# Reservoir Modeling of Production of CH<sub>4</sub> from Natural Gas Hydrates by Injection of a CO<sub>2</sub>+N<sub>2</sub> Gas Mixture\*

# Nagasree Garapati<sup>1</sup>, Patrick McGuire<sup>1</sup>, and Brian J. Anderson<sup>1</sup>

Search and Discovery Article #41183 (2013) Posted August 26, 2013

\*\*Adapted from extended abstract prepared in conjunction with poster presentation at AAPG Annual Convention and Exhibition, Pittsburgh, Pennsylvania, May 19-22, 2013, AAPG©2013

<sup>1</sup>Dept. of Chemical Engineering, West Virginia University, Morgantown, WV (<u>ngarapat@mix.wvu.edu</u>)

#### **Abstract**

Natural gas hydrates are non-stoichiometric crystalline inclusion compounds are likely to contain more carbon than in all other fossil fuel reserves combined. Different techniques that are currently being proposed for production of CH<sub>4</sub> from the gas hydrates include depressurization, thermal stimulation and injection of inhibitors (Sloan and Koh, 2007). These methods involve dissociation of gas hydrate and the release of a significant amount of water that may cause geomechanical stresses on the reservoir that could lead to subsidence. A newly proposed method is to replace CH<sub>4</sub> in the hydrate by the injection of pure CO<sub>2</sub> or CO<sub>2</sub>+N<sub>2</sub> mixtures, which serves dual purpose of long-term storage of a greenhouse gas (CO<sub>2</sub>) and the production of natural gas, while maintaining the hydrate structure in situ (Ohgaki et al., 1996), thus making the operation carbon neutral.

#### Introduction

Field-scale experiments and the equipment required for production tests on hydrate deposits are very expensive. Therefore, reservoir simulations can be used to predict the production potential of gas hydrates. HydrateResSim (HRS) (Moridis et al., 2005) is the only open-source code available for public through National Energy Technology Laboratories (NETL), written in FORTRAN. The original HydrateResSim code simulates the gas production from methane (CH<sub>4</sub>) hydrate only utilizing the following three methods: depressurization, thermal stimulation and salt inhibitor addition. The revised code Mix3HydrateResSim provides an unconventional production method by means of swapping methane with carbon dioxide and nitrogen in hydrate lattice. The revised code allows predicting gas production potential of hydrate-bearing reservoir with simultaneous CO<sub>2</sub> sequestration through the conversion into carbon dioxide hydrate. Therefore, in addition to gas production, this method provides additional benefit of carbon dioxide storage in subsurface reservoirs. Simulations have been performed to analyze the behavior of the hydrate reservoir by injecting CO<sub>2</sub> and N<sub>2</sub> mixture followed by depressurization for production of CH<sub>4</sub> gas from the reservoir.

## **Theory**

HydrateResSim (HRS) is the only open-source code available for public through National Energy Technology Laboratories (NETL), it is written in FORTRAN. This version of code can only simulate methane hydrates. The code includes both equilibrium and kinetic models of hydrate formation and dissociation which accounts for four mass components (CH<sub>4</sub>, H<sub>2</sub>O, hydrate and inhibitors) and heat distributed among four possible phases (Liquid, Gas, Ice and Hydrate). To describe the system primary variables are specified, and these variables change throughout the simulation depending on the phases present. The model can describe the hydrate dissociation by depressurization, thermal stimulation or through inhibitors either singly or in combination. The relationship between equilibrium temperature and pressure is given by regression expression parameterized by Moridis (Moridis, 2003) for CH<sub>4</sub> hydrate in HRS code.

The code is modified to simulate mixed hydrates like CH<sub>4</sub>-CO<sub>2</sub>-N<sub>2</sub> which will help to understand simultaneous CH<sub>4</sub> production rate as well as CO<sub>2</sub> sequestration rate in hydrate reservoirs, the modified code Mix3HydrateResSim, can allow distribution of heat and up to five components (H<sub>2</sub>O, CH<sub>4</sub>, CO<sub>2</sub>, N<sub>2</sub> and inhibitors) between four possible phases (gas, aqueous, ice, and hydrate). The main part of the new code is the implementation of equilibrium surface, the equilibrium pressure and hydration number for hydrate are functions of temperature and composition, The mixed hydrate data obtained using cell potential method (Garapati et al., 2011) is incorporated in to the code in tabular form and a tri-linear interpolation is used to interpolate data at given conditions. The phase equilibrium is given as input to the code in two data files.

$$Teq=f(P, y_{CH_4}, y_{CO2}) \& Peq=g(T, y_{CH_4}, y_{CO2})$$

Where T is temperature ( ${}^{\circ}$ C), P is pressure (MPa) and  $y_{CH_4}$  is  $CH_4$  composition in gas phase. Along with phase equilibrium data two extra governing equations for newly added components. With added components, the primary variables are also changed to match with the increased components and are given in Table 1. A new phase system Gas-Hydrate (GsH) was added to consider the possibility of converting all available free water to form hydrate with injected gas.

