



SPE 134178

Kinetic Simulation of CO₂ Flooding of Methane Hydrates

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This paper was prepared for presentation at the SPE Annual Technical Conference and Exhibition held in Florence, Italy, 19–22 September 2010.

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Abstract

Finding new sources of energy and curbing global warming are two of the most important current problems. CO₂ can be injected into methane-hydrate reservoirs to produce methane and sequester CO₂ simultaneously. CO₂ replaces methane in the clathrate cages producing methane. The goal of this work is to develop a compositional, thermal, and kinetic simulator to design and interpret lab and field scale CO₂ flooding experiments of methane-hydrate in porous media. Five components (water, methane, CO₂, CH₄-hydrate, CO₂-hydrate) and six phases (aqueous, gas, liquid CO₂-rich phase, CO₂-hydrate, CH₄-hydrate and ice) are considered. The equations are spatially discretized with a finite volume difference method and are solved with a Newton-Raphson method in a fully implicit manner. Primary variable switch method (PVSM) is used to track the phase transitions. 1-D core scale simulations shows that the energy produced from CO₂-hydrate formation is utilized for methane-hydrate dissociation. The methane-hydrate dissociation front moves at a slow rate of approximately 1/40 cm/hr for the kinetics assumed in the base case. High mole fractions of CO₂ lead to CO₂-hydrate formation and methane-hydrate dissociation. To dissociate methane-hydrate by CO₂ injection, either we need to keep the CO₂ mole fraction very high in the fluid phase or operate at a relatively lower pressure (shallower reservoirs of methane-hydrates).

Introduction

Hydrates are crystalline compounds of gas (e.g., CH₄, CO₂) and water molecules formed at high pressure and low temperature (Sloan 1998). The reaction for hydrate formation and dissociation can be stated as:



Hydrates of hydrocarbon gases (mostly methane) occur naturally in deep oceanic sediments or in permafrost regions. There has been a lot of interest in developing these naturally occurring methane-hydrate reservoirs as an energy resource. The amount of carbon stored in these deposits is estimated to be 2-7 times the amount of carbon in known fossil fuel deposits (Kvenvolden, 1999). The flux of methane from these reservoirs to the atmosphere also creates environmental concerns as methane is a greenhouse gas. Therefore, production effort from these methane-hydrate reservoirs has generated a lot of research in recent times.

Depressurization, thermal stimulation, inhibitor injection, and CO₂ injection are suggested methods to produce gas from methane-hydrate reservoirs (Makogon, 1997; Ji et al., 2001; Graue et al., 2006). Different simulators (TOUGH-Hydrate, from LBNL; STOMP-Hyd, from PNNL; MH-21, from Japan Oil Engineering Company, CMG-STARs, from U. Calgary and U. Alaska at Fairbanks, UH-hydrate, from University of Houston) have been developed for methane-hydrate reservoirs. UH-hydrate was developed in our lab in the past which solves mass and energy balance equations of the components (Sun and Mohanty, 2006). Depressurization and thermal stimulation can be studied using this simulator.

Apart from depressurization and warm water flooding (Phirani and Mohanty, 2009; Phirani et al., 2009), CO₂ injection is also seen as a viable method where CO₂ replaces methane in the clathrate cages. In this method, methane production and CO₂ sequestration can be achieved simultaneously. The energy required for methane-hydrate dissociation can come from the energy released from the CO₂-hydrates formation. Thermodynamically, CO₂ hydrates are found to be more stable than methane hydrates. There is a

range of temperature and pressure conditions where methane in presence of water exists as gas and CO₂ exists in hydrate form. If these pressure and temperature conditions are maintained in the methane hydrate reservoirs, then natural gas can be produced while sequestering CO₂ in these reservoirs. CO₂ in the form of hydrates in these reservoirs will be stable for many years.

In the present work, a simulator is developed to include CO₂ as a component based on UH-hydrate. CO₂ can exist in the liquid phase at the conditions where hydrates are stable. So, not only another component is added to the system but another phase is also added. Thus, a new thermal compositional kinetic simulator is developed which can handle depressurization, warm water flooding, and CO₂ flooding of methane hydrate bearing sediments based on the numerical methods used by Sun and Mohanty (2006).

Numerical Model

Five components (methane, carbon dioxide, water, methane-hydrate, CO₂-hydrate) and six phases (gas phase, aqueous phase, liquid CO₂-rich phase, ice, methane-hydrate, CO₂-hydrate) are considered in the simulator. For the conversion of gas (carbon dioxide or methane) and water to the respective gas-hydrate or vice versa, pressure-temperature phase diagram is used. The fraction of CO₂ and methane in gas and liquid phases is calculated using the Peng-Robinson equation for the two phases. The component fraction of the gases in the aqueous-phase and the water in the gas-phase is calculated using the solubility functions (Carroll and Mather, 1999).

Methane-Hydrate Phase Diagram

Figure 1 shows the pressure-temperature diagram for methane-hydrates (Sloan, 1998). The two important curves shown in the figure are the gas-hydrate equilibrium curve (P_{em} - T curve, where P_{em} is the equilibrium pressure for the methane-hydrates and T is the temperature) and the water-ice equilibrium curve (vertical line). For the phase boundary between the aqueous and the ice phases, the pressure effect on the freezing (melting) temperature is negligible under typical hydrate conditions (Sloan, 1998), and therefore it is approximated by the vertical straight line $T = 273.2$ K. The intersection of the gas-hydrate and the water-ice equilibrium curve is called the quadruple point. Above the gas-hydrate equilibrium curve (higher pressure), methane can exist as a hydrate and below the curve methane exists as a gas. Similarly, on the right side of the vertical line, the water is stable in liquid form and on the left in the solid form. Three phases can coexist on the equilibrium curve for the methane-hydrate system. If the pressure and temperature conditions lie on the equilibrium curve, gas-ice-hydrate can exist on the left side of the vertical line and water-gas-hydrate on the right. At the quadruple point (273.2 K), all the four phases can co-exist. In the present work, the correlation between P_{em} (equilibrium pressure) and T (temperature) for a salt-free system is represented with the regression formulas obtained by Moridis (2003) by fitting the experimental data reported by Sloan (1998).

In the present work, a thermodynamic equilibrium is assumed between the aqueous and ice phases. There is no kinetic barrier to the phase transition between the aqueous-phase and the ice-phase. But hydrate formation and dissociation are considered to be kinetically controlled. Thus meta-stable methane-hydrate can exist in the gas stable zone and meta-stable gas can exist in the presence of water in the hydrate stable zone. The assumption of the equilibrium between the aqueous-phase and the ice-phase is valid only when the kinetics of ice melting and water freezing is sufficiently quicker than the hydrate kinetics. This assumption is made because we are unaware of a suitable kinetic model for the phase transition between the aqueous-phase and the ice, and we believe that the incorporation of a gas molecule into the water clathrates is slow compared to freezing.

CO₂-Hydrate Phase Diagram

Figure 2(a) shows the pressure-temperature phase diagram of the CO₂-hydrates (Sloan, 1998). Two curves are shown in Figure 2(a). The points shown as triangles represent the equilibrium data of the CO₂ gas-hydrate system, while the points plotted as squares show the equilibrium data for pure CO₂ gas-liquid system. Above the CO₂ gas-liquid equilibrium curve, at high pressures, CO₂ exists as a liquid-phase while below the curve CO₂ exists as a gas. Similarly, CO₂ in the presence of water exists as a hydrate above the CO₂ gas-hydrate equilibrium curve, and as a liquid or gas below the CO₂ gas-hydrate equilibrium curve, depending on the temperature and pressure conditions.

Figure 2(a) also shows the two quadruple points for the CO₂ equilibrium diagram. The vertical line on the left passes through the left quadruple point, the freezing point of water (271.1 K, T_{qdl}). The freezing point is less because the CO₂ solubility in the water is high. Ice exists on the left side of the vertical line and water on the right side. The vertical line on the right shows the intersection of the gas-liquid equilibrium curve for pure CO₂ with the hydrate-CO₂ equilibrium curve (283.2 K, T_{qdr}). At the left quadruple point we can have aqueous, gas, hydrate and ice phases. On the right quadruple point we can have gas-CO₂, liquid-CO₂, water and hydrate. For this data we have developed a correlation (Eq. 2) to represent the equilibrium curves, similar to the correlation for methane-hydrates developed by Moridis (2003).

$$P_{ec} = \begin{cases} \exp(2.95910923520255 \times 10^{-10} T^5 - 3.11697200658458 \times 10^{-7} T^4 \\ + 0.000132144540610005 T^3 - 0.0284975863532 T^2 \\ + 3.21260589574589 T - 145.260413199229) & T \leq T_{qdl} \\ \exp(-3.90289929172812 \times 10^{-6} T^5 \\ + 0.0054246841668 T^4 - 3.01568474817701 T^3 \\ + 838.17111136993 T^2 - 116470.278754549 T \\ + 6473275.96654239) & T_{qdl} < T \leq T_{qdr} \\ \exp(0.000112579309352343 T^5 - 0.16247250385449 T^4 \\ + 93.7907178622661 T^3 - 27071.2822913195 T^2 \\ + 3906853.0872557 T - 225530302.91665) & T > T_{qdr} \end{cases} \quad (2)$$

To find the fraction of the liquid CO₂ phase and the gas CO₂ phase at a particular pressure and temperature, the flash calculation is done for the two components, methane and carbon-dioxide, and the two phases, liquid phase (CO₂-rich phase) and gas phase (methane-rich phase) using the Peng-Robinson equation of state. The formation and dissociation of the CO₂-hydrate is treated as a kinetic phenomenon similar to the formation and dissociation of the methane-hydrate.

