

# 1-D Modeling of Hydrate Decomposition in Porous Media

F. Esmailzadeh, M. E. Zeighami, and J. Fathi

**Abstract**—This paper describes a one-dimensional numerical model for natural gas production from the dissociation of methane hydrate in hydrate-capped gas reservoir under depressurization and thermal stimulation. Some of the hydrate reservoirs discovered are overlying a free-gas layer, known as hydrate-capped gas reservoirs. These reservoirs are thought to be easiest and probably the first type of hydrate reservoirs to be produced. The mathematical equations that can be described this type of reservoir include mass balance, heat balance and kinetics of hydrate decomposition. These non-linear partial differential equations are solved using finite-difference fully implicit scheme. In the model, the effect of convection and conduction heat transfer, variation change of formation porosity, the effect of using different equations of state such as PR and ER and steam or hot water injection are considered. In addition distributions of pressure, temperature, saturation of gas, hydrate and water in the reservoir are evaluated. It is shown that the gas production rate is a sensitive function of well pressure.

**Keywords**—Hydrate reservoir, numerical modeling, depressurization, thermal stimulation, gas generation.

## NOMENCLATURE

$A_{dec}$  = specific surface area per unit bulk volume,  $m^{-1}$   
 $AHS$  = specific area of hydrate particles,  $m^{-1}$   
 $E$  = activation energy, J/mol  
 $fe$  = fugacity of gas at  $T$  and  $pe$ , kPa  
 $fg$  = fugacity of gas at  $T$  and  $pg$ , kPa  
 $\dot{g}_l$  = generation rate of phase  $l$  per unit volume,  $kg/m^3s$   
 $h_l$  = specific enthalpy of phase  $l$ , J/kg  
 $K$  = absolute permeability, md  
 $K_c$  = thermal conductivity, w/m·K  
 $K_d^0$  = intrinsic decomposition rate constant,  $kmol/m^2kPa \cdot s$   
 $k_d$  = decomposition rate constant,  $kmol/m^2kPa \cdot s$   
 $k_{rl}$  = relative permeability to phase  $l$   
 $M_c$  = molar mass of component  $c$ , kg/kmol  
 $NH$  = hydrate number (= 5.75)  
 $P_l$  = pressure of phase  $l$ , kPa  
 $P_c$  = capillary pressure between gas and water, kPa  
 $P_e$  = H-V-Lw equilibrium pressure, kPa  
 $q_{ml}$  = mass production rate of phase  $l$  per unit volume,  $kg/m^3s$   
 $\dot{Q}_H$  = heat of hydrate decomposition per unit volume, J/m<sup>3</sup>s

$\dot{Q}_{in}$  = direct heat input per unit volume, J/m<sup>3</sup>s

$R$  = gas constant (= 8.314 J/mol·K)

$S_{wr}$  = irreducible water saturation

$S_{gr}$  = residual gas saturation

$S_l$  = saturation of phase  $l$

$\bar{S}_l$  = normalized saturation of phase  $l$

$t$  = time, s

$T$  = temperature, K

$v_l$  = velocity of phase  $l$ , m/s

$U_l$  = specific internal energy of phase  $l$ , J/kg

$\phi$  = porosity

$\mu_l$  = viscosity of phase  $l$ , Pa·s

$\rho_l$  = density of phase  $l$ , kg/m<sup>3</sup>

## SUBSCRIPT

$g$  = gas

$w$  = water

$H$  = hydrate

$R$  = rock

$i$  = initial condition

## I. INTRODUCTION

GAS hydrates are ice-like crystalline materials and non-stoichiometric compounds that contain water and gases with small molecules such as CH<sub>4</sub> and which can occur at temperatures above the freezing point of water. Gas hydrates are treated as a potential energy resource for the future because a large amount of methane gas is trapped in hydrates reservoirs. One volume of hydrate could release 150 to 180 volumes of gas at standard conditions. The high concentration of methane gas puts the energy content of hydrate-bearing formations on a par with bitumen and heavy-oil reservoirs, and much higher than the energy content of other unconventional sources of gas, such as coal bed [1]. According to [2], the world resources of carbon trapped in hydrates have been estimated to be twice the amount of carbon in known fossil fuel deposits. There fore, developing methods for their production behavior are attracting considerable attention.

