Oil & Natural Gas Technology

DOE Award No.: DE-FE0013889
Quarterly Research Performance Progress Report (Period ending 06/30/2014)

THCM Coupled Model For Hydrate-Bearing Sediments:
Data Analysis and Design of New Field Experiments
(Marine and Permafrost Settings)

Project Period (10/1/2013 to 09/30/2015)

Submitted by:

Marcelo Sanchez Project PI

Texas A&M University
DUNS #:  847205572
College Station, TX
979-862-6604
msanchez@civil.tamu

J. Carlos Santamarina

Georgia Institute of Technology
Atlanta, Georgia
404-894-7605
edujcs@gatech.edu

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Office of Fossil Energy
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ACCOMPLISHMENTS

The experimental study of hydrate bearing sediments has been hindered by the very low solubility of methane in water (lab testing), and inherent sampling difficulties associated with depressurization and thermal changes during core extraction. This situation has prompted more decisive developments in numerical modeling in order to advance the current understanding of hydrate bearing sediments, and to investigate/optimize production strategies and implications. The goals of this research is to addresses the complex thermo-hydro-chemo-mechanical THCM coupled phenomena in hydrate-bearing sediments, using a truly coupled numerical model that incorporates sound and proven constitutive relations, satisfies fundamental conservation principles. This tool will allow us to better analyze available data and to further enhance our understanding of hydrate bearing sediments in view of future field experiments and the development of production technology.

ACCOMPLISHED

The project management plan (PMP, Task 1) and the selection of the PhD Students working during the 1st year of the project were competed and informed in the first quarterly report. The main accomplishments for this first period address Tasks 2, 3 and 4 of the original research plan, and include:

- Student training.
- Literature review.
- Update of constitutive equations.
- Update of THCM-Hydrate.
- Close-form analytical solutions.

Training

The training of the two PhD students working in this project has continued during this period. As for Mr. Xuerui (Gary) Gai (i.e. the Ph.D. student at TAMU) the training activities have been focused on the use of “THCM-Hydrate”, the numerical code under development in this project. He also visited GT to attend a workshop on “Seismic detection natural HBS” and “Physical properties of HBS”. As for Mr. Zhonghao Sun (the Ph.D. student at GT), he training has focused on the implementation of analytical solutions in MATLAB and other pieces of software. Both students have progressed positively with their coursework at their respective universities.

Literature review

The literature review (Task 2a) has completed during this period.

Update of constitutive equations

The update of the constitutive laws for hydrate-bearing marine sediments (Task 2b–ongoing) and HBS in the permafrost (Task 2c–ongoing) have continued during this period. The section below (page 6) entitled: “1-D modeling of hydrate dissociation by depressurization–relevant factors in flow simulation” briefly presents the main findings related to the update of constitutive equations and also some of the activities performed in Task 4.
Update of THCM-Hydrate
The update of the numerical code “THCM-Hydrate” has continued during this reporting period. The main following activities for the different subtasks are highlighted:

- Validation of implemented functions (Task 3a – ongoing), including
  - Implemented soil water retention curve, thermal and hydraulic have been validated against experimental results and analytical solutions.
- Synthetic numerical tests (Task 3b – ongoing), including
  - Synthetic numerical tests looking at the validation of the proposed numerical approach have been performed. Two cases are presented in this report (page 11), one of them is related to hydrate formation and the other one with hydrate dissociation.
- Code comparison analyses (Task 3c – ongoing), including
  - We have continued with the simulations aimed at comparing our code against other ones developed to model the behavior of HBS. We are using the benchmark exercises prepared in the context of “The National Methane Hydrates R&D Program: Methane Hydrate Reservoir Simulator Code Comparison Study” (http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/MH_CodeCompare/MH_CodeCompare.html)

Close-form analytical solutions
The review on the main governing evolution laws, parameters, dimensionless ratios and simplifying assumptions for HBS dissociation has been continued.

Plan - Next reporting period
We will advance analytical and numerical fronts to enhance our code to solve coupled THCM problems involving with HBS, with renewed emphasis on simulating the natural processes under in-situ conditions and gas production.
Milestones for each budget period of the project are tabulated next. These milestones are selected to show progression towards project goals.

