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Abstract
This work deals with formation and growth of THF hydrate in porous media in a cylindrical reactor. In clear media, temperature distribution is determined and hydrate thickness is calculated by capturing images at various time intervals. Experiments in porous media are conducted using glass beads (3.5mm-4.5mm) and sand (.05mm-.9mm). Induction time are compared for different runs with same particle size. Induction time varied from one run to another for same particle size. Cooling curve is an important part of THF hydrate study in cylindrical reactor. Therefore, experimental temperature distribution for cooling curve at the centre of reactor is compared with numerical simulated and analytical results. Experimental observations are in good match with numerical simulated/analytical results which emphasized that conduction is dominant mode of heat transfer for temperature prediction at the centre of reactor. Unexpectedly, it is found that temperature starts falling after 2 h form initial hydrate formation in case of porous media (sand) and a tangible explanation is attempted to explain this observation.
Keywords*: Hydrate; reactor; Induction time; cooling curve*

I. INTRODUCTION

Clathrate hydrates are solid crystalline inclusion compounds in which guest molecules are trapped in cages formed by hydrogen bonded water molecules. Recently natural gas hydrates have received lot of attention due to ever increasing energy demands and need for cleaner fuel. They are generally found in permafrost and ocean bed.

Over the years, THF (Tetrahydrofuran) hydrate investigation has received a lot of attention. Moreover, THF forms a structure II hydrate [1] which is predominant structure in natural gas applications. Further, equilibrium melting point of THF hydrate is 4.4°C at 0.1 MPa pressure for stoichiometric ratio which is the molar ratio of THF and water at 1:17 [2]. Therefore, THF hydrate investigation does not need a pressurized reactor to form clathrate hydrate.

Hence, THF is a good substitute for studying gas hydrates. Nucleation and then subsequent hydrate growth are two important steps in hydrate formation. Hydrate nucleation is the process during which small clusters of water and gas grow and disperse in an attempt to achieve hydrate nuclei critical size for continued growth [3]. Nucleation step is a microscopic phenomenon involving tens to thousands of molecules and is difficult to observe precisely during experiments. However, induction time can be used to quantify the metastability of hydrate formation. Induction time is the period necessary for the appearance of the very first hydrate cluster of super nucleus size and capable of spontaneous overgrowth to a macroscopic size [4].

The study of THF hydrate in clear media can provide us key insights about nature of hydrate formation but in nature, methane hydrate is generally found in porous media at natural conditions. Therefore, investigation of THF hydrate in porous media is crucial to understand hydrate growth in nature. Song et al. [5] investigated THF hydrate formation and dissociation at various size of glass beads and found that presence of third surface is important for THF hydrate formation as THF hydrate crystals started to form on porous media and in their adjacent area as well as from the wall of the sample container. Xue et al. [6] investigated THF hydrate in porous media and suggested that THF hydrate grows as the cementing model when the THF and water are mixed at the molar ratio of 1:17 (19% by weight). Further, the hydrate forms preferentially at grain contacts, and then occupies the pore of the porous media gradually.

In literature, THF hydrate investigation in porous media is mainly focused on intrinsic features of hydrate growth demonstrating phenomena like memory effect, induction time but there is very scarce information on the transport phenomena which occurs inside the reactor. Here, in our study we have investigated THF hydrate growth in

cylindrical reactor with temperature variation in reactor as primary diagnostics. Experiments are designed in a way to reveal inherent features of transport phenomena inside of the reactor in porous media while also depicting intrinsic features of hydrate formation like induction time. of hydrate formation. Initially, THF hydrate growth in clear media is discussed to appreciate the influence of porous media. Further, numerical and analytical solutions of cooling THF solution are also produced and compared with experimental observations.