The technologies for recovering methane from hydrates are very challenging and are still under development. The three most practical methods are: (1) depressurization, in which the pressure of an adjacent gas phase is lowered to cause decomposition. (2) thermal stimulation, in which an external source of energy is used, and (3) inhibitor injection, in which

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inhibitor is used to de-equilibrate the system. The depressurization method is an effective method which is based on breaking the temperature-pressure equilibrium conditions of hydrate. In the depressurization method, a well is drilled into the hydrate reservoir and the well pressure is kept sufficient low to lead to dissociation of hydrate and release of natural gas.

The modeling of gas production from hydrate decomposition involves solving the coupled equations of mass and energy balances along with equilibrium and kinetics relations of hydrate decomposition.

Englezos (1993), Makogon (1974,1997) and Sloan (1998) had presented an extensive reviews of gas hydrate. Makogon (1974, 1997) viewed hydrate dissociation as a moving boundary ablation process, and used the classical Stefan's equation to describe the process of hydrate dissociation. In this model, a dissociation front is assumed to exist to separate the hydrate reservoir into a gas and a hydrate zone. Governing equations for the movement of natural gas in both zones are set up separately. A set of self-similar solutions for the pressure profiles was obtained after linearization of the governing equations. The water released during the hydrate dissociation was ignored in this model.

Verigin et al. (1980) developed Makogon's model by considering the gas and water mass balance at the dissociation front. The water released from the hydrate dissociation was assumed to be stationary and not to affect the flow of natural gas. In these earlier models, however, the process of hydrate dissociation was treated as an isothermal process.

Holder et al. (1982) simulated mass and heat transfer for the depressurization process in a hydrate reservoir overlaying a free natural gas zone. In this model, hydrate dissociation was assumed to occur only at the interface between hydrate "cap" and free natural gas layer. An energy equation involving only heat conduction was used to describe the temperature distribution in the natural gas layer. The continuity equation was used to describe the natural gas flow, in which the pressure gradient and the gas flow velocity were connected by Darcy's law. A heat balance at the interface of the hydrate "cap" and free natural gas layer was set up, from which the rate of hydrate dissociation was determined.

Water flow during the hydrate dissociation was considered by Burshears et al. (1986). They extended the model of Holder et al. (1982) by adding a mass balance of water at the dissociation front; however, the convective heat transfer in the area where gas and water coexist was not considered.

Selim and Sloan (1989) studied a thermal stimulation method for hydrate dissociation. In their one-dimensional model, convective-conductive heat transfer was considered under the assumption that the water in the reservoir remained stationary and the well temperature was kept constant.

Yousif et al. (1991) used a Kim-Bishnoi model (Kim et al., 1987) to describe a dissociation process of methane hydrate in Berea sandstone by depressurization. In a one-dimensional model, the hydrate dissociation process was assumed to be isothermal. Gas and water flow were all considered in separated continuity equations, pressure of gas and water was connected by capillary pressure. Variations of gas phase permeability and porosity during the hydrate dissociation also

were considered. The results showed distributions of pressure and hydrate saturation and the movement of the hydrate dissociation interface.

Bondarev and Cherskiy (Makogon, 1997) further developed the model of Makogon (1974) by including the heat transfer process in the porous medium. The conductive-convective energy equations in the gas and hydrate zones were used and the effects of the throttling process were included.

