Quarterly Progress Report
(January – March 2009)

Mechanisms Leading to Co-Existence of Gas and Hydrate in Ocean Sediments

Submitted by:
The University of Texas at Austin
1 University Station C0300
Austin, TX 78712-0228

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

May 1, 2009
MECHANISMS LEADING TO CO-EXISTENCE OF GAS AND HYDRATE IN OCEAN SEDIMENTS

CONTRACT NO. DE-FC26-06NT43067

QUARTERLY PROGRESS REPORT
Reporting Period: 1 Jan 09 – 31 Mar 09

Prepared by

Steven L. Bryant
Department of Petroleum and Geosystems Engineering
The University of Texas at Austin
1 University Station  C0300
Austin, TX  78712-0228
Phone: (512) 471 3250
Email: steven_bryant@mail.utexas.edu

Ruben Juanes
Department of Civil and Environmental Engineering
Massachusetts Institute of Technology
77 Massachusetts Avenue, Room 48-319
Cambridge, MA 02139
Phone: (617)253-7191
Email: juanes@mit.edu

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

Work during this quarter focused on summarizing the tool developed during this project for computing capillarity-controlled gas/water menisci in sediments and on assessing the mechanical implications of hydrate growth at those interfaces.

The tool is based on our adaptation of the level set method for interface tracking to the problem of determining constant curvature interfaces, which are the mathematical consequence of the Young-Laplace equation relating capillary pressure to meniscus curvature. In this project we also showed how the method can be extended to account for movement of grains in the sediment, a local response to the pressure difference between gas and water phases.

We show that the volume change associated with hydrate formation is not trivial and in fact in many sediments is likely to lead to pressure changes comparable to those driving sediment fracturing, drainage and imbibition. This observation adds a new dimension to the competition between drainage and fracturing. That competition has been the subject of previous reports. Work is underway to evaluate how this new aspect of hydrate formation affects the morphology of hydrate grown in sediments from gas/water interfaces.

Technology transfer: LSMPQS v.0.5 software developed during this project was made publicly available, along with the new release of LSMLIB (v. 1.0.0) which provides the kernel routines for LSMPQS.
**Activities in This Reporting Period**

**Task 7.0 - Coupled gas/water/sediment dynamics with hydrate formation**

*Volume change with hydrate formation.* A premise being tested in this project is that the gas/water interface is the site where hydrates form, and we are using the configuration of the interface to estimate hydrate growth habit in Task 7. Because hydrate formation requires stoichiometric contributions of molecules from the phases on both sides of the interface, the growth of hydrate has interesting implications for the volume occupied by the three phases (hydrate = h, gaseous = g, aqueous = a). The behavior depends on the prevailing temperature and pressure, and upon boundary conditions assumed, *i.e.* whether the gaseous phase is connected to the bulk, whether the aqueous phase is connected to the bulk, and whether the hydrate grows from the interface into the gas phase or into the water phase.

For a hypothetical closed system (fixed mass of CH₄ and H₂O), the remarkable feature of hydrate growth is that the volume occupied by CH₄ and H₂O in the hydrate is smaller than the volume occupied by those molecules in their respective phases. Consequently the total phase volume $V_h + V_a + V_g$ is a decreasing function of extent of hydrate formation. The rate of decrease depends on gaseous phase density and thus upon $P$ and $T$. Several contours of gaseous phase density (assumed to be pure methane) in kg/m³ are shown in the plot below, along with the phase boundary for methane hydrate.

![Contour plot of constant gas phase density](image)

*Figure 1. Contours of constant gas phase density (assumed pure methane) computed from the Soave-Redlich=---
Kwong equation of state. The hydrate phase boundary is shown as the heavy blue curve. Along the black line \( \rho_{CH_4} = 118 \text{ kg/m}^3 \) the gaseous phase and the hydrate phase have the same mass density of CH\(_4\), assuming hydrate density of 914 kg/m\(^3\) and a H\(_2\)O:CH\(_4\) mole ratio of \( N = 6 \).