Figure 2(b) shows the pressure-temperature phase diagram of methane-hydrate and CO₂-hydrate together. The circles show the CO₂-hydrate equilibrium curve, the triangles show the methane-hydrate equilibrium curve, and the squares show the CO₂ gas-liquid equilibrium curve. In the area between the circles and the triangles, methane exists as a gas while CO₂ exists as a hydrate.

Kinetic Model

The kinetics of hydrate formation and dissociation, written as the consumption rate of gas, is described by Eq. 3

$$r^m = k A_s (f - f_{eq}), \quad (3)$$

where r^m (mol/m³-s) is the consumption rate of methane or carbon-dioxide; k (mol/m²-Pa-s) is the kinetic constant of hydrate formation or dissociation; A_s (m²/m³) is the reaction surface area. f is the fugacity of the gas at given pressure and temperature condition and f_{eq} is the equilibrium fugacity of the gas at the given temperature. The consumption rate of water and hydrate can be calculated as:

$$r^w = n r^m, \quad r^h = -r^m \quad (4)$$

where r^w and r^h are the consumption rates of water and hydrate, respectively; n is the hydration number of the hydrate. The Peng-Robinson equation of state is used to evaluate the gas fugacity f and f_{eq} in Eq. 3. The direction of the transition between the gas, water and hydrates is determined by the driving force $(f - f_{eq})$. Hydrates tend to form when $(f - f_{eq})$ is positive, i.e., the gas pressure at a particular temperature is greater than the equilibrium pressure at that temperature ($r^m > 0$). On the other hand, if $p_G < p_e$ (where p_G is the actual gas pressure and p_e is the equilibrium pressure), the driving force $f - f_{eq}$ is negative, and hydrates tend to dissociate ($r^m < 0$). If $p_G = p_e$, then $(f - f_{eq}) = 0$, which implies reaching an equilibrium state ($r^m = 0$).

For hydrate dissociation, the kinetic constant k is written in an Arrhenius-type equation as (Kim et al., 1987)

$$k = k_0 \exp\left(-\frac{Ea}{RT}\right) \quad (5)$$

where k_0 is the intrinsic kinetic constant, Ea is the activation energy, and R is the gas constant (8.314 J/molK). For methane-hydrate in a bulk phase system without salt, $k_0 = 3.6 \times 10^4$ mol/m² Pa s, and $Ea/R = 9752.73$ K, as measured by Clarke and Bishnoi (2001). For CO₂-hydrate without salt $k_0 = 1.83 \times 10^5$ mol/m² Pa s, and $Ea/R = 12374.308$ K, as measured by Clarke and Bishnoi (2004). Measurement of the kinetic constant for the hydrate formation is more difficult than for the dissociation. Englezos et al. (1987a) measured the value for the formation of methane-hydrate from methane gas and water. The results exhibited an ambiguous dependence on temperature. In this work, the kinetic constant of the hydrate formation is assumed to be a constant and its default value takes the average of the results measured by Englezos et al. (1987a), which is 0.5875×10^{-11} mol/m²-Pa-s. For the CO₂-hydrate formation, the rate constant is taken from Malegaonkar et al. (1997) and is approximated as 0.35×10^{-10} mol/m²-Pa-s.

The determination of the reaction surface area A_s in Eq. 3 for a porous medium system is still quite uncertain, because it is difficult to visually monitor the hydrates inside the pores. Many methods have been used to calculate the area. Yousif et al. (1991) estimate the area using the relation:

$$A_s = \sqrt{\frac{\phi_e^3}{2K}} \quad (6)$$

where K is the permeability of the porous medium and ϕ_e is the effective porosity. The volume inside pores available to fluids keeps changing due to the formation and dissociation of the hydrates in the hydrate bearing porous medium. The absolute porosity (ϕ) is constant during the process and the effective porosity is calculated as:

$$\phi_e = \phi (S_{FL} + S_{AQ}) \quad (7)$$

where S_{FL} is the saturation of the fluid phase (CO₂ + CH₄ rich phase) and S_{AQ} is the saturation of the aqueous phase (water rich phase). Masuda et al. (2002) used the following equation to estimate A_s :

$$A_s = \phi S_H A_{Si}, \quad (8)$$

where A_{Si} is a constant 3.75×10^5 m²/m³. In the present study the method used by Sun and Mohanty (2005) is used. They have proposed

$$A_s = \Gamma A_p \quad (9)$$

where A_p is the pore surface area and Γ is the fraction of the pore surface area that is active in the hydrate kinetics. The value of Γ depends on the actual process and is described in detail by Sun and Mohanty (2005). In the kinetics of the hydrate formation the nucleation process is neglected in Eq. 3 and it is assumed that the porous medium provides the nucleation sites for the hydrate formation.

Phase Composition

The system can have six phases (gas, aqueous phase, CO₂-rich liquid phase, ice, methane-hydrate, CO₂-hydrate) and five components (methane, carbon dioxide, water, methane-hydrate, CO₂-hydrate). For the phase compositions, the following assumptions are made: (1) The adsorption of any component on the rock surface is neglected. (2) Hydrate phases have the respective hydrate component only, i.e., the methane-hydrate phase has only the methane-hydrate as a component and the CO₂-hydrate phase has only the CO₂-hydrate component. (3) the ice phase is composed of only the water component. (4) Gas is composed of methane, CO₂ and water. (5) The aqueous phase is composed of water, methane and CO₂. (6) the liquid phase has CO₂, methane and water (limited amount). The following symbols are used to represent the different phases and components. The phase symbols are used in the subscript for the properties and the component symbols are used in the superscript

Phases:

Methane-Hydrate: HM
CO₂-Hydrate: HC
Ice: IC

Aqueous: AQ

Fluid: FL (gas and liquid phase together which separately are represented as:)

Gas: GS

Liquid: LQ

Components

Water: w

Methane: m

CO₂: c

Methane-Hydrate: hm

CO₂-Hydrate: cm

Based on the above assumptions, mass of each component can be found in a unit volume represented as

$$\begin{aligned}
 M^w &= \rho_{AQ} S_{AQ} X_{AQ}^w + \rho_{IC} S_{IC} + \rho_{GS} S_{GS} X_{GS}^w + \rho_{LQ} S_{LQ} X_{LQ}^w \\
 M^m &= \rho_{AQ} S_{AQ} X_{AQ}^m + \rho_{GS} S_{GS} X_{GS}^m + \rho_{LQ} S_{LQ} X_{LQ}^m \\
 M^c &= \rho_{AQ} S_{AQ} X_{AQ}^c + \rho_{GS} S_{GS} X_{GS}^c + \rho_{LQ} S_{LQ} X_{LQ}^c \\
 M^{hm} &= \rho_{HM} S_{HM} \\
 M^{hc} &= \rho_{HC} S_{HC}
 \end{aligned} \tag{10}$$

where S_i is the saturation of the phase i , X_i^j is the mass fraction of the component j in the phase i and ρ_i is the density of the phase i .

For the phase saturations, the following equation must hold:

$$\sum_{i=AQ,GS,LQ,IC,HC} S_i = 1 \tag{11}$$

For the compositions of the gas, liquid, and aqueous phases,

$$\begin{aligned}
 X_{GS}^w + X_{GS}^c + X_{GS}^m &= 1 \\
 X_{LQ}^w + X_{LQ}^c + X_{LQ}^m &= 1 \\
 X_{AQ}^w + X_{AQ}^c + X_{AQ}^m &= 1
 \end{aligned} \tag{12}$$

To find the fractions of liquid and gas for a given fluid-phase saturation, where the fraction of the methane and carbon-dioxide is known, a flash calculation is done. The flash calculation also gives the fraction of the CO₂ and the methane components in both the phases. To find the equilibrium partition of the water in the fluid phase and the CO₂ and methane gases in the aqueous phase, solubility functions and Henry's law are used. The details of these functions are discussed by Sun and Mohanty (2005).

The densities of the solid phases, ρ_{HM} , ρ_{HC} and ρ_{IC} are assumed to be constant. In the present work, the values of ρ_{HM} , ρ_{HC} and ρ_{IC} are set to be 0.9, 0.91 and 0.917 g/ml, respectively (Sloan, 1998). The gas- and liquid-phase densities, ρ_{GS} and ρ_{LQ} respectively, are evaluated with the Peng–Robinson EOS, and the aqueous-phase density ρ_{AQ} is considered a function of pressure, temperature and salinity according to the data given in the CRC Handbook of Chemistry and Physics (2004/2005).

