Oil & Natural Gas Technology

DOE Award No.: DE-FE0009897

Quarterly Research Performance Progress Report (Period ending 6/30/2015)

Hydrate-Bearing Clayey Sediments: Morphology, Physical Properties, Production and Engineering/Geological Implications

Project Period (10/1/2012 to 9/30/2016)

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Office of Fossil Energy

DISCLAIMER:

ACCOMPLISHMENTS

Context – Goals. *Fine grained sediments host more than 90% of the global gas hydrate accumulations. Yet, hydrate formation in clayey sediments is least understood and characterized. This research focuses on* *hydrate bearing clayey sediments*. *The goals of this research are (1) to gain a fundamental understanding of hydrate formation and ensuing morphology, (2) to develop laboratory techniques to emulate "natural" formations, (3) to assess and develop analytical tools to predict physical properties, (4) to evaluate engineering and geological implications, and (5) to advance gas production alternatives to recover methane from these sediments.*

Accomplished

The main accomplishments for this period include:

- Formation of CO_2 hydrate in fine-grained sediment
  - Transformation from ice/water to hydrate in hydrophobic silica
- Quantified mass, and advanced thermal analysis of hydrate formation in fine-grained sediment
- Crystal formation experiments in porous media

Plan - Next reporting period

Physical understanding of hydrate formation in fine grained sediments and small pores. Evaluate the difference between gas pressure, liquid pressure and crystal pressure, and the relevance to hydrate stability. Advance Numerical model studies of physical properties of hydrate bearing sediments. Well production simulation with numerical methods.

Research in Progress

The following pages capture the slides presented at the meeting for the end of year 3, which include specific information about this quarter.

Hydrate-Bearing Clayey Sediments

Morphology, Physical Properties, Production and Engineering/Geological Implications

Transition to Phase 4 / Budget Period 4

DOE - National Energy Technology Laboratory
Agreement: DE-FE0009897

J. Carlos Santamarina

Georgia Institute of Technology
(on leave at KAUST)

Goals – Objectives - Background

Natural HBF – Fine Grained (Analogues)

Underlying Physics

Devices

Hydrate Formation in the Lab

“Reservoir” Simulation

Physical Properties

Gas Production

Next – Team – Schedule

Goals and Objectives

Background

(additional examples: see 2014 End of Year Report)

Goals and Objectives

Observation: *Fine grained sediments*

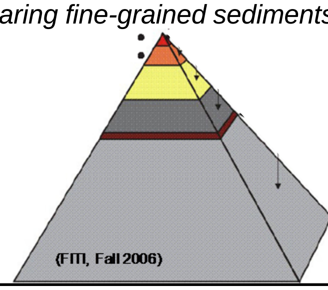
- *host more than 90% of the global gas hydrate accumulations*

State-of Knowledge: *Hydrate formation in clayey sediments*

- *least understood*
- *poorly characterized*

Objectives :

- *in-depth understanding of hydrate bearing fine-grained sediments*
- *new gas production paradigm*



Goals and Objectives

The proposed research

- focus: hydrate bearing clayey sediments
- fundamental understanding of hydrate formation
- hydrate lens topology
- laboratory techniques to emulate "natural" formations
- analytical tools to predict physical properties
- engineering and geological implications
- gas production alternatives

Project Tasks

Focus: **hydrate bearing clayey sediments**

Tasks:

- fundamental understanding of hydrate formation in fine-grained sed.
- laboratory emulation with real methane hydrate
- assessment and prediction of physical properties
- evaluation of engineering and geological implications
- possible paradigm shift in gas production from fine-grained sed.

Task 2 - Formation, distribution, topology

Guiding Questions:

- nucleation and grow in fine-grained sediments?
- continue feeding lens growth?
- underlying hydro-chemo-mechanical effects?
- sediment characteristics that control evolving hydrate topology?
- emulation in the laboratory?

Laboratory challenges

CH_4 in hydrates = 1:6 >> CH_4 in water =1:700

Hydrate formation transport-limited in water saturated sediments

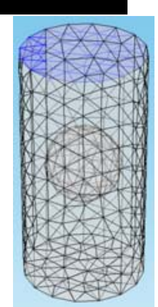
Low advective transport in clayey sediments (diffusive transport?)

Task 3 - Physical properties

Guiding Questions.

Hydro-thermo-electro-mechanical properties of fine-grained sediments with segregated hydrate?

(relevance to simulators)



SubTask 3a: Analytical estimations (two-component systems)

- upper and lower bounds
- physical models

SubTask 3b: Numerical Extension (interacting lenses)

SubTask 3c: Experimental measurements

- Form hydrate-bearing clays and measure salient physical properties
- Small strain stiffness (V_p and V_s), strength
- Thermal, hydraulic and electrical conductivity

Task 4 - Gas Production

Guiding Questions
- What are viable production strategies?
- Gas migration: from lenses towards to the production well?
- What is the role of elastic deformation of layer boundaries?
- Production strategy to keep fractures open during recovery?
- Can discontinuities become "highways" for gas flow?
- Production strategies to minimize volume contraction?

Description
- Target: *new gas production paradigm*
- From key differences with oil production
  - interconnected hydrate network
  - hydrate-to-fluid expansion
  - gas-driven openings
  - gas migration in layered stratigraphy
  - available heat

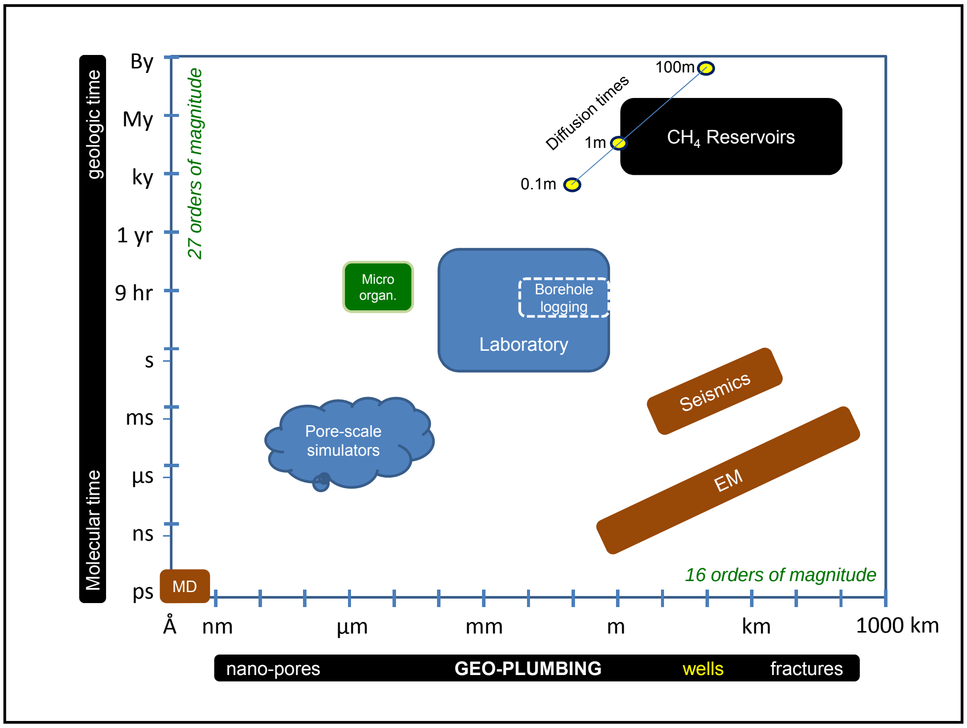
Task 5 - Implications

Guiding Question:
How does segregated hydrate in fine grained sediments affect engineering tasks (besides production) and geological processes

SubTask 5a – Seafloor infrastructure settlement

SubTask 5b – Stability (borehole and slopes)

