# **Oil & Natural Gas Technology**

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## Quarterly Progress Report Reporting Period: April-June 2007

## Detection and Production of Methane Hydrate

Submitted by: Department of Chemical and Biomolecular Engineering Rice University – MS 362 6100 Main St. Houston, TX 77251-1892

> Prepared for: United States Department of Energy National Energy Technology Laboratory

> > August, 2007





**Office of Fossil Energy** 

### **Detection and Production of Methane Hydrate**

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Reporting Period: April-June 2007

Prepared by: George Hirasaki Rice University

August 2007

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Department of Chemical and Biomolecular Engineering Rice University – MS 362 6100 Main St. Houston, TX 77251-1892 Phone: 713-348-5416; Fax: 713-348-5478; Email: gjh@rice.edu

University of Houston Department of Chemical Engineering 4800 Calhoun Street Houston, TX 77204-4004 (713) 743-4331, -4323 (fax); Email: mohanty@uh.edu

Prepared for

Richard Baker, Project Manager

U.S. Department of Energy - NETL 3610 Collins Ferry Road P.O. Box 880 Morgantown, WV 26508

### Progress during Phase 2: April-June 2007 (approved: June 21, 2007)

#### Task 1: Carbon inputs and Outputs to Gas Hydrate Systems

We have been revising and resubmitting a paper with Glen Snyder and Japanese Colleagues It is now "in press" in Deep-Sea Research. The paper is the first in our planned series of works to understand how authigenic minerals relate to methane fluxes and gas hydrate distribution in marine sediments.

We have been in collaboration with Oregan State University on Contributing Factors on Methanogenesis Rate in Sediments at Ocean Floor and their Effects on Methane Hydrate.

Meeting: April 5 -7, 2007, Oregon State University, Corvollis, Oregon

Participants:

Prof. Frederick S Colwell (Oregon State University, rcolwell@coas.oregonstate.edu)

Dr. Mark Delwiche (Idaho National Lab, mark.delwiche@inl.gov),

Dr. Bill Ussler (Monterey Bay Aquaium Research Institute, California, <u>methane@mbari.org</u>),

Prof. Gerald Dickens (Rice University, jerry@rice.edu)

Gaurav Bhatnagar (Graduate Student, Rice University, gb@rice.edu)

Guangsheng Gu (Graduate Student, Rice University, <u>gg2@rice.edu</u>)

Conclusion:

- 1. Temperature must have much effect on methanogenesis rate;
- 2. The effect of high pressure is not very clear yet, and is suspecting;
- 3. No result on methanogenesis rate at different temperature and high pressure with sediment from ocean floor as the substrate has been published till now. So such a result is very important and urgent.
- 4. All these factors may have very important effect on further modelling.

## Task 2: Numerical Models for Quantification of Hydrate and Free Gas Accumulations

## 1. Using depth of sulfate-methane transition zone as a direct proxy for quantifying methane hydrate saturation

We developed a new technique to quantify methane hydrate saturation in marine sediments by using depth of the sulfate-methane transition (SMT) zone as a proxy. This method is applicable at geologic settings where organic carbon input is low and all methane input to the gas hydrate stability zone (GHSZ) comes from a deeper source. Pore water sulfate depletion occurs in almost all hydrate settings across a relatively shallow sulfate reduction zone (SRZ) below the seafloor. Sulfate reduction in such settings occurs mainly through anaerobic methane oxidation across the SMT. Higher methane fluxes result in high hydrate saturation and shallow SMT, whereas lower methane flux causes the SMT to migrate deeper into the sediments and lower hydrate saturation.

Using a one-dimensional numerical model we show that the scaled depth to the SMT (i.e., depth of SMT below the seafloor normalized by the depth to the base of the GHSZ) as well as the average gas hydrate flux through the GHSZ is dependent on the net methane flux through the system. This feature links the scaled SMT depth to average hydrate saturation and allows estimation of the latter using the scaled depth.

We also generalize this relationship between average gas hydrate flux and scaled SMT depth through a general plot (Figure 1 below) and use it to constrain average hydrate saturation at different Cascadia Margin sites. Saturations obtained using this new method match well with interpretations of resistivity logs at these sites.



