Methane Recovery from Hydrate-bearing Sediments

Prime Recipients
J. Carlos Santamarina
Costas Tsouris
Carolyn Ruppel
Georgia Tech
ORNL/Georgia Tech
USGS (no cost)

Agreement Number
DE-PS26-06NT42820

NETL Project Manager
Timothy Grant
Objective - Expected Benefits
Hydrates

- **Energy resource**

- **Climate change**: greenhouse effect

- **Seafloor instability**

[Kvenvolden and Lorenson, 2001; www.pet.hw.ac.uk; Ballough et al.]

[USGS]
Challenge

*Methane production from hydrate-bearing sediments*

**Understanding**
- Sediment properties
- Hydrate formation history
- Phases/fluids fronts
- Effects of driving forces

**Prediction**
- Thermodynamics in confinement
- Non-equilibrium analysis
- Kinetics in confinement
- Multiphase transport
### Keys: Energy Forms + Scales + Sediment

<table>
<thead>
<tr>
<th>Mechanical - Pressure</th>
<th>Mineral surface 1D - interface</th>
<th>Porous network 2D - sub mm</th>
<th>Sediment 3D - m</th>
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<tbody>
<tr>
<td><strong>Kinetics</strong></td>
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<td>Confinement</td>
<td>Formation</td>
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<td><strong>Formation</strong></td>
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<td>Bubble formation</td>
<td>Dissociation</td>
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<td><strong>Dissociation</strong></td>
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<td>Conduction prop.</td>
<td>Granular media</td>
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<td><strong>Surface effects</strong></td>
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<td>Mass transport</td>
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<tr>
<td><strong>Miner+hydr+fluid</strong></td>
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<td>THM coupling</td>
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<tr>
<td><strong>Coupled Energy</strong></td>
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</table>

- **Mechanical - Pressure**
- **Thermal**
- **Chemical**
- **Electromagnetic**
- **Coupled Energy**

- **Mineral surface 1D - interface**
- **Porous network 2D - sub mm**
- **Sediment 3D - m**
Project Organizational Structure
Team

J. Carlos Santamarina  
*GaTech*  
*Lead: Experiments*

Costas Tsouris  
*ORNL*  
*Lead:*

Carolyn Ruppel  
*USGS (no cost)*  
*Lead: Link real systems*

---

TS Yun (Yr 1)  
PD - Experiment

P Taboada (Yr 1)  
PD - Analyses

PhD #1  
JW Jung

PhD #2  
Analyses

PhD #3  
Exper/Num

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Administrative support:  
Serelia Woods *GaTech*

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Collaborators *(no cost)*:  
Megan Madden *ORNL*  
Tommy Phelps *ORNL*  
SPS Cell Experiments
Technical Approach
Main Tasks

Task 1. Research Management Plan

Task 2. Technology Status Assessment Report

Task 3. Continuous Literature Research/Updating

Task 4. 1D Single Mineral Surface: Experimental and Analytical Studies

Task 5. 2D Porous Network Experimental Studies and Model Development

Task 6. 3D Sediment: Experimental Study Using Effective Stress Cells

--------------------- check point ------------------------------

Task 7. 3D Sediment: Experiments in Seafloor Process Simulator - Analyses
Task 4: 1D Mineral Surface

- effect of mineral surface on formation and dissociation?
- effects of different potentials?
- most relevant phenomena during dissociation?
- can robust & simple models capture observed response?

4.1: Single mineral 1-D experiments

4.2: Intrinsic kinetic model development
Task 4: 1D Mineral Surface
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Intrinsic kinetics of hydrate dissociation

Hydrate dissociation \( \Rightarrow \) system is driven outside of hydrate equilibrium & stability zone

\[ r_{\text{dis}} \propto \left[ \mu(P,T,x,\ldots) - \mu_{\text{equil}} \right] \]

driving force

Equilibrium criteria:
\[ T^I = T^{II} = T^{III} = \ldots \]
\[ P^I = P^{II} = P^{III} = \ldots \]
\[ \mu_{I_i} = \mu_{II_i} = \mu_{III_i} = \ldots \]

experimental study of dissociation kinetics
Task 5: 2D Porous Network

- phenomena that deviate from convex process (self-preservation, percolation, fingering, gas migration)?
- evolution of dissociation, spatial variability, connectivity
- implications to gas recovery? for modeling?
- production strategies: low vs. high hydrate conc.?
- effect of different potentials
- robust models to capture observed response

