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Quarterly Progress Report
(January – March 2008)

Methane Recovery from Hydrate-bearing Sediments

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INTRODUCTION - PROJECT SUMMARY – STATUS (Updated 12/2007)

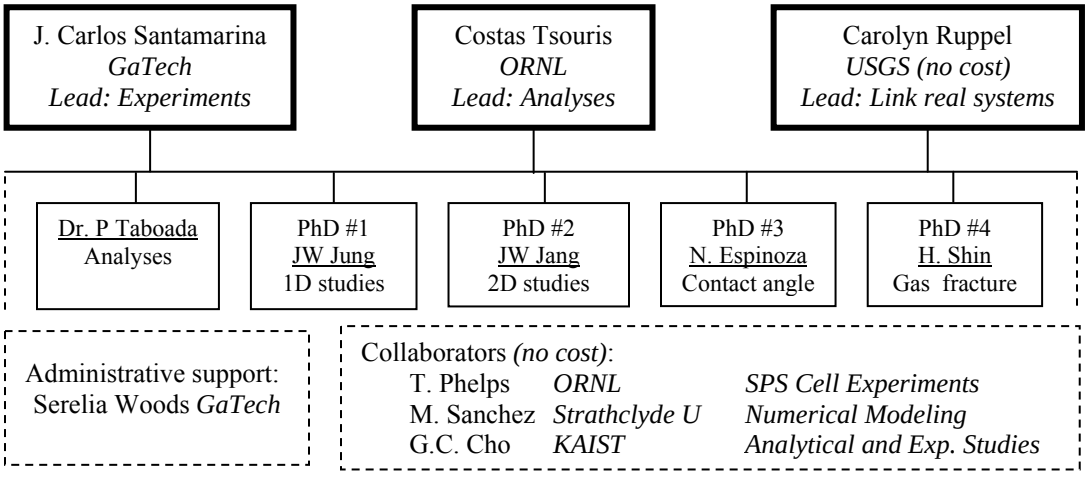
Goals: Identifying, understanding and modeling processes involved in methane production from hydrate-bearing sediments.

Approach: observation and interpretation of phenomena at multiple scales, ranging from pore-contact scale to the macro-reservoir scale, taking into consideration various possible driving forces (e.g., depressurization, thermal stimulation)

To this end, we intend to: (1) gain a thorough physical understanding of underlying phenomena associated with methane hydrate production through unique multi-scale experimentation and associated analyses; and (2) develop mathematical models that capture observed phenomena and that can be used to optimize methane hydrate production methods.

This four year project is organized into seven tasks with a "check point" before task 7. Updated tasks and team organization follow.

Task 1	Research Management Plan	Done	*(brief summary here)*
Task 2	Technology Status Assessment	Done	*(submitted report)*
Task 3	Continuous Literature	In Progress	*(submitted report)*
Task 4	1-D Single Mineral Surface Studies	In progress	*(brief summary here)*
Task 5	2-D Porous Network Studies	In progress	*(brief summary here)*
Task 6	3D Sediment: Experiments using uσ' Cell	Developments under parallel projects	
---------- check point ----------			
Task 7	3D Sediment: Experiments in SPS Cell	Developments under parallel projects	



DEVELOPMENTS DURING PRESENT QUARTER (ending April 2008)

Overview

The main developments in this quarter include:

Advances in experimental studies and corresponding analyses.

1. 1D tests in capillary tubes (new capillary cells)
2. 2D tests on hydrate formation and dissociation.
3. Contact angle studies (new cell)
4. Gas-invasion and localization (new device)

Advances on a three-front multi-scale strategy for modeling dissociation and gas production in reservoirs

5. Advances in intrinsic kinetic model
6. Advances in a robust chemo-thermo-mechanically coupled numerical model for hydrate production research.
7. Completion of the close-form analytical solution for the detailed thermo-mechanical analysis for PT evolution during production

Further development of the new laboratory facility (in Daniel Laboratory). Fully operational. Experiments are conducted 24 hrs/day and 7 days/week.

