Oil & Natural Gas Technology

DOE Award No.: DE-FC26-06NT42960

Quarterly Progress Report

Reporting Period: October-December, 2007

Detection and Production of Methane Hydrate

Submitted by: Rice University University of Houston George J. Hirasaki 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

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

> > January, 2008





Office of Fossil Energy

Table of Contents

Disclaimer	3
Executive Summary	4
Background	5
Task 5: Carbon Inputs and Outputs to Gas Hydrate Systems	. 12
Task 6: Numerical Models for Quantification of Hydrate and Free Gas Accumulations	. 13
Task 7: Analysis of Production Strategy	. 21
Task 8: Seafloor and Borehole Stability	. 22
Task 9: Geophysical Imaging of Gas Hydrate and Free Gas Accumulations	. 23
Cost Plan / Status	. 24
Milestone Plan / Status	. 25

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Executive Summary

Technical progress is reported on Tasks 5-8. Activity on Task 9 will begin in January 2008.

Task 5: Carbon Inputs and Outputs to Gas Hydrate Systems

Models concerning the abundance and distribution of gas hydrate in marine sediment require constraints on carbon inputs and outputs, fluid flow and temporal evolution. Our chemical analyses of sediment appear to be providing us reasonable constraints that we can use in our models.

Task 6: Numerical Models for Quantification of Hydrate and Free Gas Accumulations

The model development for Task 6 was largely completed in 2007. The senior graduate student on this subtask, Gaurav Bhatnagar is starting employment with Shell in February 2008. The new graduate student, Guangsheng Gu has been working on another DOE project and not yet begun work on this task. At the end of 2007 another graduate, Sayantan Chatterjee was added to this task. Funding from Shell is being negotiated to accommodate this additional expense.

A contract is being negotiated with Shell for funding to add another faculty member and graduate student to Task 8. Professor Pol Spanos of Mechanical Engineering and Material Science (member NAE) is to work on seafloor stability. The title of his project is, "Numerical/Stochastic Aspects of submarine slope stability analysis in the presence of gas hydrates."

Task 7: Analysis of Production Strategy

In the last few months, we have worked on the first four problems set up by the Code Comparison Study group. We have started the pore-level modeling of hydrate distribution in single phase flow (no free gas phase) in order to estimate transport properties of hydrate bearing sediments. We have also made 3D simulations of hydrate dissociation in a homogeneous porous medium with an underlying water saturated layer.

Task 8: Seafloor and Borehole Stability

This work has enhanced our knowledge on flow and transport properties in fine-grained sediments. We also feel it expands the use of NMR logs to get permeability in multiple lithologies. Historically the SDR equation has been employed in reservoir systems; we have adapted it for marine hydrate settings.

Background

A. Objective

This project seeks to understand regional differences in gas hydrate systems from the perspective of as an energy resource, geohazard, and long-term climate influence. Specifically, the effort will: (1) collect data and conceptual models that targets causes of gas hydrate variance, (2) construct numerical models that explain and predict regional-scale gas hydrate differences in 2- and 3-dimensions with minimal "free parameters", (3) simulate hydrocarbon production from various gas hydrate systems to establish promising resource characteristics, (4) perturb different gas hydrate systems to assess potential impacts of hot fluids on seafloor stability and well stability, and (5) develop geophysical approaches that enable remote quantification of gas hydrate heterogeneities so that they can be characterized with minimial costly drilling. Our integrated program takes advantage of the fact that we have a close working team comprised of experts in distinct disciplines.

The expected outcomes of this project are improved exploration and production technology for production of natural gas from methane hydrates and improved safety through understanding of seafloor and well bore stability in the presence of hydrates.

B. Scope of Work

The scope of this project is to more fully characterize, understand, and appreciate fundamental differences in the amount and distribution of gas hydrate and how this affects the production potential of a hydrate accumulation in the marine environment. The effort will combine existing information from locations in the ocean that are dominated by low permeability sediments with small amounts of high permeability sediments, one permafrost location where extensive hydrates exist in reservoir quality rocks and other locations deemed by mutual agreement of DOE and Rice to be appropriate. The initial ocean locations are Blake Ridge, Hydrate Ridge, Peru Margin and GOM. The permafrost location is Mallik. Although the ultimate goal of the project is to understand processes that control production potential of hydrates in marine settings, Mallik will be included because of the extensive data collected in a producible hydrate accumulation. To date, such a location has not been studied in the oceanic environment. The project will work closely with ongoing projects (e.g. GOM JIP and offshore India) that are actively investigating potentially economic hydrate accumulations in marine settings.

The overall approach is fivefold: (1) collect key data concerning hydrocarbon fluxes which is currently missing at all locations to be included in the study, (2) use this and existing data to build numerical models that can explain gas hydrate variance at all four locations, (3) simulate how natural gas could be produced from each location with different production strategies, (4) collect new sediment property data at these locations that are required for constraining fluxes, production simulations and assessing sediment stability, and (5) develop a method for remotely quantifying heterogeneities in gas hydrate and free gas distributions. While we generally restrict our efforts to the locations where key parameters can be measured or constrained, our ultimate aim is to make our efforts universally applicable to any hydrate accumulation.

Task 5: Carbon Inputs and Outputs to Gas Hydrate Systems

Responsible Party: Rice University

Subtask 5.1. Complete iodine cycling. The recipient shall collect sediment sample cores from Blake Ridge, Peru Margin, Hydrate Ridge and GOM (as well as other promising hydrate accumulation sites deemed appropriate by mutual agreement of the recipient and DOE). The recipient shall wash and freeze-dry sediments to remove pore water, and then measure them for lodine (I) and Organic Carbon (C_{org}) contents. The recipient shall conduct activities necessary to liberate and analyze the I (liberated by hydropyrolysis, collected in solution, and analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)). The recipient shall determine the content of C_{org} contents (through use of a CHNO analyzer). The recipient shall quantify how much I is incorporated into C_{org} near the seafloor and returned to pore waters at depth. The recipient shall use this information in conjunction with pore water I⁻ profiles to constrain the integrated C_{org} flux over time.