SubTask 5c – Unique implications to carbon cycle



Natural HBS - *Fine Grained* Analogues

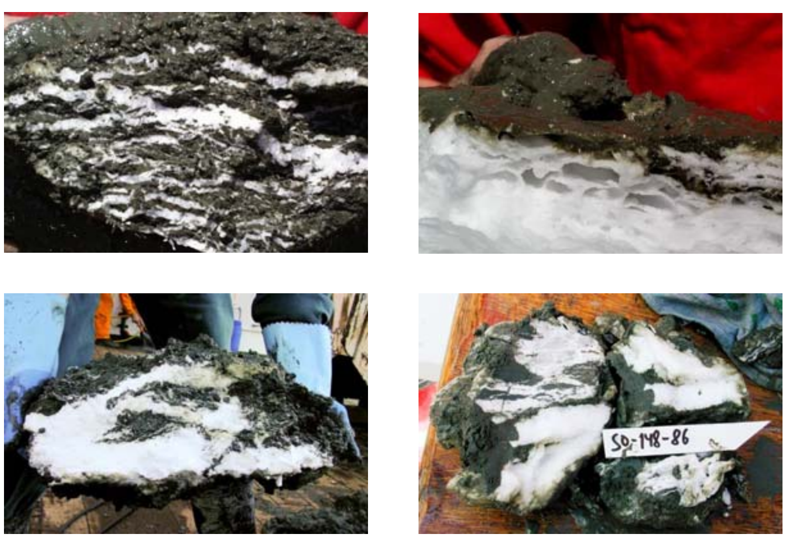
(additional examples: see 2014 End of Year Report)

Gulf of Mexico, US

smectite-dominant clay

Photos: GEOMAR

Hydrate Ridge, US



clay sediments (smectite, illite, chlorite, and kaolinite)

Photos: GEOMAR

Crystallization in Fine Grained Sediments

Ice-lens

http://bigthink.com/

http://www.page21.eu/gallery

https://woodgears.ca/cottage/foundation.html

https://woodgears.ca/cottage/foundation.html

Crystallization in Fine Grained Sediments

Emerald

Pyrite sun

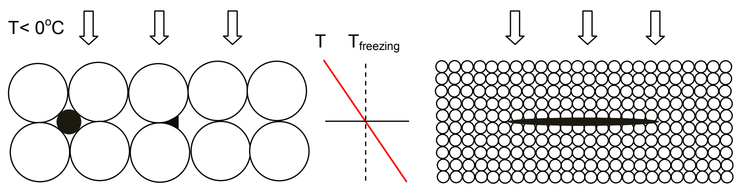
Crystallization in Fine Grained Sediments

Gypsum lenses

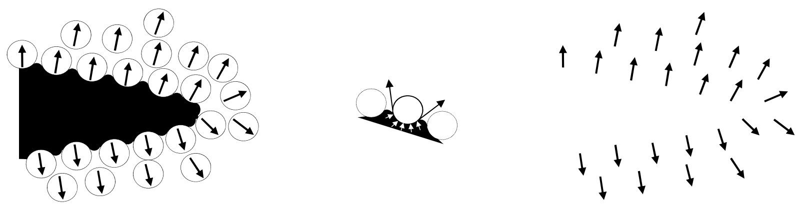
Underlying Physics

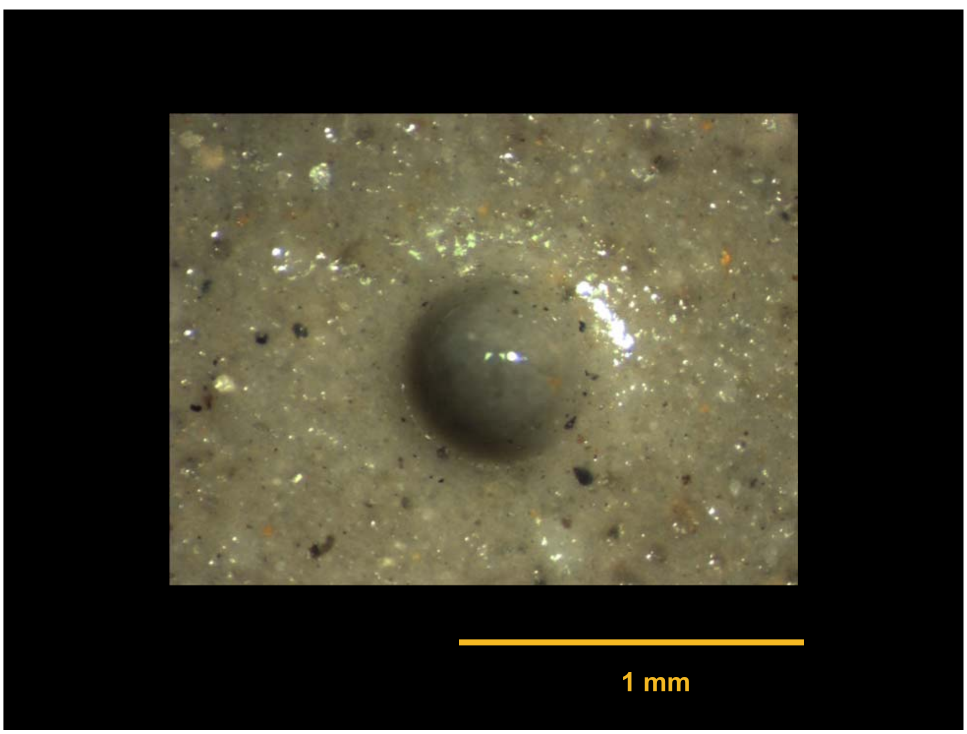
(additional information: see 2014 End of Year Report)

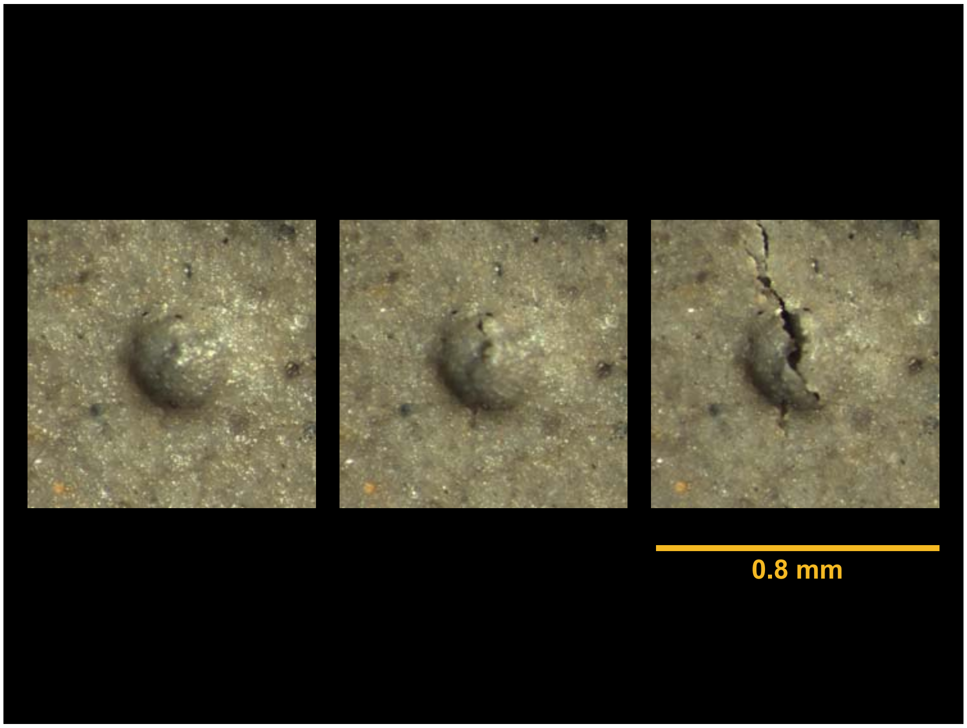
Crystal Growth in Sediments: Mechanics



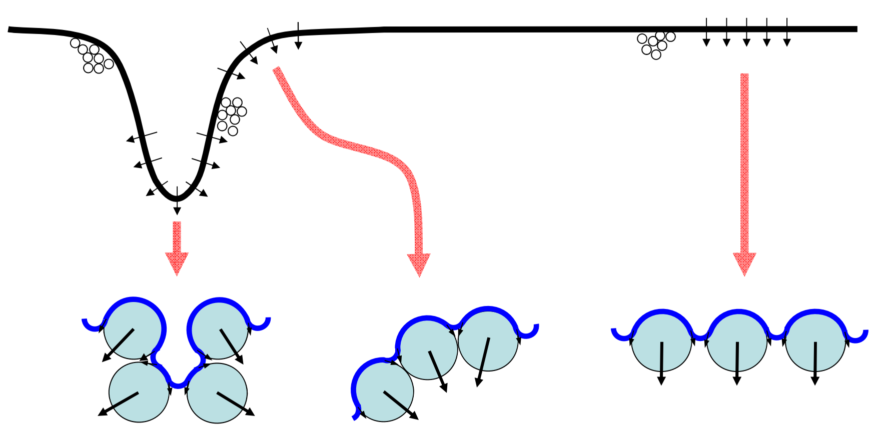
$$\gamma_{ice-soil} > \gamma_{ice-water} + \gamma_{soil-water}$$ (γ: Interfacial energy)