We assume for illustration that gaseous phase has invaded a sediment saturated with aqueous phase, and that hydrate then forms after the gaseous phase invades. (This assumption is the premise of this research project, motivated by the frequent observation of co-existence of these phases in the hydrate stability zone.) Consider then a closed system containing arbitrary initial volumes of gaseous phase (pure CH\(_4\)) and aqueous phase (pure H\(_2\)O) such that \( V_0 = V_g + V_a \). A mass balance leads to an expression for the incremental change in the total phase volume relative to \( V_h \), the volume of hydrate formed, assuming no change in \( P \) and \( T \) during hydrate formation, and assuming that both water and methane molecules have unhindered access to the growing hydrate crystal:

\[
\frac{\Delta V}{V_h} = 1 - \frac{\rho_h}{M_{CH_4} + N M_{H_2O}} \left( \frac{M_{CH_4}}{\rho_g} + \frac{\rho_h N M_{H_2O}}{\rho_a} \right)
\]

Here \( M_i \) is the molecular weight of species \( i \), \( N \) is the mole ratio of H\(_2\)O to CH\(_4\)+ in hydrate, and \( \rho_i \) is the density of phase \( i \). Putting in typical values for the second term on the right hand side yields negative quantities. Hence as shown in Figure 2 the volume change is always negative in the region of interest. That is, forming any amount of hydrate \( V_h \) decreases the volume of gaseous phase and volume of aqueous phase, and these decreases are greater in magnitude than the increase in hydrate volume.

![Figure 2. Contours of constant fractional decrease in total phase volume, relative to volume of hydrate formed, for several different gaseous phase densities, assuming a closed system at constant \( P \) and \( T \). The heavy blue line is the hydrate phase boundary. We assume hydrate density of 914 kg/m\(^3\) and a H\(_2\)O:CH\(_4\) mole ratio of \( N = 6 \). The volume occupied by hydrate, gaseous and aqueous phases decreases when hydrate forms. The rate of decrease depends on the density of the gas phase. For densities typical of the hydrate stability zone, the rate of decrease is 30% or more.](image-url)
We can carry out essentially the same calculation in terms of initial saturation of the gaseous and aqueous phases, and the results are shown in Fig. 3. The decrease in volume depends on whether CH₄ or H₂O is present in excess. This in turn depends on the gaseous phase density and hence \( P \) and \( T \). Generally, for large aqueous phase saturations, H₂O is in excess. In this case the fractional volume change is given by

\[
\frac{\Delta V}{V_0} = S_g \left( \frac{\rho_g}{\rho_H} \frac{M_g + NM_w}{M_g} - \left( 1 + \frac{\rho_g}{\rho_w} \frac{NM_w}{M_g} \right) \right)
\]

where \( V_0 \) is the pore volume. This formula applies to the upward sloping trends in Fig. 3, to the right of the minimum in each curve. When CH₄ is present in excess, the fractional volume change is given by

\[
\frac{\Delta V}{V_0} = S_w \left( \frac{\rho_w}{\rho_H} \frac{M_g + NM_w}{NM_w} - \left( 1 + \frac{\rho_w}{\rho_g} \frac{M_g}{NM_w} \right) \right)
\]

Figures 2 and 3 clearly show that substantial decreases in volume occupied by the hydrate, gaseous and aqueous phases will occur. A key underlying assumption in Figs. 2
and 3 is that $T$ and $P$ do not change. For this to happen in nature, a substantial volume of fluid -- either gas or water or both -- must enter the sediment to fill in the space vacated. This simple observation has interesting implications. Neither fluid phase is guaranteed to be connected to the corresponding bulk phase, because drainage and imbibition cause disconnections to occur at the pore scale. In this case, it may not be possible for nature to provide fluids to fill the void, and consequently the pressure would decrease locally. The pressure decrease would occur in the gas phase, if it were disconnected. This would decrease the capillary pressure and set the stage for imbibition to occur -- without any change in the larger scale conditions that caused the original gas invasion. Our conceptual model on which Task 7 is predicated anticipated the possibility of imbibition, but caused by macroscopic changes (pressure in the bulk water and/or gas phases). We also anticipated the possibility of gas phase pressure decreasing, but only because of stoichiometric consumption of CH$_4$ molecules. The volume change associated with phase densities may drive much larger pressure changes than would occur simply with stoichiometric consumption.

Another implication of this observation is that supplying either fluid phase through a low permeability sediment requires finite time. The rate is even slower in sediment in which gaseous and aqueous phases coexist (the sum of phase relative permeabilities is less than the absolute permeability), and slower still when hydrate has formed in pore space, thereby restricting flow in some pore throats. We are led to make the following conjecture: fluid supply may act as the rate-limiting step in forming hydrates from co-existing gaseous and aqueous phases. If so, it is possible that patterns of hydrate formation may emerge that overprint both the capillarity-controlled meniscus configuration and the fractured-sediment meniscus configuration. We will examine this possibility in subsequent research on this task.

We consider one other interesting situation, namely that the gas phase saturation exists as a residual phase, i.e. completely disconnected from the bulk phase. We also make the reasonable assumption (based on observations in micromodels reported in the literature) that the hydrate grows from the gas/water meniscus into the gas phase. Finally we assume that the water phase is open, in the sense that its volume remains constant. In this situation, the volume occupied by the three phases can increase or decrease, depending on the gas phase density and hence upon $T$ and $P$.

