Methane Recovery from Hydrate-bearing Sediments

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

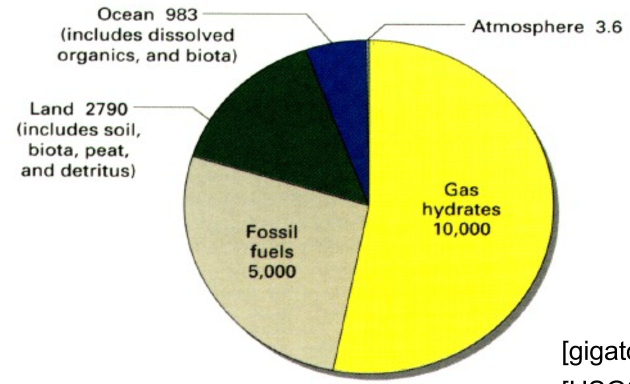
Agreement Number DE-PS26-06NT42820

NETL Project Manager Timothy Grant

Objective - Expected Benefits

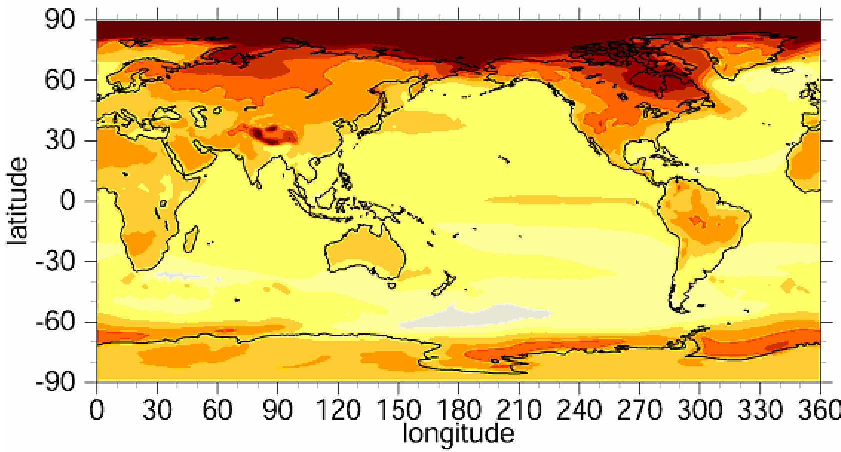
Hydrates

- ***Energy resource***

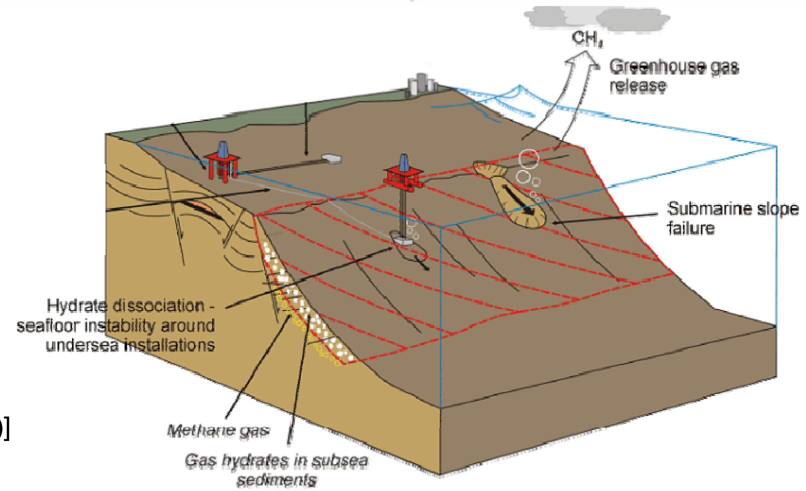


[gigaton]
[USGS]

- ***Climate change***: green house effect

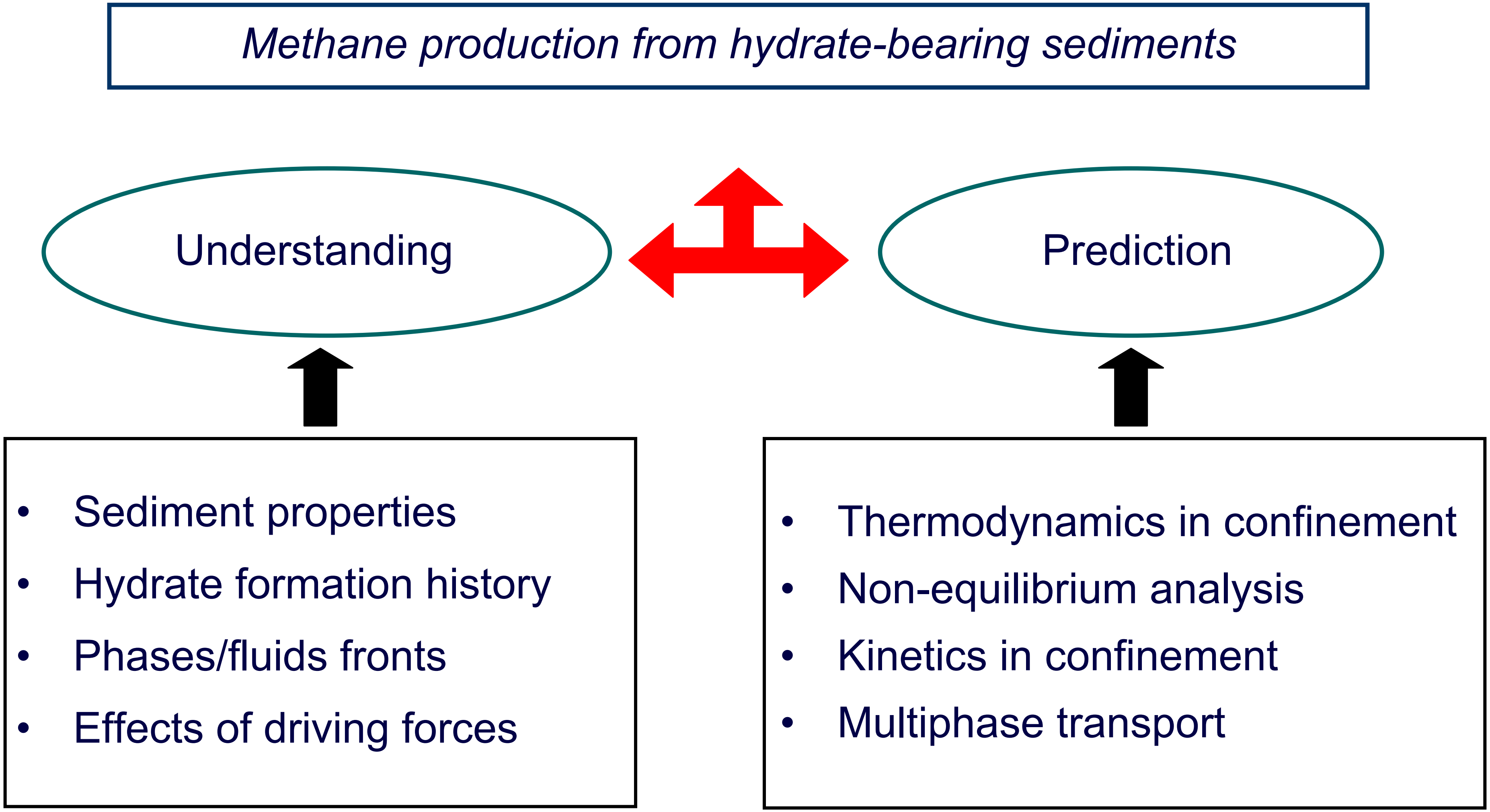


- ***Seafloor instability***



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

Challenge

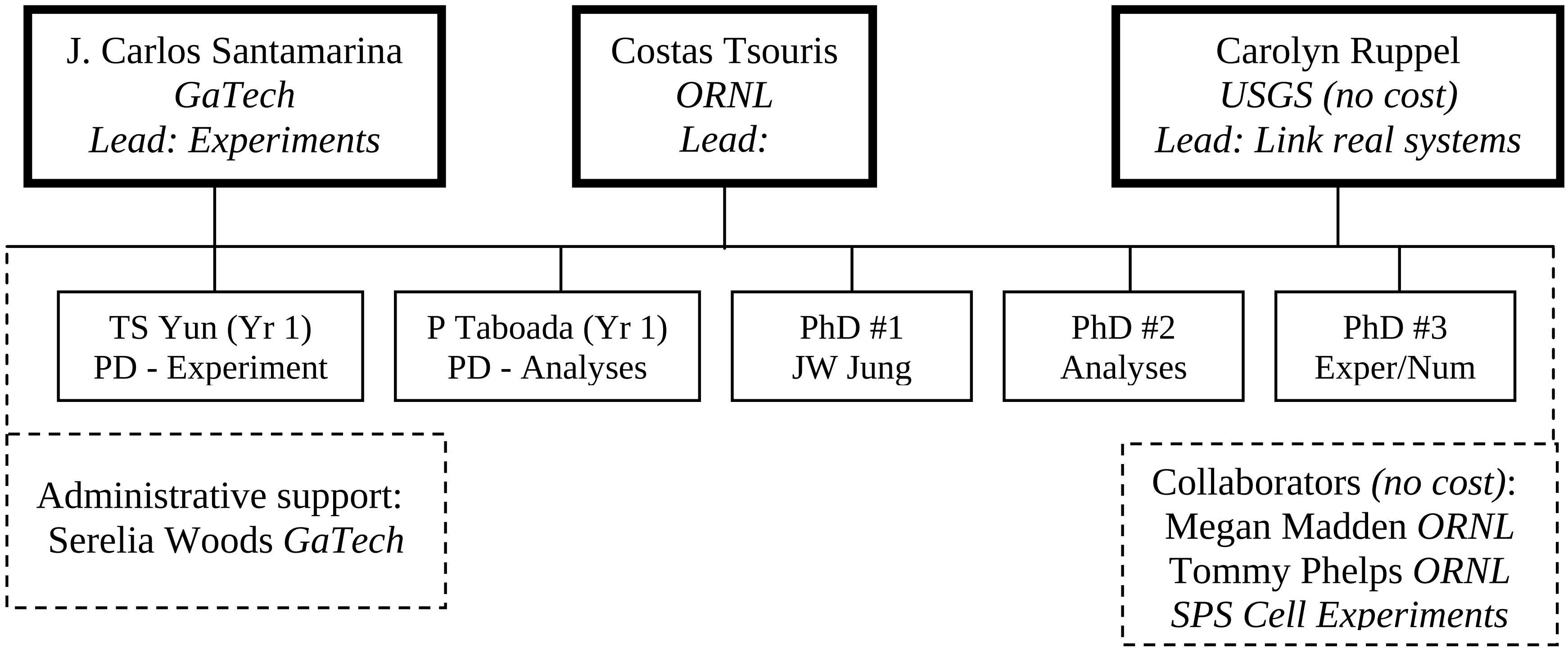

Methane production from hydrate-bearing sediments
Understanding
Prediction
• Sediment properties
• Hydrate formation history
• Phases/fluids fronts
• Effects of driving forces
• Thermodynamics in confinement
• Non-equilibrium analysis
• Kinetics in confinement
• Multiphase transport