Subtask 5.2. Authigenic minerals. The recipient shall collect sediment cores as identified in subtask 5.1, with specific focus on cores across the modern zone of Anaerobic Oxidation of Methane (AOM). After removing pore water, the recipient shall digest sediment aliquots in acetic acid and aqua regia such that the first extraction dissolves carbonate and the second dissolves barite. The recipient shall analyze the solutions for metals (e.g., Ba, Ca, Mg, Sr) using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The recipient shall use resulting sedimentary metal profiles to quantify the location and mass of authigenic minerals. The recipient shall use this information in conjunction with pore water chemistry to constrain hydrocarbon outputs through AOM.

Task 6: Numerical Models for Quantification of Hydrate and Free Gas Accumulations

Responsible Party: Rice University

Subtask 6.1: Model development. The recipient shall develop finite difference models for the accumulation of gas hydrate and free gas in natural sediment sequences on geologically relevant time scales. These models shall include hydrate precipitation, dissociation, and dissolution as influenced by parameters including, but not limited to, sedimentation, compaction, methanogenesis, salinity, multi-component hydrocarbons, momentum balance-Darcy Law, energy balance, heterogeneities geometry, geotherm, and seafloor depth. The recipient shall first model hydrate accumulation on Blake Ridge, Peru Margin, and flanks of Hydrate Ridge, where advection appears minimal and then move to the crest of Hydrate Ridge and GOM where advection from deeper sources are important. The recipient shall also model and interpret promising hydrate accumulation sites off the coast of India as well as other sites deemed appropriate by mutual agreement of the recipient and DOE. All models shall be built, tested and refined iteratively over the duration of the effort and shall incorporate new data as it becomes available.

Subtask 6.2: Conditions for existence of gas hydrate. The recipient shall summarize, quantitatively, the conditions for the absence, presence, and distribution of gas hydrates and free gas in 1-D systems by expressing the conditions in terms of dimensionless groups that combine thermodynamic, biological and lithologic transformation, and transport parameters. The recipient shall constrain quantitative

relationships between parameters by the geothermal profile, dynamic mass conservation and transport equations for sediment components, water, dissolved species and hydrocarbons.

Subtask 6.3: Compositional effect on BSR. The recipient shall add to the numerical model, developed under this task, a chloride balance and multi-hydrocarbon capability specifically to investigate how hydrocarbon fractionation might affect Bottom Simulating Reflectors (BSRs). The compositional simulator shall predict coexisting hydrate and free gas saturation profiles with change in hydrocarbon composition at the nominal Base of the Gas Hydrate Stability (BGHS) capturing the occurrence where gas hydrate and free gas can coexist over a range of temperatures when hydrocarbon composition and salinity are free to vary. The recipient shall use a rock property model to compute the vertical profile of acoustic impedance and synthetic seismograms shall be constructed to quantify the strength of the reflection as a function of frequency and angle of incidence.

Subtask 6.4: Amplitude Attenuation and chaotic zones due to hydrate distribution. The recipient shall simulate preferential formation of gas hydrate in coarse-grained, porous sediment in 2-D by linking fluid flux to the permeability distribution. The acoustic impedance shall be computed from the lithology and hydrate distribution. Synthetic seismograms shall be constructed to quantify the degree of attenuation as a function of system parameters. These simulations shall be used to test the hypothesis that preferential accumulation of hydrate in high porosity lithology may result in amplitude attenuation. If this hypothesis is shown to be valid, correlations shall be developed between degree of attenuation and system parameters. The recipient shall model focused flux of free gas into a stratified hydrate stability zone to seek conditions that will result in chaotic zones. This shall be done in an effort to simulate chaotic zones which may result from migration of free gas into the hydrate stability zone resulting in regions of strongly contrasting acoustic impedance. Activities under this subtask shall be coordinated with activities under Task 9.

Subtask 6.5: Processes leading to overpressure. The recipient shall quantify, by simulation and summarize by combination of responsible dimensionless groups, the conditions leading to overpressure to the point of sediment failure. This will be done to evaluate the occurrence of overpressure in gas hydrate systems (caused by: compacting shales that can have very low permeability, and free gas accumulation beneath the BGHS) which can lead to sediment failure by faulting and fluid leakage, or by shear failure with sliding or slumping. The recipient shall focus specifically on conditions leading to slope failure. The recipient shall correlate the maximum thickness of the free gas column with system parameters. Activities under this subtask shall be coordinated with activities under Subtask 8.2.

Subtask 6.6 Concentrated hydrate and free gas. The recipient shall, using 2-D and 3-D models, simulate lateral migration and concentration of gas hydrate and free gas in structural and stratigraphic traps. This effort will attempt to simulate the occurrence of gas hydrate systems with hydrate and free gas sufficiently concentrated for economic production which will likely form through focused fluid flow in which directed flow could occur because of lithology and geometry (i.e., stratigraphic or structural traps). The recipient shall specifically identify conditions favorable for large, concentrated accumulations of gas hydrate and free gas.

Subtask 6.7 Focused free gas, heat and salinity. The recipient shall quantify, using 2-D and 3-D model simulations and comparisons to available observations, the factors controlling the process of localized upward migration of free gas along faults and lateral

transfer to dipping strata that can lead to chaotic zones and possible accumulations of concentrated hydrate. The recipient shall seek specifically to identify if localized upwelling of free gas is only an indication of escape from a deeper accumulations or if it offers potential for concentrated accumulation of hydrate.