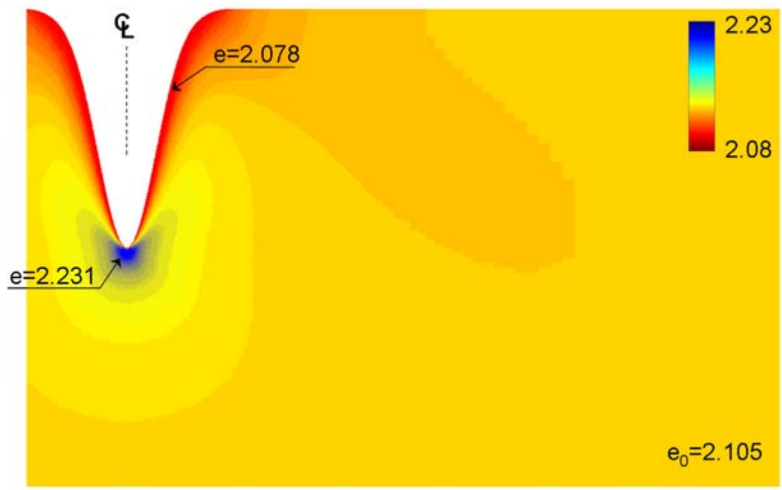


Invasion-Driven Fracture



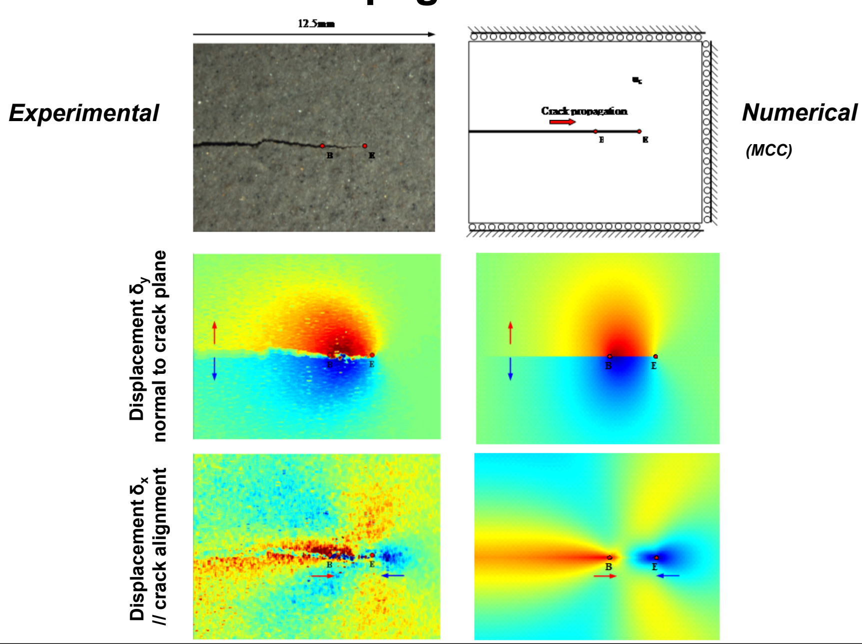
Tip Conditions

$$\Delta P = \frac{\rho \sigma_s S_s}{e}$$

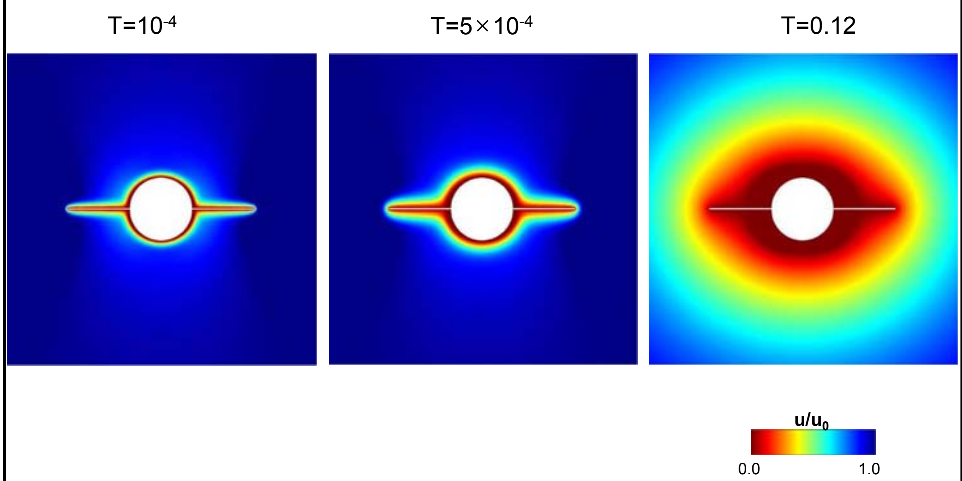


Sediment in compression EVERYwhere

Crack/Lense Propagation



Pressure Diffusion



Invasion vs. Localization

INVASION
Fluid invasion
Crystal growth in pores
Hyd.: *patchy saturation*

$$\frac{F_c}{N} = \frac{2\pi\sigma_{LV}}{\sigma' d}$$

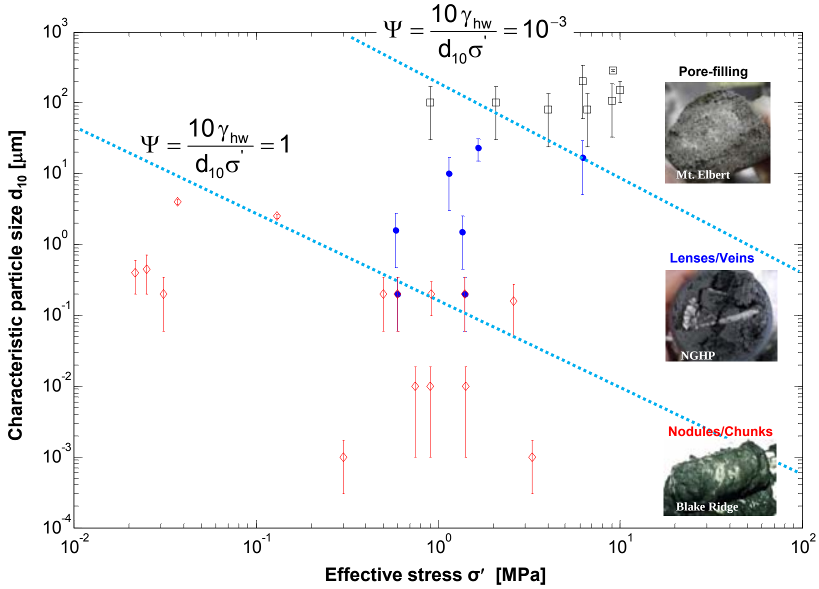
LOCALIZATION
Lenses
Fractures
Hyd.: *lenses*

0.1 — 1.0 — 10

coarse grained soils
high effective stress

fine grained soils
low effective stress

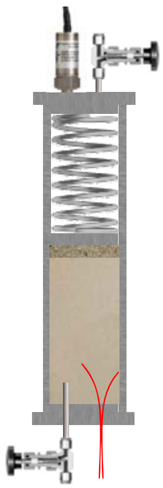
Hydrate Topology



Devices

(additional information: see 2014 End of Year Report)

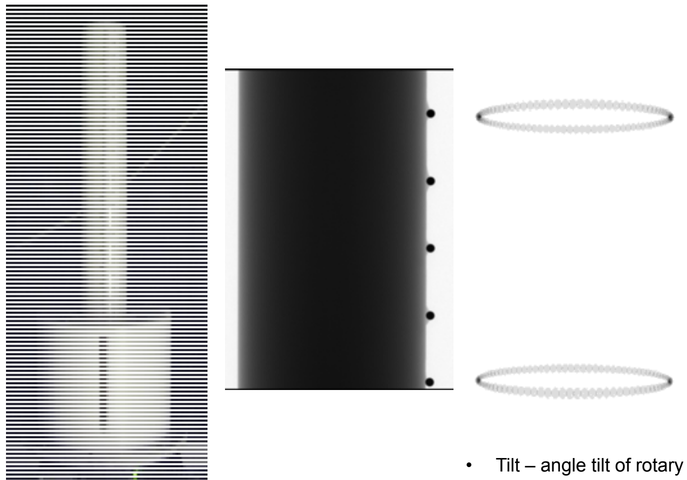
Chamber (X-ray transparent)