Figure 1: Relation between average gas hydrate flux (y-axis) and SMT depth for 5 Cascadia Margin sites

This work has been submitted for publication in Geophysical Research Letters.

### 2. Analytical theory for gas hydrate distribution and saturation in marine sediments

We have previously developed a numerical model for simulating gas hydrate accumulation due to *in-situ* biogenic methane sources or upward methane fluxes from deeper sources or a mixture of both. Motivated by the success of predicting hydrate saturation from SMT data, we tried to develop simple analytical relationships for gas hydrate systems sourced by deeper methane sources. We discovered that a gas hydrate system sourced by deeper methane can be completely described by simple analytical expressions at steady state. This approach incorporates the coupling between sulfate and methane through the anaerobic oxidation reaction.

Specifically, we use sulfate and methane mass balances in 1-D at steady state and use continuity of fluxes to obtain various system parameters. For example, we show that by specifying SMT depth as an input one can not only obtain simple expressions for the sulfate and methane profiles (Figure 2, left panel), but the entire gas hydrate saturation profile can also be constructed (Figure 2, right panel). This is done for three distinct SMT depths in Figure 2, which show that the top of the gas hydrate layer migrates to shallower depths as the SMT depth becomes smaller. Due to increased methane flux, shallow SMTs also result in greater gas hydrate saturation within the GHSZ (Figure 2, right panel). Gas hydrate saturation profiles computed analytically in Figure 2 (curves, right panel) are also compared with saturation profiles obtained from numerical simulations (crosses), which reveals very good agreement between our theory and numerical simulations.

The depth to the top of the gas hydrate layer as well as the free-gas saturation just below the BSR (assuming it to be immobile) can also be calculated from our analytical expressions. Thus, our analytical model turns out to be a fast and simple method to describe gas hydrate systems sourced by deep methane compared to expensive numerical simulations.



Figure 2: Steady-state sulfate and methane concentration profiles (left) and gas hydrate saturation profiles (right) as a function of depth for different values of scaled SMT depths.

#### 3. Overpressure development in low permeability gas hydrate systems

We have also developed a 1-D numerical model that can predict overpressure development in gas hydrate systems due to fast sedimentation and or low permeability sediments. Several natural gas hydrate systems are characterized by either of these features, which can lead to pore pressure gradients significantly higher than hydrostatic and in extreme cases approach lithostatic limits. Overpressure also limits the depth of the connected free gas column beneath the GHSZ; hydrostatically pressured systems will in general support greater thickness of free gas column than over-pressured systems before fracturing at the base of the GHSZ allows release of free gas trapped below.

To quantify such processes, we extend our earlier hydrostatically pressured numerical model to cases where pore pressure can deviate from hydrostatic values. Non-dimensionalization of this system of equations leads to the definition of a dimensionless sedimentation-compaction group,  $N_{sc}$ , that compares the permeability of the sediments to the sedimentation rate. This group is defined as:

$$N_{sc} = \frac{k_0 \rho_w g}{\mu_w \dot{S}}$$

where  $k_0$  is the absolute permeability of the sediments and  $\dot{S}$  is sedimentation rate. Thus, higher values of  $N_{sc}$  mean higher permeability or low sedimentation rate implying hydrostatic pore pressure. Conversely, lower values of  $N_{sc}$  will indicate pore pressures greater than hydrostatic. We now show results depicting the effect of this group,  $N_{sc}$ , on the gas hydrate system.

Figures 3 and 4 show the effect of decreasing  $N_{sc}$  from a large value to progressively smaller values on different depth profiles for a fixed set of biogenic input parameters. Figure 3 shows the pore pressure and lithostatic stress for different values of  $N_{sc}$ . It can be seen that decreasing  $N_{sc}$  leads to higher pore pressures and lower lithostatic stress (a result of under-compaction and higher porosities). Figure 4 shows steady-state gas hydrate and free gas saturations simulated for different  $N_{sc}$  values, which indicate lower saturations with decreasing  $N_{sc}$ . This is due to increased porosities and the higher sediment velocities through the GHSZ reduce the mass accumulation of methane and the hydrate occupying a smaller volume fraction (saturation) of the increased pore space.