Subtask 6.8 Sulfate profile as indicator of methane flux. The recipient shall compute, for systems where data on the sulfate profile is available, the oxidation of methane by sulfate and shall indicate the perceived level of effect on gas hydrate accumulation and the data's value as an indicator of methane flux. Similar interpretations shall be made for iodine and temperature.

Subtask 6.9 Application of models to interpretation of case studies. The models developed in Task 6 will be applied to case studies in the interpretation of each of the other tasks. For example, the interpretation of the depth sulfate-methane transition zone has already been used to interpret hydrate saturation. The models will be used to find favorable conditions for economic production, investigate seafloor stability, and interpret seismic profiles.

Task 7: Analysis of Production Strategy

Responsible Party: University of Houston

Subtask 7.1: Pore-scale Model for Lithology, Petrophysical and Thermophysical Parameters.

The recipient shall simulate how and where gas hydrates form in marine systems at a continuum (Darcy) scale.

The recipient shall conduct activities necessary (from several perspectives, including production and mechanical stability) to increase understanding of how gas hydrates can exist in a single pore or a collection of pores.

The recipient shall participate in the NETL methane hydrate code comparison study to evaluate the capabilities of the in-house (University of Houston) simulator with respect to other existing hydrate simulators participating in the code comparison study.

The recipient shall perform simulations of hydrate formation using the University of Houston in-house simulator.

- The recipient shall simulate, within the context of available geological constraints and numerical models of accumulation, the formation of hydrates at the pore-scale in an effort to ascertain plausible spatial distributions of hydrates as a function of pore-scale saturation.
- Once the hydrate distribution is specified, effective conductivity of each pore to single-phase flow, multi-phase flow, and heat transfer shall be calculated.
- The pores shall be combined in a network model and the effective properties of the medium calculated at this initial saturation.
- Small amounts of hydrates shall be decomposed by depressurization and evolving distributions of hydrate generated.
- Again, effective conductivity of each pore to single-phase flow, multi-phase flow, and heat transfer shall be calculated at each hydrate saturation.
- Sediment grain size distribution shall be a parameter of this study.

The pore-scale results shall be compared with applicable published experimental results.

The recipient shall generate pore-scale models that match experimental single phase (no hydrate) permeability data from reservoir quality sediments found in the cores used in Task 8 (or other sources deemed appropriate by mutual agreement of the Recipient and DOE) and shall estimate the multiphase transport properties at various hydrate saturations. The recipient shall incorporate these petrophysical and thermophysical property correlations in reservoir-scale simulation models in subtask 7.2 to estimate gas production from hydrate reservoirs.

Subtask 7.2: Evaluation of Production Strategy. The recipient shall simulate gas production by depressurization and thermal stimulation for heterogeneous reservoirs and shall identify a perceived optimal production strategy.

- Efforts for simulation of gas production shall focus on marine hydrate reservoirs (Class 2).
- Reservoir heterogeneity anticipated in marine environments (known or determined through other tasks) shall be incorporated.
- Discrete features in the sediment (e.g. depth variations in composition and physical properties, fractures, reservoir dips etc.) shall be included.
- Appropriate hydrate distributions, either constrained from experimental data or mechanistic simulations (Task 5) shall be incorporated.
- A 3D in-house (University of Houston) simulator shall be used to simulate possible means of depressurization taking advantage of the capabilities of the simulator.
- Addition of heat shall be simulated in heterogeneous marine hydrate reservoirs to evaluate the hypothesis that natural gas production from hydrate deposits may be limited by the transfer of the heat needed for dissociation.
- The perceived optimal strategy for producing gas, based on these efforts, shall be identified for each marine hydrate system.
- The recipient shall identify key criteria of each system that can be used to evaluate the resource potential of other hydrate systems.

Task 8: Seafloor and Borehole Stability.

Responsible Party: Rice University

Subtask 8.1: Sediment-hydrate properties. The recipient shall establish a sediment properties database that defines how geomechanical and flow properties of different lithologies behave at varying hydrate concentrations and states of effective stress.

- Database construction shall begin by assimilating available properties from the five focus hydrate regions outlined in the description of project scope (as well as other promising hydrate accumulation sites deemed appropriate by mutual agreement of the recipient and DOE).
- The recipient shall separate mechanical properties into deformation properties (elastic, plastic, and brittle) associated with the yielding behavior and hydrologic properties (permeability).

- In addition to existing data, the recipient shall complete triaxial, uniaxial, and permeability experiments on existing cores to evaluate how properties change with stress. These experiments will provide a reference dataset for zero hydrate saturation which can be compared to existing data on hydrate-bearing systems.
- In collaboration with the USGS Woods Hole Science Center, the recipient shall complete triaxial strength measurements on NGHP cores from offshore India. Laboratory experiments shall constrain shear strength and cohesive properties of hydrate-bearing specimens near in situ effective stress and temperature conditions. These experiments will provide crucial information on strength behavior under which natural or induced (i.e., production related) failure could create hazards.
- In conjunction with wireline logging, LWD, IPTC data, and experiments on nonhydrate bearing samples the recipient shall characterize strength and flow properties of sediments with and without hydrate. The recipient shall provide these properties at varying hydrate saturations as they are necessary constraints and inputs of geomechanical and flow models that address geologic accumulation and production of gas hydrate.

Subtask 8.2: Modeling (In)stability. Physical properties of hydrate-bearing sediment (from subtask 8.1) shall be incorporated into numerical models for accumulation (geologic timescales) and production (human timescales) in gas hydrate systems.

- The recipient shall create a deformation and strength model to understand feedbacks between the formation and dissociation of gas hydrate, and sediment properties that control fluid flow, sediment deformation, and sediment stability.
- Sensitivity analyses shall be completed to evaluate how initial hydrate and gas concentrations, permeability / strength / compressibility of the system components, and rate of gas generation influence pressure/stress responses and system dynamics (flow, stability).
- Ultimately the recipient shall couple the flow behavior that exists in the accumulation and reservoir models with well tested, but simple calculations of stability (e.g., infinite slope analyses, Bishop or Janbu methods).

