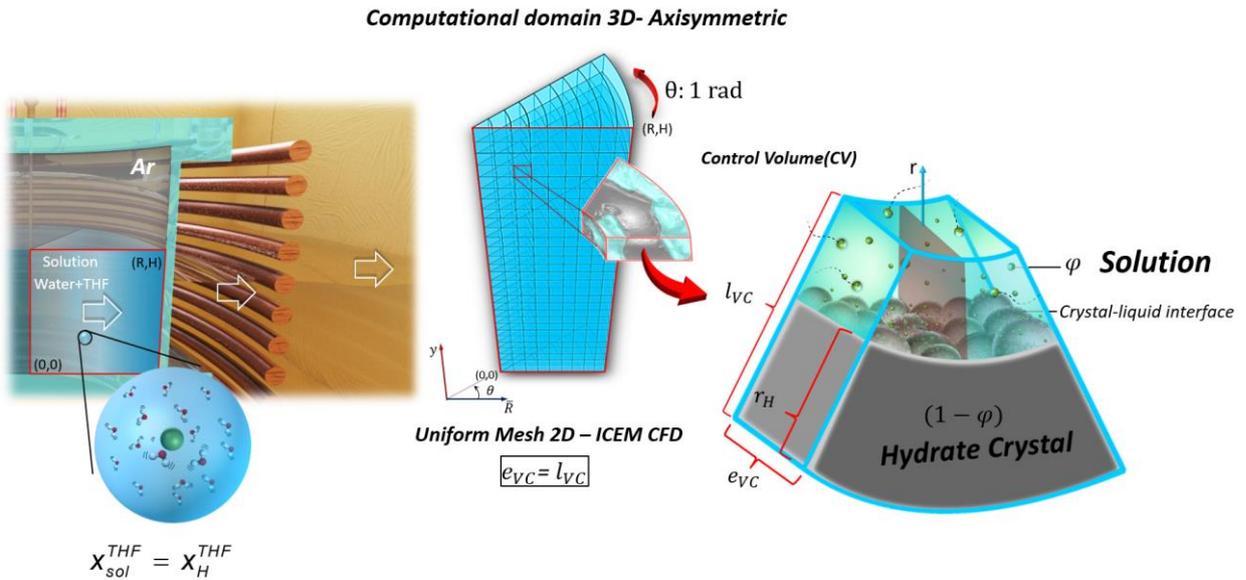


Figure 4. Axisymmetric domain ANSYS/FLUENT-Student®.

Moreover, for the boundary conditions of the problem were considered the following:

for all $y = H$;

$$\frac{\partial T}{\partial y_H} \approx 0 \quad (8.a)$$

$$\frac{\partial \phi}{\partial y_H} = 0 \quad (8.b)$$

for all $\bar{R} = R$;

$$T_{y=R} = T_{(T_3)} \quad (9.a)$$

$$\frac{\partial \phi}{\partial \bar{R}_R} = 0 \quad (9.b)$$

for all $y = 0$;

$$T_{y=-e} = T_{(T_1)} \quad (10.a)$$

$$\frac{\partial \phi}{\partial y_0} = 0 \quad (10.b)$$

where, for the top of the solution was considered heat flux zero, Equation (8.a); for the lateral wall of the cylinder was defined a transient function via UDF using a data registered by the thermocouple T₃, Equation (9.a) and for the cylinder base, was imposed the bath temperature (thermocouple T₁) taking into account a wall thickness e of 7 cm, Equation (10.a).

The initial condition for THF hydrate growth assume as initial system porosity the value of one (without presence of hydrate) and for the initial system temperature, the experimental reports indicate which hydrate growth starts with a temperature approximately of 4.1°C.

The relevant physical properties used at the simulation are specified in Tab 1.

Table 1. Properties for THF hydrate systems.

	Properties	Unit	THF Hydrate	THF + H2O
R	Internal radius of pipeline	mm	70.0	
p	Pressure	bar	1.0	
T_{eq}	Equilibrium temperature	K	277.55	
ΔT_{min}	Subcooling minimum	K	0.4	
ρ	Mass density	kg/m ³	997	997
c_p	Specific heat capacity	J/kg.K	2123	4210
K	Kinetic parameter	(m/s)	6E-06	-
M	Molar weight	kg/mol	0.3783	21.02
\bar{L}	Latent heat formation	kJ/mol	100	-
k	Thermal conductivity	W/m.k	0.525	0.562
n	Hydration number	-	17	-
ϕ_F	Final hydrate porosity	-	0.1	-

5. RESULTS AND DISCUSSION

The experimental runs were made with three different bath temperatures (1.0°C, -1.0°C and -3.0°C) to analyze the influence of the subcooling effects on hydrate formation, comparing the temperature registered of thermocouples T4 and T5 for the experimental procedure with the obtained of numerical simulation, Figures 5-7.