X-ray CT Scanner

X-ray CT Scanner

Calibration: specimen and protocol



- Tilt – angle tilt of rotary stage relative to detector
- SDD – source-to-detector distance
- SOD – source-to-object distance

Hydrate Formation in the Lab

(additional information: see 2014 End of Year Report)

Task 2

Laboratory protocol to form hydrate bearing clayey sediments

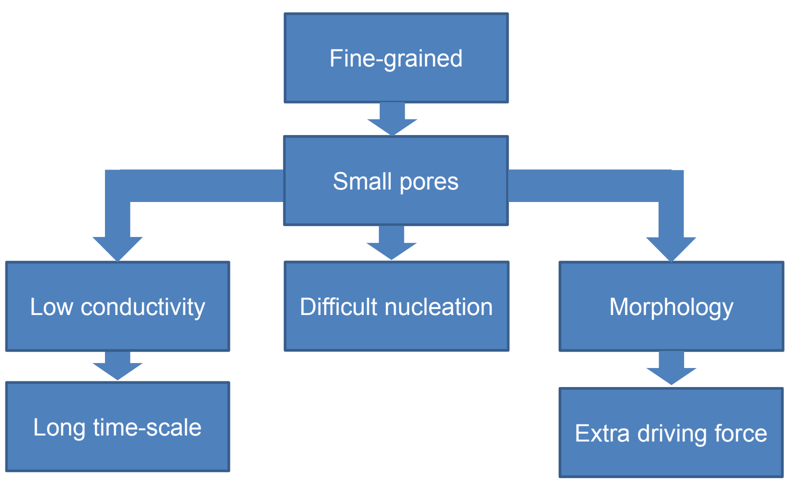
Dispersed nucleation followed by increased in effective stress and aging

- dispersed nucleation (partial water saturation, ice-seeding, and ground hydrate premixing)
- aging (e.g., thermal cycling) + stress: segregation into lenses?

Saturated blocky sediment + hydrate formation along discontinuities

- gas-driven fractures
- shear bands
- sediment slicing with intersecting planes
- pre-flushing freezing air ➔ gas flow + pressurization

Challenges in Fine-grained Sediments



Method 1: Spontaneous nucleation

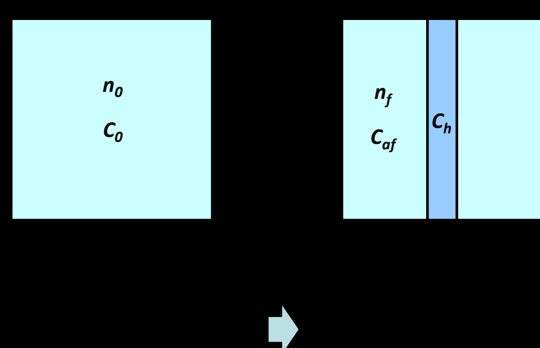
Henry's law:

$$M_{P,T} = P_{applied}\, k_H^0 \cdot \exp\left[\frac{-\Delta H}{R}\left(\frac{1}{T} - \frac{1}{298.15K}\right)\right]$$

concentration	M [mol/m^3]
enthalpy of the solution	ΔH=-14130 J/mol
Henry's law constant	k_H^o=1.3×10^3 M/atm at 298.15 K
universal gas constant	R=8.314 J/(mol·K).

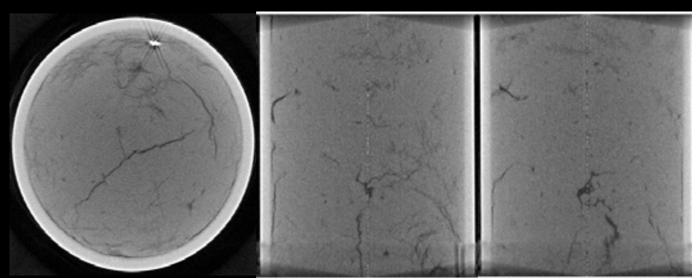
	Without hydrate (C_{bh})		**With hydrate (C_{ah})**	
	Pure water	Salt water (con. of NaCl)	Pure water	Salt water (con. of NaCl)
Methane concentration [mol/kg]	0.11 (273K,3MPa) 0.0974 (273K,50MPa)	0.00177 (1m) (273K,0.1MPa)	0.065 (274K,3.5MPa)	0.05184 (273K,10MPa)
	0.12 (276K,6.6MPa)		0.066 (274K,5MPa)	
	0.13 (285K,10MPa)		0.067 (275K,6.5MPa)	0.09689 (283K,10MPa)
	0.00247 (273K,0.1MPa)			

Method 1: Spontaneous nucleation

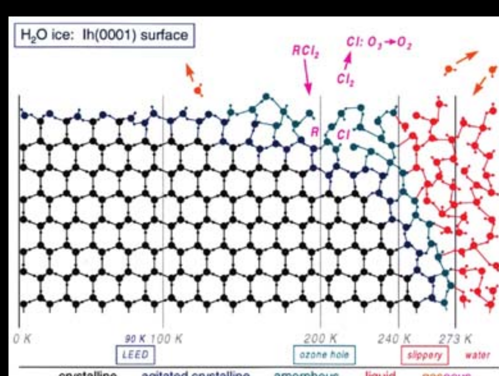


initial methane concentration:	C_0=0.14mol/kg (P=12MPa and T=288K)	***Lense λ*=4mm every *L*=1m**
CH_4 solubility – hydrate present:	C_{ah}=0.063mol/kg	
CH_4concentration in hydrate	C_h=8.06mol/kg	

Method 2: Avoid Diffusion ➔ THF Hydrate

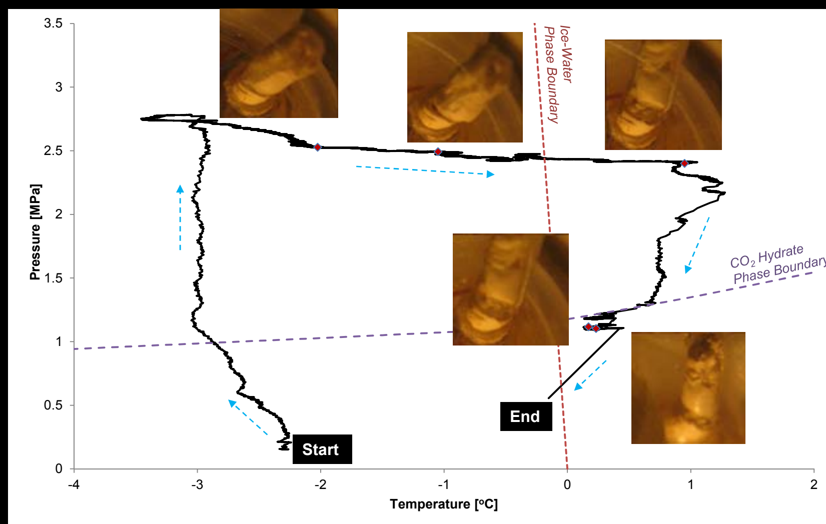


Multiple Methods: Ice ➔ Hydrate

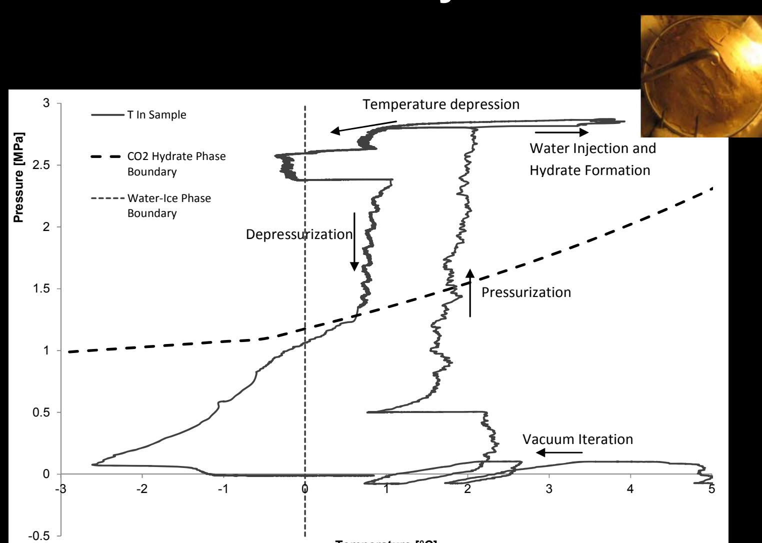


Ice starts pre-melting at the surface when T= -33 °C
The structure does not fuly solidify until 0K (Li, and Somorjai, 2007)