Subtask 8.3: Integrating geomechanical studies. The proposed stability evaluation shall complement and expand upon ongoing (separately funded) DOE studies of geomechanics. Recipient generated laboratory and field characterization shall be used to define bulk properties incorporated into geological models to evaluate bulk regional trends of flow and (in)stability and into production models to assess borehole stability.

This effort is to expand upon the pore- and grain-scale geomechanical and flow studies of Bryant & Juanes (Mechanisms Leading to the Co-Existence of Gas and Hydrate in Ocean Sediment, DE-FC26-05NT42958) and Holditch et al. (Geomechanical Performance of Hydrate-Bearing Sediments in Offshore Environments, DE-FC26-05NT42664). These ongoing studies are advancing our understanding of hydrate formation at the grain-pore interface and how this impacts porosity, permeability, and strength evolution near grain boundaries.

Work under this award shall focus on bulk/average analyses as necessary for largerscale modeling and analysis.

• The recipient shall develop a database of geomechanical and flow properties against which the ongoing studies can be tested.

• The recipient shall participate in continued discussion among all groups with a focus toward development of a testing and modeling program that can describe flow, strength and instability in hydrate systems at the granular-, borehole- and regional-scales; an understanding that is necessary for evaluating hydrate accumulation and production.

Task 9: Geophysical Imaging of Gas Hydrate and Free Gas Accumulations

Responsible Party: Rice University

Subtask 9.1: Preliminary processing and inversion of seismic data.

The recipient shall obtain seismic data from locations offshore eastern India from NGRI focusing on areas believed to contain potentially economic hydrate accumulations in a marine setting. After data acquisition, the recipient shall perform conventional seismic reflection processing, velocity analysis, travel time tomography, and other analyses as deemed appropriate and necessary. The recipient shall focus efforts on providing the best possible structural image and starting velocity models for waveform inversion of the seismic data to be performed in Subtask 9.2.

Subtask 9.2: Final 1-D elastic and 2-D acoustic waveform inversion.

The recipient shall apply 1-D elastic inversions on data obtained under Subtask 9.1 to derive compressional and shear velocities. The compressional velocities shall also serve as a benchmark against which to measure the improved lateral resolution of P-wave velocity from the 2D acoustic inversion.

Subtask 9.3: Rock physics modeling.

The recipient shall apply current and generally accepted rock physics models to the developed velocity models. The recipient shall estimate hydrate saturation and lithology through application of well log data in conjunction with data resultant from the application of rock physics models to the developed velocity models.

The recipient shall actively seek to collaborate with and expand upon research in this field being conducted under separately funded DOE-NETL projects (DE-FC26-05NT42663 with Stanford University, "Seismic-Scale Rock Physics of Methane Hydrate" and others as applicable) as such this effort should not require development of new rock physics models, but shall apply those rock physics models deemed, by the recipient, to be most appropriate based on consultations with DOE and other researchers.

Task 5: Carbon Inputs and Outputs to Gas Hydrate Systems

Approach

The amount and distribution of gas hydrate in marine sediment depends on several factors. Our project-related modeling efforts (Bhatnagar et al., 2007a, 2007b), as well as results from other studies, show that two particularly important factors are: (1) the flux of labile organic carbon over time, and (2) fluid flow, particularly because it impacts gas output via anaerobic oxidation of methane. We are trying to constrain these factors by generating key chemical data sets using sediment obtained from present-day gas hydrate systems.

Results and Discussion

We have generated a series of iodine profiles for sediment and pore waters through several gas hydrate systems (Blake Ridge, Peru Margin, Gulf of Mexico, Japan Sea). The profiles at Blake Ridge and Peru Margin have a fairly straightforward interpretation. Organic carbon lands on the seafloor with iodine. During burial, iodine is released from the organic carbon, contributing to iodide in pore water. This iodide moves upward toward the seafloor, by diffusion, advection or both. Here, it is converted to iodate and re-scavenged by organic carbon. The consequence is a system where the amount of iodine in pore waters is proportional to carbon input and fluid dynamics over time. We have begun writing these results. The iodine in the GOM and Japan Sea is not so easy to understand because, so far, it appears that there are external sources of iodine

We have generated a series of sediment data (metals and carbonate) across the sulfate-methane transition at a site with gas hydrate on the Peru Margin. This site was chosen because it already has very detailed pore water data. There is a 2-m thick horizon with high amounts of authigenic carbonate (calcite) and barite across the sulfate-methane transition. This horizon attests to a methane output that has been similar to present-day over a long time (>100,000 years) interval (i.e., steady-state). We are now collecting samples for carbon isotope measurements so that we can determine the relative fluxes of methane and bicarbonate into and out of this horizon. We have modeled the abundance of gas hydrate at this location. The results of our sediment chemistry work will enable us to evaluate whether key model parameters are reasonable.

Conclusions

Models concerning the abundance and distribution of gas hydrate in marine sediment require constraints on carbon inputs and outputs, fluid flow and temporal evolution. Our chemical analyses of sediment appear to be providing us reasonable constraints that we can use in our models.

Task 6: Numerical Models for Quantification of Hydrate and Free Gas Accumulations

Subtask 6.8: Sulfate profile as indicator of methane flux.

Numerical and analytical models have been developed for inferring gas hydrate saturation in marine sediments from pore water sulfate profiles. These models utilize the depth of the sulfate-methane transition (SMT) as the primary input variable and are valid for systems dominated by methane supply from deeper sources. Results from these models are in agreement with gas hydrate saturations estimated from resistivity logs/chloride data at several sites along Cascadia Margin.