5.1: 2-D porous matrix experiments

5.2: 2-D porous matrix model development
Hydrate dissociation and CH4 transport

Hydrate dissociation:
- “shrinkage” of hydrate phase
- changes in phase distribution
- local thermal variations

Analysis of multiphase flow with thermal gradients ⇒
coupled momentum, mass, and energy balances
Task 6: 3D Sediment – $\sigma'$ Cell

- poro-mechanical 3D effects
- suitable production strategies
- effect of specimen preparation on gas recovery
- promising production strategies to facilitate recovery control?
- criteria for the experiments in Task 7.0
Instrumentation

\( u, \sigma', \varepsilon_{\text{vol}}, \varepsilon_{\text{dev}}, V_{\text{gas}}, V_{\text{liq}} \)

\( \kappa', \sigma_{\text{el}}, \text{ERT} \)

\( V_P, V_S \)

\( k_T, k_{\text{hyd}} \)
Phase Transformation – $V_p$ and $V_s$

(Kaolinite + THF + H₂O)
Phase Transformation - Real Permittivity

(Kaolinite + THF + H\textsubscript{2}O)

Temperature [°C]

Real permittivity $k'$

Time [min]

hydrate

ice

F. Francisca
Experimental Results

Sand

Crushed silt

Precipitated silt

Kaolinite

a: $\sigma_c' = 0.03$ MPa
b: $\sigma_c' = 0.5$ MPa
c: $\sigma_c' = 1$ MPa
3-D transport and CH₄ production

3-D Extension of coupled momentum, mass, & energy balances

CH₄ production rate:

\[ Q = \iiint_S \left( \dot{N}_{CH_4} \cdot \vec{n} \right) dS \]
Task 7: 3D Sediment – SPS and Model

• specimen preparation and gas recovery
• evolution of de-stabilization fronts – all potentials
• role of reservoir geometry? optimal production strategies?
• emergent phenomena? HF, percolation/coning, compaction/collapse?
• simple yet predictive models (include THF coupling)

7.1: Hydrate formation
7.2: 3D Sediment Experiments
7.3: Analysis and model
Model Verification → Instrumentation

PT – pressure transducer
TC – thermocouple
FM – flowmeter (mass or vol.)

CH₄ and CO₂ monitor (GC or FTIR)

Back-pressure regulator

Water source and high-pressure pump

Sapphire windows

Fluid distributor

Sediment

High-pressure gas source
Analyses at different length scales

Types of Gas Hydrate Deposits

Although all factors controlling the type, distribution, and amount of natural hydrate accumulations are poorly understood, geologic environment is known to play a significant role. In particular, gas hydrate formation is influenced by the porosity, permeability and degree of lithification of the enclosing medium.

Methane Recovery

Dissociation and Transport (2-D & 3-D)

Intrinsic Kinetics
Why Use Chemical Potential?

**Strategy I** ⇒ Thermal stimulation

\[ d\mu = \left( \frac{\partial \mu}{\partial T} \right)_{P,N_i,Z_i} dT - S \]

**Strategy II** ⇒ Depressurization

\[ d\mu = \left( \frac{\partial \mu}{\partial P} \right)_{T,N_i,Z_i} dP \]

**Strategy III** ⇒ Thermal + Depres.

\[ d\mu = \left( \frac{\partial \mu}{\partial T} \right)_{P,N_i,Z_i} dT + \left( \frac{\partial \mu}{\partial P} \right)_{T,N_i,Z_i} dP \]

**Fundamental Equation of Thermodynamics**

\[ du = T ds - P dv + \sum_j [\delta W_{rev}]_j + \sum_i \mu_i dN_i \]