#### **Simulation Details**

Using Mix3HydrateResSim, a methane hydrate reservoir with coexisting pure- CH<sub>4</sub> hydrate and aqueous phases, is modeled for the Ignik Sikumi conditions: (i) 14-day injection of CO<sub>2</sub> and N<sub>2</sub> followed by (ii) 30-day production of CH<sub>4</sub> (by depressurization of the well). The system considered is a 1-D 20m block divided into 20 grid blocks logarithmically as shown in Figure 1 whose parameters are specified in Table 2. Initially the system is considered as a pure CH<sub>4</sub> hydrate with coexisting aqueous phase at 7.0 MPa and 5.5 °C. During the injection phase, the injection well is modeled as a fixed-condition boundary maintained as a gas phase (23% CO<sub>2</sub>+ 77% N<sub>2</sub>) at 9.65 MPa and 5.5 °C and for depressurization was modeled by maintaining fixed-state boundary as aqueous phase at the bottom-hole pressure of 5.5 MPa.

#### **Results and Discussion**

During injection, the domain becomes pressurized, with a pressure front reaching out to the ninth grid element of the reservoir, and an exothermic temperature pulse in grid elements 9-18 as shown in <u>Figure 2</u>. During production, the domain becomes depressurized and hydrate starts dissociating, hence a decrease in temperature is observed.

During the injection, initially there is an increase in the saturation of hydrate, indicating the formation of secondary hydrate due to the injected gas and the available free water. As the hydrate becomes saturated with the injected gases it releases CH<sub>4</sub>, and there is hydrate dissociation and gas production as signified by non-zero gas saturations, as shown in <u>Figure 3</u>.

Cumulative amounts of gases released from the hydrate during the injection and production are given in <u>Figure 4</u>. The negative numbers implies the gas is absorbed to form hydrate while the positive numbers means that gas is released by hydrate dissociation.

During injection of the gas mixture,  $N_2$  and  $CO_2$  are absorbed into hydrate while the  $CH_4$  gas is released from the hydrate, but during the production, there is a reformation of  $CH_4$  hydrate, which can be seen from the decrease in the amount of  $CH_4$  released in Figure 4. While production the pressure of the reservoir decreases and reaches to the  $CH_4$  hydrate stability region causing  $CH_4$  hydrate to reform. From the figure, it is also clear that some of the injected  $N_2$  and  $CO_2$  are sequestered as hydrate.

#### **Conclusion**

HydrateResSim is modified for modeling Ternary hydrate and is known as Mix3HydrateResSim. Simulations are conducted on a one dimensional methane hydrate domain for injection of  $CO_2$  and  $N_2$  mixture followed by depressurization using a single well. It is found that during the injection period  $CH_4$  gas is released from the hydrate and  $CO_2/N_2$  gases are absorbed to form hydrate and during depressurization the released  $CH_4$  gas reforms hydrate. Currently, history matching for the Ignik Sikumi, first field test for gas hydrate exchange trial using Mix3HydrateResSim is in progress.

# Acknowledgement

This technical effort was performed in support of the National Energy Technology laboratory's on-going research in methane hydrates under the RES contract DE-FE0004000.

### **Selected References**

Garapati, N., S. Velaga, and B.J. Anderson, 2011, Development of a Thermodynamic Framework for the Simulation of Mixed Gas Hydrates: Formation, Dissociation, and CO<sub>2</sub>-CH<sub>4</sub> Exchange: Proceedings of the 7th International Conference on Gas Hydrates, Edinburgh, Scotland, UK, 7 p.

Moridis, G., M. Kowalsky, and K. Pruess, 2005, HydrateResSim Users Manual: A Numerical Simulator for Modeling the Behavior of Hydrates in Geologic Media. Contract No. DE-AC03-76SF00098: Department of Energy, Lawrence Berkeley National Laboratory, Berkeley, CA.