Related and complementary activities:

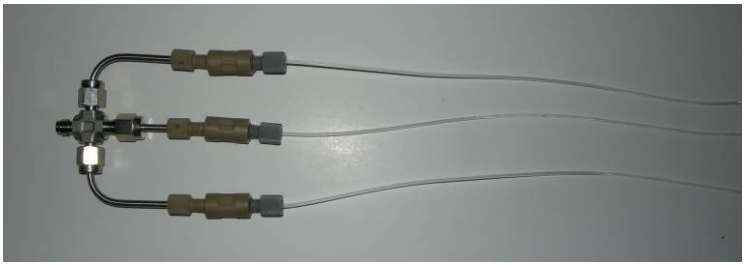
8. Testing of Korean pressure cores (in South Korea – KIGAM support)
9. Workshop on physical properties (organized with Bill Waite at USGS – DOE support)

Details on research progress are documented next. The presentation is separated into

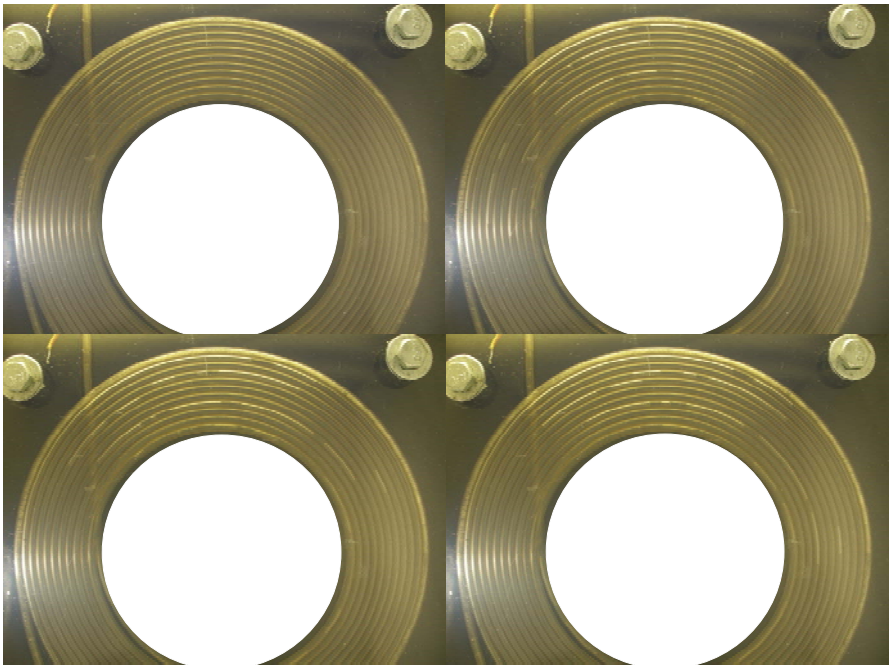
Experiments: 1D tests in capillary tubes

The long time required for hydrate formation stimulated the development of alternative experimental solutions to explore a wider range of conditions within the available time. Therefore, while we continue our test program with the original 1D chamber, we have been running tests in high capacity capillary tubes. We have built two sets.

The first set consists of a manifold with multiple tubes (no flow through). These "cells" are being used in long-term diffusion tests.



The second capillary cell is a 5m long tube with flow through. We can flush gas, water or other chemicals, form hydrates, and later change T or P conditions to monitor gas production. The following sequence of images shows (1) hydrate in the outer loop and (2-4) gas production and bubble migration as depressurization in imposed at the end of the inner loop.