Tsyarkin (2000) also assumed the presence of a dissociation front and separated the hydrate reservoir into hydrate and gas zones during hydrate dissociation by depressurization. In his multiphase one-dimensional model, movement of water and gas in the reservoir was described and heat and mass balance at the dissociation front were included. Masuda et al. (1999) treated the process of hydrate dissociation as a Kim et al. (1987) kinetic process. In this model the driving force for hydrate dissociation is the difference between the equilibrium pressure and gas pressure. Their numerical results were in agreement with their experimental data. Moridis et al. (1998) added a module for hydrate dissociation into the TOUGH2 general-purpose reservoir simulator. The flow of gas and water were considered and the conductive-convective heat transfer equation was used.

Durgut and Parlaktuna (1996) described a thermal stimulation method for natural gas production in a hydrate reservoir. Their two-dimensional model included heat conduction and convection, and both water and gas flows. Swinkels and Drenth (1999) studied the behavior of a hydrate capped gas reservoir using a 3-D thermal reservoir simulator.

Ahmadi et al. (2000) and Ji et al. (2001) used the combined models of Verigin et al. (1980) and Bondarev and Cherskiy as reported by Makogon (1997). In this model, a set of self-similar solutions for temperature and pressure was obtained after linearization of the governing equations.

Pooladi-Darvish and Hong (2004) and Hong and Pooladi-Darvish (2005) have shown that in the presence of a mobile (gas or water) phase in the hydrate cap, pressure reduction propagates from the interface into the hydrate zone, leading to decomposition of the hydrate within the hydrate zone. Under these conditions, decomposition occurs over a zone rather than on an interface and the assumption of sharp dissociation interface becomes invalid.

In this work, natural gas production from hydrate-capped gas reservoir is studied. The reservoir is partially saturated with hydrate, and the reservoir contains pressurized natural gas and thermal stimulation is analyzed. The energy balance including both heat conduction and convection was used in the analysis. The mass balance and heat balance at the dissociation front are included in the analysis. Governing equations are solved using a finite-difference numerical scheme. In the model, the effect of convection and conduction heat transfer, variation change of formation porosity, the effect of using different equations of state such as PR and ER and steam or hot water injection are considered. In addition distributions of pressure, temperature, saturation of gas, hydrate and water in the reservoir are evaluated.

## II. PHYSICAL MODEL

Referring to Fig. 1, we consider a gas reservoir capped with a partially saturated hydrate layer in contact with cap and base rocks. The pressure and temperature conditions at the base of the hydrate layer are determined by the prevailing equilibrium relation. A well is drilled through the hydrate layer and is completed in the free-gas zone. At time  $t=0$ , gas is produced from the reservoir, causing the pressure in the free-gas zone to be reduced gradually to pressure below the equilibrium pressure at initial temperature.

Fig. 2 shows a hydrate three-phase equilibrium curve. Since the decomposition of hydrate is an endothermic process, the temperature of the hydrate will decrease to the new equilibrium pressure that provides the driving force for the kinetic decomposition of the hydrate. The heat of decomposition is provided by the sensible heat within the hydrate layer and adjacent base and cap rocks.

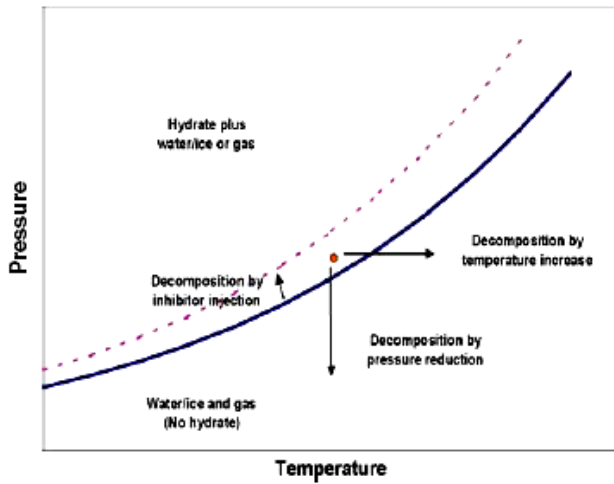


Fig. 2 Hydrate three-phase equilibrium curve [4]

In the present study, it is assumed that the pressure and temperature at the dissociation front are respectively the equilibrium pressure and temperature, which vary slowly with time.