Moridis, G.J., 2003. Numerical Studies of Gas Production from Methane Hydrates: SPE Journal, v. 8, p. 359-370.

Ohgaki, K., K. Takano, H. Sangawa, T. Matsubara, and S. Nakano, 1996, Methane exploitation by carbon dioxide from gas hydrates-phase equilibria for CO<sub>2</sub> -CH<sub>4</sub> mixed hydrate system: Journal of Chemical Engineering of Japan, v. 29, p. 478-483.

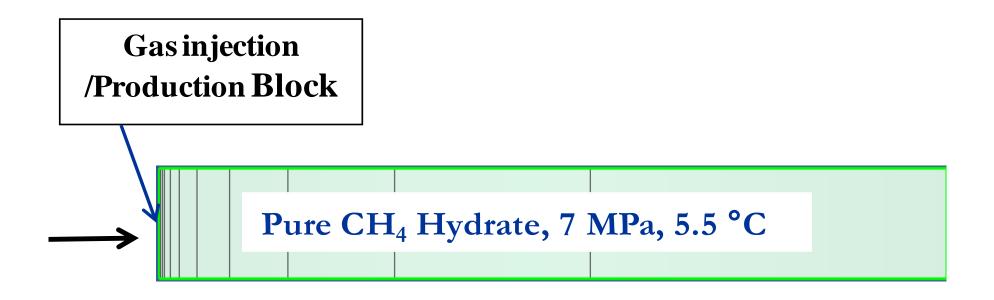


Figure 1. System used for simulation of CH<sub>4</sub> production using N<sub>2</sub>+CO<sub>2</sub> injection followed by depressurization.

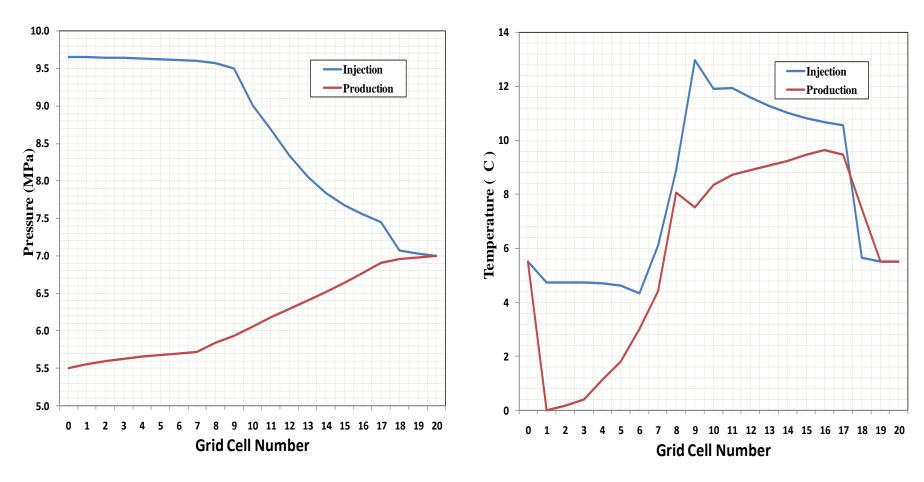


Figure 2. Pressure and temperature distribution along the domain.

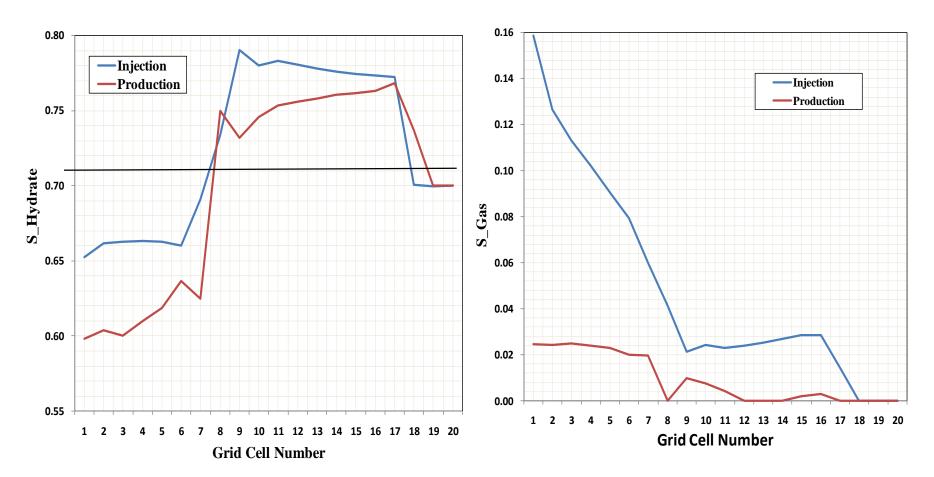


Figure 3. Hydrate and gas saturation profile along the domain.