Internal Energy

The total internal energy per unit volume U is given by

$$U = \phi (\rho_{GS} S_{GS} U_{GS} + \rho_{AQ} S_{AQ} U_{AQ} + \rho_{HM} S_{HM} U_{HM} + \rho_{IC} S_{IC} U_{IC} + \rho_{HC} S_{HC} U_{HC} + \rho_{LQ} S_{LQ} U_{LQ}) + (1 - \phi) \rho_S U_S, \quad (13)$$

where U_j is the specific internal energy of the phase j in J/kg and ϕ is the porosity of the porous medium. Note, the subscript S in the above equation represents the sediment phase, which is inactive in the mass transfer but plays an important role in the heat transfer. The sediment density ρ_S is assigned according to the rock mineralogy. The evaluations of U_{AQ} , U_{HM} , U_{HC} , U_{IC} and U_S have been described in detail by Sun and Mohanty (2005). U_{LQ} and U_{GS} are calculated by the Peng-Robinson EOS and thermodynamic evaluations of the enthalpy.

Flow Models

The solid phases (HM , HC and IC) are assumed to be immobile. The convection of the fluid phases (GS , LQ and AQ) during the hydrate formation - dissociation process is usually slow; hence Darcy's law for multiphase flow can be used to find the convection of different phases (Lake, 1989).

$$\bar{v}_j = -\frac{\bar{K} k_{rj}}{\mu_j} \cdot (\nabla p_j + \rho_j \bar{g}) \quad (14)$$

where v_j is the Darcy velocity of the phase j ($j = GS$, AQ and LQ); K is the absolute permeability tensor; k_{rj} , μ_j and p_j are, respectively, the relative permeability, the viscosity and the pressure of phase j ; g is the gravitational acceleration.

The absolute permeability is estimated by using Civan (2001) power law model which is described in Phirani and Mohanty (2009). To find relative permeabilities, a two-phase system is considered, i.e., aqueous-phase and fluid-phase. For the two-phase system, the Brooks-Corey correlations are used to find relative permeabilities. To find the relative permeability of the gas-phase, which is a fraction of the fluid phase, a factor of (S_{GS}/S_{FL}) is multiplied to the fluid phase relative permeability while for the liquid phase system a factor of (S_{LQ}/S_{FL}) is used. The Brooks-Corey correlations used in this work are described in detail by Sun and Mohanty (2005). No capillary pressure is assumed between the liquid and gas phases, while the capillary pressure is assumed to be non-zero between fluid and aqueous phases and found using the Brooks-Corey model.

Gas viscosity μ_{GS} in Eq. 14 is considered to be a function of the temperature T and the density ρ_{GS} with the empirical model by Selim and Sloan (1989). The viscosity of the aqueous-phase μ_{AQ} is assumed to be a constant at 1 cp. The liquid viscosity μ_{LQ} is calculated using a correlation by Fong et al. (1996). The mass transfer is presumed to occur through only convection. Physical dispersion and diffusion are assumed to be equal to the numerical dispersion. The mass flux for the component i ($i = m, w, c$), F^i , is

$$F^i = \rho_{GS} v_{GS} X_{GS}^i + \rho_{AQ} v_{AQ} X_{AQ}^i + \rho_{LQ} v_{LQ} X_{LQ}^i. \quad (15)$$

The heat transfer can take place by both convection and conduction. The heat flux is calculated by

$$F^i = \rho_{GS} v_{GS} H_{GS} + \rho_{AQ} v_{AQ} H_{AQ} + \rho_{LQ} v_{LQ} H_{LQ} - \lambda \nabla T, \quad (16)$$

where H_j (J/kg) is the specific enthalpy of the phase j ($j = GS, AQ$ and LQ) and λ (W/m K) is the effective thermal conductivity. The evaluation of H_{GS} , H_{LQ} and H_{AQ} are described in Sun and Mohanty (2005). Energy is treated as a pseudo-component in the present work and is represented by the superscript "e". λ is the volume average of the conductivity of the phases present in the unit volume.

Governing Equations and Numerical Solution

Mass Balance equations are:

$$\frac{\partial}{\partial t} (\phi M^m) + \nabla \cdot \bar{F}^m = -MW^m r^m + q^m \quad (17a)$$

$$\frac{\partial}{\partial t} (\phi M^c) + \nabla \cdot \bar{F}^c = -MW^c r^c + q^c \quad (17b)$$

$$\frac{\partial}{\partial t}(\phi M^w) + \nabla \cdot \bar{F}^w = -MW^w r^w + q^w \quad (17c)$$

$$\frac{\partial}{\partial t}(\phi M^{hm}) = -MW^{hm} r^{hm} \quad (17d)$$

$$\frac{\partial}{\partial t}(\phi M^{hc}) = -MW^{hc} r^{hc} \quad (17a)$$

The energy balance equation is:

$$\frac{\partial}{\partial t}(\phi U) + \nabla \cdot \bar{F}^e = -q^e \quad (18)$$

The simulator solves the above equations along with the thermodynamic properties of CO₂ and methane, the phase diagrams of the CO₂-hydrate and the methane-hydrate, the phase compositions, internal energy, kinetics of the hydrate formation and dissociation, and the flow and transport models described in the ‘flow models’ section. In the above equation MW^i is the molecular weight of the component i . The heat of formation and dissociation of the hydrate is incorporated in the energy balance equation through the internal energy calculations. Any in-situ sources of the components and energy are neglected, and hence the source term is determined by the boundary conditions applied. For the mass transfer equations, pressure or flow rate are used as the boundary conditions in the simulator, while for the energy balance equation, temperature is specified as the boundary condition.

A finite volume method is used to discretize the governing equations spatially. This discretization method provides the flexibility to use any co-ordinate system of our choice. The governing equations are discretized using backward Euler method in time, giving a fully implicit solution scheme. The phase mobility is calculated by single upstream averaging. In the discretized system every grid-block is governed by the six non-linear equations corresponding to the mass and energy balance equations. For each grid block, these equations are coupled with the thermodynamic, kinetic, flow and transport models. Mass transfer and heat transfer couple the equations for different grid-blocks.

Primary variable switch method is used to define the primary variables depending on the phase conditions in a particular grid-block. Three cases are considered in the present case, depending on the temperature and saturation conditions. This method is similar to the method used by Sun and Mohanty (2005). In the present work the three cases considered are described in Table 1.

Table 1: Cases considered in the primary variable switch method

Case	Water-rich phase	Variables
1	AQ	P, S _{AQ} , S _{HM} , S _{FL} , X ^C _{FL} , T (S _{IC} =0)
2	AQ-IC	P, S _{AQ} , S _{HM} , S _{FL} , X ^C _{FL} , S _{IC} (T=T _{qd})
3	IC	P, S _{IC} , S _{HM} , S _{FL} , X ^C _{FL} , T (S _{AQ} =0)

S_{FL} is the saturation of the fluid phase and X^C_{FL} is the fraction of CO₂ in the fluid phase. The flash calculation at a particular temperature and pressure condition gives the S_{GS} and S_{LQ} which are secondary variables. The primary variables are found by solving the governing equations. The secondary variables are calculated using the equations described above or from the thermodynamic calculations. The phase status or the case is determined by S_{AQ} and S_{IC}. If S_{AQ} > 0 and S_{IC} > 0, then we are in case 2 and the corresponding primary variables are used. If only S_{AQ} > 0, then we are in case 1, and the corresponding primary variables are chosen. If only S_{IC} > 0, then we are in case 3, and the corresponding primary variables are chosen. If S_{AQ} = 0 and S_{IC} = 0, then the temperature of the grid block is checked to determine the phase status. If T > T_{qd}, then case 1 is used, if T < T_{qd} then case 3 is used and if T = T_{qd} then case 2 is used. The primary variables are switched according to the change in the phase status of the grid block, which is the status of the water-rich phase. If a grid block has ice and water present, then the temperature has to be the quadruple point temperature where ice and water can co-exist. Thus, temperature is not a primary variable, which is case 2 in Table 1. If during the simulation the ice-phase disappears, then we are no longer on the quadruple point. The aqueous phase saturation and temperature are the primary variables, while the ice saturation is known and equals 0. If the aqueous-phase disappears, then we move from case 2 to case 3 in Table 1.

The Newton Raphson method is used to solve the discretized equations after ascertaining the variables similar to the method used by Sun and Mohanty (2005). The PVSM method is used inside the Newton-Raphson method where the phase status is checked for each Newton-Raphson iteration.

Results and Discussion

Using the model developed above, core scale CO₂ flooding of methane-hydrate bearing sediments is simulated. A 12 cm core saturated with water and methane-hydrates is considered. The initial saturation of water is 0.6 and the initial saturation of methane-hydrate is 0.4. The initial pressure in the core is assumed to be 6.1MPa at a temperature of 278K. At this pressure and temperature conditions, methane exists in the hydrate form. **Figure 3** shows the schematic of the core used for the simulations. To dissociate the methane-hydrates, pure CO₂ is injected from the left boundary at 6.11MPa and 278K. At this pressure and temperature conditions, CO₂ exists in the liquid form. The pressure at the right boundary is maintained at 6.09MPa. The pressure drop across the core is 0.02MPa. 1-D simulations are performed for CO₂ injection in the above described methane-hydrate bearing core. The simulation was carried out for 50hrs of CO₂ injection. The domain is discretized in 10 gridblocks.