## III. NUMERICAL MODELING

The mathematical equations that govern the above physical process include mass transfer, heat transfer and kinetics of hydrate decomposition. These equations are coupled non-linear partial differential equations. It is impossible to obtain the exact solution to these mathematical equations. However, a numerical technique such as the finite-difference fully implicit scheme is an effective tool to obtain an approximate solution. The accuracy of the solution can also be evaluated.

Hydrate decomposition reaction is modeled by the Kim-Bishnoi kinetics equation (Kim et al 1987).

$$\dot{g}_g = k_d M_g A_{dec} (f_e - f_g) \quad (1)$$

where  $\dot{g}_g$  is the mass rate of gas generated per unit bulk volume.  $M_g$  is the molar mass of methane gas.  $f_e$  and  $f_g$  are the fugacities of methane at equilibrium condition and gas phase. The fugacity of methane gas in the kinetic model is computed from the modified ER equation of state. The kinetic rate constant is a function of reaction temperature:

$$k_d = k_d^0 \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where  $k_d^0$  is the intrinsic rate constant,  $E$  is the activation energy, and  $R$  is the universal gas constant.

The specific area of the hydrate decomposition,  $A_{dec}$ , is incorporated using the following equation:

$$A_{dec} = \phi S_h A_{hs} \quad (3)$$

where  $A_{hs}$  is specific surface area per unit hydrate volume.

$\phi$  is the porosity of the formation.  $S_h$  is saturation of hydrate in the porous media. The fugacities are calculated using PR (Peng and Robinson 1976) or modified ER (Esmailzadeh and Roshanfekr 2007) equation of state.

The rate of water generated is given by:

$$\dot{g}_w = \dot{g}_g N_H \frac{M_w}{M_g} \quad (4)$$

where  $M_w$  is the molar mass of water, and  $N_H$  is the ratio of water molecules to methane molecules, chosen in this work to be 5.75.

The rate of hydrate decomposition is given by:

$$\dot{g}_H = -\dot{g}_g \frac{M_H}{M_g} \quad (5)$$

where  $M_H$  is the molar mass of methane hydrate.

The heat of decomposition is given by:

$$\dot{Q}_H = \frac{\dot{g}_H}{M_H} (56599 - 16.744T) \quad (6)$$

where  $T$  is temperature of porous media.

The mass balance equations for gas, water and hydrate in porous medium can be written as:

$$-\frac{\partial}{\partial z}(\rho_g v_g) + \dot{q}_{mg} + \dot{g}_g = \frac{\partial}{\partial t}(\phi \rho_g S_g) \quad (7)$$

$$-\frac{\partial}{\partial z}(\rho_w v_w) + \dot{q}_{mw} + \dot{g}_w = \frac{\partial}{\partial t}(\phi \rho_w S_w) \quad (8)$$

$$\dot{g}_H = \frac{\partial}{\partial t}(\phi \rho_H S_h) \quad (9)$$

Auxiliary relations:

$$S_g + S_w + S_h = 1 \quad (10)$$

$$P_w = P_g - P_c$$

where  $\dot{q}_{mg}$  and  $\dot{q}_{mw}$  are the source/sink in terms of injection/production of gas and water and  $P_c$  is capillary pressure between gaseous and aqueous phases. The velocities of gas and water are given by the Darcy's law for multiphase flow.