Method 3: Water sat + Freeze + I➔H

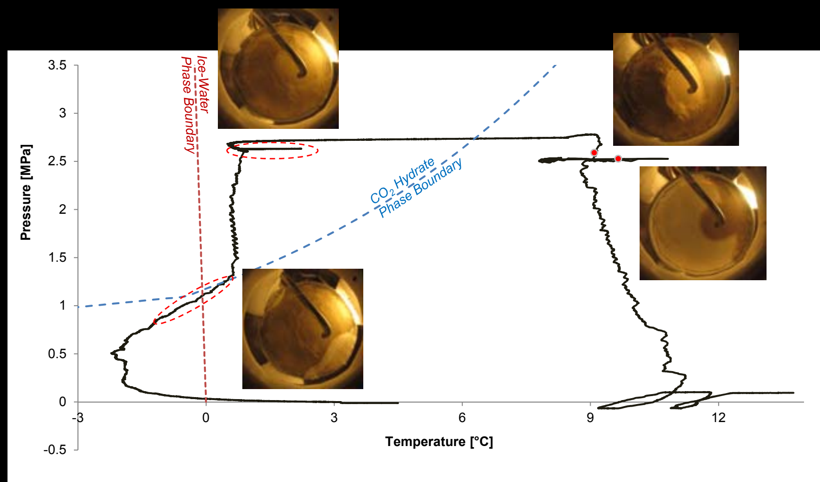


Method 4: Gas sat + Stability PT + Water



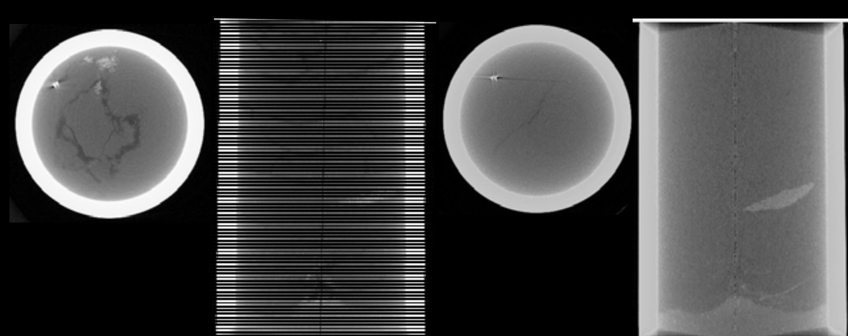
Store gas into diatom inner pores
Stimulated by diatoms found in NanKai Trough

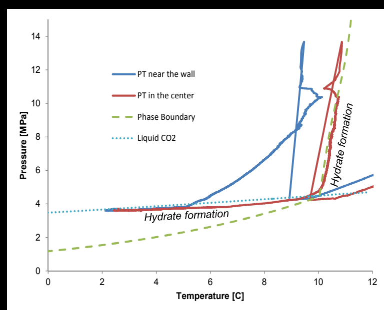
Method 5: Gas sat + Water + Stability PT

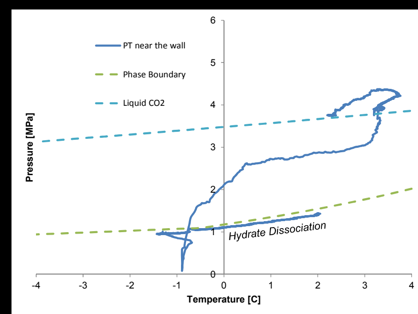


Store gas into diatom inner pores
Stimulated by diatoms found in NanKai Trough

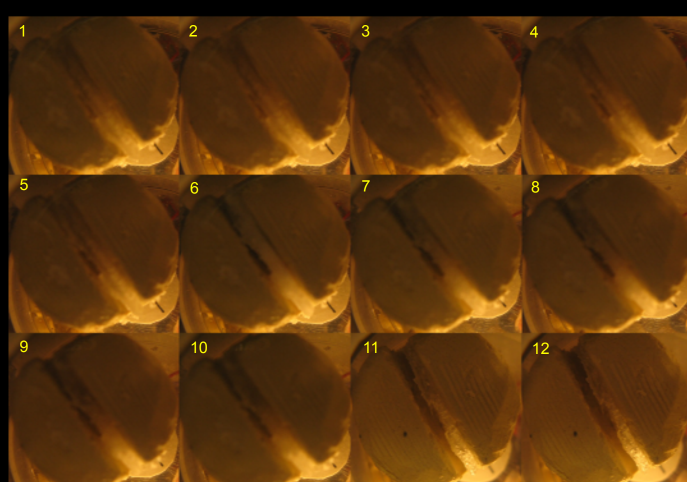
Method 5: Gas sat + Water + Stability PT