As the CO₂ liquid phase goes in the core, the saturation of the fluid phase increases with a high mole fraction of CO₂ and the partial pressure of methane decreases in the fluid phase. This implies that equilibrium fugacity of methane (fugacity at the current temperature and equilibrium pressure of the hydrate formation) is greater than the actual fugacity of methane gas. To equilibrate the two fugacities, methane-hydrate dissociates and the mole fraction of methane in the fluid phase increases. The injection of pure CO₂ pushes the dissociated methane downstream. 15% of the total methane-hydrate present in the system dissociates within 50 hrs of CO₂ injection. **Figure 4** shows the cumulative production and injection from the core in terms of pore volumes. If all the pores are filled with hydrate then the total amount of gas (CO₂ or methane) present is about 160 pore volumes. Methane-hydrate saturation is 0.4, hence about 40 pore volumes of methane are present. Figure 4 shows that we are able to produce 0.8 pore volumes of methane and 2.6 pore volumes of CO₂ while we inject about 15 pore volumes of CO₂ in the core in 50 hrs. A small amount of water is also pushed through the production boundary. In situ profiles of saturations and temperature provide some insight into this process.

In situ Profiles

Figure 5 shows the longitudinal in-situ profiles. Figure 5(a) shows the saturation profiles while Figure 5(b) shows the temperature profile and fraction of CO₂ in fluid phase after 5 hrs of CO₂ injection. As CO₂ is injected from the left side, the fluid phases displace water and hence water saturation decreases and fluid saturation increases. The fluid phase is a mixture of the gas (methane rich) and the liquid (CO₂ rich) phases. At the very initial stages when CO₂ mole fraction in the injected fluid phase is very high (~1.0) the fluid phase is liquid CO₂, but soon methane-hydrate starts dissociating which releases methane and the mixture of the CO₂ and methane exists as a gas phase at the temperature and pressure conditions of the core. In the present simulation, the mole fraction of methane is usually high in the fluid phase which leads to the existence of only the gas phase. Gas has high mobility than the aqueous phase. Thus, due to the adverse mobility ratio, the saturation of the gas/fluid phase does not increase rapidly.

Figure 5(a) shows the methane-hydrate saturation profile and Figure 5(b) shows the CO₂ mole fraction in the gas phase. On the left side, the equilibrium fugacity of the methane in the fluid phase is higher than actual fugacity because of the high mole fraction of CO₂ being injected at the left boundary. To equilibrate the fugacity, the methane-hydrates dissociate decreasing the methane-hydrate saturation near the left boundary, as shown in Figure 5(a). Due to methane gas formation the fraction of methane in the fluid phase increases and is pushed toward the right due to the pressure drop along the length, as shown by the mole fraction of CO₂ in the fluid phase in Figure 5(b).

The CO₂-hydrate starts forming near the injection boundary (Figure 5(a)) as the fugacity of CO₂ in the fluid phase is greater than the equilibrium CO₂ fugacity but the saturation is small. Figure 5(b) shows the temperature profile after 5 hrs of the CO₂ injection. The dissociation of the methane-hydrate near the injection boundary decreases the temperature as dissociation is an endothermic process.

Figure 6 shows the in-situ profiles after 50 hrs of CO₂ injection. Figure 6(a) shows the saturation profiles after 50 hrs. The saturation profiles show that gas breaks through the core early and saturation keeps increasing near the injection boundary. This is a typical case of an adverse mobility ratio displacement in Buckley-Leverette type problems. In the present case, the displacement of the water with the gas is coupled with the formation of methane from methane-hydrates and the consumption of CO₂ in the form of CO₂-hydrate. In Figure 6(a) the aqueous saturation first decreases towards the right and then increases. The average aqueous phase saturation is about 0.5 along the length which shows the decrease all along the length owing to the fluid phase break

through. In the first few grid blocks, we see increased aqueous phase saturation because methane-hydrates have dissociated in the first few gridblocks (Figure 6(a)) and the volume is occupied by the fluid-phase, aqueous phase or CO₂-hydrate phase which leads to a little increase in aqueous phase saturation. Figure 6(b) shows the mole fraction CO₂ in the gas phase; the methane fraction has build up all along the length in the gas phase and is the least near the injection boundary. Figure 6(b) shows the CO₂-hydrate saturation after 50 hrs of the injection; the CO₂-hydrate saturation increases along the length as the mole fraction of CO₂ in the fluid phase increases with time along the length. Figure 6(b) also shows that near the injection boundary the temperature increases because the methane-hydrate dissociation is slow there after 50 hrs, as most of the methane-hydrates have dissociated, while CO₂ fraction in the gas phase is high leading to a high rate of CO₂-hydrate formation which leads to a net release of heat (exothermic reaction). The methane-hydrate dissociation front moves at a slow rate of approximately 1/40 cm/hr for the kinetics assumed in the base case. The core scale experimental data of CO₂ injection in methane-hydrate bearing core is not readily available (Graue et al., 2006) to verify these simulation results.

Sensitivity Analysis

Sensitivity analysis is done for initial pressure, temperature, methane-hydrate dissociation rate and CO₂-hydrate formation rate.

Reaction rate

Figure 7 shows methane-hydrate and CO₂-hydrate saturation profiles after 50 hrs for 3 cases: base case, methane-hydrate reaction rates 1/10th of the base case (represented by 'CH₄ less' in the figure) and CO₂-hydrate reaction rates 1/10th of the base case (represented by 'CO₂ less' in the figure). Figure 7(a) shows the methane-hydrate saturation profiles. Methane-hydrate dissociation is the least when methane-hydrate dissociation rate is 1/10th of the base case. But the methane-hydrate dissociation decreases even only the CO₂-hydrate dissociation rate is decreased. The CO₂-hydrate formation is least when the rate is less but decreases when only the methane-hydrate dissociation rate is decreased (Figure 7(b)). This is due to the energy required for the formation and dissociation of hydrates. When the CO₂-hydrate formation rate is decreased then the energy released is less due to decrease in the CO₂-hydrate formation. Hence, the energy delivered for methane-hydrate dissociation is less leading to less methane-hydrates dissociation. If methane-hydrate dissociation rate is less then the energy released by CO₂-hydrate formation is not utilized efficiently and the temperature increases leading to less CO₂-hydrate formation.

Initial pressure and temperature

Figure 8 shows methane-hydrate and CO₂-hydrate saturation profiles after 50 hrs for different initial temperature and pressure conditions. Figure 8(a) shows methane-hydrate saturation profiles. If the temperature is kept same and pressure is increased (5.1MPa, 6.1MPa and 7.1MPa), the methane dissociation decreases. In the case when just the temperature is increased to 280K from 278K, the initial conditions of pressure and temperature are not in equilibrium. Initially the hydrate saturation all along decreases a little to reach equilibrium (temperature decreases due to hydrate dissociation). Then the dissociation follows the same path as in the base case. Finally there is not much difference in the methane saturation profiles. For the case of initial condition (P=7.1MPa and T=280K), the methane dissociation decreases. So as the initial condition moves up along the methane-hydrate equilibrium line, methane dissociation becomes difficult.

Figure 8(b) shows the CO₂ saturation profiles for the same cases after 50 hrs. It shows that CO₂-hydrate forms easily when we have high pressure. The CO₂-hydrate forms near the injection boundary and blocks the the rest of the core. With decreasing pressure the hydrate formation along the core becomes more gradual. When initial temperature is high, a small amount of methane exists in the gas phase which accounts for low partial pressure of CO₂ and hence less CO₂ formation initially, but final saturation profile of CO₂-hydrate is not much different.

In the case when the initial condition moves up on the equilibrium line of methane-hydrate, the fluid phase exists as a liquid phase. The viscosity of the liquid phase is more than the gas phase hence the displacement of water from the liquid CO₂ is more efficient. Figure 8(c) shows the fluid saturation profiles for both the cases. Figure 2(b) shows that for pressures above 10MPa the methane-hydrates become more stable than the CO₂-hydrates. This means that to dissociate methane-hydrate and form CO₂-hydrate, either a high CO₂ mole fraction is needed in the fluid phase or a low pressure of operation is required (shallow reservoirs of methane-hydrates).

Conclusions

A thermal, compositional, kinetic simulator for CO₂ flooding of the methane-hydrate bearing sediments is developed. 1-D simulations of CO₂ injection shows that the fluid saturation remains low due to the adverse mobility ratio of the displacement of water with gas/liquid CO₂. To form CO₂-hydrate a specific fraction of CO₂ should be present in the fluid phase which is continuously decreased by the release of methane (due to the methane-hydrate dissociation). The energy of formation of the CO₂-

hydrate is utilized in the methane-hydrate dissociation which maintains the temperature of the core. The methane-hydrate dissociation front moves at a slow rate of approximately 1/40 cm/hr for the kinetics assumed in the base case. To dissociate methane-hydrate by CO₂ injection, either we need to keep the CO₂ mole fraction very high in the fluid phase or operate at a relatively lower pressure (shallower reservoirs of methane-hydrates).