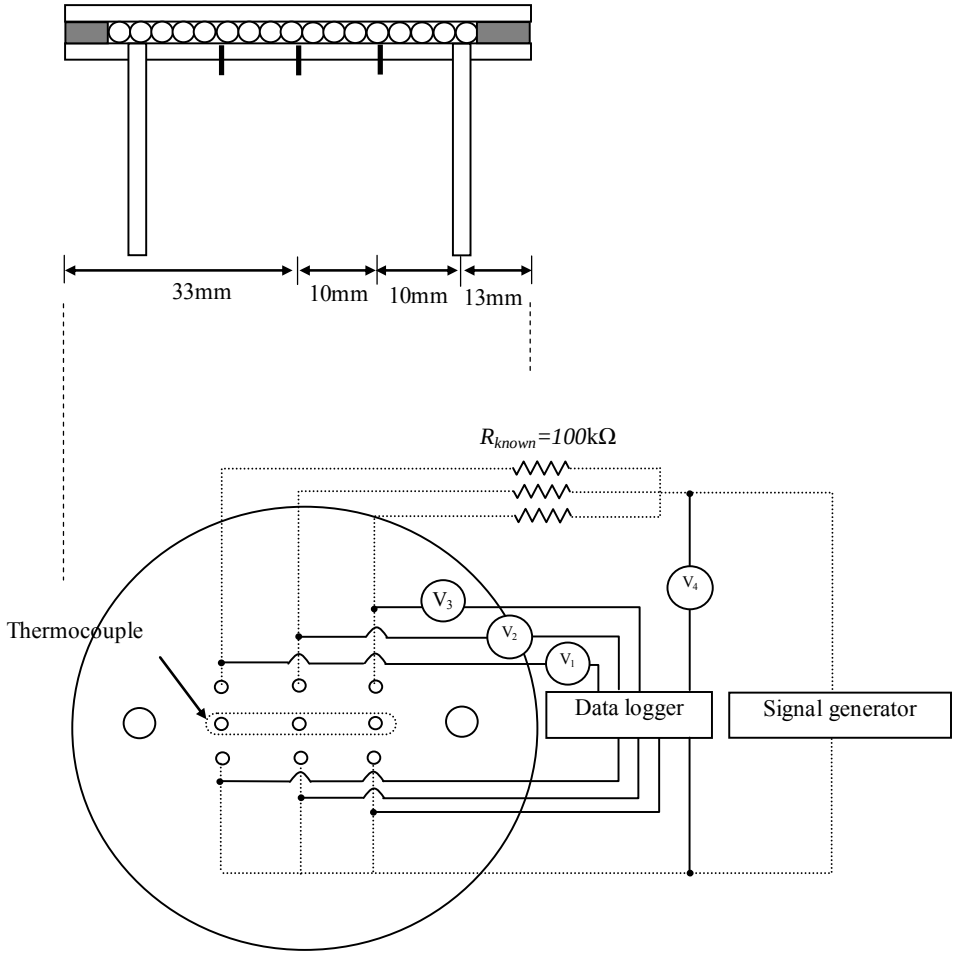


We are currently extending this study to

- automate image processing and data reduction
- tube filled with grains
- alternative production strategies
- development of governing equations and numerical simulation

Experiments: 2D tests on hydrate formation and dissociation.

These tests continue providing fascinating data, both during formation as well as during dissociation and gas production. The instrumented 2D plate is sketched next. Snapshots at different states of a test are summarized on the following page.



We are currently extending this study to

- gain in-depth understanding of observed results (solubility, diffusion, formation, dissociation, transients) leading to the identification of governing equations in support of numerical simulation.
- extend the study to include fine grained media and the formation of lenses in view of unique production strategies (also, complemented with governing equations and numerical simulation).

1. Hydrate triggered by gas injection

2.Hydrate triggered by forcing circulation(?)