**Surface:** \( \sigma \leftrightarrow a \)

**Electric:** \( E \leftrightarrow D \)

**Magnetic:** \( H \leftrightarrow B \)
Hydrate Equilibrium Thermodynamics

**Multiphase equilibrium**

\[
\begin{align*}
\mu^H_w &= \mu^I_w = \mu^H_w = \ldots \\
\mu^1_w &= \mu^I_1 = \mu^H_1 = \ldots \\
\mu^2_w &= \mu^I_2 = \mu^H_2 = \ldots \\
\end{align*}
\]

**Water in hydrate phase**

“If a standard state hydrate chemical potential is known at conditions \((P,T)\), the only accountable change in energy is due to the occupation of hydrate cavities by guest gases.”

\[
\frac{\mu^H_w}{RT} = \frac{\mu^\beta_w}{RT} + \sum_m \nu_m \ln \left[ 1 - \sum_j \theta_{jm} \right]
\]


**Cage occupancy**

\[
\theta_{jm} = \frac{C_{jm}}{1 + \sum_k C_{km} f_{km}}
\]

**Cell potential function:** Kihara potential

\[
C_{jm} = \frac{4\pi}{kT} \int_0^{R_{m-a_j}} \exp \left[ -\frac{\omega_{jm}(r)}{kT} \right] r^2 dr
\]

(Ballard & Sloan, *Fluid Phase Equil.* 2002)

**Empty hydrate cage**

\[
\frac{\mu^\beta_w}{RT} = \frac{\mu^O_w}{RT_O} - \int_{T_0}^T \frac{\Delta h_w}{RT^2} dT + \int_0^P \frac{\Delta v_w}{RT} dP - \ln a_w
\]

Solving the model

Hydrate equilibrium

Flash calculation
Nonlinear optimization

Intrinsic Kinetics

Ordinary diff. equation
Runge-Kutta solution

Experiments

Validation

Dissociation & CH₄ transport

Partial diff. equations
Finite differences

Experiments

Validation

Decision point
Schedule

Milestones

Deliverables
<table>
<thead>
<tr>
<th>Task</th>
<th>Description</th>
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<tbody>
<tr>
<td><strong>Task 1.0:</strong> Research Management Plan</td>
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<td><strong>Task 2.0:</strong> Initial Technology Status Assessment</td>
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<td><strong>Task 3.0:</strong> Continuous Literature Research/Updating</td>
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<tr>
<td><strong>Task 4.0:</strong> 1D Single Mineral Surface</td>
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<tr>
<td><strong>Subtask 4.1:</strong> Experimental studies</td>
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<tr>
<td>1. Design and manufacture the instrumented pressure vessel</td>
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<tr>
<td>2. Prototype and first set of data</td>
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<tr>
<td>3. Complete the experiments and data analysis</td>
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<tr>
<td><strong>Subtask 4.2:</strong> Analytical studies</td>
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<tr>
<td>1. Intrinsic kinetic model</td>
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<tr>
<td>Development of theoretical framework for kinetic model</td>
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<tr>
<td>Formulation of general mathematical expressions</td>
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<tr>
<td>Derivation of particular expressions for formation/dissociation</td>
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<tr>
<td>2. Validation of modeling results with experimental data</td>
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<tr>
<td><strong>Task 5.0:</strong> 2D Porous Network - Single Grain Layer</td>
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<td><strong>Subtask 5.1:</strong> Experimental studies</td>
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<tr>
<td>4. Supplement tests tasks 4 and 5</td>
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<tr>
<td><strong>Subtask 5.2:</strong> Analytical study</td>
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<tr>
<td>1. Thermodynamic model, mass transport and energy coupled mode</td>
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<tr>
<td>Mathematical modeling of confinement effects</td>
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<tr>
<td>Development of coupled equations of mass and energy transport</td>
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<tr>
<td>Development of numerical solution strategies for the 2-D model</td>
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<tr>
<td>2. Validation of 2-D model</td>
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<tr>
<td><strong>Task 6.0:</strong> 3D - Effective Stress Cell</td>
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<td>3. Complete the experiments and data analysis</td>
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<td><strong>Task 7.0:</strong> 3D - SPS Cell and Analyses</td>
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<tr>
<td><strong>Subtask 7.1:</strong> Hydrate formation in SPS</td>
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<tr>
<td><strong>Subtask 7.2:</strong> Experimental studies in SPS</td>
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<tr>
<td>1. ORNL’s SPS Production Studies</td>
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<tr>
<td>First data set with selected formation</td>
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<tr>
<td>Complete experiments study and data analysis</td>
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<tr>
<td><strong>Subtask 7.3:</strong> Analytical study</td>
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<tr>
<td>1. 3-D mathematical model</td>
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<tr>
<td>Extension of the 2-D model and numerical solution to 3-D</td>
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<tr>
<td>2. Validation of 3-D model via comparison</td>
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<tr>
<td>4. Integration of analyses of hydrate formation</td>
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<td>4. Simulation of different scenarios</td>
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## Milestones