II. METHODOLOGY
A. Experimental details

Experiment apparatus is shown in fig. 1 contains: (1) reactor cell made up of glass with a diameter 13.5cm and volume 3L, (2) Plexiglas tank of dimensions 37×37×26 cm3, (3) two "T- type" thermocouples placed in Plexiglas guides, (4) camera, (5) data acquisition system for recording temperature. The reactor cell was housed in a Plexiglas tank which was covered with insulating material for decreasing heat transfer to the surrounding. Two "T-type" thermocouples are located at radial distance of 5mm and one at the canter of reactor cell, connected to a data acquisition system of National Instruments to collect temperature information with the help of LabVIEW program and temperature value recorded after every 4s. A camera is used to capture images of THF hydrate growth at various time intervals and a cooling jacket around reactor cell is used to maintain the low temperature at the reactor wall at 1±0.3°C.
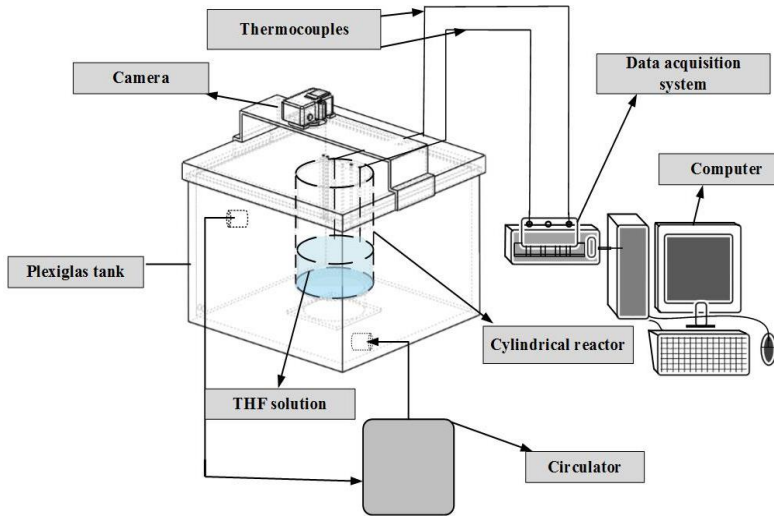

Figure 1: Schematic diagram of experimental set up

B. Numerical details

Mathematical modelling of cooling of THF solution is done for stoichiometric concentration at atmospheric pressure. Further, we have made following assumptions for developing the mathematical model: -

(a) The heat transfer between the THF hydrate and solution is taken as one dimensional i.e., only in radial direction.
(b) The dominant mode of heat transfer is conduction (neglecting the effect of natural convection).
(c) Variation of properties with temperature is negligible.
(d) Local thermodynamic equilibrium and volume averaged temperature is used in all the equations.

Considering above assumptions, governing equation can be written in porous media

$$(\rho c)_{eff} \frac{\partial \langle T \rangle}{\partial t} = \nabla.\left(k_{eff} \nabla \langle T \rangle\right), \tag{1}$$

$$(\rho c)_{eff} = (1-\phi)(\rho c)_s + \phi(\rho c)_f, \tag{2}$$

$$k_{eff} = (1-\phi)(k)_s + \phi(k)_f, \tag{3}$$

where c_f is the specific heat of fluid, c_s is the specific heat of solid, ρ_f is the density of fluid, ρ_s is the density of solid, k_f is the thermal conductivity of fluid, k_s is the thermal conductivity of solid, ϕ is the porosity. The initial and boundary conditions can be written as: -

$$r = 0, \ \frac{\partial \langle T \rangle}{\partial r} = 0$$
$$r = R, \langle T \rangle = 274.35 \text{ K}$$
$$t = 0, \langle T \rangle = 298.65 \text{ K}$$

where r is the radial distance from centre of the reactor and R is the radius of the rector. The thermo-physical properties of THF solution are adopted from Iida et al.[7] and are mentioned in the table 1.

Table 1: Thermophysical properties of THF solution and glass beads

Property	Liquid Solution	Glass beads
Thermal conductivity k (W m^{-1} K^{-1})	0.562	1
Specific heat C_p (J kg^{-1} K^{-1})	4210	510.204
Density ρ (kg m^{-3})	997	2520

Mathematical model is numerical simulated using Comsol Multphysics®.Further an analytical solution is also developed using variable separable approach, given by (4):

$$\theta = 2\sum_0^\infty \frac{\theta_i J_0(\lambda_n r)}{\lambda_n R} e^{-\frac{(1-\phi)(k)_s + \phi(k)_f}{(1-\phi)(\rho c)_s + \phi(\rho c)_f}}, \tag{4}$$

The values of "λ" are given by (5)

$$J_0(\lambda_n R) = 0, \tag{5}$$

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III.   RESULTS AND DISCUSSION