$$v_g = -\frac{Kk_{rg}}{\mu_g} \frac{\partial}{\partial z}(P_g) \quad (11)$$

$$v_w = -\frac{Kk_{rw}}{\mu_w} \frac{\partial}{\partial z}(P_w) \quad (12)$$

where  $K$  is the absolute permeability and  $k_{rw}$  and  $k_{rg}$  are the relative permeability of water phase and gas phase. In this work the relative permeabilities are evaluated with Corey model:

$$k_{rw} = \left( \frac{\frac{S_w}{S_w + S_g} - S_{wr}}{1 - S_{wr} - S_{gr}} \right)^4 \quad (13)$$

$$k_{rg} = \left( \frac{\frac{S_g}{S_w + S_g} - S_{gr}}{1 - S_{wr} - S_{gr}} \right)^2 \quad (14)$$

In these equations, the residual water saturation and gas saturation,  $S_{wr}$  and  $S_{gr}$ , are based on the pore volume occupied by fluid phases (namely effective pore volume). We assumed a value of 0.2 for  $S_{wr}$  and 0 for  $S_{gr}$  respectively [3].

For water pressure calculation we use capillary pressure and capillary pressure is calculated from Paker et al (1987) model.

$$P_c = \left[ \left( \bar{S}_w \right)^{\frac{1}{0.45}} - 1 \right]^{0.55} \quad (15)$$

where

$$\bar{S}_w = \frac{S_w - S_{wr}}{1 - S_{wr} - S_{gr}} \quad (16)$$

Equilibrium conditions (P,T) of the methane gas, methane hydrate and water are computed using the Kamath and Holder (1987) correlation [5].

$$P[kpa] = \exp \left( 38.98 - \frac{8533.8}{T[k]} \right) \quad (17)$$

Hydrate dissociation is an endothermic process and the dissociation rate depends strongly upon the temperature. In this work, we adopt a 1D continuum heat transfer model with conduction, convection and heat flow from the surrounding

sediments. This model is based on the assumption of no inter-phase heat resistance between gas, water, hydrate and the sand forming the medium. Heat balance equation is:

$$\frac{\partial}{\partial z} \left( K_c \frac{\partial T}{\partial z} \right) - \frac{\partial}{\partial z} (\rho_g v_g h_g + \rho_w v_w h_w) + \dot{q}_{mg} h_g + \dot{q}_{mw} h_w + \dot{Q}_H + \dot{Q}_{in} = \frac{\partial}{\partial t} [(1-\phi)\rho_{rock}u_{rock} + \phi S_H \rho_H u_H + \phi S_g \rho_g u_g + \phi S_w \rho_w u_w] \quad (18)$$

where  $h_g$  and  $h_w$  are the enthalpies of gas and water phase.

$u_{rock}$ ,  $u_H$ ,  $u_g$  and  $u_w$  are internal energy of rock, hydrate,

gas and water.  $\dot{Q}_{in}$  is heat from the cap or base rock and  $K_c$  is the thermal conductivity of the porous media. Thermal conductivities of rock, hydrate, water and gas are constant.

$$K_c = k_{c,rock}(1-\phi) + \phi(k_{c,H}S_H + k_{c,w}S_w + k_{c,g}S_g) \quad (19)$$

$$C_{p,g} = 1.238 + 0.00313T + 7.905 \times 10^{-7}T^2 - 6.858 \times 10^{-10}T^3 \quad (20)$$

$$C_{p,w} = 4.18 \frac{kJ}{kg.k}$$

$$C_{p,H} = 2.22 \frac{kJ}{kg.k}$$

$$C_{p,rock} = 0.8 \frac{kJ}{kg.k}$$

The enthalpy of water, gas, rock and hydrate phase is computed by the following correlation:

$$h = \int_{T_{ref}}^T C_p dt \quad (21)$$

Internal energy of water, hydrate and rock phases are equal with its enthalpy, but internal energy of gas phase is computed by following equation:

$$u_g = h_g - \frac{P_g}{\rho_g} \quad (22)$$

Initial and boundary conditions are as follows:

$$\begin{array}{lll} \text{at} & t = 0 & 0 \leq z \leq h & T = T_i \\ \text{at} & t = 0 & 0 \leq z \leq h & P = P_i \\ \text{at} & t = 0 & 0 \leq z \leq h & S_H = S_{H,i} \\ \text{at} & t = 0 & 0 \leq z \leq h & S_w = S_{w,i} \end{array} \quad (23)$$

$$\begin{array}{lll} \text{at} & z = 0, h & \frac{\partial P}{\partial z} = 0 \\ \text{at} & z = 0, h & \frac{\partial T}{\partial z} = 0 \end{array} \quad (24)$$