3. Hydrate without triggering

4. Hydrate without triggering

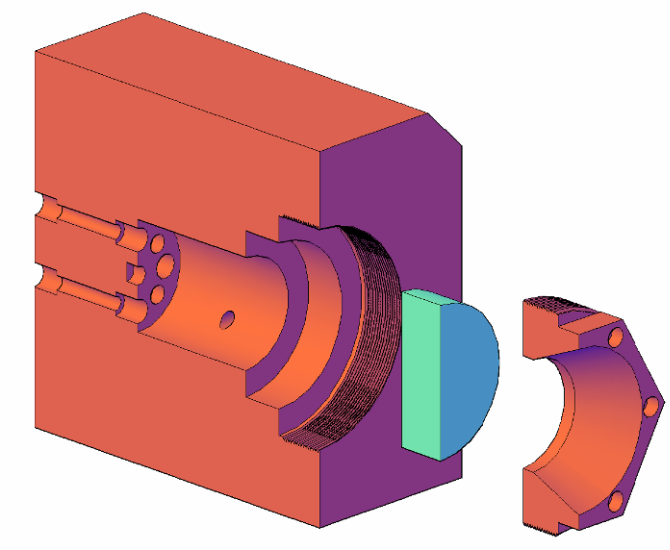
5. Hydrate without triggering

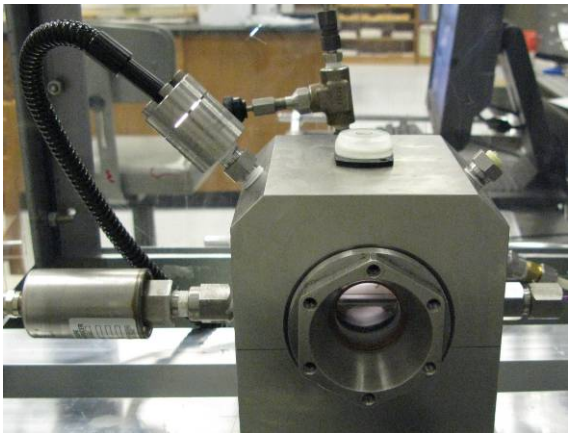
6. Hydrate triggered by depressurization

Experiments: Contact angle studies (new cell)

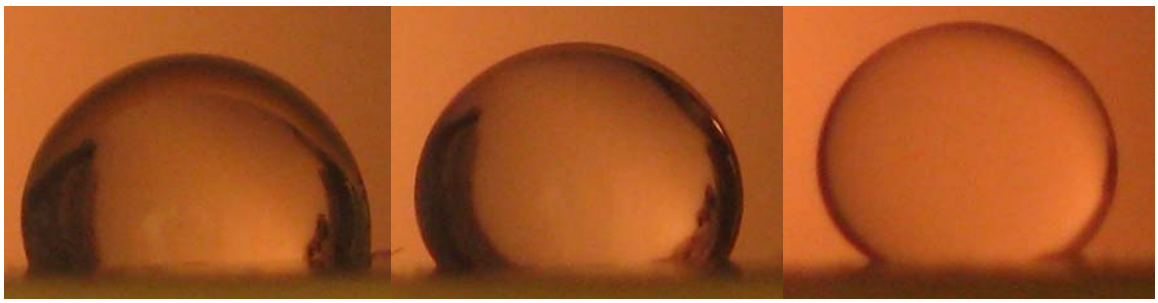
Changes in gas-fluid-mineral interaction observed in the 2D models (see previous report) have prompted additional studies on contact angle and surface tension as a function of pressure.

We designed and built a third high-pressure chamber to perform these studies:





Preliminary results shown in the following figure confirm changes in interfacial tension and contact angle as the gas pressure in the surrounding CO2 atmosphere is raised.