<table>
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<tr>
<th>Year</th>
<th>Month</th>
<th>Event Description</th>
</tr>
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<tbody>
<tr>
<td>2006</td>
<td>December</td>
<td>Experimental: 1D cell machined</td>
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<tr>
<td>2007</td>
<td>March</td>
<td>Experimental: First formation/production test in 1D cell (+instr.)</td>
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<tr>
<td></td>
<td>December</td>
<td>Experimental: First formation/production test in 2D cell (+instr.)</td>
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<td>Analytical: Model for 1D production – coupled energy</td>
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<td>2008</td>
<td>September</td>
<td>Experimental: First formation/production test in $\sigma'$ cell (+instr.)</td>
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<tr>
<td>2009</td>
<td>March</td>
<td>Experimental: Results coupled energy production in 2D cell</td>
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<td>2009</td>
<td>June</td>
<td>Analytical: Model for production in 2D networks</td>
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<td>2009</td>
<td>December</td>
<td>Experimental: First production study in ORNL's SPS</td>
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<td>2010</td>
<td>June</td>
<td>Experimental: Insightful production-related results from SPS cell</td>
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<tr>
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<td></td>
<td>Analytical: Predict &amp; optimize 3D production results</td>
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<td>2010</td>
<td>September</td>
<td>PROJECT COMPLETION</td>
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<tr>
<th>Deliverable</th>
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<tr>
<td>Research Management Plan</td>
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<td>Pressurized vessel design</td>
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<td>Quarterly Report</td>
<td>02/28/2007</td>
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<td>Annual Report</td>
<td>08/31/2007</td>
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<td>Quarterly Report</td>
<td>02/28/2008</td>
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<td>Annual Report</td>
<td>08/31/2008</td>
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<td>Quarterly Report</td>
<td>02/28/2009</td>
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<td>Annual Report</td>
<td>08/31/2009</td>
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<td>Recommendation</td>
<td>08/31/2009</td>
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<td>Review of Recommendation</td>
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<td>Quarterly Report</td>
<td>02/28/2010</td>
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<tr>
<td>Final Report</td>
<td>09/30/2010</td>
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Problems and Risks

Hydrate formation in sediments - history

Instrumentation

System identification / Inversion

Model verification

Laboratory → field? (field test with MBARI?)

…

Unknowns!
Possible opportunities

Production test – India cores

Field tests (e.g., with MBARI)?
Budget Period Slide
# Budget: Government and Cost Share

<table>
<thead>
<tr>
<th>Task</th>
<th>Task Description</th>
<th>DOE</th>
<th>Cost Share</th>
<th>Task Total</th>
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<td>1D Single Mineral Surface: Experimental and Analytical Studies</td>
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<td>2D Porous Network – Single Grain Layer: Experimental and Analytical Studies</td>
<td>277,675</td>
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<td>6.0</td>
<td>3D Sediment: Experiments in Effective Stress Cell</td>
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<td>3D Sediment: Experiments in SPS Cell – Analyses</td>
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<td>8.0</td>
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<th>BP 2 - 12 months</th>
<th>BP 3 - 12 months</th>
<th>BP 4 - 15 months</th>
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<td>247661</td>
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<td>332271</td>
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Final Products
Main Products:
• Technology to recover natural gas from hydrates
• Predictive models – Analysis/design/optimization
• Unprecedented database of production-related parameters

Groundwork:
• ...towards field demonstration with Industry

Byproducts:
• Enhanced understanding of hydrate bearing sediments
• Algorithm and software for process simulation
• Possible implications to seafloor stability, climate