The numerical model is explained in a short article in Geophysical Research Letters, titled "*Sulfate-methane transition as a proxy for average methane hydrate saturation in marine sediments*". This article is currently in press.

Analytical theory has also been developed to predict steady-state gas hydrate saturation in deep-source systems using the depth of the SMT as the primary input. This theory allows calculation of the gas hydrate saturation profile, as well as the sulfate and methane concentration profiles, using simple analytical expressions. Figure 1 below shows gas hydrate saturation profiles as a function of scaled depth below the seafloor for different values of the SMT depth \tilde{L}_s , which is the ratio of the SMT depth to the depth to the base of the gas hydrate stability zone (GHSZ). Shallow SMT depths indicate higher methane flux and, consequently, higher gas hydrate saturation. Results from our numerical models (crosses) compare favorably with our analytical results (curves).

Several interesting aspects of gas hydrate systems can also be explained using our analytical theory. For example, we show why the depth to the first occurrence of gas hydrate below the seafloor is often 10-12 times the depth of the SMT (Figure 2) using our analytical theory. This "10 x SMT" relationship has been often hypothesized in the literature based on field observations. Figure 2 shows this ratio as a function of scaled SMT depth and demonstrates that the ratio is close to 10-12 for relatively large SMT depths, but increases to higher values for relatively shallower SMT depths.

This analytical theory has been written into a longer manuscript during this quarter and will be submitted shortly for publication in *Geochemistry, Geophysics, Geosystems*. This work has also been accepted for oral presentation at the 6th International Conference on Gas Hydrates, Vancouver, British Columbia, 2008. The abstract for this presentation is titled "*Relating Gas Hydrate Saturation to Depth of Sulfate-Methane Transition*".



Figure 1: Steady-state gas hydrate saturation profiles for different scaled SMT depths \tilde{L}_s . Crosses denote numerical model results, while curves represent the analytical model.



Figure 2: Relationship between the ratio of depth to the first occurrence of gas hydrate $(L_t - L_h)$ to the SMT depth (L_s) as a function of the scaled SMT depth (L_s / L_t) for two different seafloor depths.

Subtask 6.5: Processes leading to overpressure

Work has continued in this subtask through one-dimensional numerical modeling to ascertain the factors and dimensionless groups responsible for overpressure generation in gas hydrate systems. Previously, we had determined through numerical simulations that the ratio of sediment absolute permeability to the sedimentation rate was the key dimensionless group controlling overpressure generation. This group, N_{sc} , was defined as:

$$\mathsf{N}_{\mathsf{sc}} = \frac{k_0 \rho_w g}{\mu_w \dot{S}}$$

where k_0 is the sediment permeability, ρ_w is seawater density, μ_w is viscosity and \dot{S} is sedimentation rate. Figure 3 shows that higher values of N_{sc} indicate high permeability and/or low sedimentation rate, leading to hydrostatic pore pressures. As N_{sc} decreases, pore pressure starts to increase towards lithostatic values.



Figure 3: Effect of the dimensionless group N_{sc} on pore pressure evolution. P_{lith} , P_w and P_{hydro} denote lithostatic, pore pressure and hydrostatic pressure profiles, respectively. Relatively higher values of N_{sc} lead to almost hydrostatic pore pressure, while N_{sc} close to unity results in pore pressure that is very close to the lithostatic limit.

The effect of overpressure, in turn, limits the amount (thickness) of free gas that can accumulate below the GHSZ. This situation is depicted schematically in Figure 4a, where hydrostatic pore pressures allow a relatively long connected gas column to form. On the other hand, Figure 4b shows that overpressure generation can significantly reduce the thickness of this connected gas column before gas pressure reaches the lithostatic limit at the BHSZ and causes sediments to fracture.



Figure 4: Schematic illustration of the effect of overpressure on the maximum thickness of the connected free gas column beneath the GHSZ. P_{lith} , P_w , P_{hydro} and P_g denote lithostatic, pore pressure, hydrostatic and gas pressure profiles, respectively. Development of overpressure can significantly reduce the thickness of the connected gas column before fracturing occurs.

We have now modeled this effect of N_{sc} on gas column thickness by allowing free gas to migrate buoyantly upwards when the critical gas saturation is exceeded. Two test cases are presented next. The first case (Figure 5), simulated for a relatively high value of N_{sc} , shows a thick connected gas column beneath the GHSZ due to low overpressure development. At the simulation time shown in Figure 5, gas pressure becomes equal to the lithostatic stress at the base of the GHSZ, causing sediments to fracture. Figure 6 shows a case simulated for N_{sc} =10, which shows that only a short gas column develops before sediment fracturing is initiated. Thus, low values of this ratio N_{sc} , which physically translates to settings with low sediment permeability and/or fast sedimentation rates, will only allow short gas columns to develop before sediment fracture occurs and vents the gas. This work has been accepted for a poster presentation at the 6th International Conference on Gas Hydrates, Vancouver, British Columbia, 2008. The abstract for this presentation is titled "*Effect of Overpressure on Gas Hydrate Distribution*".



Figure 5: Normalized pressure profiles (left) and gas hydrate and free gas saturation profiles (right) for N_{sc} =1000. Gas pressure at this time is just equal to the lithostatic stress. A relatively deep connected gas column exists beneath the GHSZ at this state.



Figure 6: Normalized pressure profiles (left) and gas hydrate and free gas saturation profiles (right) for N_{sc} =10. Gas pressure at this time is just equal to the lithostatic stress. Compared to Figure 5, a relatively short connected gas column exists beneath the GHSZ at this state.