Keys: Energy Forms + Scales + Sediment

<table>
<tr><th></th><th>Mineral surface
1D - interface</th><th>Porous network
2D - sub mm</th><th>Sediment
3D - m</th></tr>
<tr><td>Mechanical - Pressure</td><td rowspan="5">Kinetics
Formation
Dissociation
Surface effects
Miner+hydr+fluid</td><td rowspan="5">Confinement
Bubble formation
Conduction prop.
Mass transport</td><td rowspan="5">Formation
Dissociation
Granular media
Mass transport
THM coupling</td></tr>
<tr><td>Thermal</td></tr>
<tr><td>Chemical</td></tr>
<tr><td>Electromagnetic</td></tr>
<tr><td>Coupled Energy</td></tr>
</table>

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
Administrative support:
Serelia Woods *GaTech*
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 --

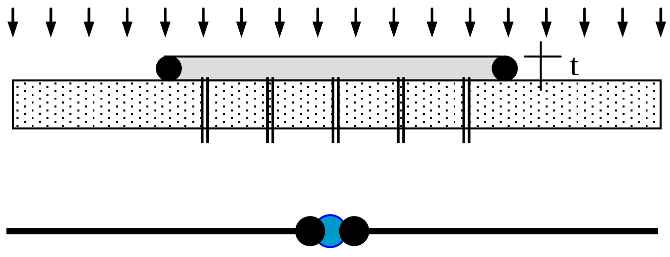
Task 7. 3D Sediment: Experiments in Seafloor Process Simulator - Analyses