Figure 2(a) and 2(b) shows a schematic diagram of conceptualized THF hydrate formation in porous media and actual THF hydrate formed in porous media (glass beads (3.5mm-4.5 mm)). Figure 2(b) shows THF hydrate grows in porous media like a cementing model. The hydrate forms preferentially at grain contacts, and then occupies the pore of the porous media gradually.
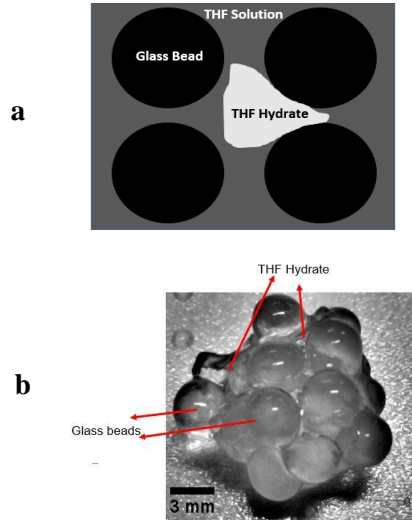
Figure 2: Conceptual (a) and actual hydrate formation (b) in porous media

Figure 3 shows temperature distribution of THF hydrate formation in clear media at close to the wall (r/R=.93) and centre of the reactor (r/R=0). Temperature drops from 23°C to around 1.5 °C which is the cooling regime (a-b). At the starting of the cooling curve, the temperature decreases steeply because initially there is a large temperature difference between the THF solution and reactor wall temperature, so higher heat transfer takes place from the THF solution to reactor wall. After an initial cooling period of 2 hours, nucleation takes place and hydrate growth happens (b-c) from the wall towards centre of the reactor. The temperature increases until it reaches equilibrium temperature. The temperature close to the wall starts decreasing because of the continuous cooling from the wall but the temperature at the centre (r/R=0) almost remains constant throughout the growth of THF hydrate. The nearly constant nature of temperature at the centre may be explained by considering the heat generation due to continuous hydrate formation towards the centre of the reactor from the wall and further decreased heat transfer due to hydrate formation at the periphery of the reactor. Earlier we stated that nucleation of THF hydrate is stochastic which is quite evident in experiments involving hydrate growth in sand as porous media. Sand used in the present study as porous media has particle size: .05mm to. 9mm.Induction time varied from one experiment to another

Induction time varied from one experiment to another run. Induction from 3 runs are 2 hr 36 min, 57.6 min ,45 min which shows its stochastic nature. This can be attributed to the fact that THF hydrate is in metastable stage below equilibrium temperature (4.4°C at stoichiometric concentration), therefore hydrate can form at any time below the equilibrium temperature with the help of external impurity.
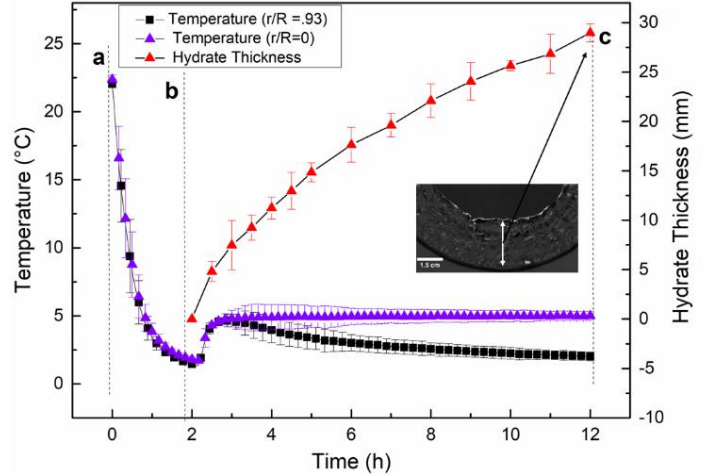
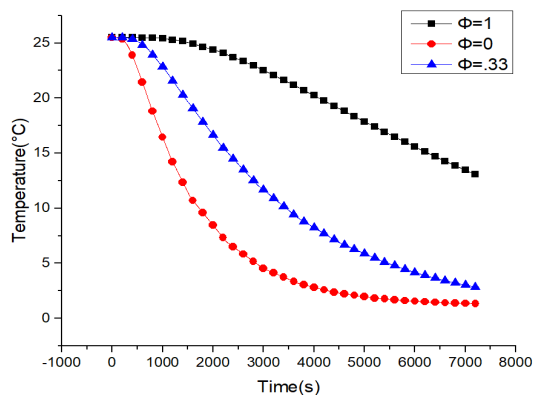Figure 3: Temperature distribution at two locations in clear media