More interesting, however, is the fact that the base of the GHSZ shifts by a relatively small depth even when the formation is close to lithostatic pore pressures. Thus, the pressure state of a gas hydrate system (i.e., hydrostatic or over-pressured) cannot be inferred from the fact that the theoretical base of the GHSZ is in agreement with the BSR. In other words, the system might be almost lithostatic and close to failure, yet the thermodynamically predicted base of the GHSZ could match well with the seismic BSR.



Figure 3: Normalized pore pressure (solid) and lithostatic stress (dashed) profiles as a function of the dimensionless group  $N_{sc}$ .



Figure 4: Gas hydrate (solid) and free gas (dashed) saturation profiles for different values of  $N_{sc}$ 

#### Task 3: Analysis of Production Strategy

J. Phirani & K. K. Mohanty

University of Houston

#### Abstract

In subtask 7.1, we are participating in the NETL methane code comparison study. In the last month, we have worked on the first two problems set up by the Code Comparison Study group. The brief statement of the problems and our simulator results are described below.

#### Problem 1

This is a problem of gas-liquid equilibrium (no hydrates) inside a one-dimensional porous medium without any mass or heat transfer outside the domain. The initial pressure and temperature are set outside the stability region of gas hydrates and ice. The domain is of length 20 meters, divided in 20 grid blocks of equal dimension. The problem is initialized with a gradient in temperature and aqueous / gas pressures such that, the first half of the domain, i.e., first 10 grid blocks, is saturated with water and the second half has both gas and water. The system is left to equilibrate and the parameters are recorded at 1 day, 10 days, 100 days, 1000 days and 10000 days.

The results from our simulator are plotted in Figs. 1-4. Fig. 1 shows the temperature evolution. There is an initial temperature gradient. It takes more than 1000 days for the temperature to equilibrate. Fig. 2 shows the aqueous phase pressure. It is constant in the left half of the domain and has a gradient in the right half initially. It equilibrates in about 1000 days. Fig. 3 shows the aqueous phase saturation. It is 100% in the left half of the domain and has a gradient in the right half initially. Again, it reaches a steady state in about 1000 days. Fig. 4 shows the methane dissolved in water. Initially it has a gradient because pressure and temperature vary within the domain initially. It equilibrates in about 1000 days.



Fig. 1: Temperature evolution in problem 1



Fig. 2: Aqueous pressure evolution in problem 1





Fig. 3: Aqueous saturation evolution in problem 1



Methane mass fraction in aqueous phase

Fig. 4: Methane mass fraction evolution in problem 1

#### Problem 2

This is a base case problem with hydrate-gas-liquid equilibrium. The domain is the same as in problem 1 and with no flow or heat transfer boundary conditions. The problem is initialized with hydrate and aqueous phases in the left half and aqueous and gas phases in the right half. Pressures and temperatures vary accordingly. The system is left to equilibrate and the parameters are recorded at 1 day, 10 days, 100 days, 1000 days and 10000 days.



**Temperature (C)** 

Fig. 5: Temperature evolution in problem 2

### **Hydrate Saturation**



Fig. 6: Hydrate saturation evolution in problem 2

**Gas Saturation** 



#### **Gas Pressure**



Fig. 8: Gas pressure evolution in problem 2

The results from our simulator for the problem 2 are plotted in Figs. 5-8. Fig. 5 shows the temperature evolution. There is an initial temperature discontinuity at the middle of the domain. It takes more than 1000 days for the temperature to equilibrate. Fig. 6 shows the hydrate phase saturation. It is present and constant in the left half of the domain and absent in the right half initially. Hydrate melts on its right side front which releases gas and increases pressure. Thus new hydrates form to the left of the front; hydrate saturation increases at the left side of the domain. Fig. 7 shows the gas phase saturation. Gas phase saturation goes up because some of the hydrates melt. Again, it reaches a steady state in more than 1000 days. Fig. 8 shows the gas phase pressure. The gas pressure equilibrates spatially very fast, but it increases as hydrates melt.

#### **Future Work**

We will finish up the other two problems and start on modeling of pore-scale accumulation of hydrates (Subtask 7.1).