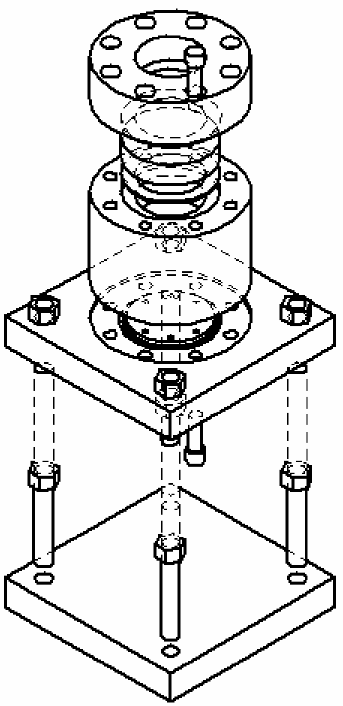
Task 4:   1D Mineral Surface

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

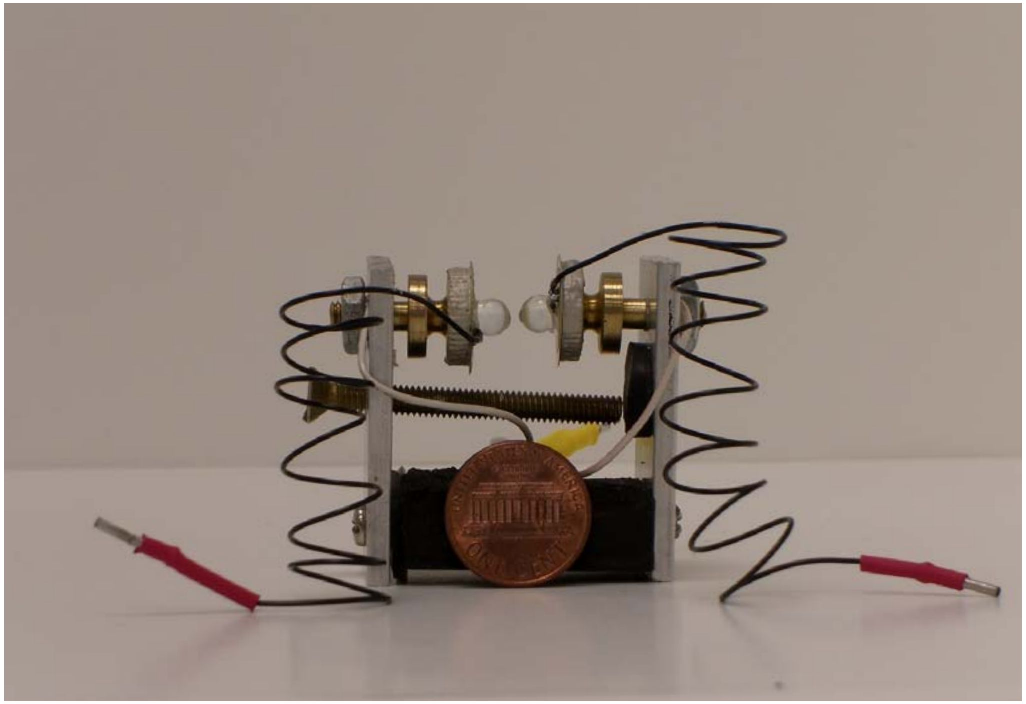
4.1: Single mineral 1-D experiments

4.2: Intrinsic kinetic model development

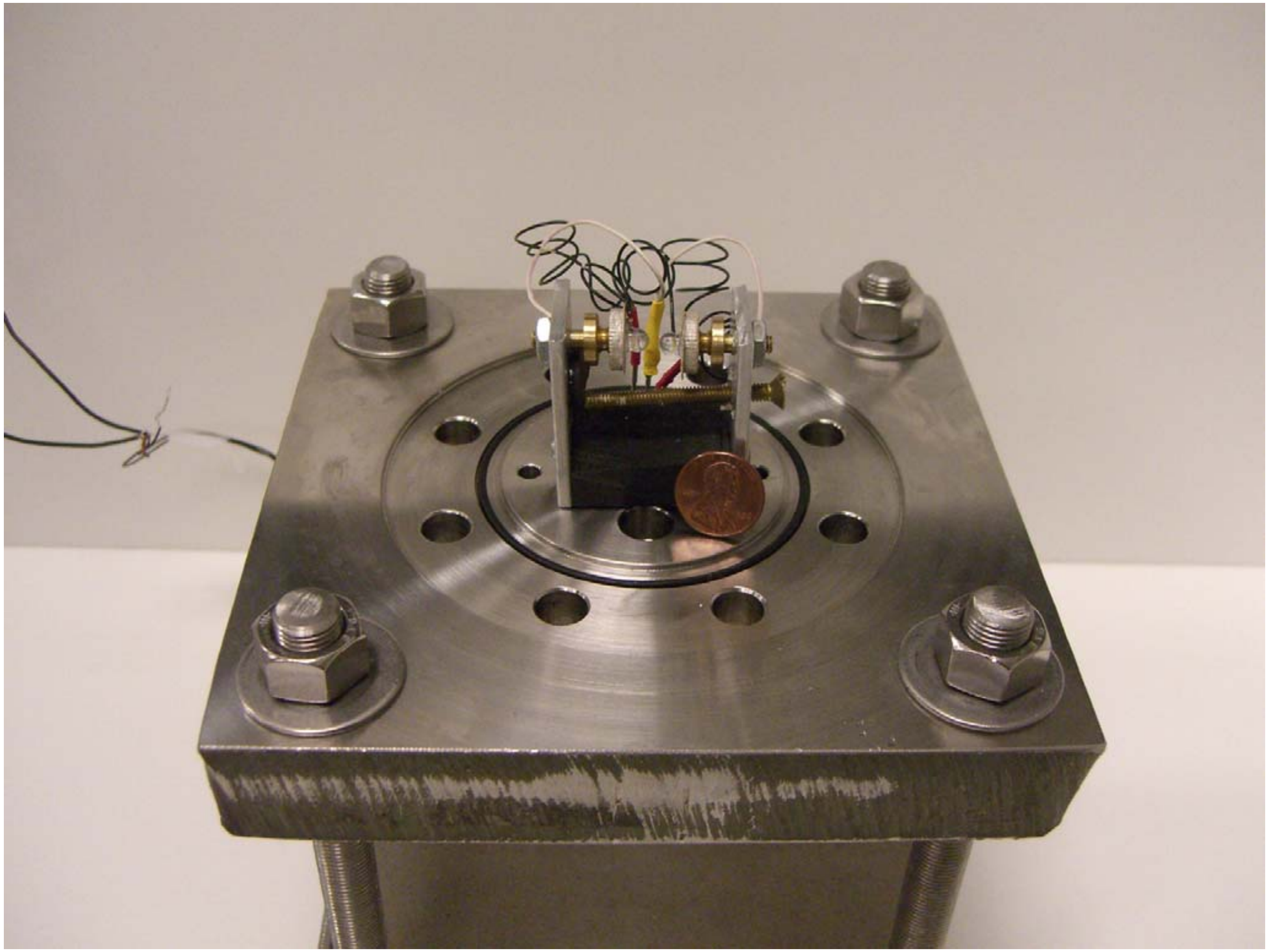




Task 4: 1D Mineral Surface

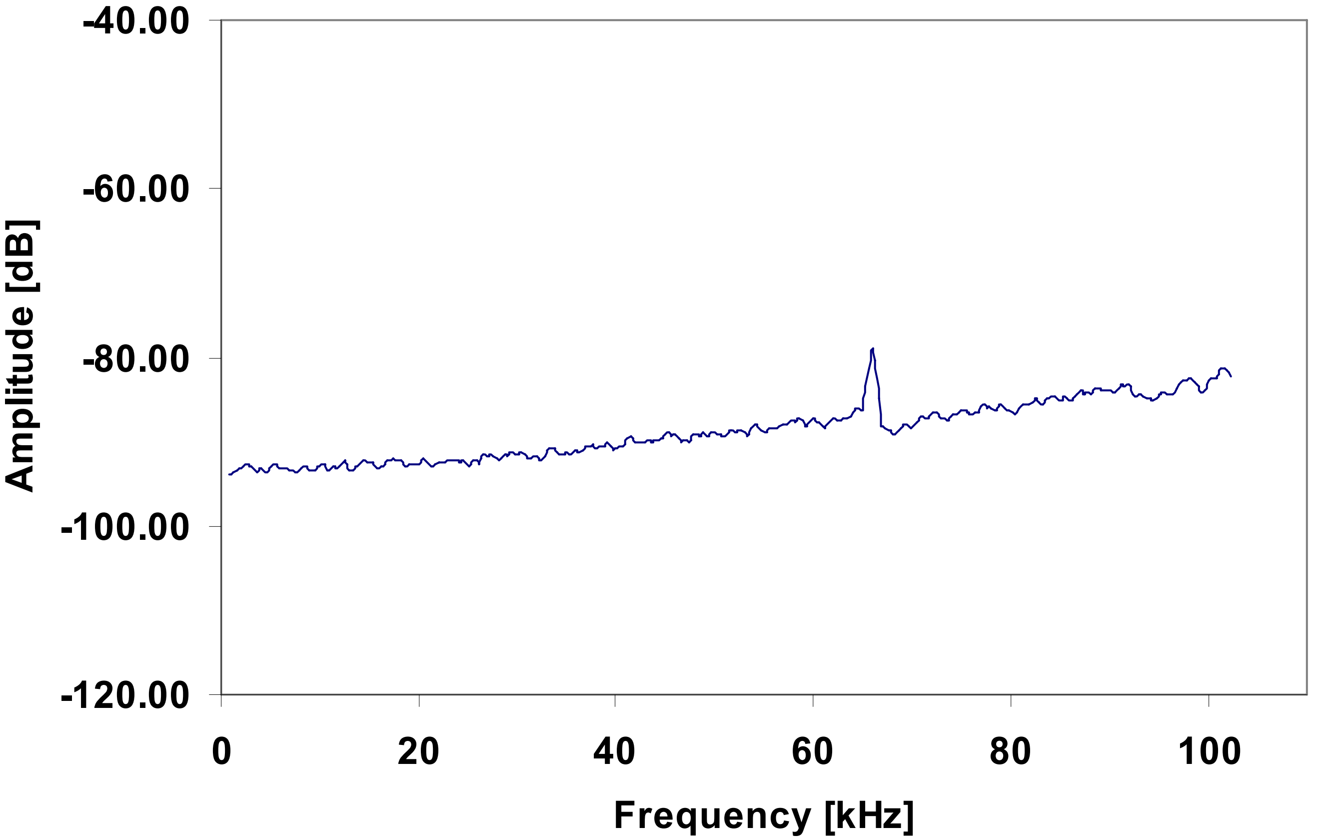


Task 4: 1D Mineral Surface

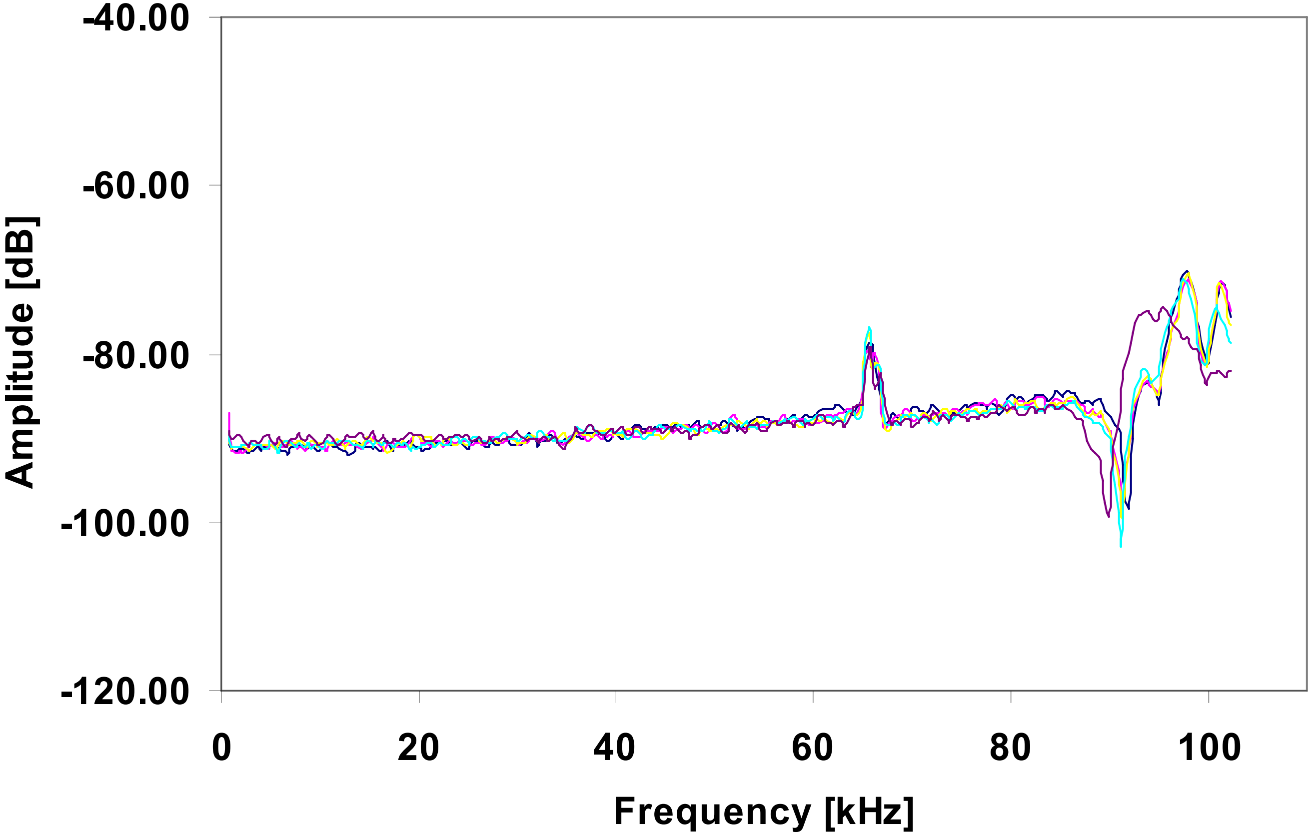


Task 4:   1D Mineral Surface

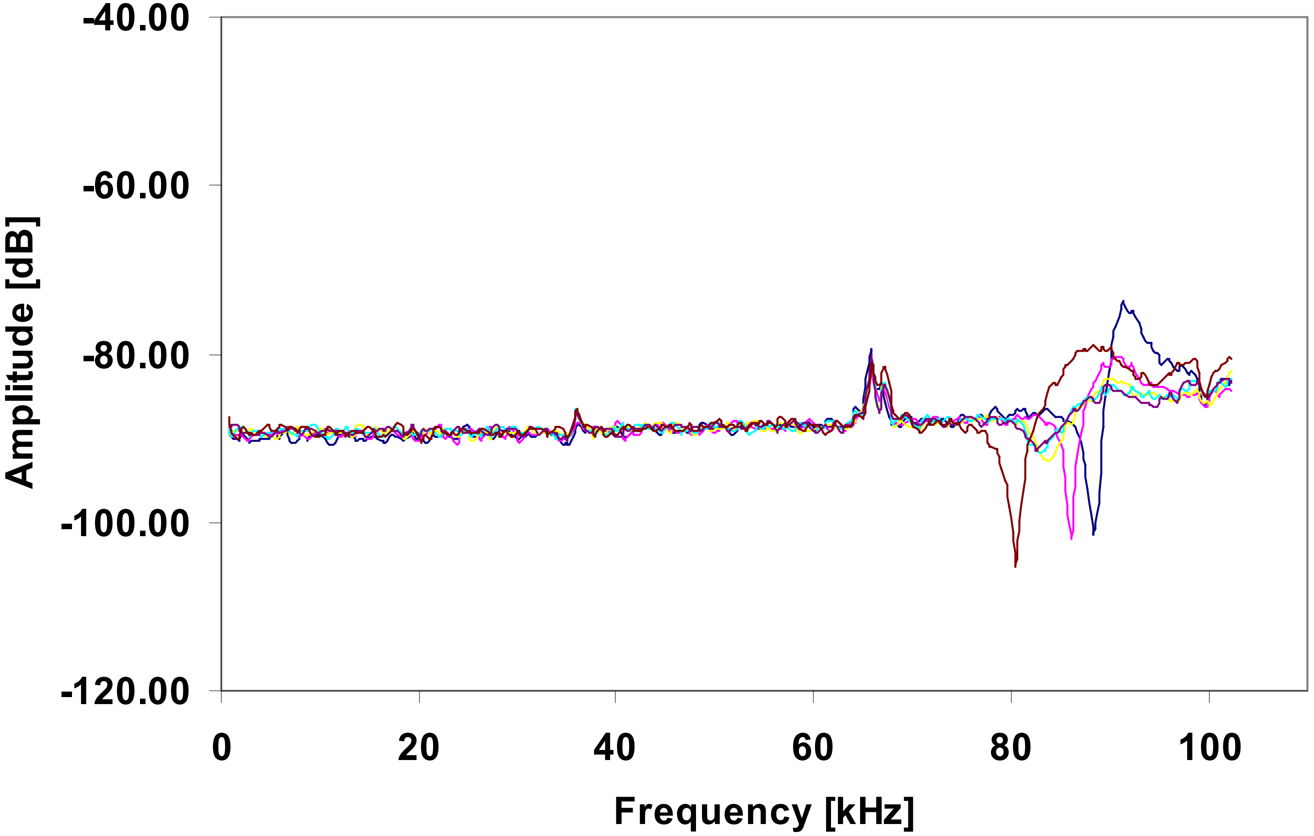
Task 4:   1D Mineral Surface



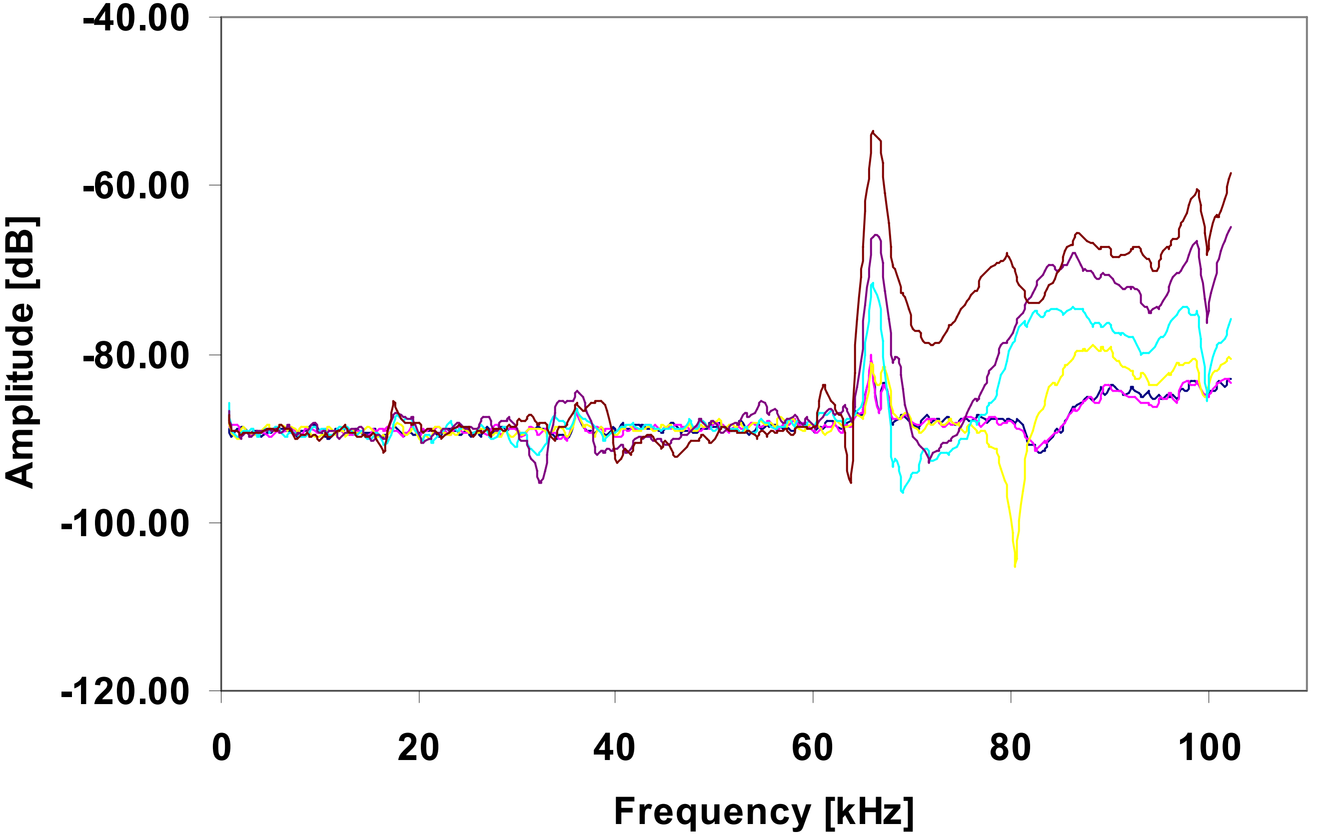
Task 4: 1D Mineral Surface



Task 4: 1D Mineral Surface



Task 4: 1D Mineral Surface



Intrinsic kinetics of hydrate dissociation

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

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

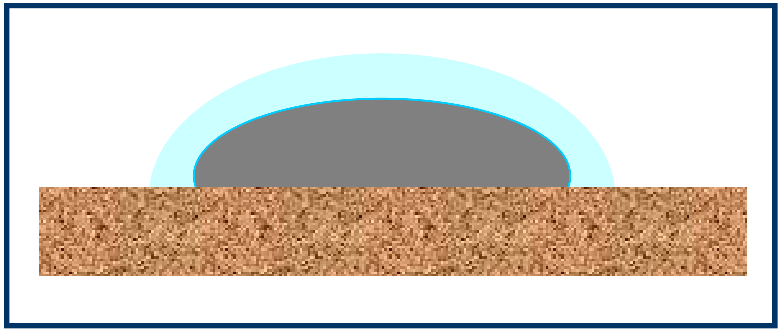
driving force

Equilibrium criteria:

$T^{I} = T^{II} = T^{III} = \ldots$

$P^{I} = P^{II} = P^{III} = \ldots$

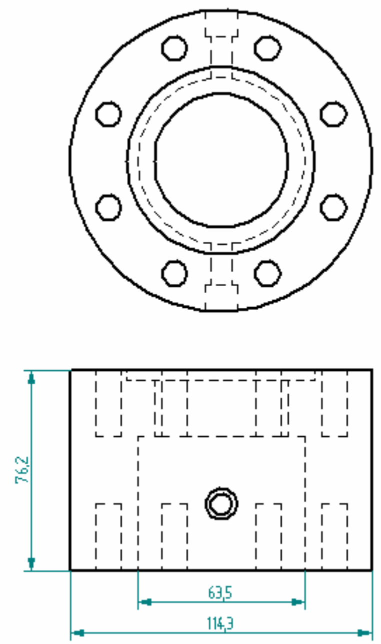
$\mu^{I}_{i} = \mu^{II}_{i} = \mu^{III}_{i} = \ldots$



experimental study of dissociation kinetics

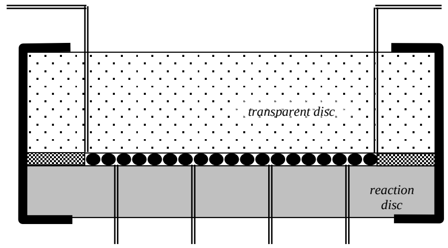
Task 5:   2D Porous Network

- *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*

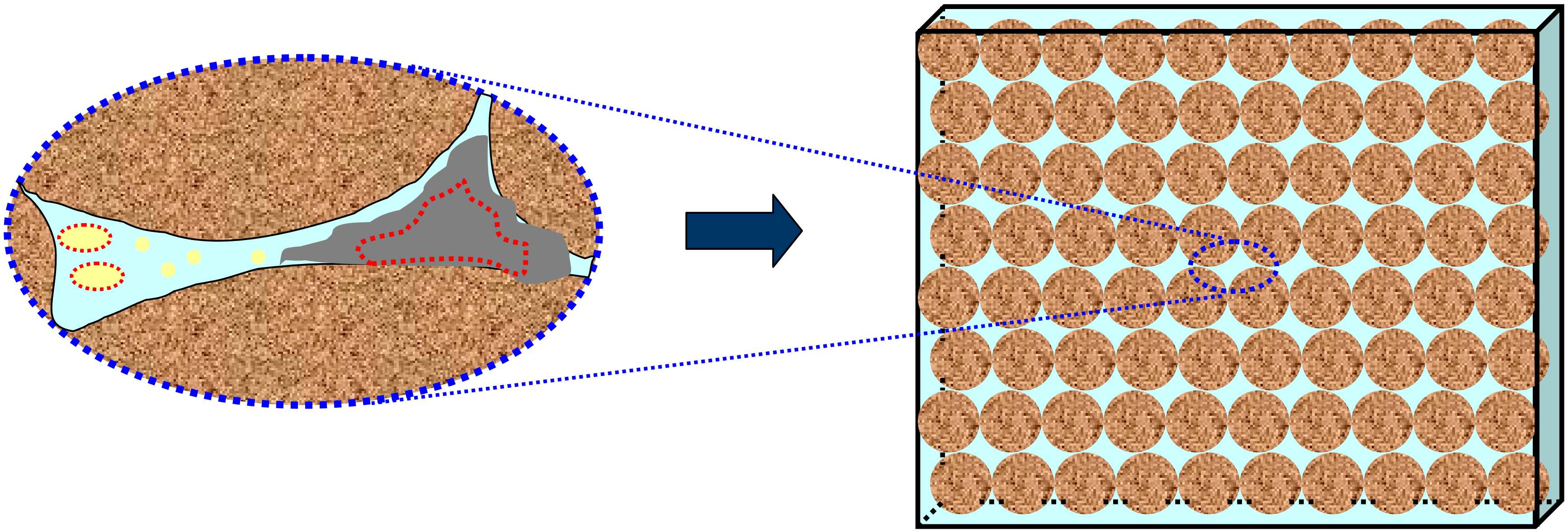


5.1: 2-D porous matrix experiments

5.2:   2-D porous matrix model development



Hydrate dissociation and CH4 transport



Hydrate dissociation :

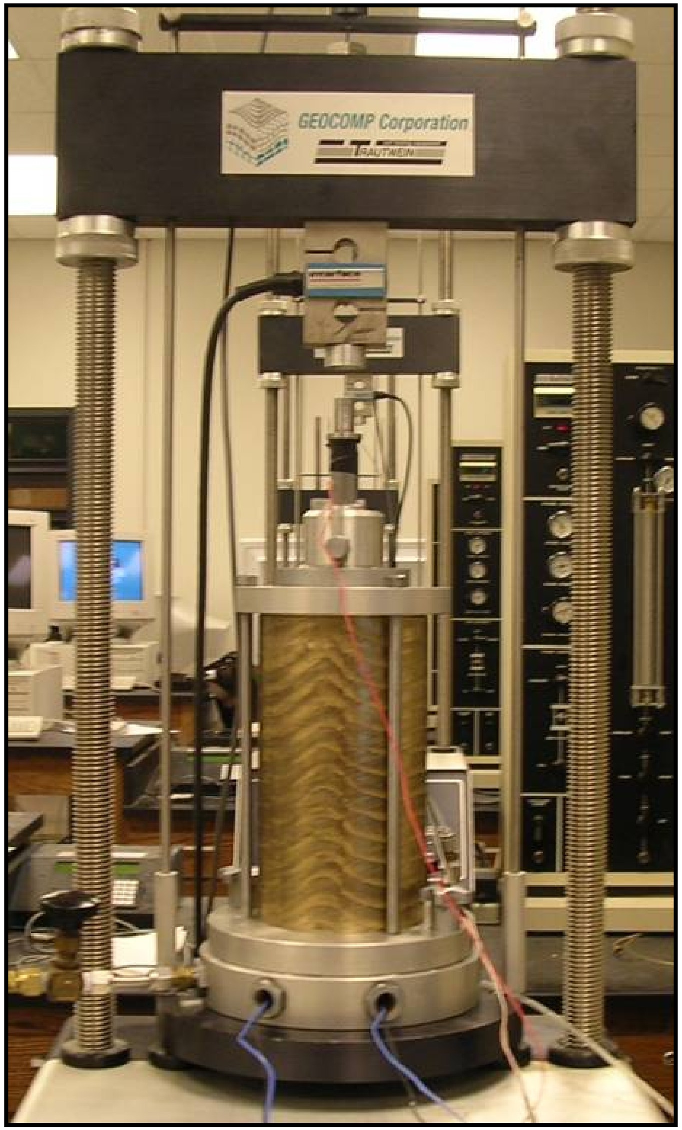
- “shrinkage” of hydrate phase
- changes in phase distribution
- local thermal variations