Figure 4 shows temperature distribution in sand as porous media (.05mm to. 9mm) for three experimental runs at the centre of the reactor. The nature of cooling curve is same in all three runs but difference lies in the hydrate nucleation and growth. Induction time is different in all three runs which is expected. However, after initial temperature rise after hydrate nucleation, suddenly temperature starts dropping around 2 h during hydrate growth period in all the three runs which is quite unexpected. Moreover, after temperature drop, temperature becomes almost equal in all the three runs.
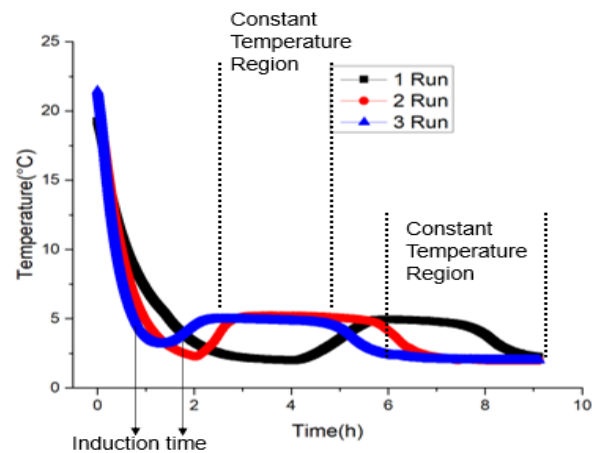
Figure 4: Temperature time profile for three experimental runs at the centre of the reactor in sand as a porous media
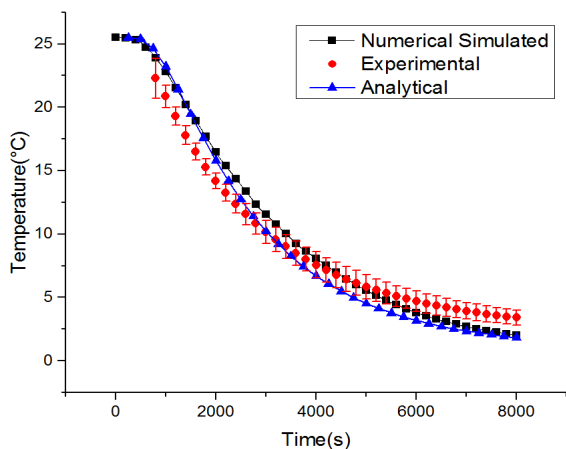
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This sudden drop can be explained by the fact that that hydrate formation at the centre of reactor in clear media takes a long time but for porous media formation of hydrate happens quickly because of present of third surface (porous media). Therefore, due to quick hydrate formation at the centre of reactor, there will be no longer heat generation due to hydrate formation at the centre of reactor which will result in reduction of temperature after some time due to lower temperature maintained at the wall. This observation also emphasizes that initially there will be tendency of hydrate to form at the wall but eventually its formation will become random throughout the reactor as critical size nucleus to form and sustain growth.

Figure 5 shows temperature distribution at the centre of reactor with different porosity which shows as porosity decreases, decrease in temperature becomes steeper. This can be explained by the fact that thermal diffusivity of matrix is 5.81 times than THF solution. Therefore, as the porosity decreases, the effective thermal diffusivity increases which results in higher cooling rates.

Figure 5: Comparison of Temperature profile at the center of the reactor for different porosities

Figure 6 shows experimental, analytical and numerical simulated temperature distribution at the centre of the reactor. There is excellent agreement between experimental and numerical simulated/analytical results which emphasize that dominant mode of heat transfer away from the wall is conduction

Figure 6: Comparison of numerical, experimental, analytical results for cooling of THF solution in porous media at the center of the reactor

The following conclusions can be made from our work**:**

1) Temperature at the centre of the reactor in case of clear media after hydrate formation is constant because of continuous heat generation as hydrate front moves from wall to the centre. However, in case of porous media it is found that temperature starts reducing after approximately 2 h from initial hydrate formation. This is because hydrate formation at the centre of reactor in clear media takes a long time but for porous media formation of hydrate happens quickly because of present of third surface (porous media).

2) Modelling conduction as dominant mode of heat transfer for prediction of temperature at the centre of reactor is a good approximation. This is well supported by fact that experimental temperature data is found in agreement with numerically simulated and analytical solutions.

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