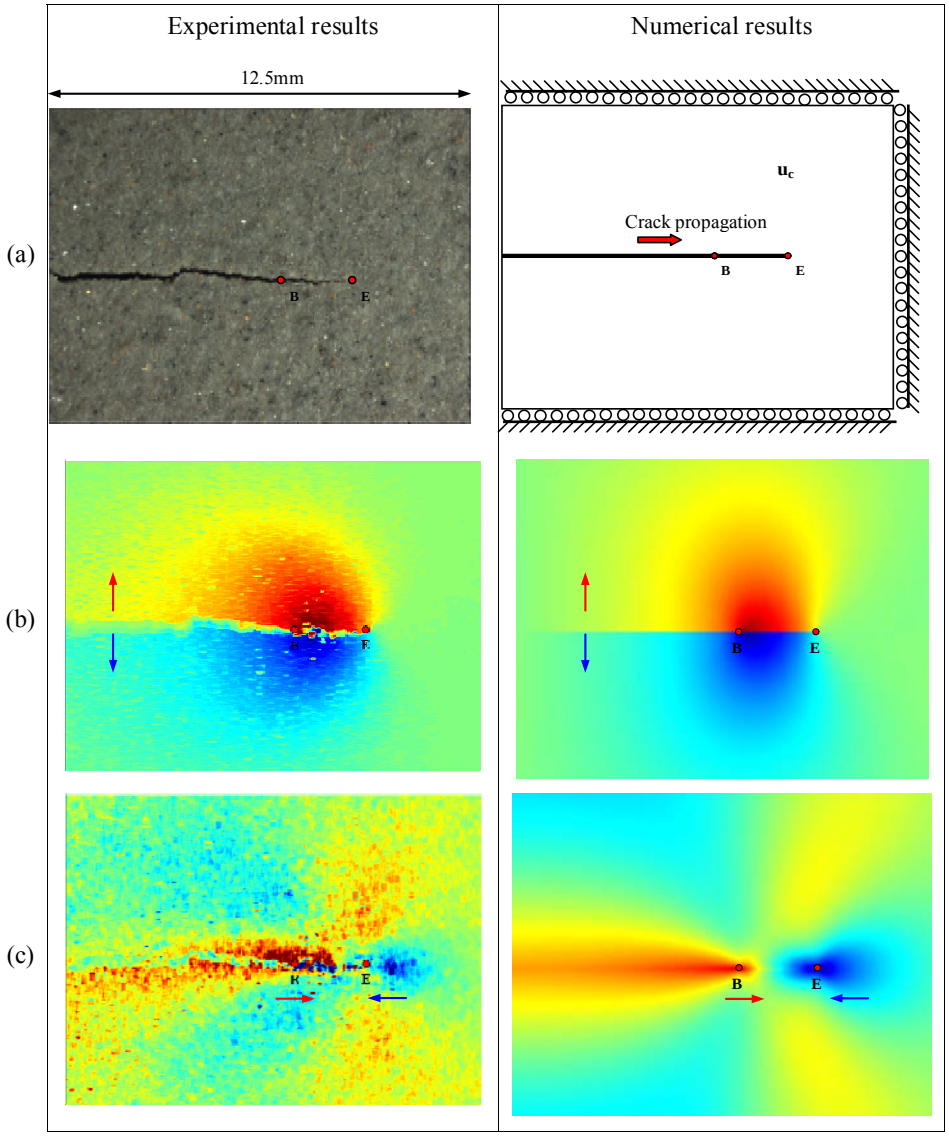


We are currently extending this study to

- methane gas
- various mineral substrates
- data reduction algorithms to infer surface tension and contact angle from digital images
- production simulation taking these results into consideration in network model studies.

Experiments: Gas-invasion and localization (new device)

Based on prior research on desiccation cracks in our group, we have extended our research on methane production to consider the development and propagation of high permeability discontinuities in sediments (Note: complementary to Bryant and Juanes). The sequence of figures shows preliminary numerical and experimental results of the displacement fields associated to a crack propagating from a beginning point B to the end point E: (a) Photograph and FEM model. (b) Displacement δ_y normal to the crack plane. (c) Displacement δ_x parallel to the crack propagation alignment.



Analytical: Advances in intrinsic kinetic model

After careful consideration of the set of variables that would need to be optimized in the model in order to compare the model predictions to experimental data, we concluded that the optimization routine may produce a set of results instead of a unique result for each experimental condition. Therefore, we would not be able to discriminate between actual physical effects and numerical effects. It was then decided to pursue simpler experiments and modeling that would directly contribute to the work on hydrate dissociation in sediments. Multiple gas-hydrate equilibrium, formation and dissociation experiments inside capillary tubes of varying diameters and compositions were planned. Figure 1 presents a simple schematic of one of the capillary systems under study through a set of experiments and which is also the focus of the current model development.

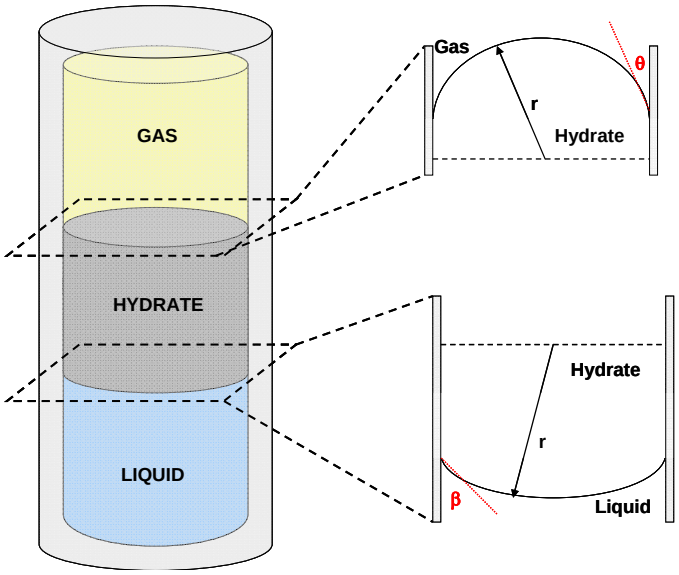


Figure 1 Schematic of the system under study via experiments at Georgia Tech and modeling at ORNL.