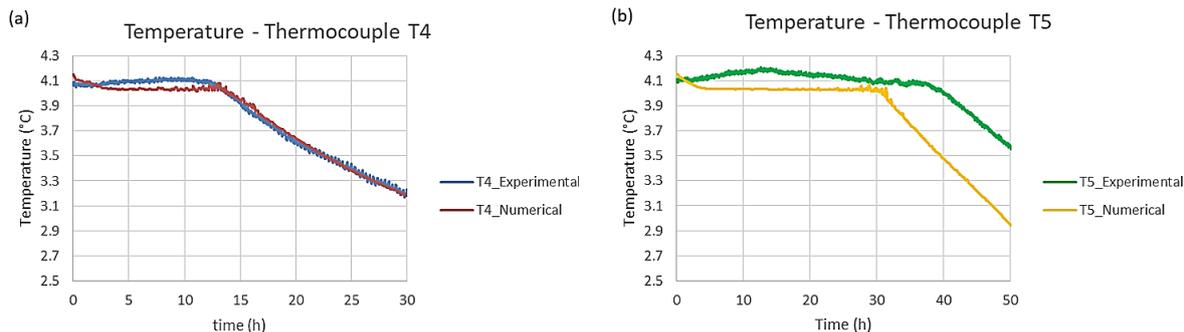


Figure 5. Bath temperature 1.0°C. Thermocouple T₄ and T₅.

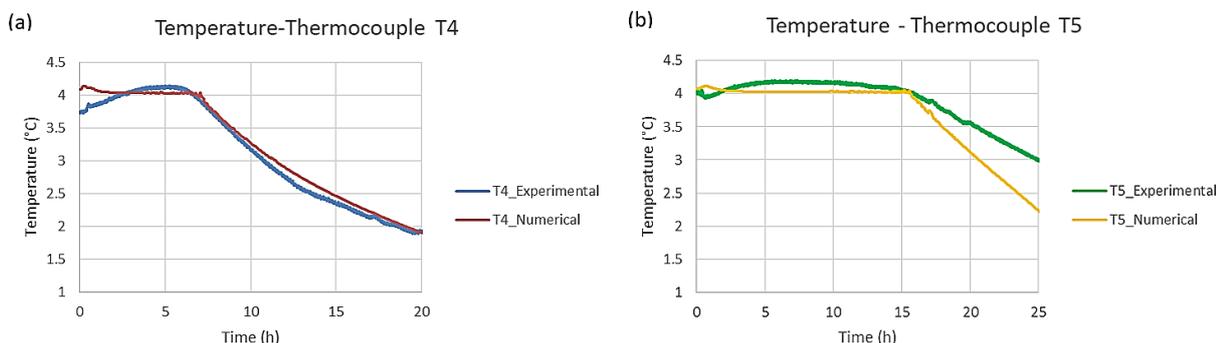


Figure 6. Bath temperature -1.0°C. Thermocouple T₄ and T₅.

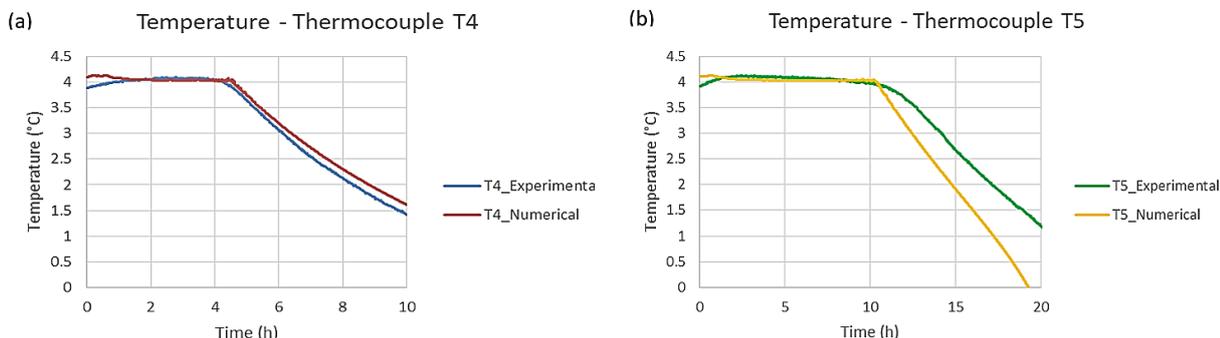


Figure 7. Bath temperature -3.0°C. Thermocouple T₄ and T₅.

Of the Figures 5-7 can be observed for the experimental and numerical results the temperature drop of thermocouples T₄ and T₅, which is related with the hydrate overtake each thermocouple due the growth from wall cylinder. The times related to the temperature drop are reported at Table 2 -3.

Table 2. Thermocouple T₄.

Bath temperature (°C)	Experimental time (h)	Numerical time (h)	Error (%)
1.0	13.00	13.24	1.85%
-1.0	6.82	7.00	2.64%
-3.0	4.21	4.57	8.55%

Table 3. Thermocouple T₅.

Bath temperature (°C)	Experimental time (h)	Numerical time (h)	Error (%)
1.0	37.80	31.43	16.85%
-1.0	15.48	15.39	0.58%
-3.0	10.00	10.15	1.50%

6. CONCLUSION

THF-hydrate growth rate was investigated experimentally and numerically in this paper. The experimental facility was constructed to permit thermal monitoring in hydrate growth evolution along the time. A time-lapse study of the hydrate growth rate was done and the results are compared with numerical model. In spite of an observed difference between the numerical and the experimental, the numerical model could represent the THF hydrate growth. As a result, the constant of the model was adjusted in order to fit the experimental data.

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8. RESPONSIBILITY NOTICE

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