## IV. SOLUTION METHOD

Substituting equation 11 and 12 into equation 7 and 8 and multiplying by  $\frac{1}{\rho_{gsc}}$  and  $\frac{1}{\rho_{wsc}}$  respectively, give

$$\frac{\partial}{\partial z} \left[ \beta_c \frac{Kk_{rg}}{\mu_g B_g} \frac{\partial}{\partial z} (P_g) \right] + \dot{q}_{gsc} + \dot{g}_{gsc} = \frac{\partial}{\partial t} \left( \frac{\phi S_g}{B_g} \right) \quad (25)$$

$$\frac{\partial}{\partial z} \left[ \beta_c \frac{Kk_{rw}}{\mu_w B_w} \frac{\partial}{\partial z} (P_g - P_c) \right] + \dot{q}_{wsc} + \dot{g}_{wsc} = \frac{\partial}{\partial t} \left( \frac{\phi S_w}{B_e} \right) \quad (26)$$

Multiplying equation 9 by  $\frac{1}{\rho_{Hsc}}$  gives:

$$\dot{g}_{Hsc} = \frac{\partial}{\partial t} \left( \frac{\phi \rho_H S_H}{\rho_{Hsc}} \right) \quad (27)$$

Numerical techniques must be used to solve these equations. After non-linear partial differential equations are discretized into non-linear algebraic equations, Newton's method is used to linearize the fully-implicit equations and these equations are solved simultaneously to obtain the solutions of pressure, saturations of gas, water and hydrate phases and temperature.

## V. RESULTS AND DISCUSSION

The model developed herein can be used to estimate the reservoir parameters in lifetime of the reservoir simulation. The inputs to the model are related to initial pressure, porosity, drainage area, thermo-physical properties of reservoir components and production rate.

In this section, we study the effects of important parameters including reservoir porosity, rock thermal conductivity, production rate, reservoir permeability and initial reservoir temperature on hydrate reservoir behavior.

TABLE I  
BASE CASE PARAMETERS OF MODEL

$\phi = 0.16$
$K(\text{md}) = 20$
$T_i(\text{k}) = 285$
$k_{cr}(\text{w/m.k}) = 1.5$
$q(\text{std m}^3/\text{day}) = 6500$

Fig. 3 shows the comparison between the base case model results and Uddin et al(2006), HYDRSIM software model and Gerami et al (2006) model.

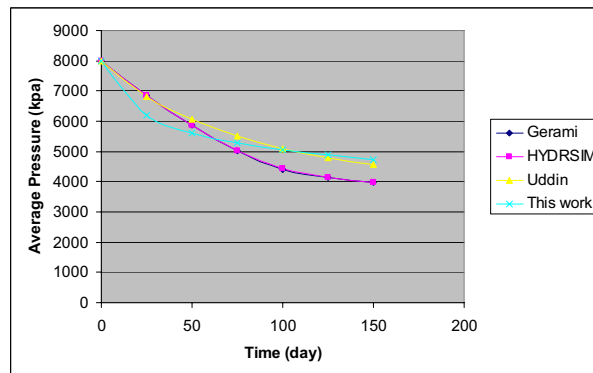


Fig. 3 Comparison between the models results

Fig. 4 shows the effect of varying the base case porosity. The comparison between these curves reveals that the reservoir pressure in the low porosity system is slightly lower than that of high porosity.