Method 6: Water sat + Ice + I➔H



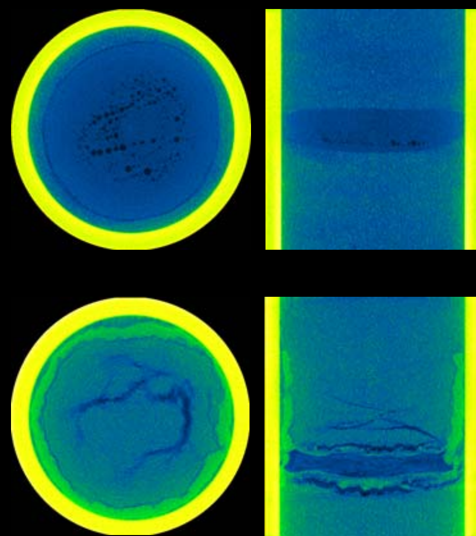
kaolin

Method 7: Dry + Ice + Stability PT

Strategy: Supply gas through dry sediment

before

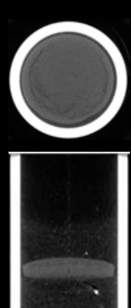
after

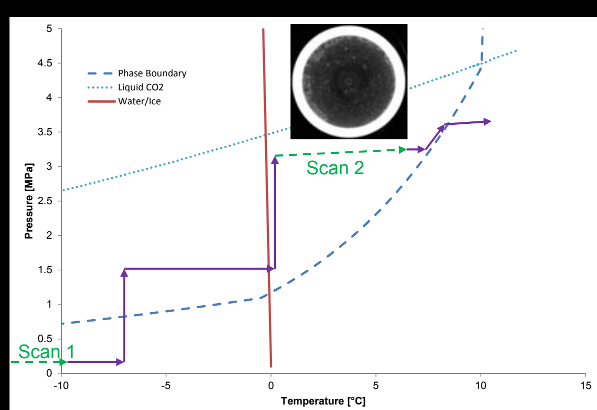


Kaolin

Method 8: Hydrophobic + Ice Lens + I➔H

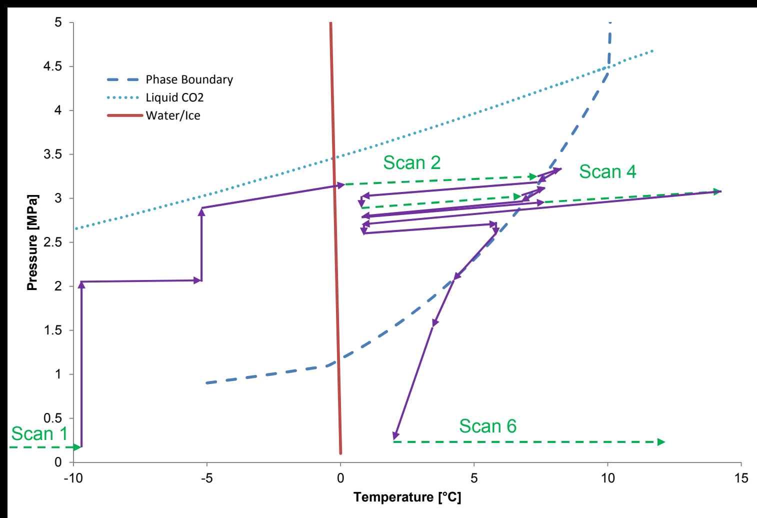
large lense



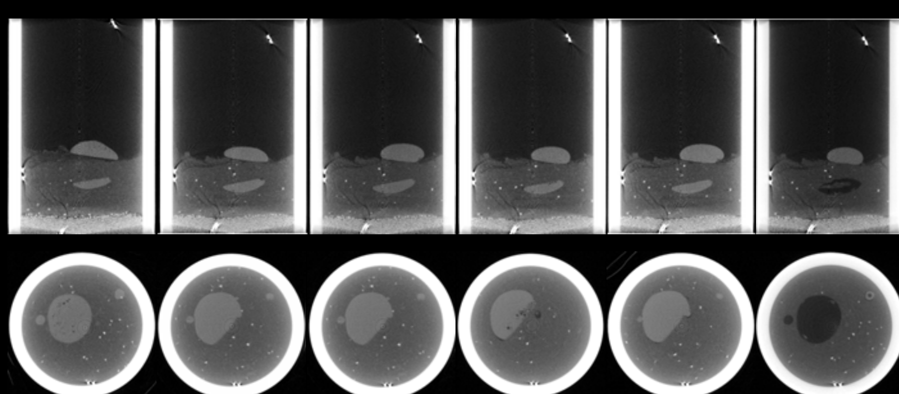


Method 8: Hydrophobic + Ice Lens + I➔H

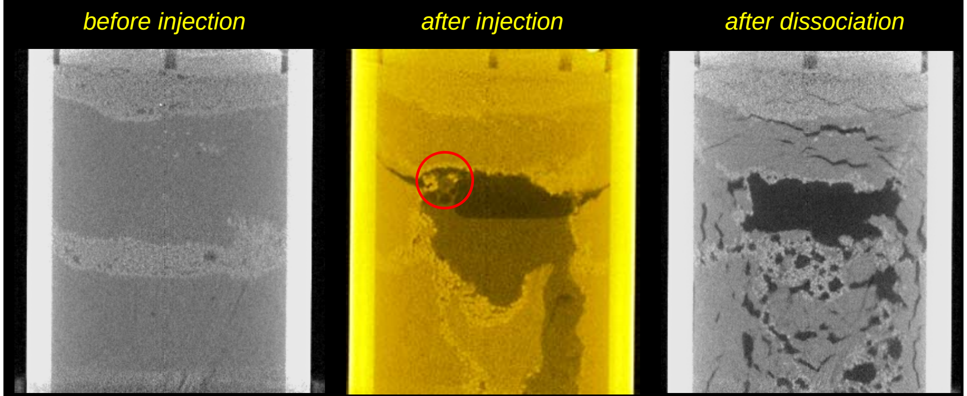
small lense



small lense

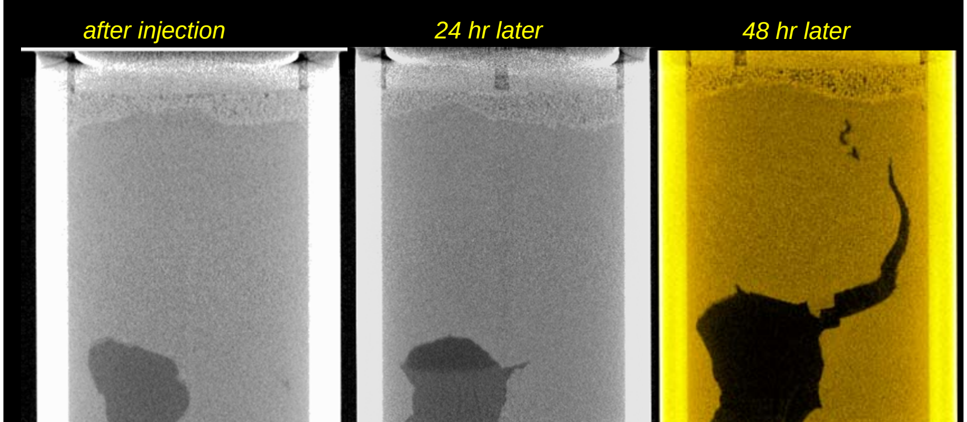


Method 9: Water sat + Stability + CO_2^L inject



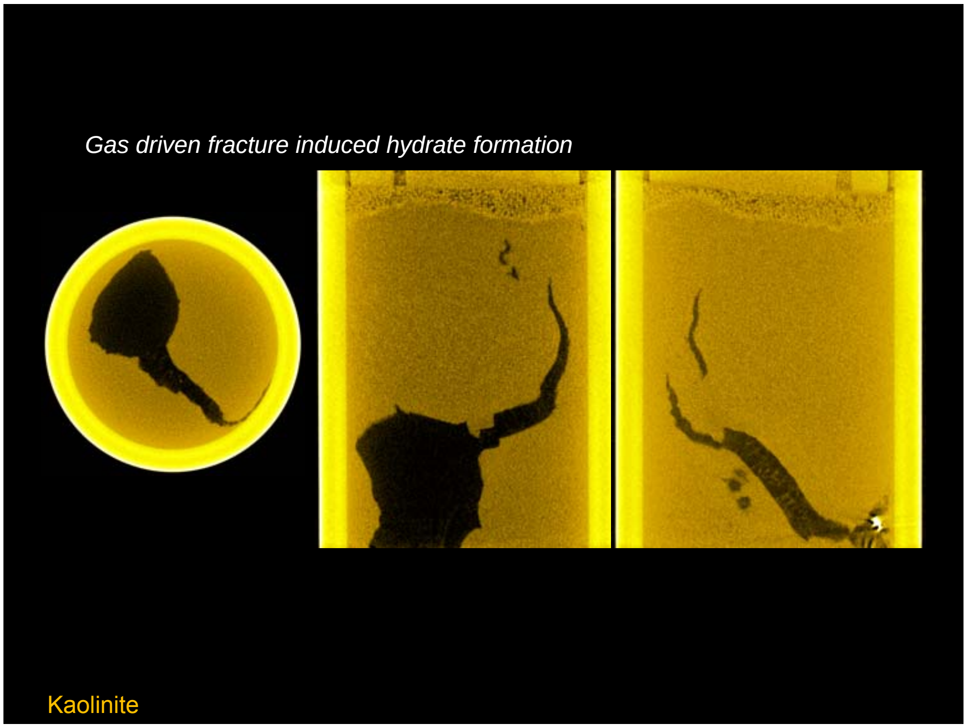
Diatom-sand layers

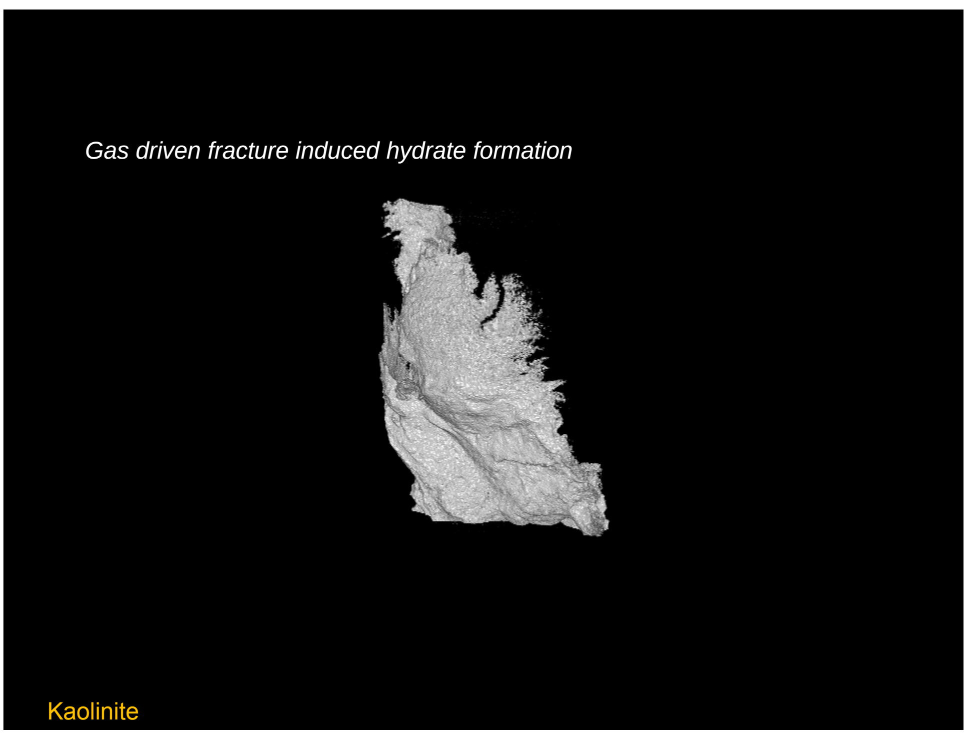
Method 9: Water sat + Stability + CO_2^L inject