Subtask 6.1: Model Development

Work has continued during this quarter towards extending the onedimensional numerical model to two spatial dimensions. Upward free gas migration due to buoyancy has also been included in the model. We have also developed the capability to model the effect of heterogeneities in focusing fluid flow and concentrating gas hydrate/free gas in two dimensions. We present two simple test cases to illustrate how gas hydrate/free gas is concentrated along high permeability conduits.

The first case models a system with a single vertical fracture located along the center of the grid that extends from the seafloor down to the bottom of the simulation domain. The fracture permeability is assumed to be 100 times greater than that of the surrounding sediment. Over geologic time, this fracture gets buried away from the seafloor with the downward moving sediment. Figure 7 shows the position of the fracture at a later time and the effect of focused fluid flow on gas hydrate and free gas saturation contours. It can be clearly seen from Figure 7 that gas hydrate as well as free gas is concentrated within and around the fracture compared to the surrounding sediment.



Figure 7: Gas hydrate (left) and free gas (right) saturation contours at dimensionless time $\tilde{t} = 0.1$ after the fracture is introduced in the system. Dashed lines show the position of the fracture within the system.

Figure 8 shows the evolution of gas hydrate and free gas saturation at a later time ($\tilde{t} = 0.5$). Peak gas hydrate saturation occurs within the fracture and close to the base of the GHSZ (~20%), which is almost twice the value in surrounding sediments at the same normalized depth. Free gas also accumulates in greater amount within the fracture, with peak saturation of about 50% beneath the GHSZ. Compared to Figure 7, the fracture has moved down to about half of the depth of the GHSZ. Consequently, the gas hydrate saturation in the upper half of the GHSZ becomes relatively homogeneous. At later times, the fracture gradually moves out of the GHSZ causing sediments to have a much more homogeneous hydrate distribution within the entire GHSZ.



Figure 8: Gas hydrate (left) and free gas (right) saturation contours at dimensionless time $\tilde{t} = 0.5$ after the fracture is introduced in the system. Dashed lines show the position of the fracture within the system.

We also study the effect of preferential gas hydrate accumulation in lithology of varying permeabilities. To model this scenario, we introduce a high permeability dipping sand layer within relatively low permeability clay sediments. The sand layer shown in simulations below has a dip of about 2.5 degrees and permeability 100 times greater than the clay permeability. Figure 9 shows the gas hydrate and free gas saturation contours at time $\tilde{t} = 0.25$ after deposition. Continuous sedimentation buries the sand layer towards the base of the GHSZ, but the effect of fluid focusing in concentrating gas hydrate within the sand layer is clearly seen. The color axis for the hydrate saturation contour plot (Figure 9) is scaled to a maximum of 15% to show the hydrate distribution more clearly; otherwise the contour plot gets dominated by the high saturation gridblocks. Peak hydrate saturation increases to about 30% within the sand layer near the base of the GHSZ, while hydrate saturation at the same depth in neighboring clay sediments is only about 8%. The y-axis in the contour plots in Figure 9 has a vertical exaggeration (VE) of about 2:1, so that the sand layer appears to have a dip greater than the true dip of 2.5 deg.

At a later time (\tilde{t} =0.75), the sand layer almost passes completely through the GHSZ (Figure 10). Consequently, hydrate saturation returns to a more homogeneous distribution within the GHSZ. Free gas saturation increase to about 60% within the sand layer just below the GHSZ and also migrates laterally to increase peak gas saturation in the lower permeability sediments to about 30 % (Figure 10).

The above simulations were relatively simple test cases performed to validate our two-dimensional model and code. Effect of different system parameters, such as thickness of beds, permeability contrasts, dip angles, and combination of different permeability beds with fracture networks are planned as future work.



Figure 9: Gas hydrate and free gas saturation contours at dimensionless time $\tilde{t} = 0.25$ after deposition of the sand layer within low permeability clay sediments. Peak hydrate saturation within the sand layer increases to about 30%, but the color axis is scaled to a maximum of 15% to show the other contours more clearly. Vertical exaggeration is about 2:1.



Figure 10: Gas hydrate and free gas saturation contours at dimensionless time $\tilde{t} = 0.75$. Sand layer almost passes through the GHSZ, causing hydrate saturation to become more homogeneous laterally within the GHSZ. Vertical exaggeration is about 2:1.

Task 7: Analysis of Production Strategy

J. Phirani & K. K. Mohanty, University of Houston

In subtask 7.1, we are participating in the NETL methane code comparison study. In the last few months, we have worked on the first four problems set up by the Code Comparison Study group. Our results for the first four problems have been communicated to Prof. Brian Anderson, the coordinator of the Code Comparison Study group in October, 2007.

We have started the pore-level modeling of hydrate distribution in single phase flow (no free gas phase) in order to estimate transport properties of hydrate bearing sediments. A basic element of porous media is a pore throat. We have assumed a simplified cylindrical geometry for a pore throat. We have also assumed that this cylindrical throat is at a temperature and pressure where hydrates can form if the methane content is high enough. Water saturated with methane at a higher temperature flows into this pore throat. As the water passes through this throat, temperature falls, hydrates can form at a low-enough temperature region. Characteristic times for diffusion, heat conduction, reaction and flow are compared.

Results from this study indicate that temperature is the coldest near the pore wall because heat is removed through the wall. Hydrate forms near on the wall and builds up. The rate at which hydrate layer builds up depend on the temperature gradient, flow rate etc. These observations will be used to build a model for hydrate deposition in a medium with distributed pore size distribution. As the cold water passes through a collection of pores, the hydrate saturation at the pore scale will vary from pore to pore. We will use these results to calculate permeability of porous media as a function of overall hydrate saturation. We will also develop models for multiphase flow during hydrate deposition.