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INTRODUCTION

Hydrate dissociation is a dynamic process. We built a MATLAB code to investigate the impact of dynamic effects on the capillary pressure-saturation relationship. The simulator takes into consideration parameters such as specific surface area of hydrate in porous media, permeability of hydrate-bearing sediments and their effect on flow during hydrate dissociation.

MODEL DEVELOPMENT

In this study, we couple a kinetic model of hydrate decomposition and two-phase flow in porous media equations. We start by solving equations for two-phase flow in porous media, and then include dynamic effects on the capillary pressure-saturation relationship and hydrate decomposition model into the code. Table 1 list the equations solved. Some constitutive relations needed to solve these equations are also considered, e.g. specific surface area of hydrate and permeability of hydrate-bearing sediments.

NUMERICAL FORMULATIONS

The solution scheme resembles the one proposed by Celia et al. (1990) and Celia and Binning (1992) to solve the 1-D traditional two-phase flow in porous media. It employs a fully implicit finite difference method but it is modified to consider dynamic capillary effects and a kinetic model. The proposed method is simple and robust, and it is readily implemented in MATLAB.

Boundary conditions

Fixed pressure boundary and flow-free boundary conditions are considered:

- Fixed pressure boundary: \( P_o = P_b \) for \( t > 0 \)
- Flow free boundary: \( P_o = P_a \) for \( t > 0 \)

where \( P_b \) is the pressure at the boundary, \( P_a \) is the pressure of the node adjacent to the boundary. After the pressure is known, saturation and relative permeability are calculated.
Table 1. Equations for two-phase flow in porous media.

<table>
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<tr>
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<th>Two-phase flow in porous media</th>
<th>Two-phase flow with dynamic effect</th>
<th>Two-phase flow with hydrate dissociation</th>
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<td>(\frac{\partial \phi w S_w}{\partial t} - \nabla \left[ \rho_w k_{rw} \frac{K}{\mu_w} (\nabla P_w - \rho_w \mathbf{g}) \right] = 0)</td>
<td>(\frac{\partial \phi w S_w}{\partial t} - \nabla \left[ \rho_w k_{rw} \frac{K}{\mu_w} (\nabla P_w - \rho_w \mathbf{g}) \right] = 0)</td>
<td>(\frac{\partial \phi w S_w}{\partial t} - \nabla \left[ \rho_w k_{rw} \frac{K}{\mu_w} (\nabla P_w - \rho_w \mathbf{g}) \right] - \dot{m}_w = 0)</td>
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<td>Mass balance of gas</td>
<td>(\frac{\partial \phi g S_g}{\partial t} - \nabla \left[ \rho_g k_{rg} \frac{K}{\mu_g} (\nabla P_g - \rho_g \mathbf{g}) \right] = 0)</td>
<td>(\frac{\partial \phi g S_g}{\partial t} - \nabla \left[ \rho_g k_{rg} \frac{K}{\mu_g} (\nabla P_g - \rho_g \mathbf{g}) \right] = 0)</td>
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<td>Pressure-S saturation relation</td>
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<td>(P_g - P_w = \rho \left( S_w \right) - \tau \frac{dS_w}{dt})</td>
<td>(P_g - P_w = \rho \left( S_w \right) - \tau \frac{dS_w}{dt})</td>
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\(K\) is intrinsic permeability, \(k_{\alpha}\) is relative permeability of water \((w)\) or gas \((g)\), \(\mu_\alpha\) is the viscosity of water or gas, \(\tau\) is dynamic coefficient, \(S\) is saturation, \(P\) is pressure, \(\phi\) is porosity, and \(\rho\) is density. The expressions of terms related to hydrate dissociation are listed following. \(M_\alpha\) is molar mass of water \((w)\), gas \((g)\), and hydrate \((h)\), \(N_H\) is the hydration number, which is chosen as 6.

\[
\dot{m}_w = -N_H M_w \frac{dn_h}{dt}
\]

\[
\dot{m}_g = -M_g \frac{dn_h}{dt}
\]

\[
\frac{dn_h}{dt} = -K_d(T)A_h \left( P_{eq} - P_g \right)
\]
**Convergence criterion and Time-stepping method**

The convergence criterion proposed by Huang et al. (1996) with an adaptive time-stepping method was adopted to make the scheme more efficient and robust. If the iteration number in the last time step is less than 3, the time step times 1.05; if the iteration number is more than 6, the time step is divided by 1.04. If the iteration dose not convergence after 10 iterations, the iteration is stopped and the time step is divided by 2 to recalculate (Kaluarachchi and Parker, 1989). Figure 3 shows the flow chart for the numerical algorithm.