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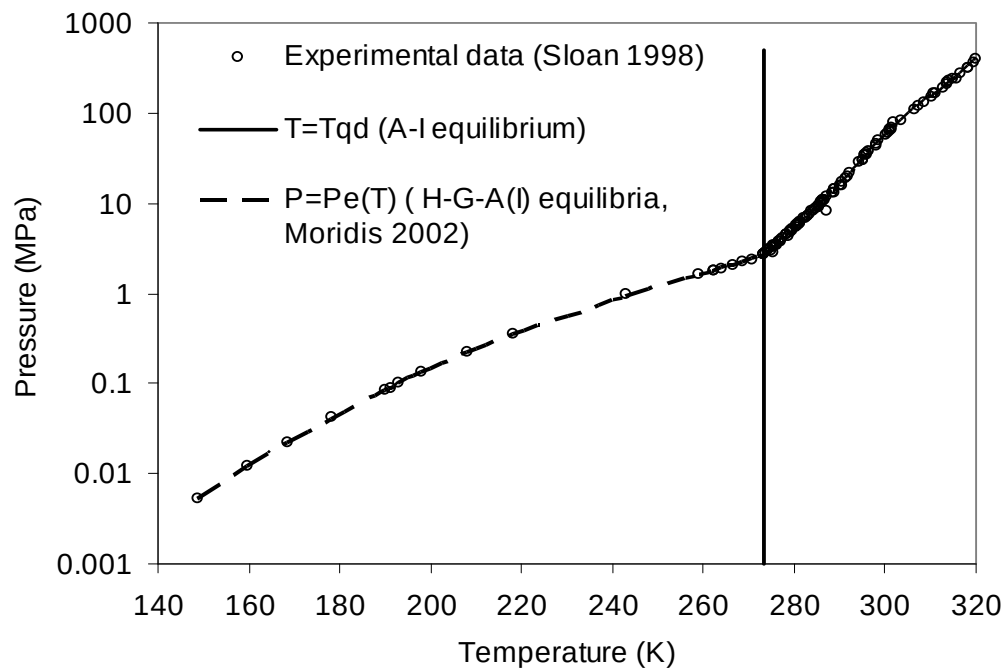


Figure 1: Equilibrium curve for methane hydrate stability zone

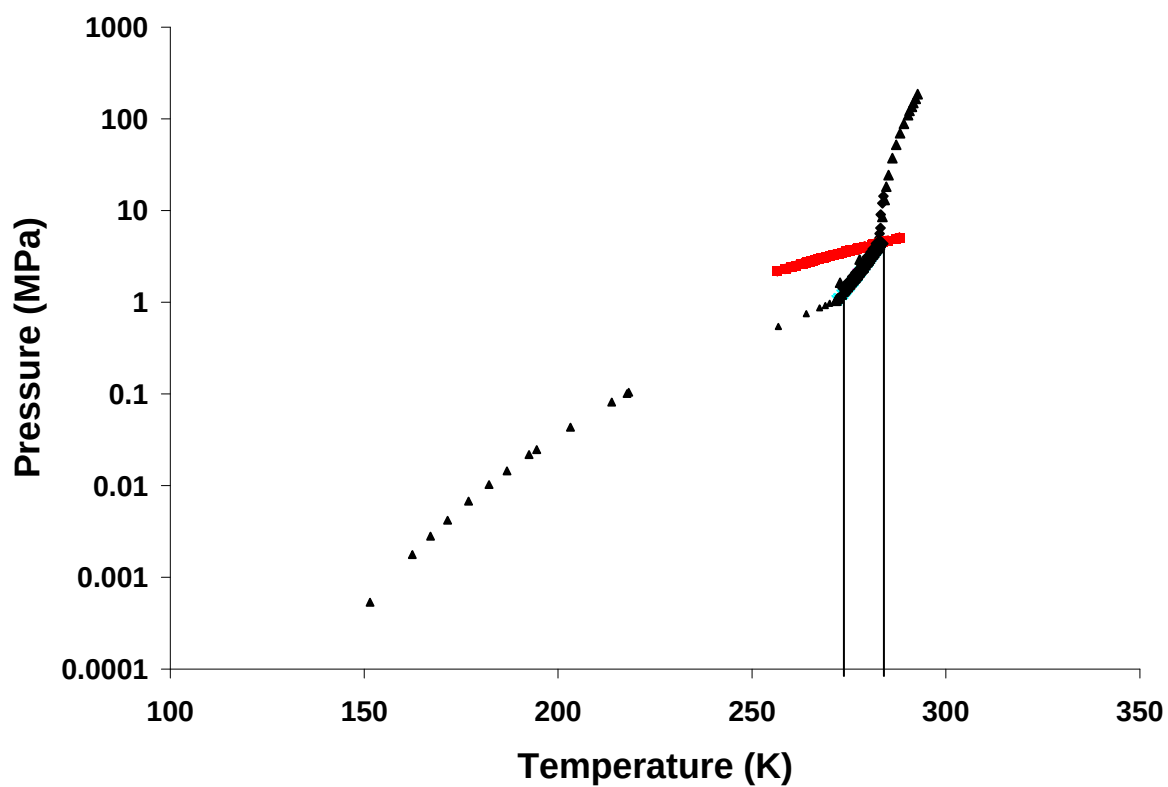


Figure 2(a): Equilibrium data for CO₂-hydrate system

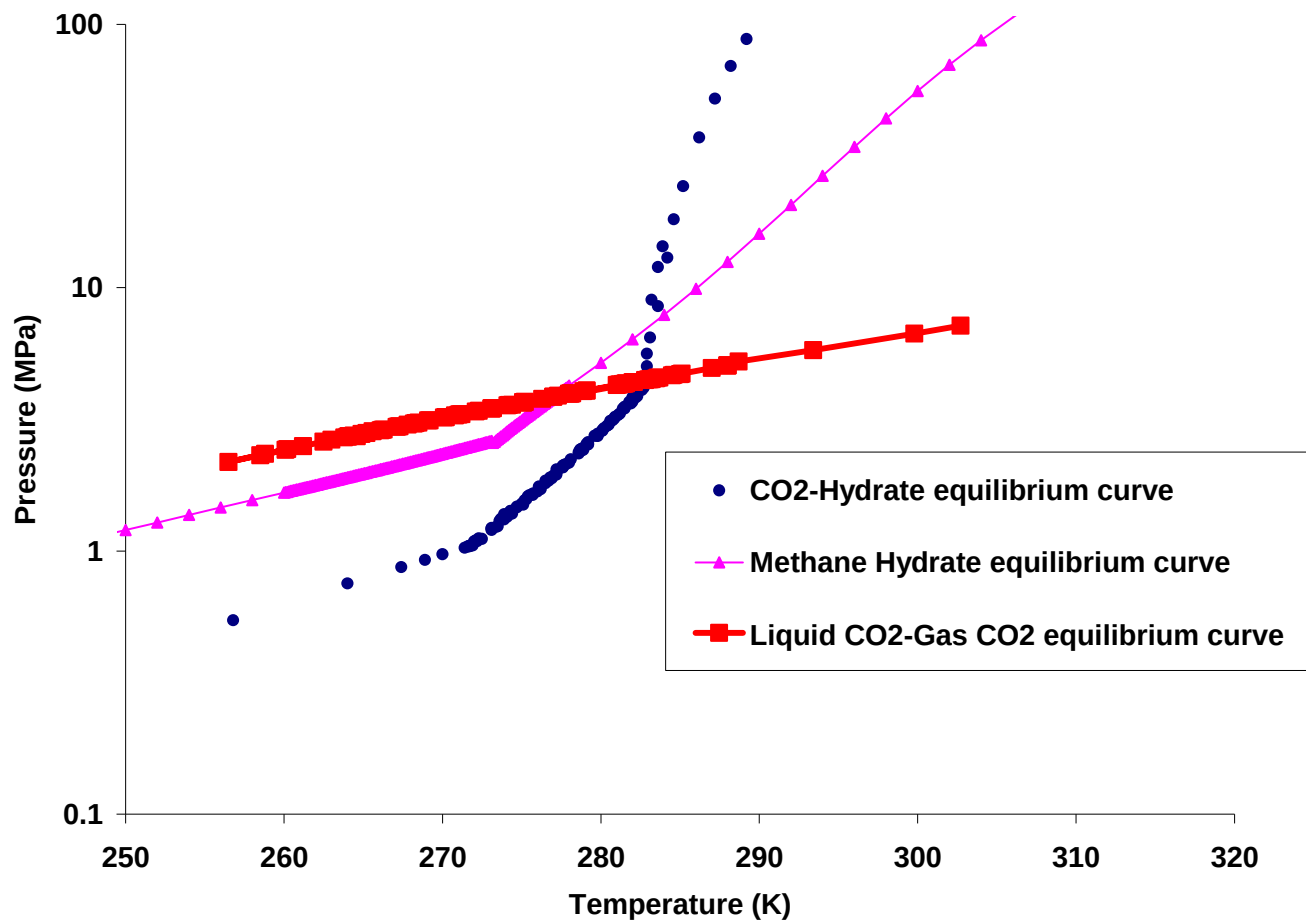


Figure 2(b): The equilibrium data for methane and CO₂ hydrates

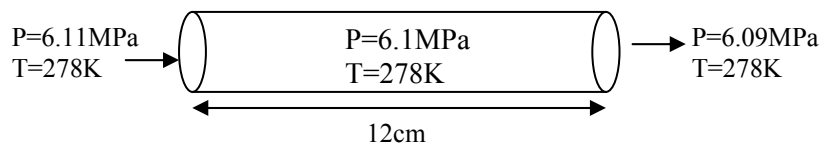


Figure 3: Schematic of the core used for simulations.