We have also made 3D simulations of hydrate dissociation in a homogeneous porous medium with an underlying water saturated layer. A field unit of 120mx120mx10m is simulated with a single production well in one corner. The initial saturation in the top 8m is assumed to be 0.6 hydrate and 0.4 water. The bottom 2m is fully saturated with water. Pressure is reduced from the initial value of 9MPa to 2 MPa at the well. This simulation shows the typical saturation history in hydrate depressurization. Similar calculations will be made for hot water injection to produce hydrates. The saturation histories encountered in these simulations will be modeled at the pore scale for transport properties.

In the next quarter, we will work on the pore-scale model to estimate the transport properties.

Task 8: Seafloor and Borehole Stability

Approach

We have continued to expand our database on flow properties of finegrained sediments from oceanic hydrate settings. For Keathley Canyon we used constant rate of strain consolidation experiments to measure vertical permeability on individual sediment samples. We have integrated those measurements with the NMR (nuclear magnetic resonance) log data from the field to develop a complete permeability profile for Keathley Canyon. We have also developed a technique to measure horizontal permeability on sediment samples.

Results and Discussion

The correlation of the permeability measurements and the NMR log data (T_2 relaxation times) has allowed us to develop a permeability model for Keathley Canyon. We based our model on the Schlumberger-Doll Research (SDR) equation relating permeability and T_2 (Kenyon et al., 1989). In the traditional equation, a constant coefficient (A) is employed, implying a constant lithology. In Keathley Canyon, we had to deal with lithologic variability in the basin which ranges from clay to sand. We modified the SDR equation by redefining the A coefficient. This new model has a variable A based on the gamma ray log which defines lithologic variations. The parameter A is a quantitative measure of the porosity-permeability behavior of a sediment, and was found to decrease with increasing clay content; this suggests that the parameter A accounts for variations in pore structure and NMR properties such as surface relaxivity. Permeabilities calculated with a variable A provided a better fit to experimental data than those calculated using a fixed value of A. We are trying to advance our understanding of this behavior by making NMR measurements on the same samples used in our permeability studies. We have only completed one horizontal permeability measurement, but anticipate completing more to develop a quantitative assessment of anisotropy in the basin as a function of stress and consolidation state. Permeability architecture is important for understand flow and transport in basins which affects hydrate distribution and saturation. Our basin models are being expanded to two-dimensions (Task 6). These models require inputs on permeability heterogeneity and anisotropy.

Conclusions

This work has enhanced our knowledge on flow and transport properties in fine-grained sediments. We also feel it expands the use of NMR logs to get permeability in multiple lithologies. Historically the SDR equation has been employed in reservoir systems; we have adapted it for marine hydrate settings.

References

Kenyon, W.E., Howard, J.J., Sezinger, A., Straley, C., Matteson, A., Horkowitz, K., Ehrlich, R., 1989, Pore-size distribution and NMR in Microporous Cherty Sandstones, Transactions of the SPWLA 30th Annual Logging Symposium, Denver CO (USA), 11-14 June 1989, paper LL.

Task 9: Geophysical Imaging of Gas Hydrate and Free Gas Accumulations

Although Priyank Jaiswal has done considerable work that is directly related to this grant, Priyank and Colin Zelt have not been funded by this DOE grant until January 2008. His work to date involves testing and applying seismic imaging and inversion algorithms to real data from two non-hydrate sites in India using exactly the same methods we propose to apply to the hydate data; one paper has been published in Geophys. J. Int. in 2007 and one paper is about to be submitted to the journal called Geophysics.

Priyank is currently in India to meet with the DGH (Directorate General of Hydrocarbon) to secure the geophysical data (seismic and well data) that we proposed to work on for this project.

COST PLAN / STATUS									
	Phase 1	Phase 2: Year 1 (June 2007 - May 2008)							
Baseline Quarter Reporting		7/1/0	7 TO 9/30/07	10/*	1/07 TO 12/31/07	1/1/	08 TO 3/31/08	4/1/()8 TO 6/30/08
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 Cos	\$ 4,628	\$	113,284	\$	221,940	\$	330,596	\$	439,252
Actual Incurred Cost									
Federal Share	\$ 3,082	\$	56,282	\$	76,882				
Non-Federal Share	\$ 1,091	\$	18,616	\$	52,263				
Total Planned	\$ 4,173	\$	74,898	\$	129,145	\$	-	\$	-
Cumulative Costs	\$ 4,173	\$	79,071	\$	208,216	\$	208,216	\$	208,216
Variance (plan-actual)									
Federal Share	\$ 542	\$	23,721	\$	3,121				
Non-Federal Share	\$ (87)	\$	10,037	\$	(23,610)				
Total Variance	\$ 455	\$	33,758	\$	(20,489)	\$	-	\$	-
Cumulative Variance	\$ 455	\$	34,213	\$	13,724				

Milestone Plan/Status

Task	Milestone: Status and Results	Date	Status
5. Carbon inputs and outputs to gas hydrate systems	5.1a Measure iodine in sediments We have measured iodine concentrations in pore waters from several gas hydrate systems. We hope to complete the analyses this month and write up intitial results over the next month.	12/07	1/08
	 5.1b Constrain C_{org} inputs from iodine We will measure the content and isotopic composition of organic carbon and carbonate in sediment from cores of several gas hydrate systems. We have collected most of the samples, although plan to visit the ODP repository (College Station) in late spring or early summer to collect additional samples. Most analyses will be done this summer, although we anticipate examination of a small "trial batch" of samples from the Peru Margin in the next month. 	10/08	
	5.2a Construct metal profiles in sediments We will measure metal contents in sediment from cores of several gas hydrate systems to constrain past hydrocarbon outputs via anaerobic oxidation of methane (AOM). Because initiation of project funding was slowed, we began some of this work last year with scientists from Japan using samples of opportunity from the Sea of Japan. This work was published in the fall (Snyder et al., 2007).	12/09	
	5.2b Modeling/integrating profiles We will use the metal and iodine profiles to constrain models for gas hydrate formation. We have discussed data and models but	12/10	