Analysis of <u>multiphase flow with thermal gradients</u> $\Rightarrow$

coupled momentum, mass, and energy balances

Task 6: 3D Sediment – σ’ 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*



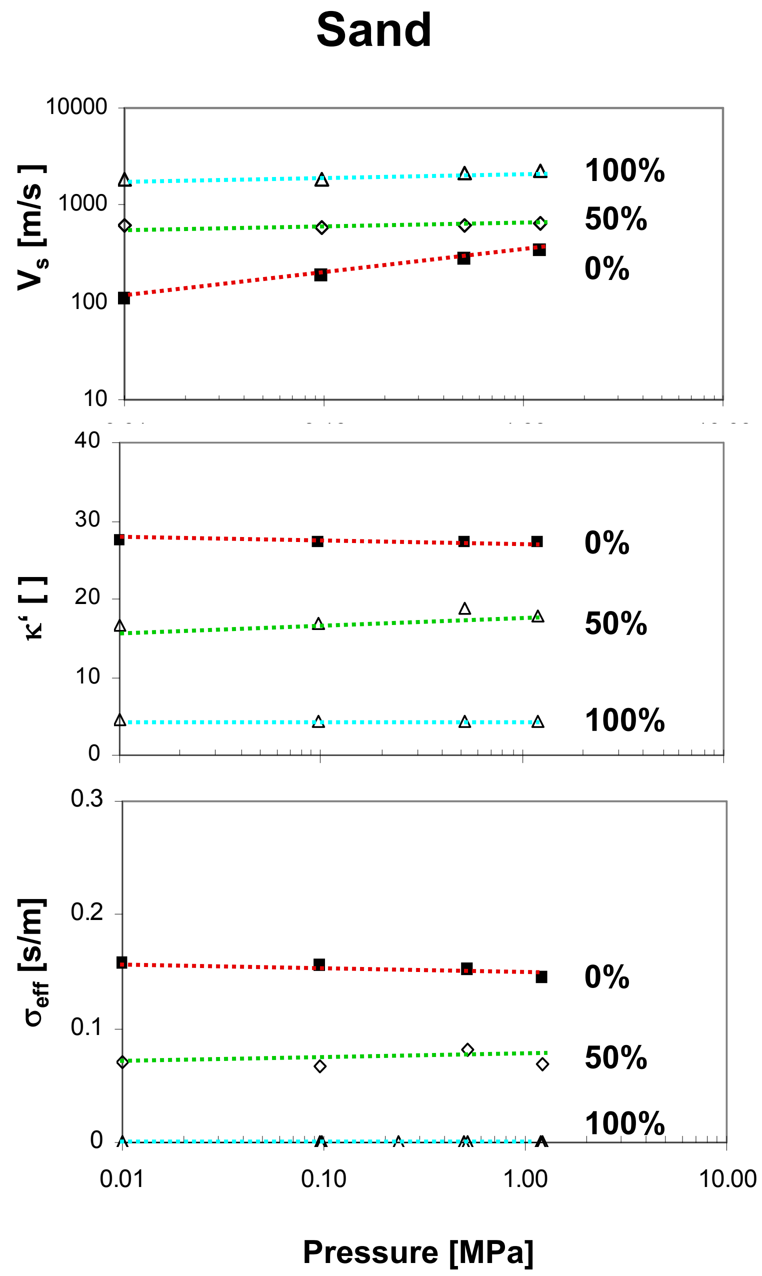
Instrumentation

u, σ', ε_{vol}, ε_{dev}, V_{gas}, V_{liq}

κ', σ_{el}, ERT

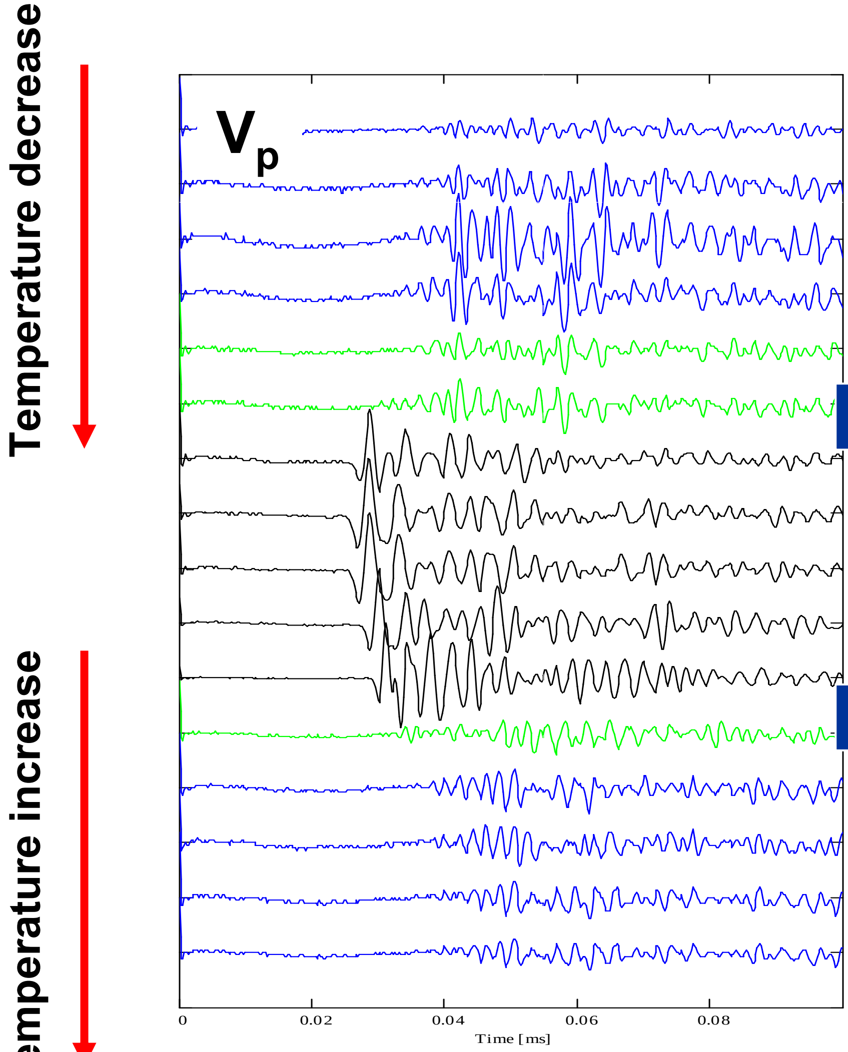
V_P, V_S

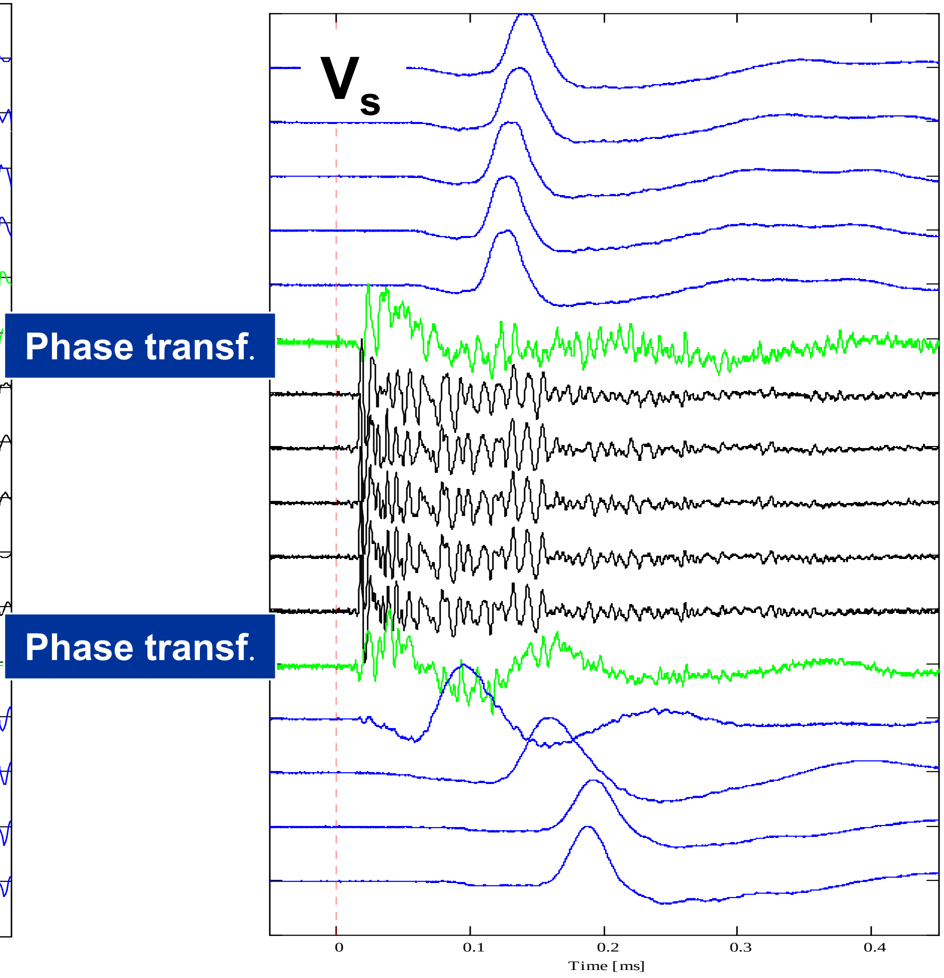
k_T, k_{hyd}



Phase Transformation – V_p and V_s

(Kaolinite + THF + H_2O)

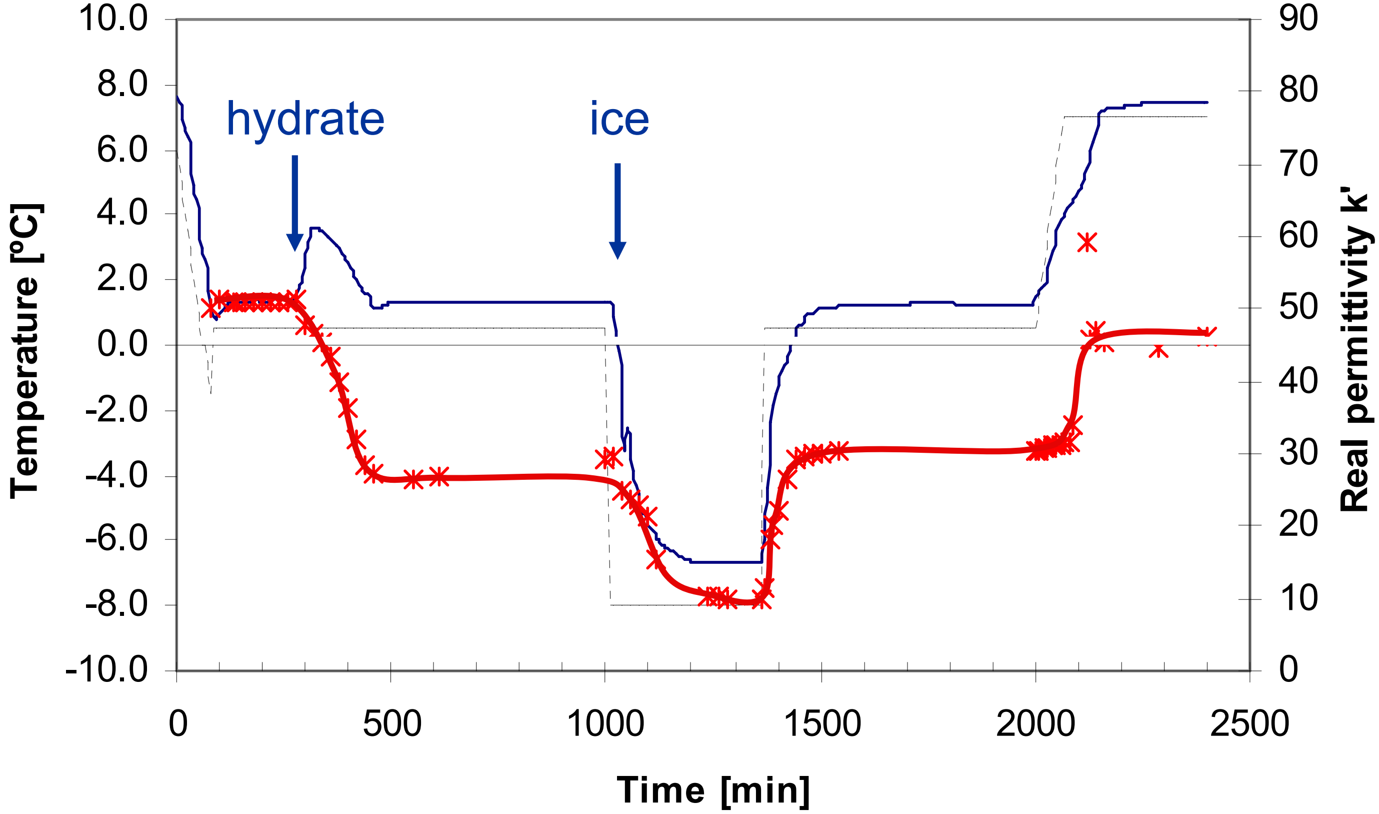




TS. Yun

Phase Transformation - Real Permittivity

(Kaolinite + THF + H_2O)