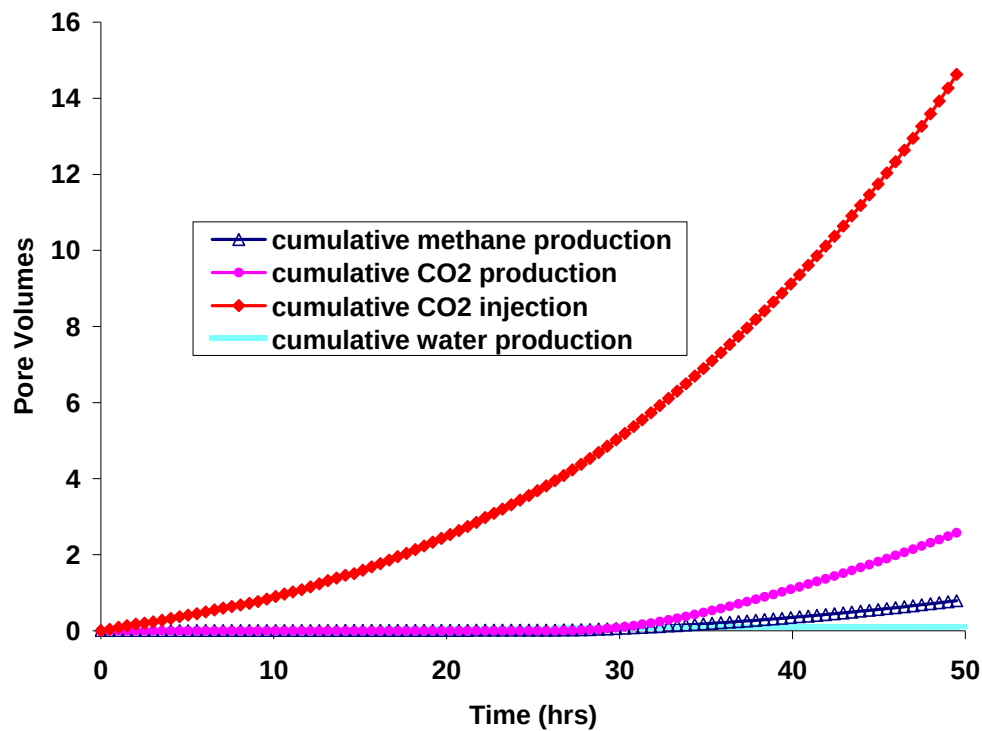


Figure 4: Cumulative methane production, CO₂ production and CO₂ injection

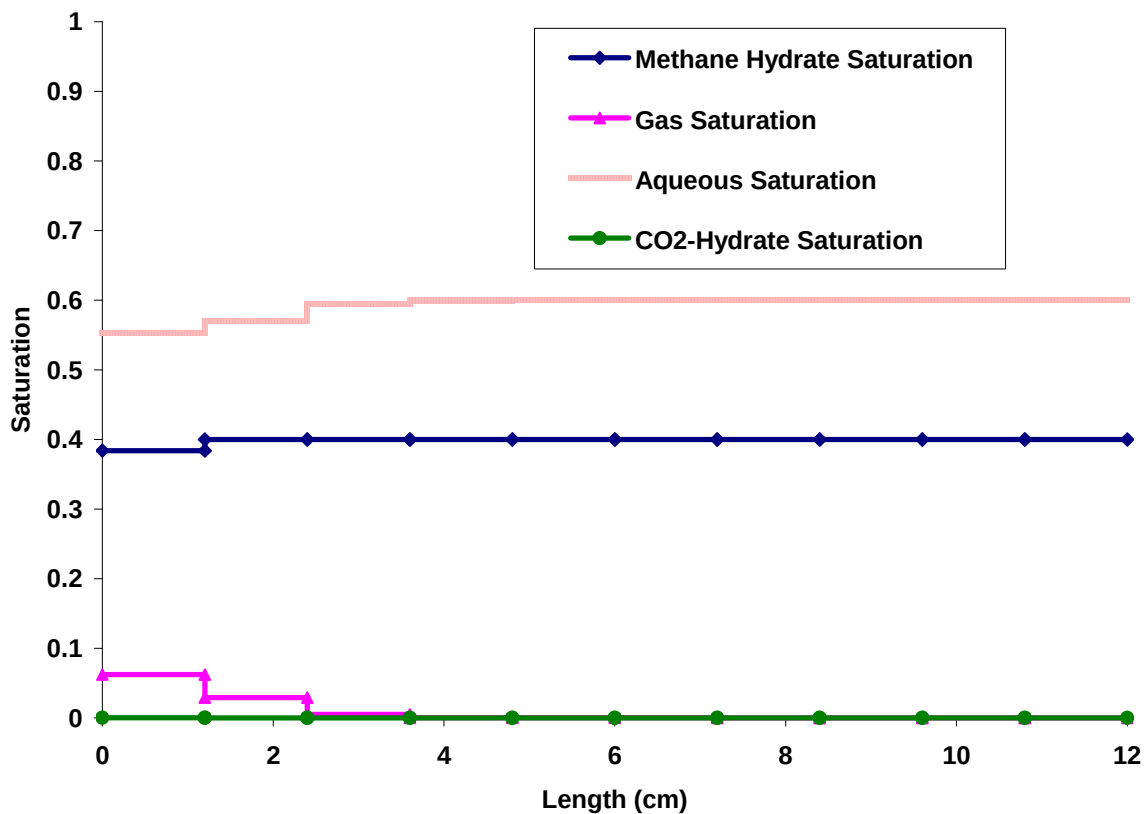


Figure 5(a): Saturation profiles after 5 hrs

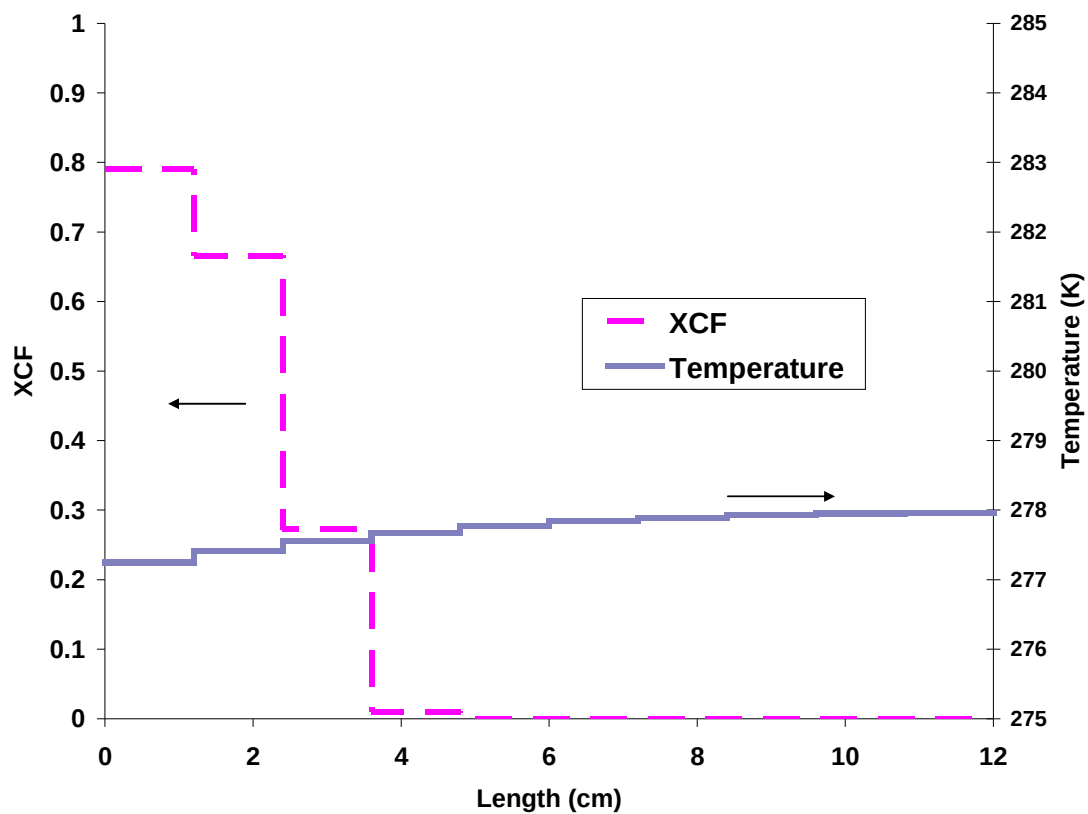


Figure 5(b): XCF (mole fraction of CO₂ in fluid phase) and temperature profile after 5 hrs