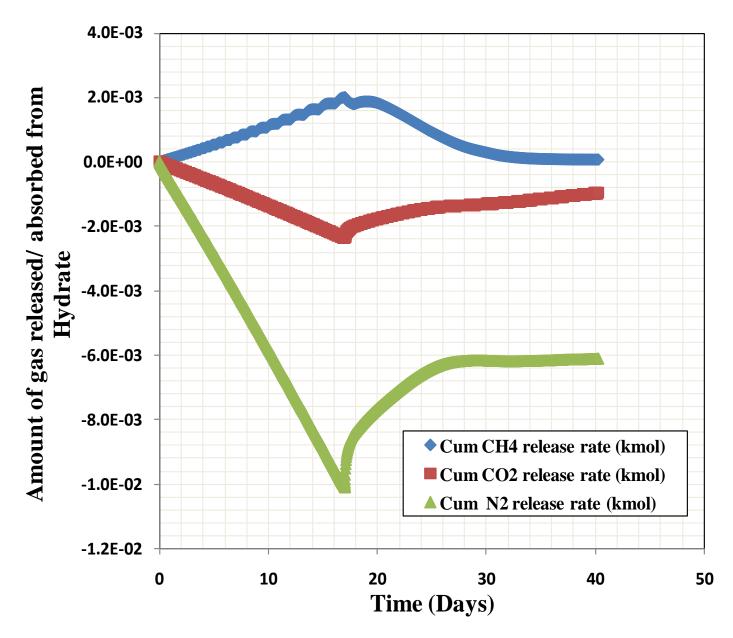


Figure 4. Cumulative amount of gases released or absorbed into the hydrate during injection and production phases.

1 Phase Agu 1.Px, 2.X mA, 3.Tx, 4.X cA, 5.X nA 1.Px, 2.Xmol mG, 3.Tx, 4.Xmol cG, 5.Xmol nG 1 Phase Gas 2 Phases AqG 1.Px, 2.S\_aqu, 3.Tx, 4.Xmol\_cG, 5.Xmol\_nG 2 Phases AqH 1.Px, 2.S\_aqu, 3.Tx, 4.Xmol\_cH, 5.Xmol\_nH 2 Phases IcG 1.Px, 2.S ice, 3.Tx, 4.Xmol cG, 5.Xmol nG 2 Phases IcH 1.Px, 2.S\_ice, 3.Tx, 4.Xmol\_cH, 5.Xmol\_nH 1.S gas, 2.S aqu, 3.Tx, 4.Xmol cH, 5.Xmol nH 3 Phases AGH 1.Px, 2.S\_aqu, 3.S\_gas, 4.Xmol\_cG, 5.Xmol\_nG 3 Phases AIG 1.Px, 2.S\_aqu, 3.S\_ice, 4.Xmol\_cH, 5.Xmol\_nH 3 Phases AIH 1.S gas, 2.S ice, 3.Tx, 4.Xmol cH, 5.Xmol nH 3 Phases IGH 1.S\_gas, 2.S\_aqu, 3.S\_ice, 4.Xmol\_cH, 5.Xmol\_nH 4 Phases Qup 1.Px, 2.S gas, 3.Tx, 4.Xmol cH, 5.Xmol nH 2 Phases GsH

Table 1. Primary variables for different phase states.

Parameter	Value
Porosity	0.3
Density	2650 kg/m³
Specific heat	750 J/kg K
Dry thermal conductivity	2.0 W/m K
Wet thermal conductivity	2.18 W/m K
Pore compressibility	5.0 × 10 <sup>-10</sup> Pa <sup>-1</sup>
Capillary Pressure Model	van genuchten function
S <sub>irA</sub>	0.14
n	1.84
α	10
Relative Permeability Model	Stone first three phase
S <sub>irA</sub>	0.15
$S_{irG}$	0.001
n	3

Table 2. Parameters and specifications of domain.