#### Task 4: Seafloor and Borehole Stability.

- Worked with USGS Woods Hole to develop testing procedure and preparation technique for working with pressurized hydrate cores from India hydrates program (NGHP)
- Worked with W. Waite (USGS Woods Hole) to develope data processing stream and interface for working with data from the Gas Hydrate and Sediment Testing Laboratory Instrument (GHASTLI)
- Assisted with sample set-up and experiments on sample from NGHP in GHASTLI

Two papers are in review for in Marine and Petroleum Geology (special volume on the scientific results from the 2005 JIP drilling for gas hydrates in the Gulf of Mexico) Dugan, B., in review, Fluid Flow in Keathley Canyon, Northern Gulf of Mexico, Marine and Petroleum Geology.

Winters, W.J., Dugan, B., Collett, T.S., in review, Physical Properties of Sediments from Keathley Canyon and Atwater Valley, JIP Gulf of Mexico Gas Hydrate Drilling Program, Marine and Petroleum Geology

#### Task 5: Geophysical Imaging of Gas Hydrate and Free Gas Accumulations

We have submitted a paper to *Geophysical Journal International*<sup>1</sup> that includes the same seismic waveform inversion methodology that we will apply to the seismic data for imaging gas hydrates. The Ph.D student (Priyank Jaiswal) has also given a presentation at the 69th Annual EAGE conference in London (11–14 June, 2007) on the seismic waveform inversion methodology<sup>2</sup>. He will also be presenting the methodology and its application again at the 77th SEG Annual Meeting in San Antonio (23-28 September)<sup>3</sup>. The application of the waveform inversion methodology is currently being made on additional onshore reflection seismic data from the North-East India.

We have made contacts in the Directorate General of Hydrocarbon, the Indian hydrocarbon regulative authority, requesting seismic and well data from the Krishna-Godavari Basin offshore west coast of India, but we are only aware that our request is under review. This location is where successful drilling for gas hydrates was completed in 2006.

Mr. Jaiswal's work to date is funded by other sources, and will continue to be until we acquire the gas hydrate data referred to above. At that time, Mr. Jaiswal may be finished his Ph.D. and will therefore begin his work under this grant as a postdoc (there is funding in the grant for his work as a postdoc).

1. Jaiswal, P., C. A. Zelt, A. W. Bally, and R. Dasgupta, 2-D traveltime and waveform inversion for improved seismic imaging: Naga Thrust and Fold Best, India, **Geophys. J. Int.**, submitted, 2007.

- 2. Jaiswal, P., and <u>C. A. Zelt</u>, Traveltime and full-waveform inversion for improved seismic imaging in geologically complex areas, **EAGE**, Annual meeting, London, 2007.
- 3. Jaiswal, P., Zelt, C. A., and Dasgupta, R., 2-D waveform and traveltime inversion for seismic imaging of the Naga thrust fault, India. **SEG** Expanded Abstracts, Vol. 77, 2007.

COST PLAN / STATUS					
	Phase 1	Phase 2; Year 1 (June 2007-May 2008)			
Baseline Reporting Quarter		Q2	Q3	Q4	Q1
Baseline Cost Plan (SF-424A)					
Federal Share	\$3,624	\$80,003	\$80,003	\$80,003	\$80,003
Non-Federal Share	\$1,004	\$28,653	\$28,653	\$28,653	\$28,653
Total Planned	\$4,628	\$108,656	\$108,656	\$108,656	\$108,656
Cumulative Baseline Cost	\$4,628	\$113,284	\$221,940	\$330,596	\$439,252
Actual Incurred Cost					
Federal Share	\$3,082	0			
Non-Federal Share		0			
Total Incurred Cost		0			
Cumulative Costs	\$3,082	\$3,082			
Variance (plan-actual)					
Federal Share	\$542	\$80,003			
Non-Federal Share	\$1,004	\$28,653			
Total Variance	\$1,546	\$108,656			
Cumulative Variance	\$1,546	\$110,202			

Milestone Plan/Status



### 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

One West Third Street, Suite 1400 Tulsa, OK 74103-3519

1450 Queen Avenue SW Albany, OR 97321-2198

2175 University Ave. South Suite 201 Fairbanks, AK 99709

Visit the NETL website at: www.netl.doe.gov

Customer Service: 1-800-553-7681