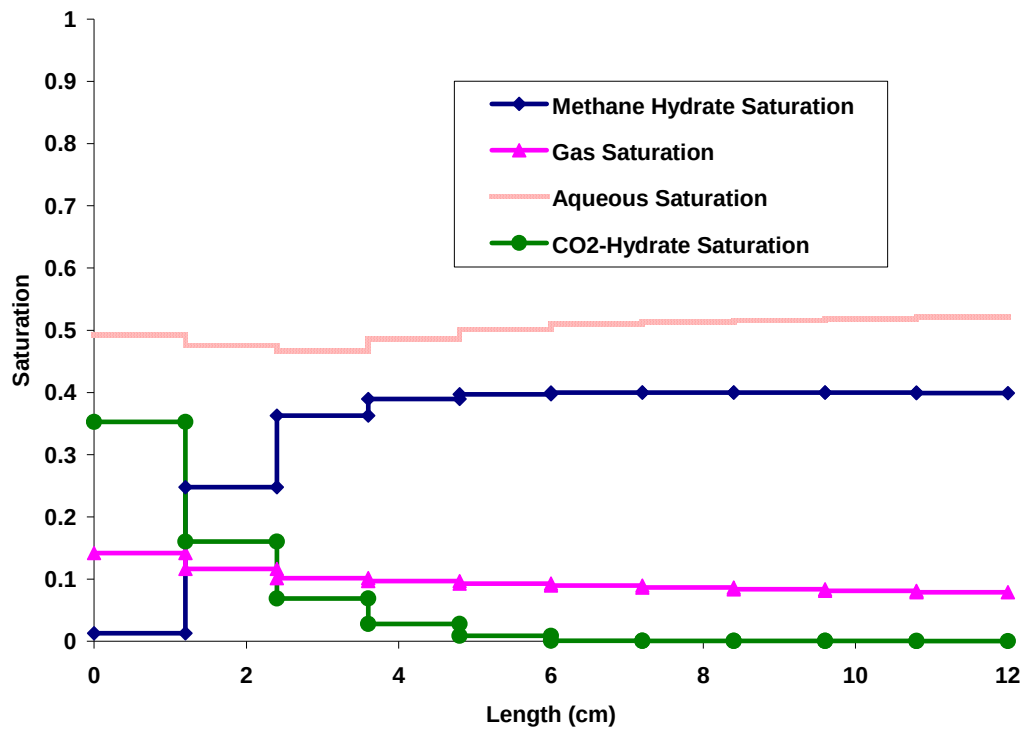


Figure 6(a): Saturation profiles after 50 hrs

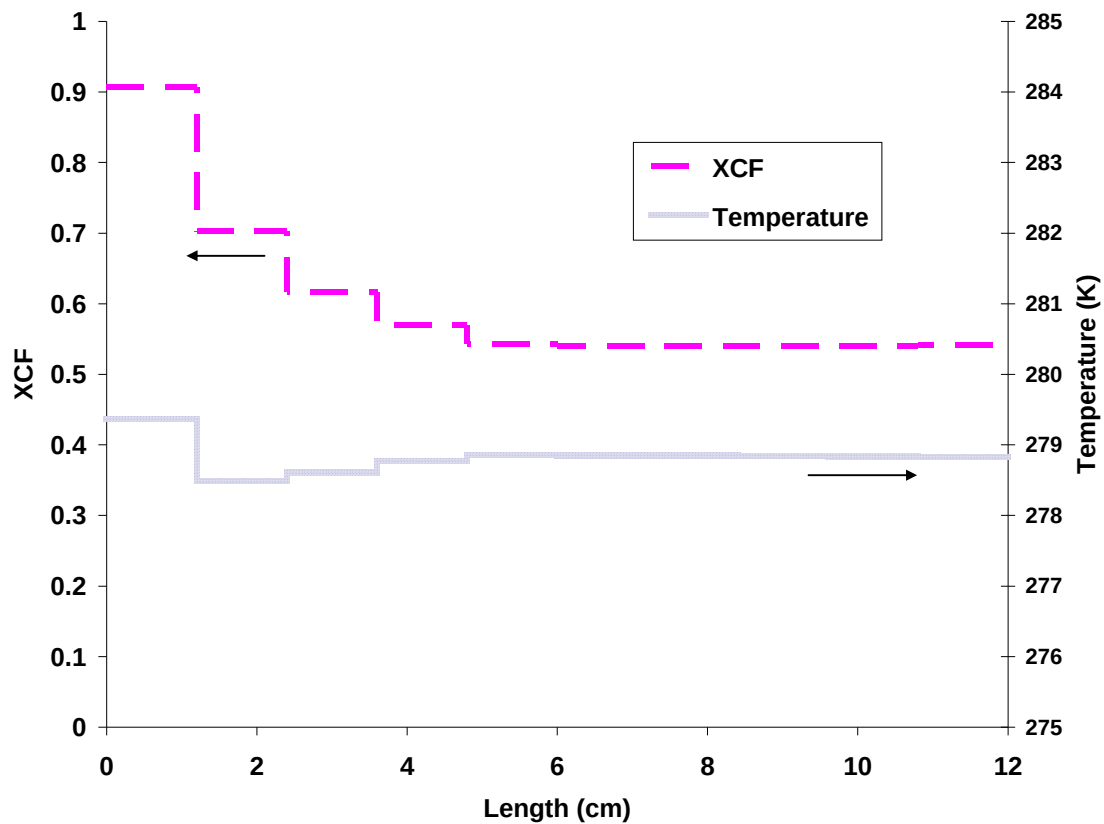


Figure 6(b): XCF (mole fraction of CO₂ in fluid phase) and temperature profile after 50 hrs

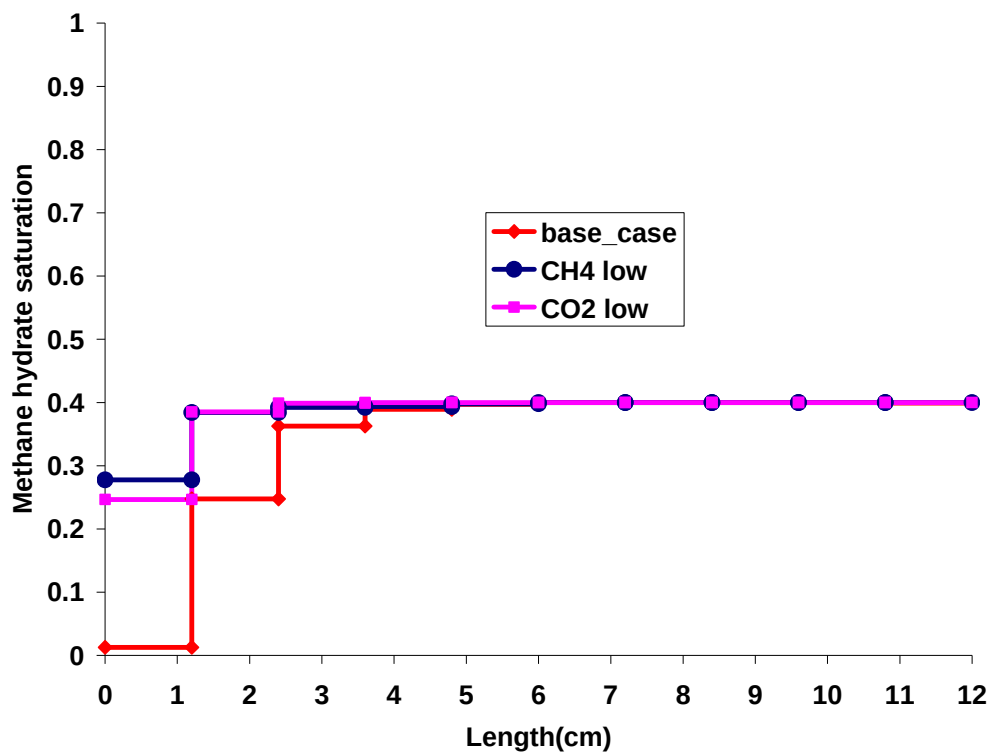


Figure 7(a): Methane hydrate saturation after 50 hrs for different reaction rates after 50 hrs

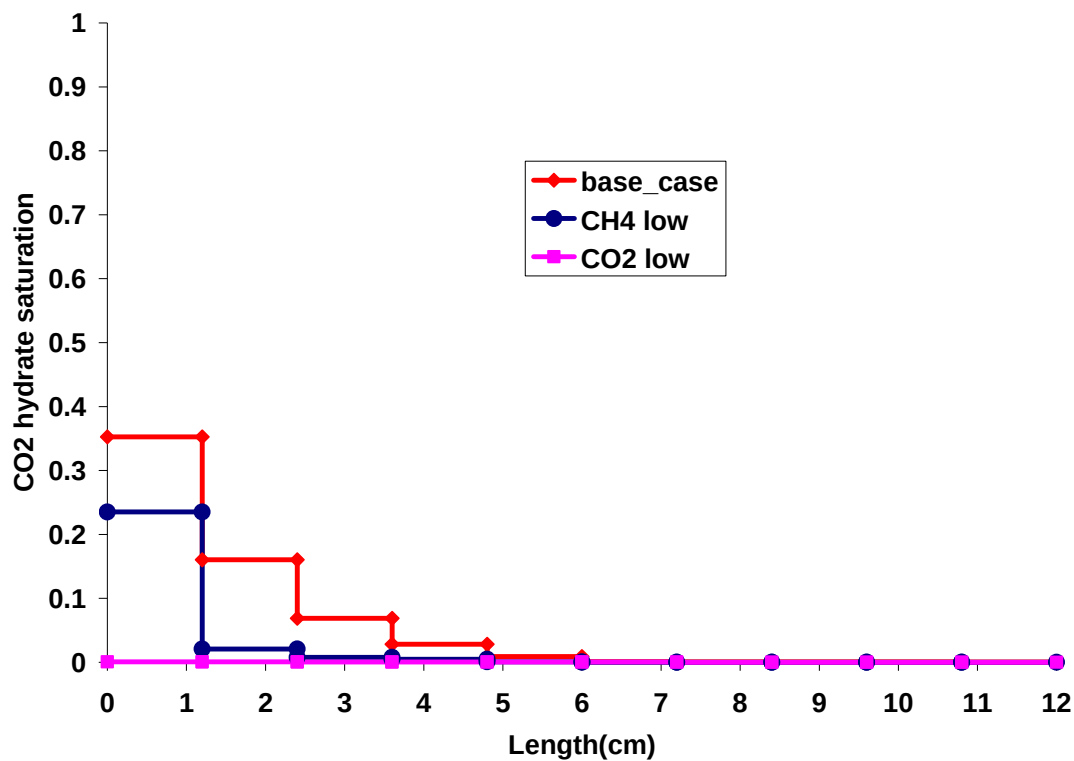


Figure 7(b): CO₂- hydrate saturation after 50 hrs for different reaction rates after 50 hrs