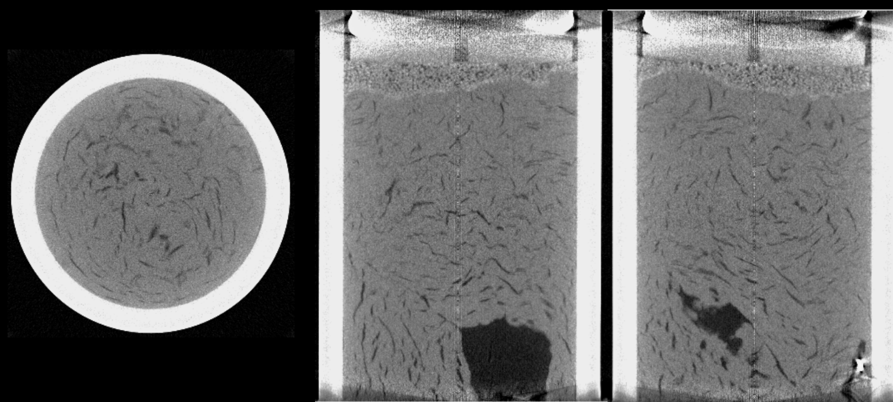
Gas driven fracture induced hydrate formation

Kaolinite


Gas driven fracture induced hydrate formation
Kaolinite

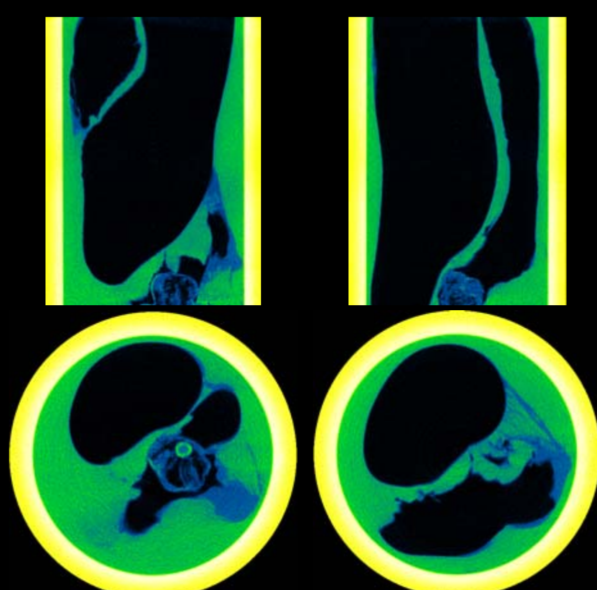

Gas driven fracture induced hydrate formation
Kaolinite

After dissociation



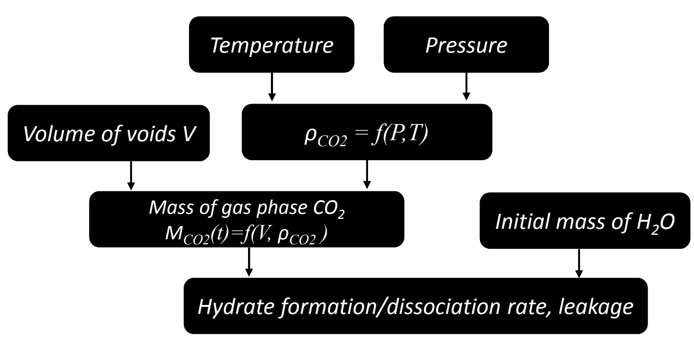
Kaolinite

Method 10: Gas-injection into Clay Slurry

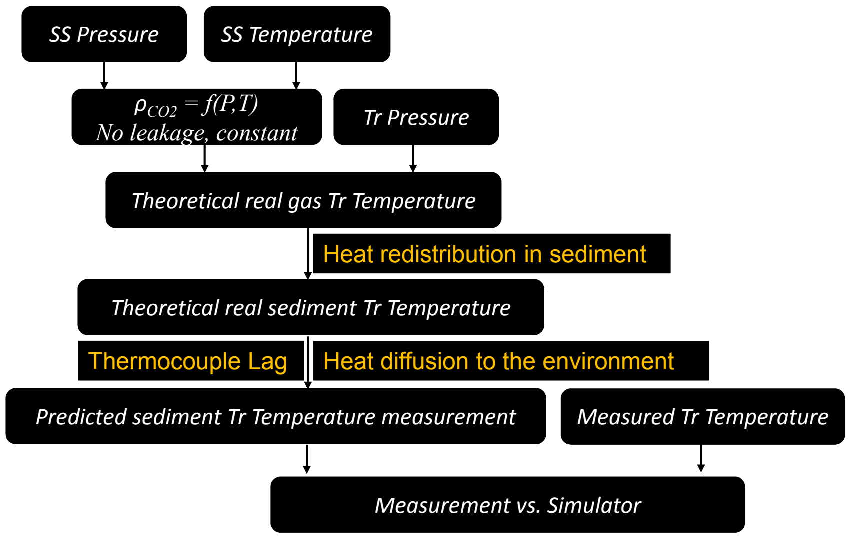


“Reservoir” Simulation

Mass: Measurement vs. Simulation



Thermal Analysis



Thermal Analysis - Thermocouple Response

$$\frac{dQ}{dt} = \pi r_t^2 l \rho_t c_t \frac{d(T_t(t))}{dt} \qquad q[t] = \frac{dQ}{dt} = h 2\pi r_t l [T_{tc}(t) - T_t(t)]$$

$$q^i = h 2\pi r_t l \left[\frac{(T_{tc}^{\,i} - T_t^{\,i}) + (T_{tc}^{\,i+1} - T_t^{\,i+1})}{2} \right]$$

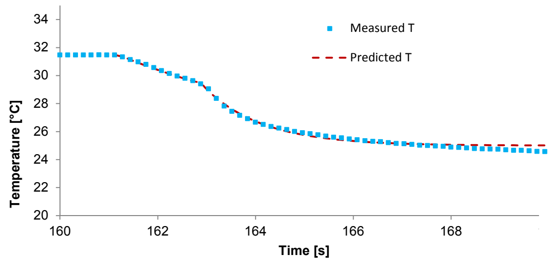
$$T_t^{i+1} = T_t^i + \frac{q^i \Delta t}{\pi r_t^2 l \rho_t c_t}$$

$$T_t^{i+1} = \frac{T_t^i + \alpha (T_{tc}^i - T_t^i + T_{tc}^{i+1})}{1+\alpha}$$

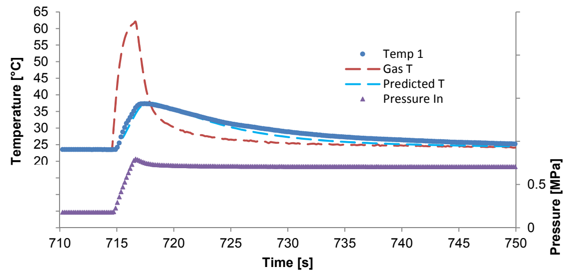
Where: $\alpha = \frac{h \Delta t}{r_t \rho_t c_t}$

Thermal Analysis-Thermocouple Lag

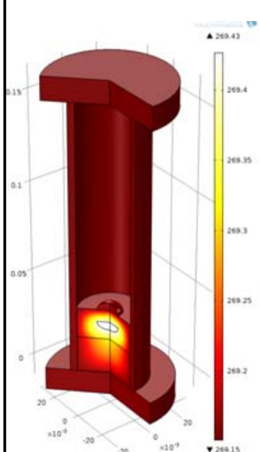
Thermocouple response during step temperature change in sediment