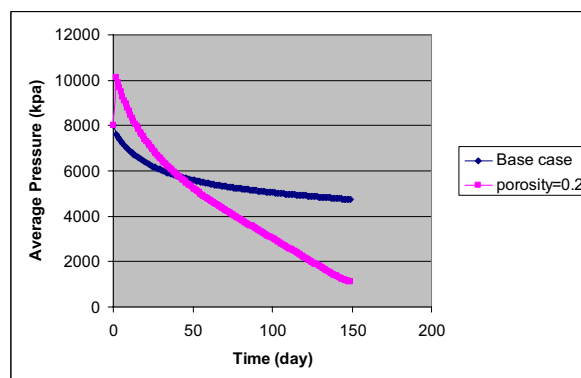


Fig. 4 Effect of varying the base case porosity

Fig. 5 shows the effect of doubling rock thermal conductivity. This comparison shows that in this range, thermal conductivity has an insignificant effect on reservoir performance.

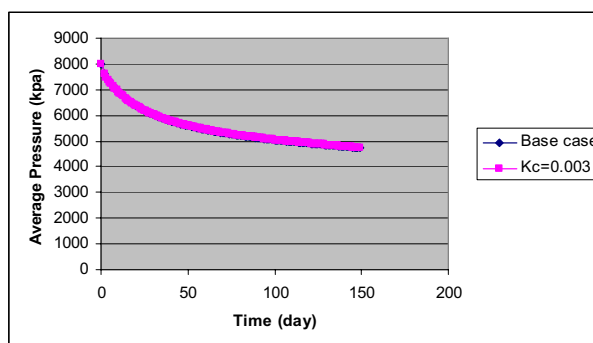


Fig. 5 Effect of doubling rock thermal conductivity

Fig. 6 shows the effect of increasing the base case production rate. This figure shows that, as production rate increase, reservoir pressure drops faster. Therefore, the corresponding equilibrium temperature drops faster.

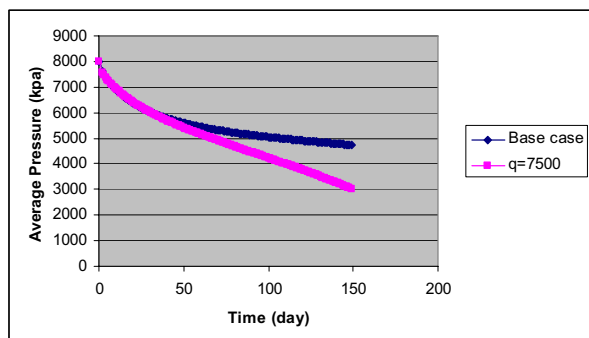


Fig. 6 Effect of increase in production rate

Fig. 7 shows the effect of varying the rock absolute permeability. Fig. 7 shows that, as rock absolute permeability decreases, reservoir pressure drops slowly.

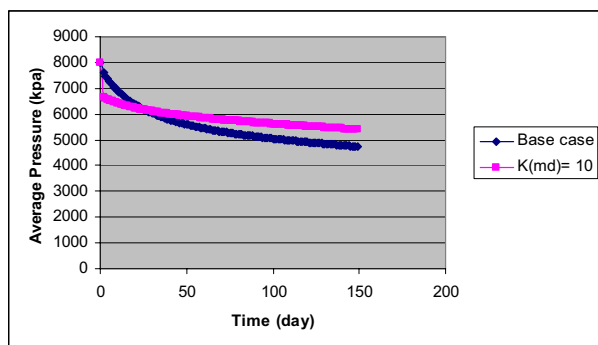


Fig. 7 Effect of decreasing rock absolute permeability

Fig. 8 shows the effect of varying the initial reservoir temperature. As reservoir temperature increases, the corresponding equilibrium pressure increases, leading to an increase in the amount of initial free gas-in-place. Therefore, reservoir pressure is sustained longer.