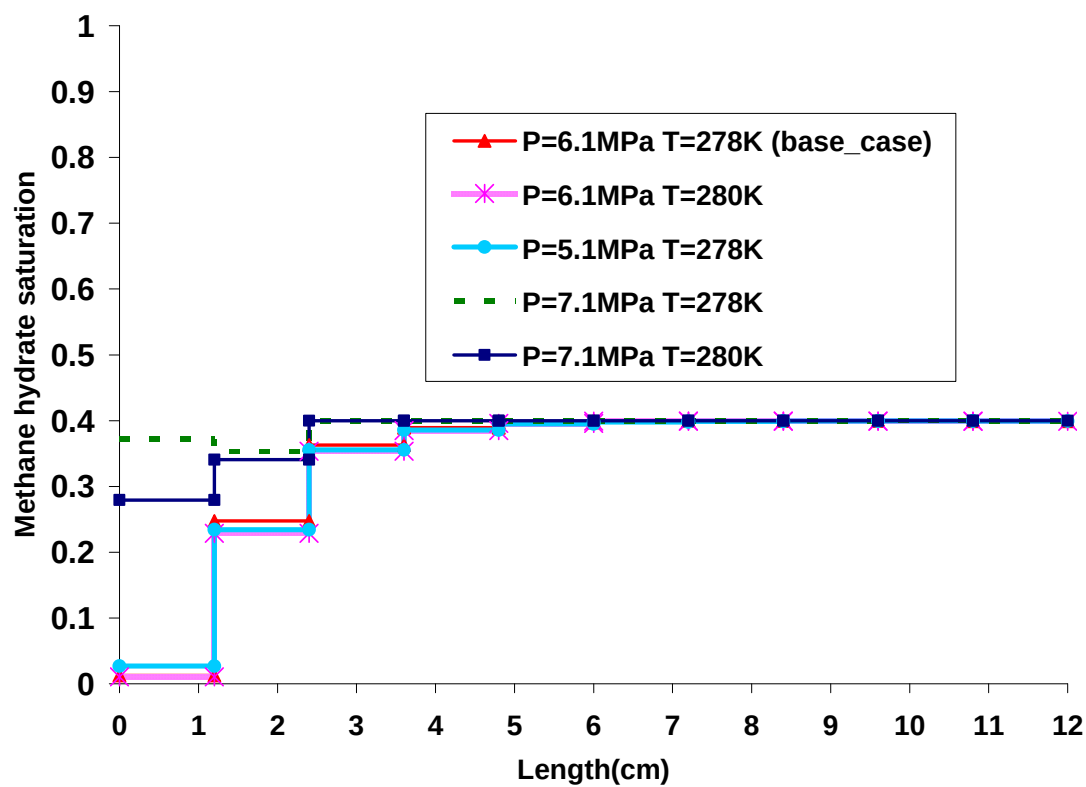


Figure 8(a): Methane hydrate saturation profiles for different initial conditions after 50 hrs

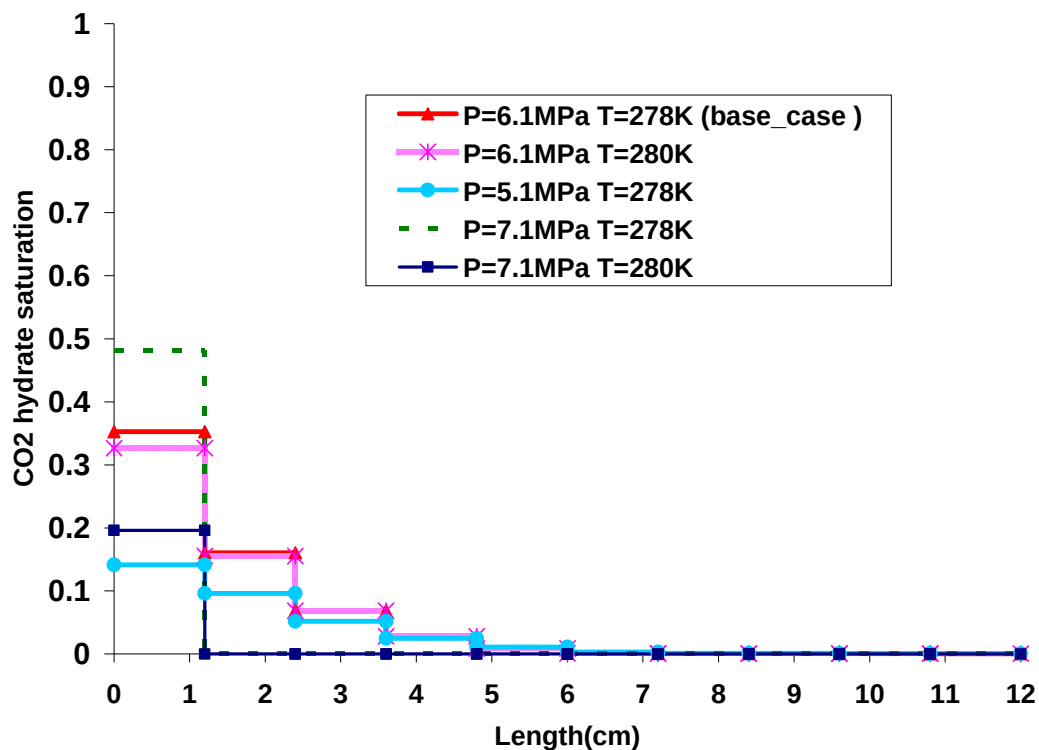


Figure 8(b): CO₂ hydrate saturation profiles for different initial conditions after 50 hrs

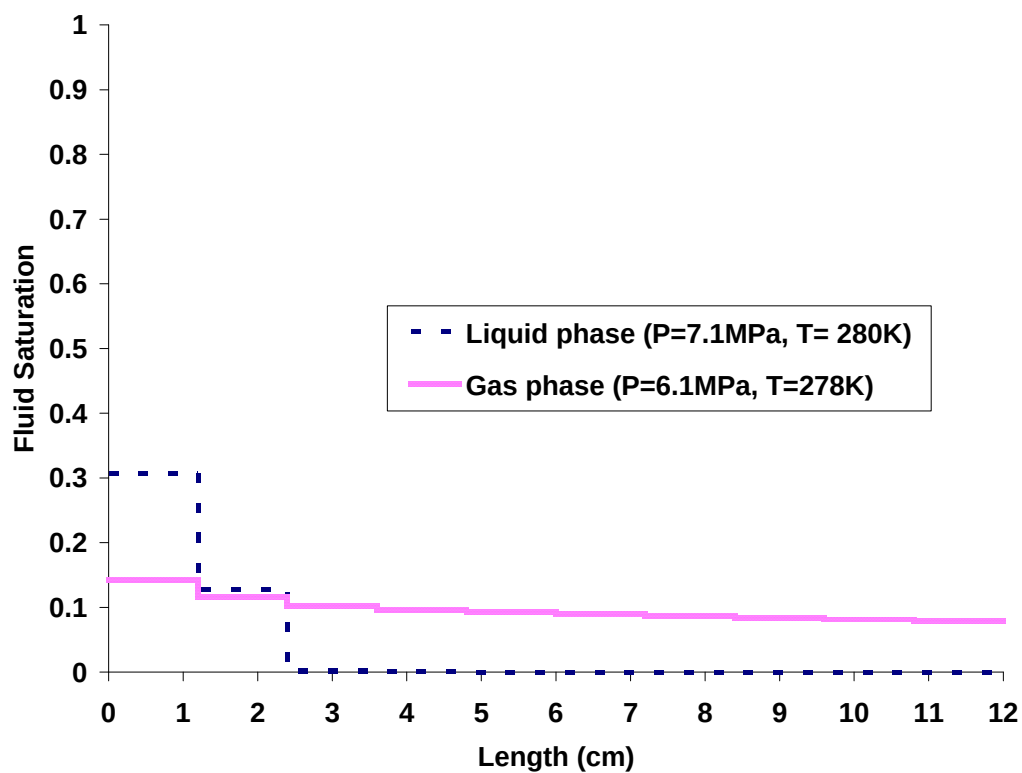


Figure 8(c): Fluid phase saturation profiles for different initial equilibrium conditions after 50 hrs