Figure 3. Flow chart for numerical algorithm.
MODEL VALIDATION

We validated the algorithm by comparing numerical results against a semi-analytical solution proposed by McWhorter and Sunada (1990). The semi-analytical solution was calculated by applying the code proposed by Bjornara and Mathias (2013). Figure 4 shows the results for horizontal displacement (soil permeability: $10 \times 10^{-12}$ m$^2$). Simulation results agree well with the semi-analytical solution.

![Saturation profile for the horizontal displacement example at t=5000s.](image)

Figure 4. Saturation profile for the horizontal displacement example at t=5000s.

PRELIMINARY RESULTS FOR DYNAMIC EFFECT

Figures 5 and 6 compare our numerical results with published simulation results (Manthey et al., 2008). It should be noted that Manthey et al. (2008) used a 3-D simulator. Results compare favorably. Figure 7 shows the pressure difference versus saturation for cell at x=0.09m. Since the wetting phase replaces the nonwetting phase in this problem, the pressure difference under dynamic conditions is lower than the static capillary pressure.

![Initial and boundary conditions for calculated example (Manthey et al., 2008).](image)

Figure 5. Initial and boundary conditions for calculated example (Manthey et al., 2008).
Figure 6. Comparison between simulation results of (a) this study and (b) Manthey et al. (2008).

Figure 7. Pressure difference-saturation curve for cell at x=0.09m in example 3.
The upgrading of the *THCM-hydrate* is being performed to capture all species and phases encountered in hydrate bearing sediments, and new equations are added to properly account for the behavior of hydrate bearing sediments and all phases involved. The main aspects of this implementation are: (1) The state variables are: solid velocity, $u$ (one, two or three spatial directions); liquid pressure $P_l$, gas pressure $P_g$, temperature $T$ and chemical species concentration. (2) Thermal equilibrium between phases in a given element is assumed. (3) We consider kinetics in hydrate formation/dissociation as a function of the driving temperature and fluid pressure deviations from the phase boundary, considering the mass fraction of methane in hydrate as the associated variable.

A critical component of a THCM formulation for HBS is to model properly the possible phase changes that may occur in the PT space under different field/laboratory conditions. We present first different formation and dissociation paths to explore the performance of the proposed kinetic algorithm for a wide range of situations, including special cases when hydrate and ice may coexist, such as the formation of secondary ice and hydrate during production. These qualitative validation studies allow us to introduce code details relevant to the simulation.

**Case 1: Hydrate formation under cooling at constant volume.** Hydrate formation in the presence of free gas can be either gas- or water-limited. The amount of hydrate $\Delta S_h$ that can form in each case follows:

\[
\begin{align*}
\text{gas limited (excess water)} & \quad \frac{\rho_l S_l}{\rho_g S_g} \geq \frac{\alpha}{1 - \alpha} \quad \Rightarrow \quad \Delta S_h = \frac{1 - \rho_g}{1 - \alpha \rho_h} S_g \\
\text{water limited (excess gas)} & \quad \frac{\rho_l S_l}{\rho_g S_g} \leq \frac{\alpha}{1 - \alpha} \quad \Rightarrow \quad \Delta S_h = \frac{1}{\alpha \rho_h} S_g
\end{align*}
\]

where $\rho_l$ and $\rho_g$ are the liquid and gas density, respectively, $\alpha$ is the mass fraction of water in hydrate; and $S_l$ and $S_g$ are the liquid and gas degree of saturations. Changes in saturation for a given time step follow from the kinetics, For example, when going across the hydrate phase boundary

\[
S_h^{i+1} = S_h^i + \beta \Delta S_h
\]

where $\beta$ is related to the rate of hydrate dissociation, coming from the kinetic law. Hydrate occupies less volume than the combined volume of the water and gas that reacted to make the hydrate. The algorithm attempts to refill the pore to satisfy the effective saturation ($S_e^i$) that corresponds to the water retention curve for the prevailing capillary pressure:

\[
\begin{align*}
S_e^{i+1} &= S_e^i \left[ 1 - \left( S_h^i + S_l^i \right) \right] \\
S_g^{i+1} &= 1 - \left( S_h^i + S_l^i + S_g^i \right)
\end{align*}
\]

where $S_l$ is the ice saturation. However, flow conditions will determine the availability of water and gas, changes in temperature, gas, liquid and capillary pressures.