When $T$ and $P$ are such that the gas phase density exceeds 118 kg/m$^3$ (the mass density of CH$_4$ in hydrate), the change in volume is positive, as shown in Fig. 4. Conversely, for gas phase densities below this threshold, the change in volume is negative. As above, this calculation assumes that $P$ and $T$ do not change. In nature, however, the gas phase pressure will increase or decrease as the hydrate grows, depending on whether the volume change is positive or negative.

Increasing the gas pressure raises the possibility of rupturing the incipient hydrate skin from within the trapped gas volume. This would push hydrate and gas out into the water phase. Subsequent hydrate formation would be thus be distributed away from the initial gas-filled pores. Conversely, decreasing the gaseous phase pressure would raise the
possibility of rupturing the incipient hydrate skin into the trapped gas. In this case, hydrate and water would encroach into the gas-filled pores. Subsequent hydrate formation would thus tend to fill in the initially gas-filled pores. We are therefore led to predict two distinct morphologies for hydrate growing at the gas/water interface in sediment in which imbibition has occurred. We will seek experimental (in)validation of this prediction in future work.

![Figure 4](image.png)

**Figure 4.** Contours of constant fractional change in total phase volume, relative to volume of hydrate formed, for several different gaseous phase densities. The heavy blue line is the hydrate phase boundary. Assumptions: gas phase is disconnected from the bulk but water is connected; hydrate grows from the gas/water interface into the gas phase; constant $P$ and $T$; hydrate density of 914 kg/m$^3$ and a H$_2$O:CH$_4$ mole ratio of $N = 6$. When the gas phase density exceeds 118 kg/m$^3$, the volume occupied by hydrate, gaseous and aqueous phases increases when hydrate forms. Conversely, the total phase volume decreases when hydrate grows into gas phase having density less than 118 kg/m$^3$. In nature, the assumption of constant $P$ is poor: the gas phase pressure will increase or decrease depending on the sign of the phase volume change. Thus depending on the mechanical strength of the hydrate film along the gas water interface, the incipient film is more likely to rupture.

Tool for gas/water/sediment dynamics. A powerful enabling technology for this research has been the level set method adapted for computing gas/water interfaces during drainage and imbibition, LSMPQS (Prodanovic and Bryant, 2006). The most recent example of its continuing development and application in this project was to account for the displacement of solid grains in contact with the gas phase. As shown in Figure 5, (reproduced from previous quarterly report) simulations with LSMPQS reveal the emergence of channels of invading gas phase, with no increase in gas pressure once a threshold value is reached.
As part of the technology transfer in this project, LSMPQS was recently made publicly available. This has the additional benefit of ensures reusability, higher standards, and better transparency of any computational effort.

LSMPQS is a software package for simulating capillarity controlled, immiscible fluid displacement (drainage and imbibition) in porous media. The first release is v 0.5. of April 2009.

Fig 6. (left) Medial surface extracted from a micro CT image of a naturally fractured carbonate rock. Rainbow coloring indicates the distance from the closest grain surface (red=3.1µm, velvet=55.8µm). (right) Simulation of an oil interface in the fracture at imbibition at mean curvature 0.09µm⁻¹. The red shows oil-water interface, gray is oil-rock contact and the snapped-off (residual) oil blobs are in blue.
Features

- Porous medium can be of arbitrary complexity, described analytically (e.g. sphere packs) or from segmented images of real rocks.
- No pre-set parameters other than detailed description of the porous medium are needed.
- The fluid configurations obtained from LSMPQS simulation are detailed (see above figure) and quantifying saturation, volumes, interfacial areas etc. is straightforward. Having suitable geometry, you can obtain capillary-pressure curves or study pore scale phenomena in a small ensemble of pores.
- LSMPQS is developed on Linux, and should compile on any Unix-like system. C/C++ and FORTRAN compilers are required.

Author: Dr. M. Prodanović, masa.prodanovic@gmail.com
Webpage: http://users.ices.utexas.edu/~masha/lsmpqs/index.html
Download detailed manual:
   http://users.ices.utexas.edu/~masha/lsmpqs/LSMPQS-v0.5-Manual.pdf
In addition, Dr. Prodanović has been a developer of the library of level set methods LSMLIB since 2006 and this library had a new release 1.0.0. in February 2009.
LSMLIB webpage: http://ktchu.serendipityresearch.org/software/lsmlib/index.html
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