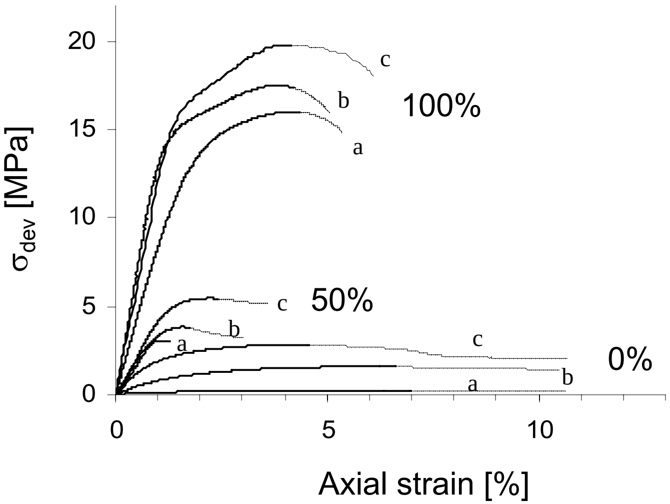


F. Francisca

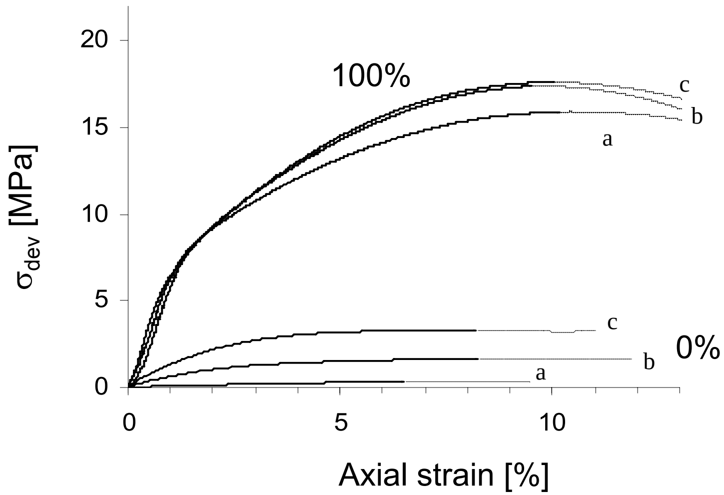
Experimental Results

a: σ'_c=0.03 MPa
b: σ'_c=0.5 MPa
c: σ'_c=1 MPa

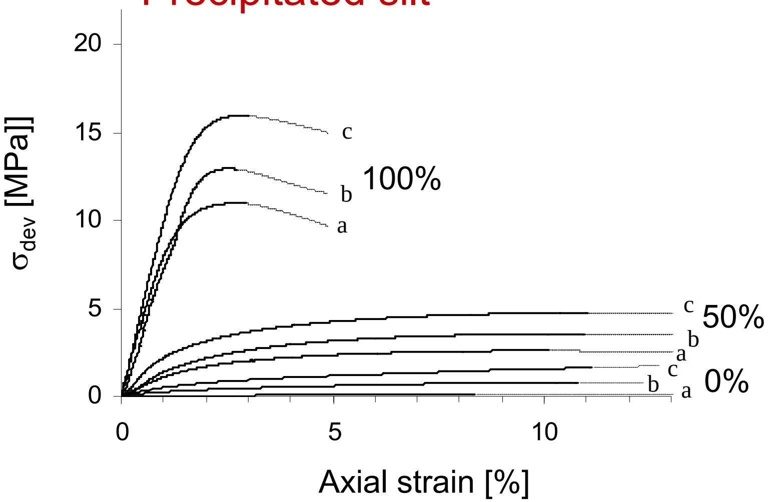
Sand



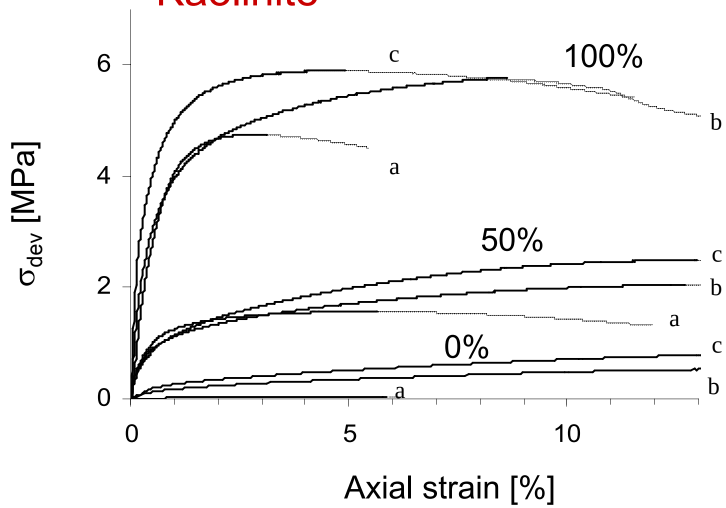
Crushed silt



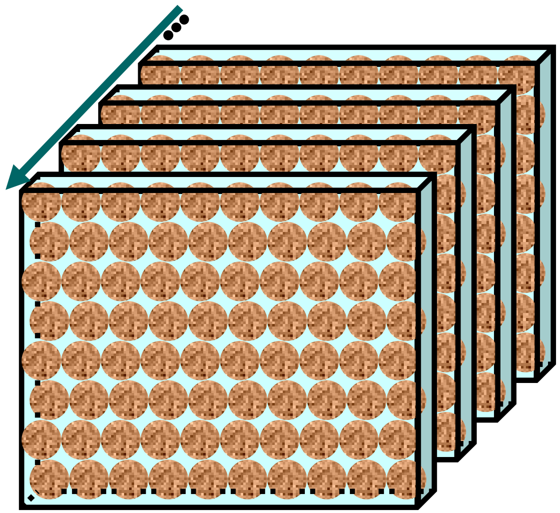
Precipitated silt

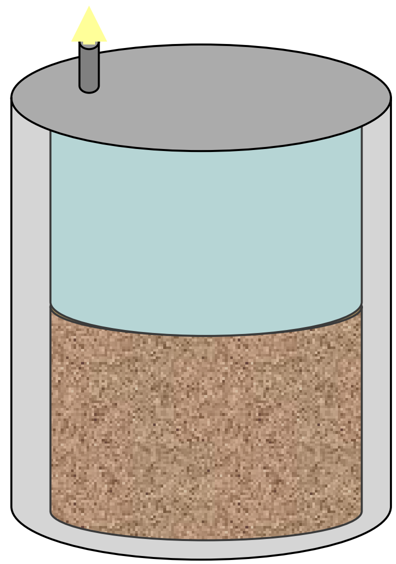


Kaolinite



3-D transport and CH4 production





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

CH_4 production rate: $$Q = \iint_S \left(\dot{N}_{CH_4} \cdot \vec{n} \right) dS$$

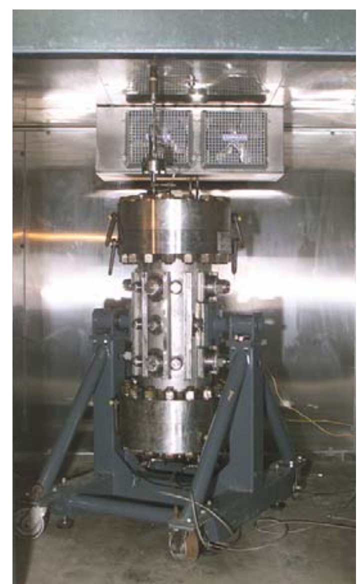
Task 7: 3D Sediment – SPS and Model

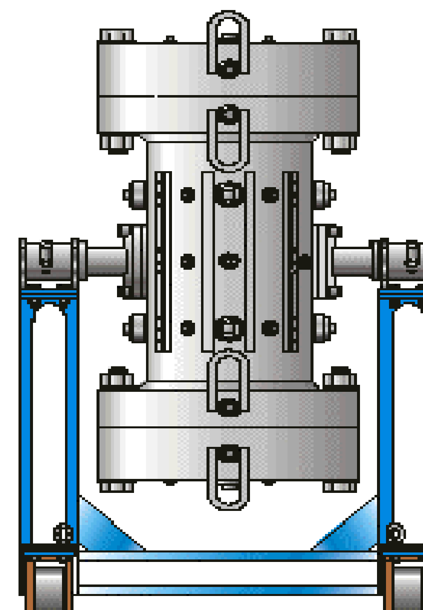
- *specimen preparation and gas recovery*
- *evolution of de-stabilization fronts – all potentials*
- *role of reservoir geometry? optimal production strategies?*
- *emergent phenomena? HF, percolation/coning, compaction/collapse?*
- *simple yet predictive models (include THF coupling)*