The energy-based representation of the fundamental equation of thermodynamics is applied to determine the equilibrium criteria for the equilibrium of gas/hydrate/liquid inside a single capillary tube. It is assumed that the interfaces between hydrate and gas, and hydrate and liquid (i.e., water) present different curvatures due to differences in surface energy. Properties of ice will be used for preliminary calculations.

The Peng-Robinson equation of state is used to describe the gas phase, and Henry's Law is used to describe the solubility of gas in the liquid (i.e., the solubility of methane in water is very small even at high pressures). The estimates for the fugacity of water in both liquid and hydrate phase are based on improvements to the original Parrish and Prausnitz (1972) expressions proposed by Klauda and Sandler (2003) and Zhang et al. (2006) for hydrates in the bulk. The updates just mentioned are based on ab-initio calculations of interaction potentials for hydrate structures. The improvements include the consideration of three crystalline shells during the calculation of the Kihara potential for the interaction of the guest molecule and the water cages, and the consideration of expansion/contraction of hydrate cages.

An algorithm to find the equilibrium pressure for a given temperature based on the fulfillment of the equilibrium criteria for the capillary tube is under development. One of the main challenges in this part of the work is finding a numerical algorithm that is stable, robust, and capable of converging into a unique solution (i.e., a global energy minimum). Therefore, efforts will be concentrated in developing numerical solution and computer codes for the solution of the equilibrium problem in upcoming months.

Numerical: Robust chemo-thermo-mechanically coupled simulation of production

(collaboration with Dr. M. Sanchez - Strathclyde University)

We have started the development of a comprehensive numerical simulator based on the robust Code_Bright platform. This platform will allow us to simultaneously solve all transport, mass balance and energy balance equations taking into consideration the inherent behavior of the sediment using the simple yet most robust Cam-clay model (adapted for hydrate bearing sediments). Experimental and analytical developments in the previous tasks will be incorporated in this simulator.

We have completed: the formulation, the development of constitutive equations specifically calibrated to hydrates and hydrate bearing sediments, and we already have a 1D working version of the algorithm. For completeness, the balance equations included in the algorithm are listed next.

Mass Balance: Water

$$\frac{\partial}{\partial t}[\underbrace{(\rho_\ell S_\ell + \alpha\rho_h S_h + \rho_i S_i)\phi}_{\text{mass water per unit volume}}] + \nabla.[\underbrace{\rho_\ell \mathbf{q}_\ell + \rho_\ell S_\ell \phi \mathbf{v}}_{\text{w in liquid}} + \underbrace{\alpha\rho_h S_h \phi \mathbf{v}}_{\text{w in hydrate}} + \underbrace{\rho_i S_i \phi \mathbf{v}}_{\text{w in ice}}] = f^w$$

Mass Balance: Methane

$$\frac{\partial}{\partial t}\underbrace{\left\{\left[\rho_g S_g + (1-\alpha)\rho_h S_h\right]\phi\right\}}_{\text{mass of methane per unit volume}} + \nabla.[\underbrace{\rho_g \mathbf{q}_g + \rho_g S_g \phi \mathbf{v}}_{\text{m in gas}} + \underbrace{(1-\alpha)\rho_h S_h \phi \mathbf{v}}_{\text{m in hydrate}}] = f^m$$

Mass Balance: Salt

$$\frac{\partial}{\partial t}\underbrace{(c_\ell^d S_\ell \phi)}_{\substack{\text{mass of salt}\\ \text{unit volume}}} + \nabla.(\underbrace{c_\ell^d \mathbf{q}_\ell + c_\ell^d S_\ell \phi \mathbf{v}}_{\text{d in liquid}}) = 0$$

Mass Balance: Mineral

$$\frac{\partial}{\partial t}\underbrace{[\rho_s(1-\phi)]}_{\substack{\text{mass mineral}\\ \text{per unit volume}}} + \nabla\cdot\underbrace{[\rho_s(1-\phi)\mathbf{v}]}_{\text{m in solid}} = 0$$