We simulate hydrate and ice formation following an isochoric cooling path (Fig. 8a). The initial conditions are identified as ‘0’ (Fig. 8): $T=292.1$ °K; $P_c=0.18$ MPa (i.e. $P_l=15$ MPa and $P_g=15.18$ MPa); $S_l=S_g=0.5$. As expected, changes in $S_h$, $S_l$ and $S_g$ start when the P-T path touches the phase boundary, at point ‘1’ (Fig. 8b & 8d). Water and gas consume during hydrate formation, $S_g$
and $S_l^*$ always decrease (Fig. 8c). At point ‘2’ (Fig. 8b & d), all the methane available for hydrate formation consumes and the P-T path departs from the phase boundary. Note the capability of the proposed algorithm to successfully maintain the P-T path on the phase boundary during dissociation (Fig. 8b). This behavior is mainly controlled by the kinetic law. At ‘3’ (Fig. 8b) the P-T path touches the ice-water phase boundary and the liquid water transforms into ice (Fig. 8d).

Figure 8. Hydrate formation by cooling. The extreme case of isochoric conditions is presented herein to compare results with the analytical solution in Kwon et al (2008)
**Case 2: Thermal dissociation at constant volume and mass.** Isochoric heating is the extreme case of constrained volume expansion and it causes high pore fluid generation under undrained conditions (i.e. the rate of heating is higher than the rate of pore fluid pressure dissipation). The following simulation parameters are selected to compare results to the analytical solution in Kwon et al (2008): $S_h = 0.2$, rigid sediment skeleton, no mass flux. Results are summarized in Figure 9. The PT state remains on the phase boundary until all hydrate either dissociates or forms; numerical results are identical to the close-form predictions.

**Figure 9**  Gas production by heating. The extreme case of isochoric conditions is presented herein to compare results with the analytical solution in Kwon et al. (2008).
References


PRODUCTS

Publications – Presentations:

- A conference paper has been accepted for the 14th IACMAG (International Conference of the International Association for Computer Methods and Advances in Geomechanics). Kyoto Japan 22-25 September 2014 Title: “Coupled Modeling of Gas Hydrate Bearing Sediments”. Authors: M. Sanchez, J. C. Santamarina, A. Shastri & Xuerui Gai.
- A session on “Hydrate bearing soils: characterization, modeling and geomechanical implications”, has been accepted for the forthcoming AGU Fall meeting 2015, San Francisco, 15th to 19th December 2014. Marcelo Sanchez is one of the session conveners.
- Carlos Santamarina has been invited to deliver invited lecture on hydrate bearing Sediments at AGU Fall meeting 2015.

Website: Publications (for academic purposes only) and key presentations are included in http://pmrl.ce.gatech.edu/; http://engineering.tamu.edu/civil/people/msanchez

Technologies or techniques: None at this point.

Inventions, patent applications, and/or licenses: None at this point.

Other products: None at this point.

PARTICIPANTS

Research Team: The current team is shown next.

IMPACT

- While it is still too early to assess impact, we can already highlight the computational platform extensively validated in a wide range of coupled thermo-hydro-chemo-mechanical coupled problems (CB_Hydrate).

CHANGES/PROBLEMS:

None so far.
SPECIAL REPORTING REQUIREMENTS:
Nothing to report
# BUDGETARY INFORMATION:

## TAMU

**Grant No.DE-FE0013889**  
**TEES Project 32525-C3870 CE**  
**COST PLAN/STATUS**

### EXHIBIT 2 - COST PLAN/STATUS

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National Energy Technology Laboratory

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880

13131 Dairy Ashford Road, Suite 225
Sugar Land, TX 77478

1450 Queen Avenue SW
Albany, OR 97321-2198

Arctic Energy Office
420 L Street, Suite 305
Anchorage, AK 99501

Visit the NETL website at:
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