7.1: Hydrate formation

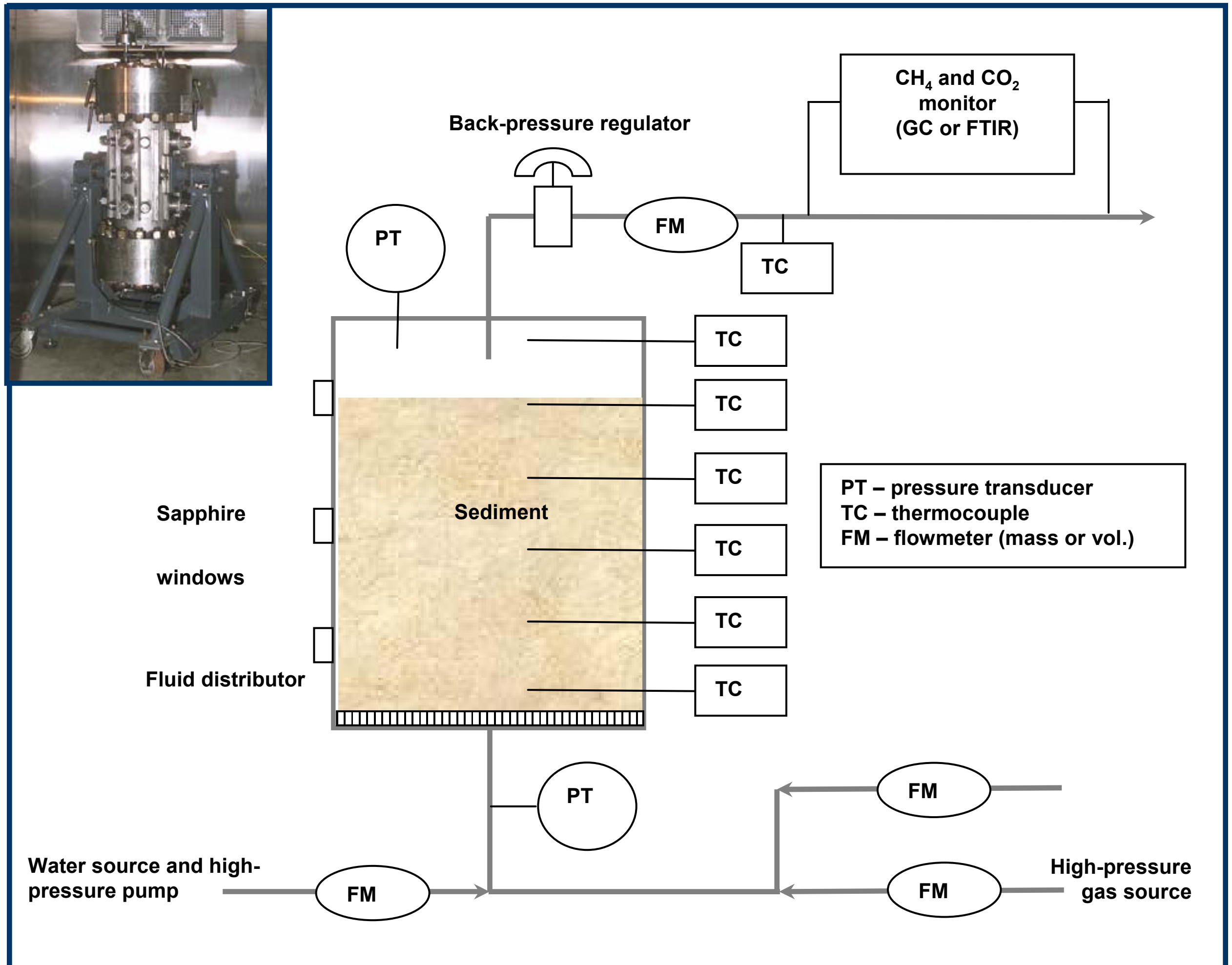
7.2: 3D Sediment Experiments

7.3: Analysis and model

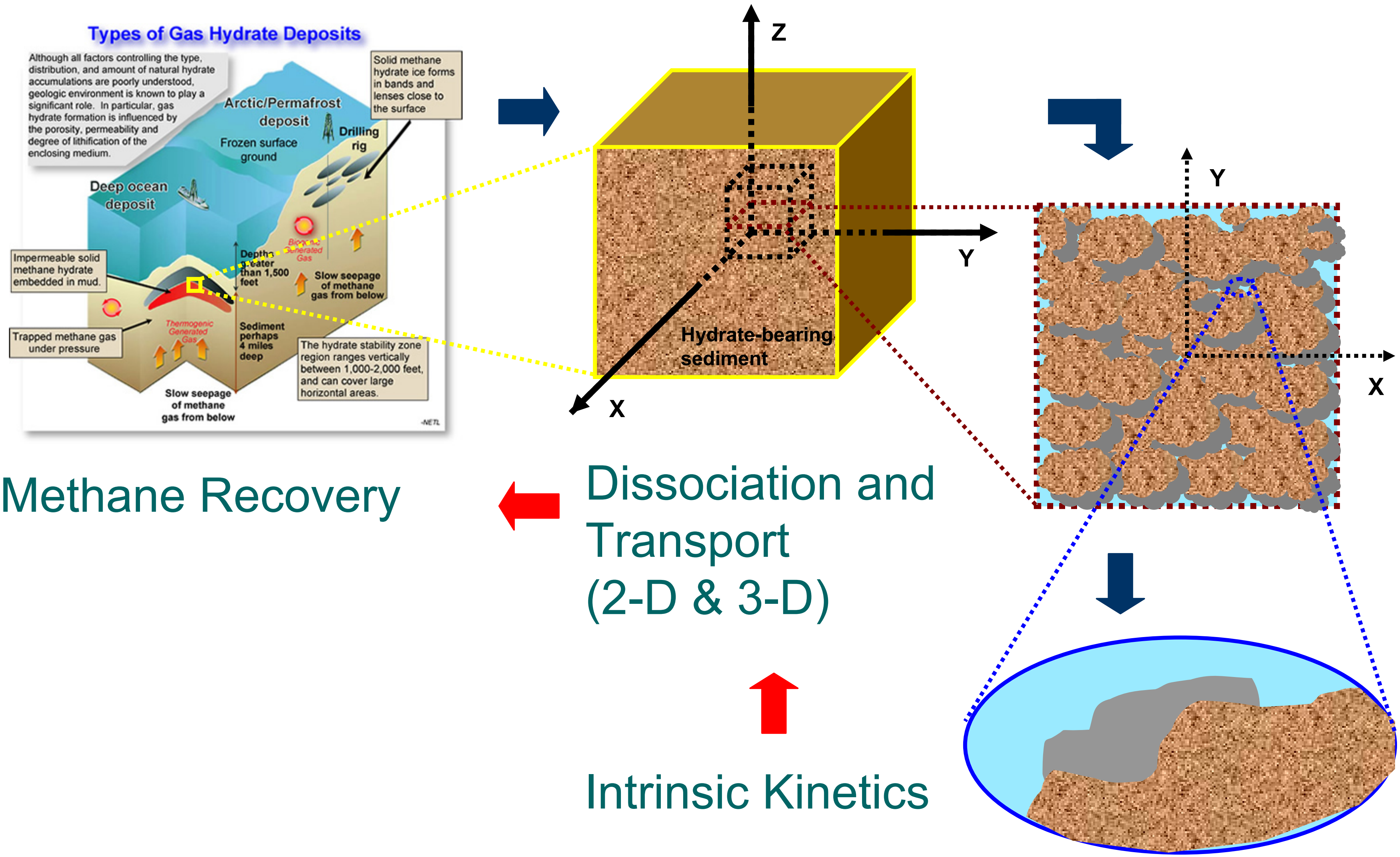




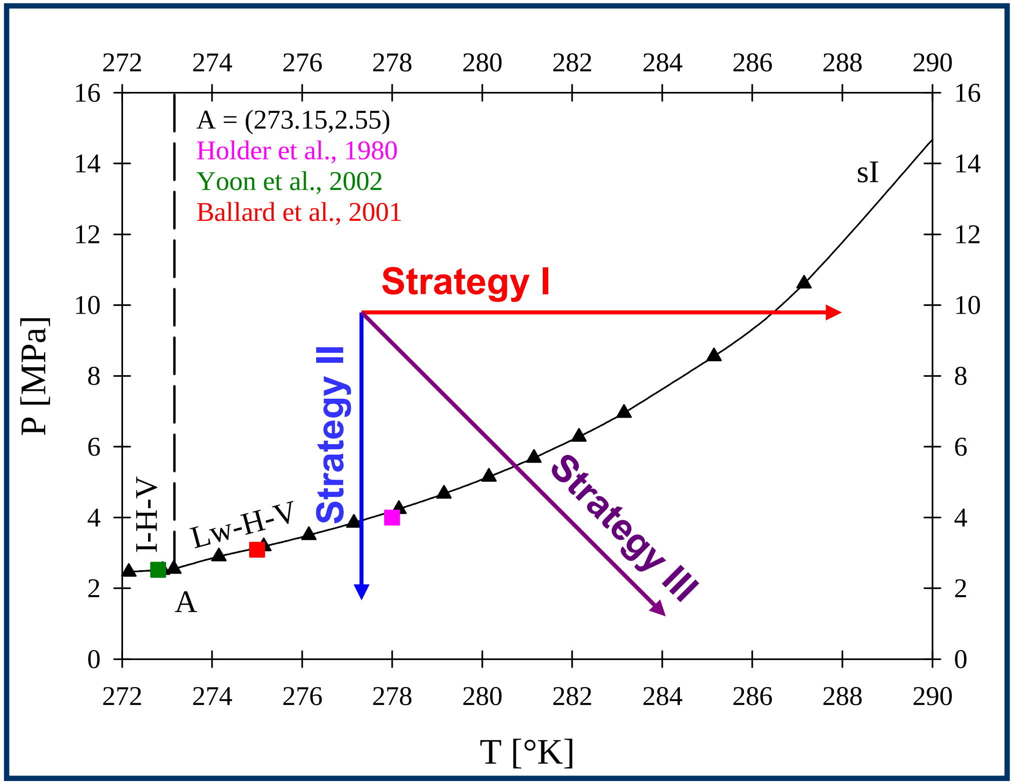
Model Verification → Instrumentation



Analyses at different length scales



Why Use Chemical Potential?



Strategy I ⇒ Thermal stimulation

$$d\mu = \left(\frac{\partial \mu}{\partial T}\right)_{P,N_i,Z_i} dT \quad \rightarrow -s$$

Strategy II ⇒ Depressurization

$$d\mu = \left(\frac{\partial \mu}{\partial P}\right)_{T,N_i,Z_i} dP \quad \rightarrow v$$

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

$$du = Tds - Pdv + \sum_j \left[\delta W_{rev}\right]_j + \sum_i \mu_i dN_i$$

Surface: $\sigma \leftrightarrow a$
Electric: $\boldsymbol{E} \leftrightarrow D$
Magnetic: $\boldsymbol{H} \leftrightarrow B$

Hydrate Equilibrium Thermodynamics

Multiphase equilibrium

$$\mu_w^H = \mu_w^I = \mu_w^{II} = \ldots$$

$$\mu_1^H = \mu_1^I = \mu_1^{II} = \ldots$$

$$\mu_2^H = \mu_2^I = \mu_2^{II} = \ldots$$

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."

$$\frac{\mu_w^H}{RT} = \frac{\mu_w^\beta}{RT} + \sum_m \upsilon_m \ln\left[1 - \sum_J \theta_{Jm}\right]$$

(Parrish & Prausnitz, *IEC Proc. Des. Dev.* **1972**)

Cage occupancy

$$\theta_{Jm} = \frac{C_{Jm}}{1 + \sum_k C_{km} f_{km}}$$

(Van der Waals & Platteeuw, *Adv. Chem. Phys.* **1959**)

$$C_{Jm} = \frac{4\pi}{kT} \int_0^{Rm-a_J} \exp\left[-\frac{\omega_{Jm}(r)}{kT}\right] r^2 dr$$

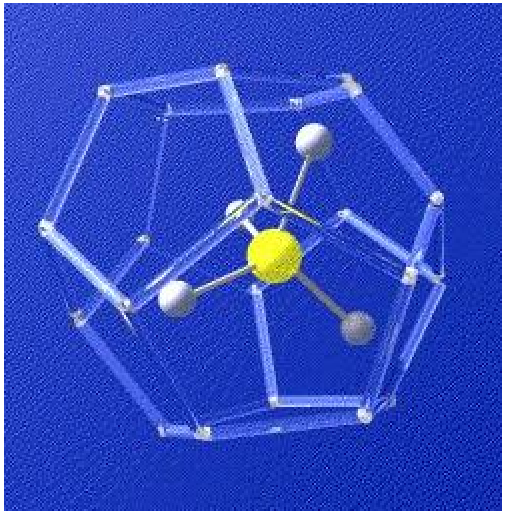
Cell potential function: Kihara potential

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

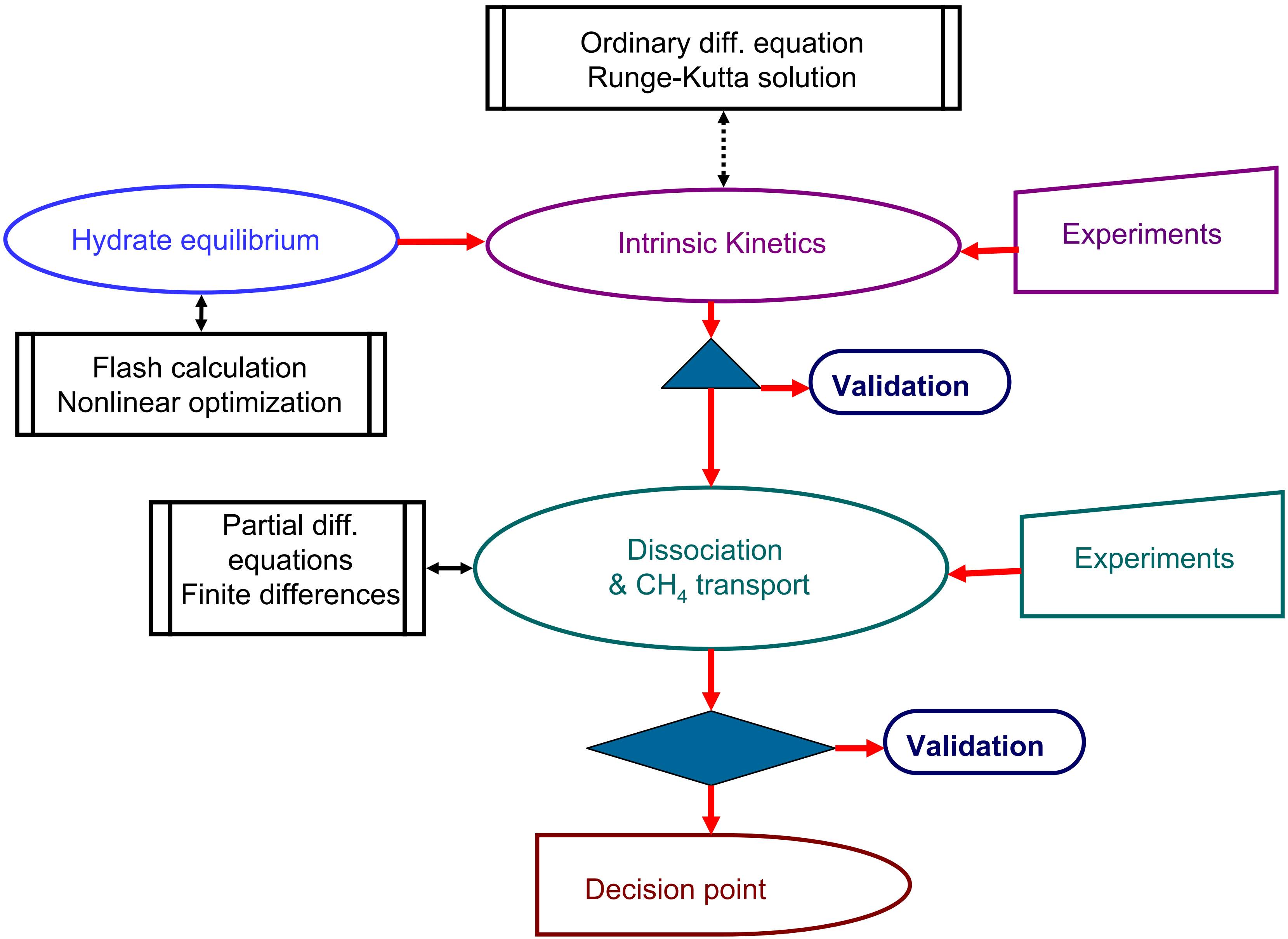
Empty hydrate cage

$$\frac{\mu_w^\beta}{RT} = \frac{\mu_w^O}{RT_O} - \int_{T_O}^{T} \frac{\Delta h_w}{RT^2} dT + \int_0^P \frac{\Delta v_w}{RT} dP - \ln a_w$$