Energy Balance

$$f^E = \frac{\partial}{\partial t}\overbrace{\left\{\left[e_s\rho_s(1-\phi)\right] + \left(e_\ell\rho_\ell S_\ell + e_g\rho_g S_g + e_h\rho_h S_h + e_i\rho_i S_i\right)\phi\right\}}^{\text{energy per unit volume of the hydrate bearing sediment}} +$$
$$+\nabla.\mathbf{i}_c +$$
$$+\nabla.[\underbrace{e_\ell\rho_\ell(\mathbf{q}_\ell + S_\ell\phi\mathbf{v})}_{\text{transport in }\ell} + \underbrace{e_g\rho_g(\mathbf{q}_g + S_g\phi\mathbf{v})}_{\text{transport in g}} + \underbrace{e_h\rho_h S_h\phi\mathbf{v}}_{\text{transport in h}} + \underbrace{e_i\rho_i S_i\phi\mathbf{v}}_{\text{transport in i}} + \underbrace{e_s\rho_s(1-\phi)\mathbf{v}}_{\text{transport in s}}]$$

Momentum Balance (equilibrium)

$$\nabla.\boldsymbol{\sigma}_t + \mathbf{b} = 0$$

Analytical: Thermo-mechanical analysis for PT evolution during production
(collaboration with Dr. Cho at KAIST)

A comprehensive formulation was derived for the prediction of fluid pressure evolution in hydrate-bearing sediments subjected to thermal stimulation without mass transfer. The formulation considers pressure and temperature-dependent volume changes in all phases, effective stress-controlled sediment compressibility, capillarity, and the relative solubilities of fluids. The model properly reproduces experimental data, including the PT evolution along the phase boundary during dissociation, and the effect of capillarity.

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Gas hydrate dissociation in sediments: Pressure-temperature evolution

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[1] Hydrate-bearing sediments may destabilize spontaneously as part of geological processes, unavoidably during petroleum drilling/production operations or intentionally as part of gas extraction from the hydrate itself. In all cases, high pore fluid pressure generation is anticipated during hydrate dissociation. A comprehensive formulation is derived for the prediction of fluid pressure evolution in hydrate-bearing sediments subjected to thermal stimulation without mass transfer. The formulation considers pressure- and temperature-dependent volume changes in all phases, effective stress-controlled sediment compressibility, capillarity, and the relative solubilities of fluids. Salient implications are explored through parametric studies. The model properly reproduces experimental data, including the PT evolution along the phase boundary during dissociation and the effect of capillarity. Pore fluid pressure generation is proportional to the initial hydrate fraction and the sediment bulk stiffness; is inversely proportional to the initial gas fraction and gas solubility; and is limited by changes in effective stress that cause the failure of the sediment. When the sediment stiffness is high, the generated pore pressure reflects thermal and pressure changes in water, hydrate, and mineral densities. Comparative analyses for CO_2 and CH_4 highlight the role of gas solubility in excess pore fluid pressure generation. Dissociation in small pores experiences melting point depression due to changes in water activity, and lower pore fluid pressure generation due to the higher gas pressure in small gas bubbles. Capillarity effects may be disregarded in silts and sands, when hydrates are present in nodules and lenses and when the sediment experiences hydraulic fracture.

Related Activities

Workshop on physical properties - Organized together with Bill Waite (USGS – DOE support). Participants included: Bill Waite (USGS), Jack Germaine (MIT), Tae Sup Yun (Lehigh U.), Brandon Dugan (Rice U), Tim Kneafsey (LBNL), Bill Winters (USGS), Kenichi Soga (Cambridge U.), Carlos Santamarina (Georgia Tech). In addition, 5 PhD students Georgia tech were an integral part of the exercise: J. Jong, J. Jun, N. Espinoza, H. Shin, and D. Cortes. Well prepared with assignments before arrival, we worked with great dedication for 3 days to draft a comprehensive summary of the most relevant physical properties of hydrate bearing sediments. The document will be opened to the public and circulated in the summer 2008.

Testing of Korean pressure cores. While this project was supported by KIGAM, it had great relevance to this research because it made us deeply aware of real sediment and field conditions. As part of this study, we run 3 fully monitored production studies.

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