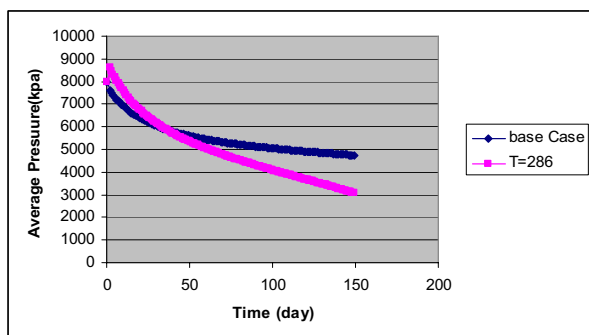


Fig. 8 Effect of increase in initial temperature

Effects of hot water injection in pressure distribution shows in Fig. 9 as hot water injection, the reservoir temperature increases, therefore pressure drops faster.

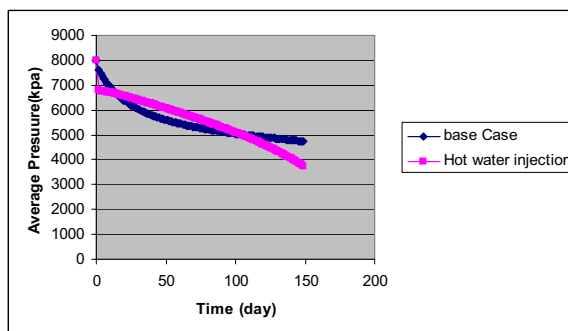


Fig. 9 Effect of hot water injection

## VI. CONCLUSION

Methane gas production from hydrate containing porous media is studied. A non-isothermal one-dimensional simulator is developed. This model taking into account the complete heat balance equation, heat transfer from surroundings, kinetics associated to hydrate decomposition and flow of water as a result of hydrate dissociation. The following are the conclusions drawn from the results:

1. The decomposition of hydrates can contribute significantly to the total production of a gas reservoir.
2. The gas production rate is a sensitive function of well pressure.
3. The presence of solid hydrate on top of a free gas reservoir had a significant impact on improving the productivity of the underlying gas reservoir.
4. When a mobile phase was present to transmit the low pressures caused by production, the hydrate decomposed deep within the hydrate layer allowing for more decomposition as compared with decomposition at the interface between the hydrate and the underlying free gas zone.

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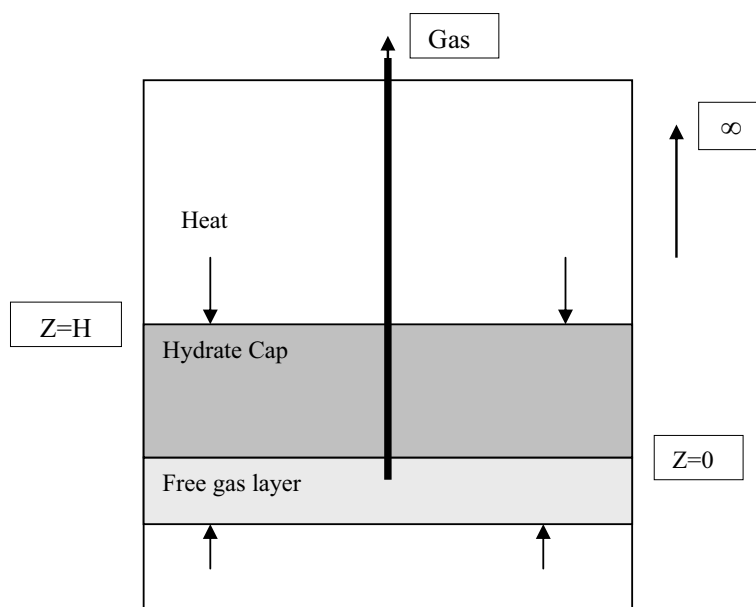


Fig. 1 Schematic of gas production model of the hydrate-capped gas reservoir