(Parrish & Prausnitz, *IEC Proc. Des. Dev.* **1972**)



Solving the model

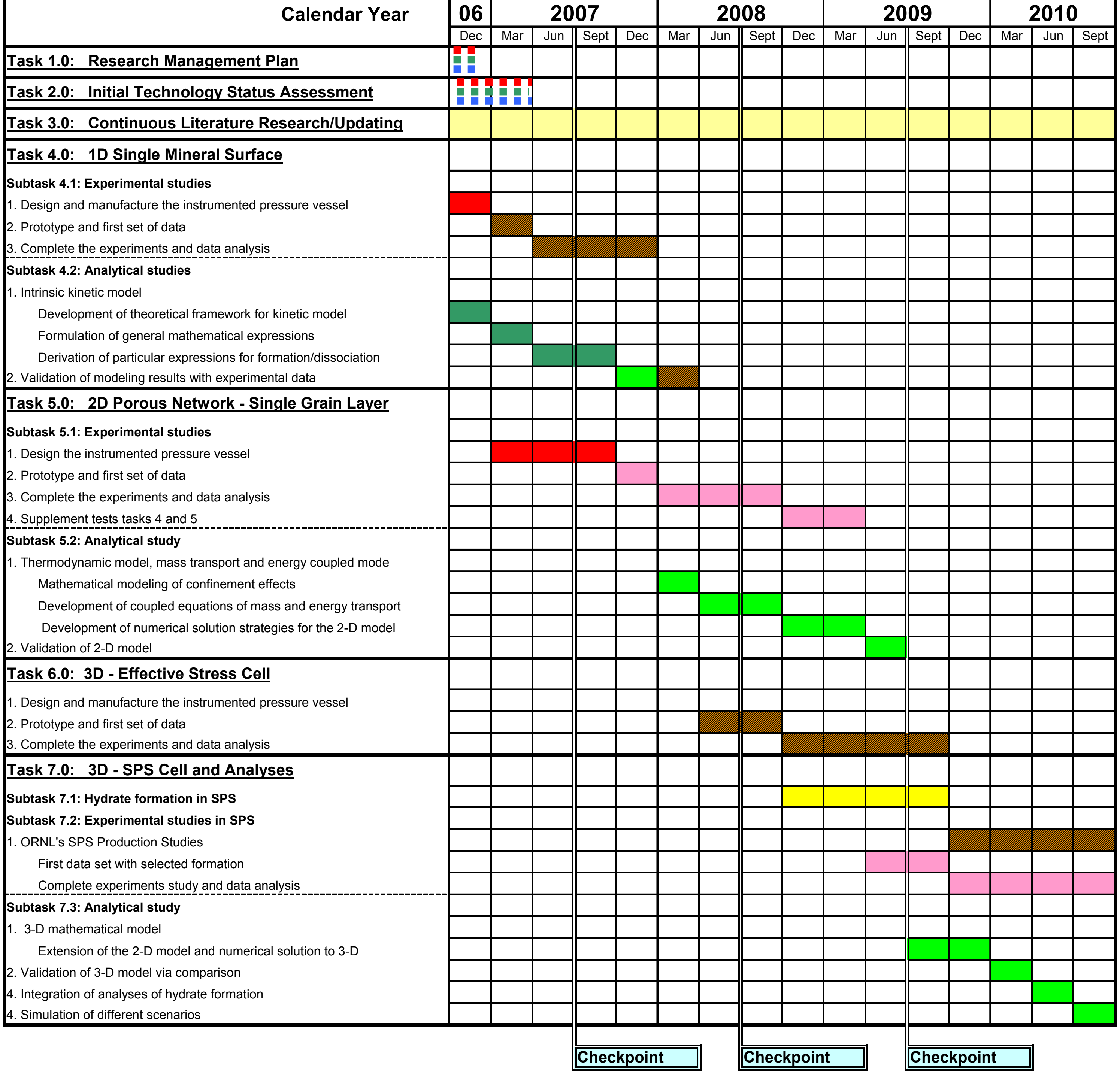


Schedule

Milestones

Deliverables

Schedule



Calendar Year
06
2007
2008
2009
2010
Dec
Mar
Jun
Sept
Dec
Mar
Jun
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Mar
Jun
Sept
Task 1.0: Research Management Plan
Task 2.0: Initial Technology Status Assessment
Task 3.0: Continuous Literature Research/Updating
Task 4.0: 1D Single Mineral Surface
Subtask 4.1: Experimental studies
1. Design and manufacture the instrumented pressure vessel
2. Prototype and first set of data
3. Complete the experiments and data analysis
Subtask 4.2: Analytical studies
1. Intrinsic kinetic model
Development of theoretical framework for kinetic model
Formulation of general mathematical expressions
Derivation of particular expressions for formation/dissociation
2. Validation of modeling results with experimental data
Task 5.0: 2D Porous Network - Single Grain Layer
Subtask 5.1: Experimental studies
1. Design the instrumented pressure vessel
2. Prototype and first set of data
3. Complete the experiments and data analysis
4. Supplement tests tasks 4 and 5
Subtask 5.2: Analytical study
1. Thermodynamic model, mass transport and energy coupled mode
Mathematical modeling of confinement effects
Development of coupled equations of mass and energy transport
Development of numerical solution strategies for the 2-D model
2. Validation of 2-D model
Task 6.0: 3D - Effective Stress Cell
1. Design and manufacture the instrumented pressure vessel
2. Prototype and first set of data
3. Complete the experiments and data analysis
Task 7.0: 3D - SPS Cell and Analyses
Subtask 7.1: Hydrate formation in SPS
Subtask 7.2: Experimental studies in SPS
1. ORNL's SPS Production Studies
First data set with selected formation
Complete experiments study and data analysis
Subtask 7.3: Analytical study
1. 3-D mathematical model
Extension of the 2-D model and numerical solution to 3-D
2. Validation of 3-D model via comparison
4. Integration of analyses of hydrate formation
4. Simulation of different scenarios
Checkpoint
Checkpoint
Checkpoint

Milestones

2006	December	Experimental: 1D cell machined
2007	March	Experimental: First formation/production test in 1D cell (+instr.)
2007	December	Experimental: First formation/production test in 2D cell (+instr.) Analytical: Model for 1D production – coupled energy
2008	September	Experimental: First formation/production test in σ' cell (+instr.)
2009	March	Experimental: Results coupled energy production in 2D cell
2009	June	Analytical: Model for production in 2D networks
2009	December	Experimental: First production study in ORNL's SPS
2010	June	Experimental: Insightful production-related results from SPS cell Analytical: Predict & optimize 3D production results
2010	September	PROJECT COMPLETION

Deliverables

Deliverable	Approx. Submission Date
Research Management Plan	10/31/2006
Technology Status Assessment Report	11/30/2007
Pressurized vessel design	
Quarterly Report	02/28/2007
Annual Report	08/31/2007
Quarterly Report	02/28/2008
Annual Report	08/31/2008
Quarterly Report	02/28/2009
Annual Report	08/31/2009
Recommendation	08/31/2009
Review of Recommendation	09/30/2009
Quarterly Report	02/28/2010
Final Report	09/30/2010

Problems and Risks

Hydrate formation in sediments - history

Instrumentation

System identification / Inversion

Model verification

Laboratory → field? (field test with MBARI?)

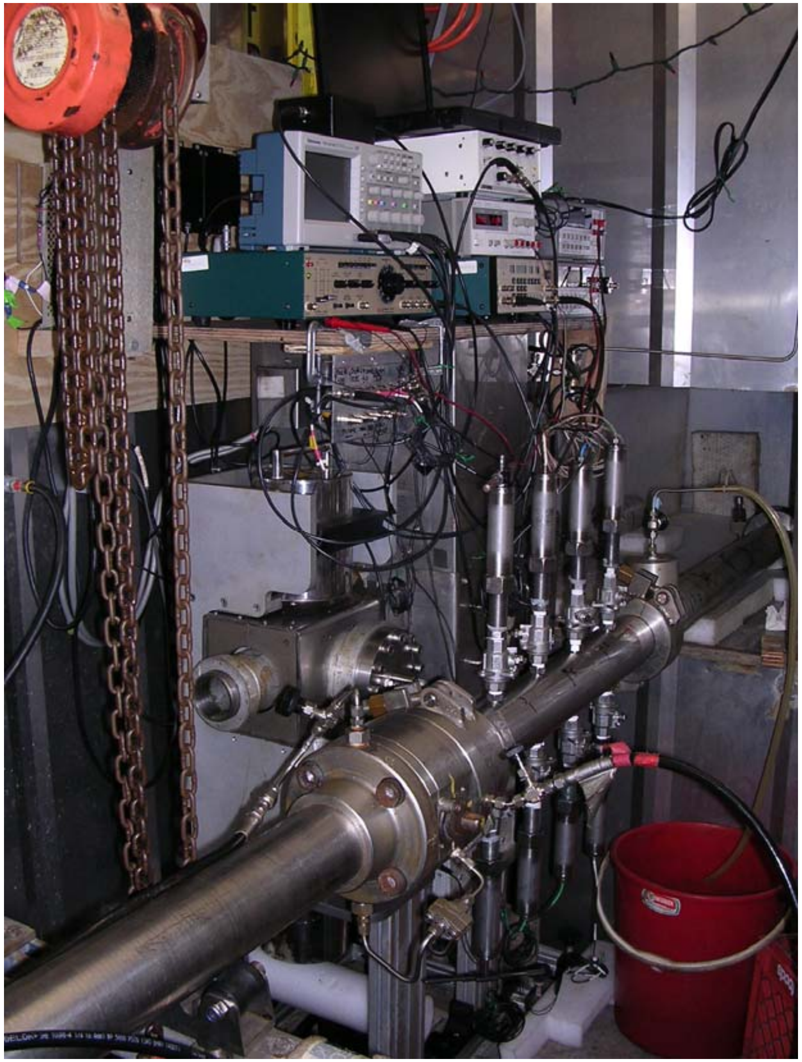
…

Unknowns !

Possible opportunities

Production test – India cores

Field tests (e.g., with MBARI)?



Budget Period Slide

Budget: Government and Cost Share

Task	Task Description	DOE	Cost Share	Task Total
1.0	Research Management Plan			
2.0	Technology Status Assessment			
3.0	Continuous Literature Research/Updating			
4.0	1D Single Mineral Surface: Experimental and Analytical Studies	368,550	114,420	482,970
5.0	2D Porous Network – Single Grain Layer: Experimental and Analytical Studies	277,675	86,205	363,880
6.0	3D Sediment: Experiments in Effective Stress Cell	40,388	12,538	52,926
7.0	3D Sediment: Experiments in SPS Cell – Analyses	100,972	31,347	132,319
8.0	Final Report / Deliverables			
	Total	787,585	244,510	1,032,095

BP 1 - 9 months			BP 2 - 12 months			BP 3 - 12 months			BP 4 - 15 months			Totals		
DOE	GIT	Total	DOE	GIT	Total	DOE	GIT	Total	DOE	GIT	Total	DOE	GIT	Total
155319	49170	204490	184260	63401	247661	187670	60004	247673	260336	71935	332271	787585	244510	1032095

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**