	have not begun this work so far.		
6. Numerical	6.1 Model development.	9/07	1/08
models for quantification of hydrate and free gas accumulations	The recipient shall develop finite difference models for the accumulation of gas hydrate and free gas in natural sediment sequences on geologically relevant time scales.		
	6.2: Conditions for existence of gas hydrate	3/07	done
	The recipient shall summarize, quantitatively, the conditions for the absence, presence, and distribution of gas hydrates and free gas in 1-D systems by expressing the conditions in terms of dimensionless groups that combine thermodynamic, biological and lithologic transformation, and transport parameters.		
	6.3 Compositional effect on BSR	7/07	12/08
	The recipient shall add to the numerical model, developed under this task, a chloride balance and multi-hydrocarbon capability specifically to investigate how hydrocarbon fractionation might affect Bottom Simulating Reflectors (BSRs).		
	6.4: Amplitude Attenuation and chaotic zones due to hydrate distribution	3/09	
	The recipient shall simulate preferential formation of gas hydrate in coarse-grained, porous sediment in 2-D by linking fluid flux to the permeability distribution.		
	6.5: Processes leading to overpressure	3/08	
	The recipient shall quantify, by simulation and summarize by combination of responsible dimensionless groups, the conditions leading to overpressure to the point of sediment failure.		
	6.6 Concentrated hydrate and free gas	3/08	
	The recipient shall, using 2-D and 3-D models, simulate lateral migration and concentration of gas hydrate and free gas in structural and stratigraphic traps.		

	6.7 Focused free gas, heat and salinity The recipient shall quantify, using 2-D and 3-D model simulations and comparisons to available observations, the factors controlling the process of localized upward migration of free gas along faults and lateral transfer to dipping strata that can lead to chaotic zones and possible accumulations of concentrated hydrate.	9/09	
	6.8 Sulfate profile as indicator of methane flux The recipient shall compute, for systems where data on the sulfate profile is available, the oxidation of methane by sulfate and shall indicate the perceived level of effect on gas hydrate accumulation and the data's value as an indicator of methane flux.	7/07	done
	6.9 Application of models to interpretation of case studies.The models developed in Task 6 will be applied to case studies in the interpretation of each of the other tasks.	6/10	6/10
7. Analysis of production strategy	 7.1a Pore scale model development and Hydrate code comparison For this milestone, we will develop pore- scale models of hydrate accumulation by simulation. Our hydrate code will be used to solve a set of problems formulated by the Code Comparison Study group. Our results will be compared with those of other hydrate codes. Should be changed to: 6/08 Reason: The starting date was moved to 6/07 Status: Code comparison study is 80% complete. 	1/08	6/08 Code compa rison is done.
	7.1b Petrophysical and thermophysical properties of hydrate sediments from pore- scale model For this milestone, we will assume the	1/09	6/09

	pore-scale models of hydrate accumulation developed in the last milestone and estimate transport properties as a function of hydrate and gas saturations. Should be changed to: 6/09 Reason: The starting date was moved to 6/07		
	Status: Have not started		
	7.2a Modeling of several production strategies to recover gas from marine hydrates	1/10	6/10
	Several production strategies would be modelled using the transport property correlations developed in the previous milestone. Optimal strategies will be identified.		
	Should be changed to: 6/10 Reason: The starting date was moved to 6/07 Status: Have not started		
	7.2b Effect of marine reservoir heterogeneities on production of methane	12/10	6/10
	Reservoir heterogeneity anticipated in marine environments (known or determined through other tasks) would be incorporated. Appropriate hydrate distributions, either constrained from experimental data or mechanistic simulations (Task 5) would be used. Sensitivity of gas production to the heterogeneities would be calculated.		
	Should be changed to: 6/11 Reason: The starting date was moved to 6/07 Status: Have not started		
8. Seafloor and	8.1a Collection of data	10/07	05/08
borehole stability	Status: 05/08 (large shift according to anticipated start date and dispersement of funds to Rice) To achieve this milestone, we will perform a literature and database search of existing geomechanical properties of sediments with hydrate and sediments without hydrate from hydrate		

	settings. This will include laboratory experiments, field data, published results, and unpublished data.		
	8.1c Complete database Status: 1/09 (some shift due to delay of data collection)	10/08	01/09
	We will organize the data from task 8.1a into a format that can be easily searched and used by any researchers trying to understand mechanical behavior of hydrate-bearing sediment. We will also identify key gaps in the database for focusing future hydrate research endeavors.		
	8.2a Link database with models Status: 8/08	3/08	8/08
	From the database we will assess how hydrate saturation affects different geomechanical properties. These relationships can then be input into models of basin development or production.		
	8.2b Add sediment stability to models Status: 10/08	10/08	
	Standard stability calculations will be coupled with basin scale and production models. The strength characteristics that influence stability will be imported from the relations developed in 7.2a.		
	8.2c Conditions for (in)stability	9/09	
9 Geophysical imaging of hydrate and free gas	9.1 Preliminary processing and inversion of seismic data.	8/08	
	processing, velocity analysis, travel time tomography, and other analyses as deemed appropriate and necessary.		
	9.2: Final 1-D elastic and 2-D acoustic waveform inversion.	8/09	
	Apply 1-D elastic and 2D acoustic inversions on data obtained from subtask 9.1 to derive determine high-resolution elastic and acoustic properties.		

9.3: Rock physics modeling.	8/10	
Apply rock physics models to the developed seismic models to estimate hydrate saturation and lithology through application of well log data in conjunction with data from subtask 9.2. For this subtask we shall seek to collaborate with research being conducted under separately funded DOE-NETL projects (DE-FC26-05NT42663 with Stanford University, "Seismic-Scale Rock Physics of Methane Hydrate" and others as applicable).		

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