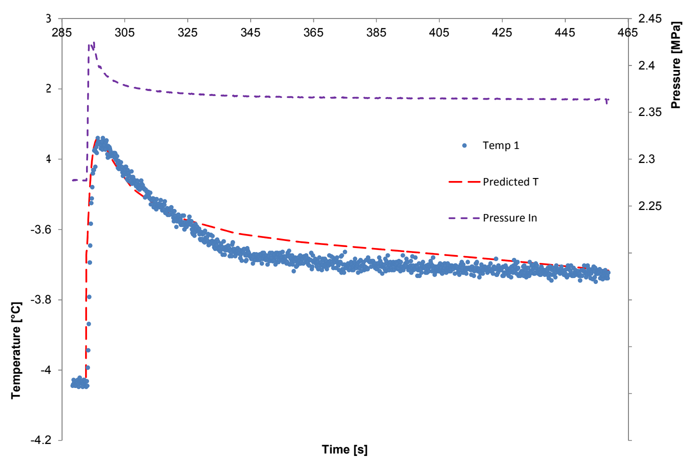


Thermocouple response during gas injection in air



Thermal Analysis – 3D FEM



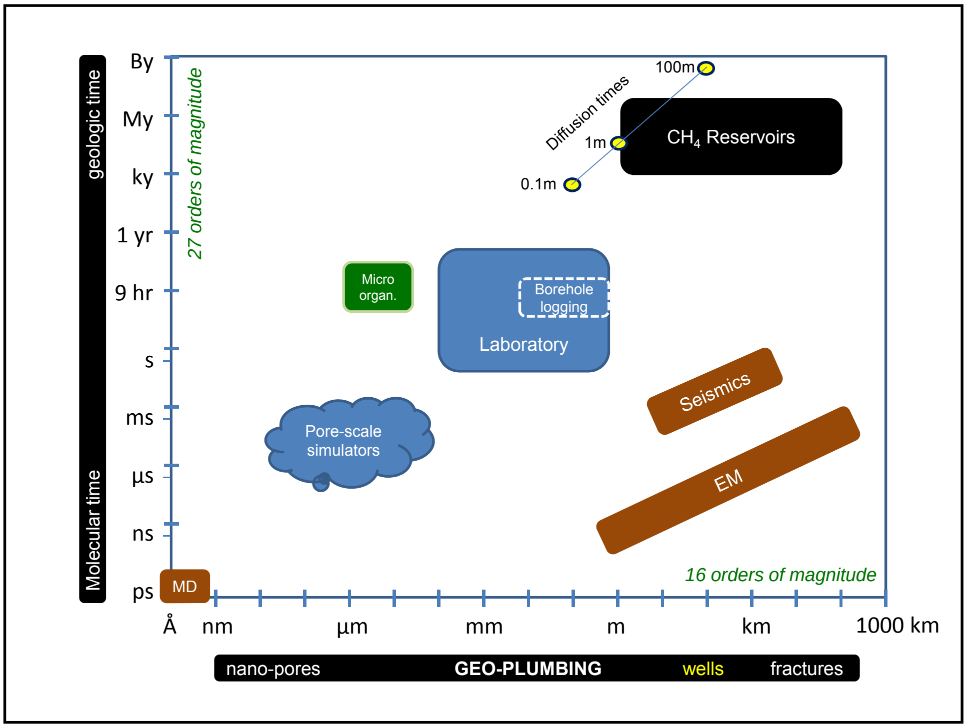


Physical properties

(additional information: see 2014 End of Year Report)

Properties - Needs

Mechanical	- Borehole stability - Seafloor subsidence - Slope stability / Submarine landslides
Thermal	- Reservoir modeling - Production enhancement
Hydraulic	- Hydraulic fracturing - Water production
Electrical	- Saturation estimations - Fracture tomography



Physical Properties

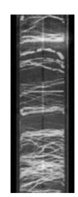
Numerical Simulations

Idealized topologies

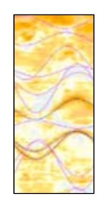
Physics inspired

Logging

Pressure core

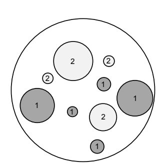


(Lee et al. 2013)



(Cook 2010)

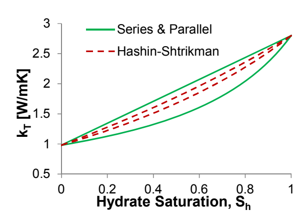
Effective Media Models



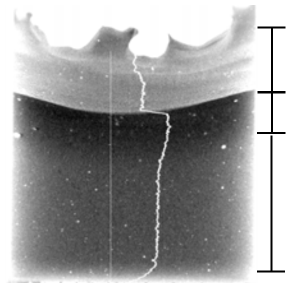
Bounds

$$k_{parallel} = \sum x_i \cdot k_i$$

$$k_{series} = \left(\sum \frac{x_i}{k_i} \right)^{-1}$$



Cryogenic Suction Induced Consolidation



Gas Production

(additional information: see 2014 End of Year Report)

Gas Production

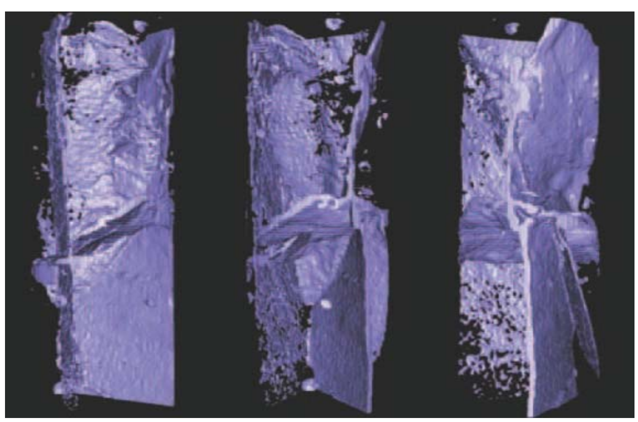
Prevailing Paradigm:
- Based on oil production

Consequently: Clayey sediments are not considered good prospects
- low permeability
- unacceptable high settlements if production by depressurization
- available technology driven by petroleum production
- lack of economically viable production concepts

Gas production from hydrate-bearing – All tested in sands
- depressurization
- heating
- inhibitors (including CO_2-CH_4 replacement)

Keys for a Paradigm Shift ?

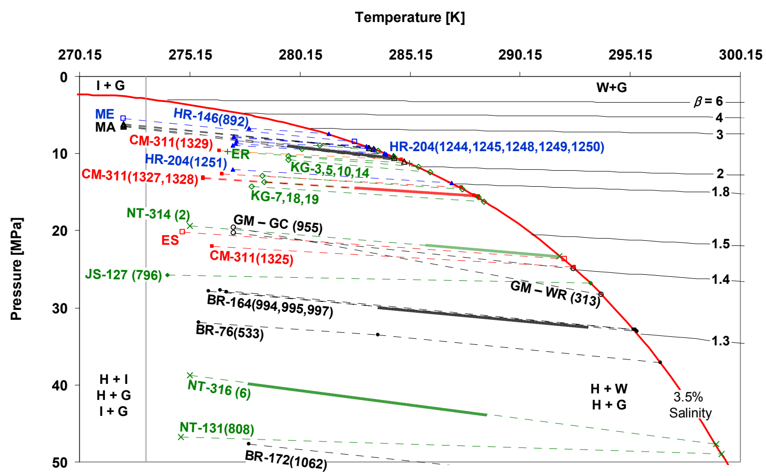
Key #1: Interconnected hydrate lenses



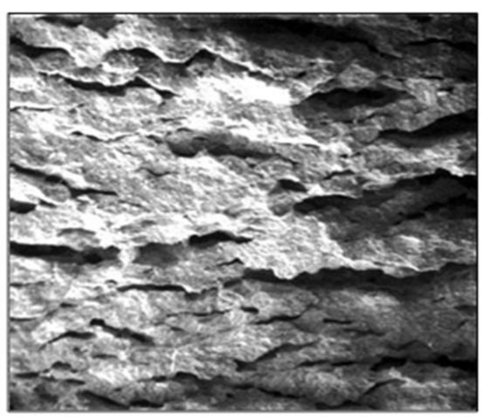
Korean cores - Park et al., 2009

Key #2: Volume expansion

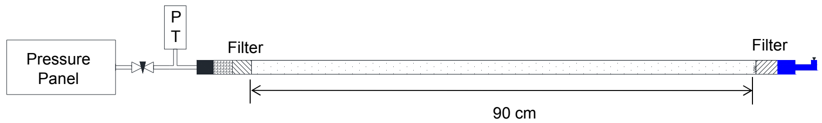
$$\beta = \frac{V_g + V_w}{V_h} = \frac{z\lambda RT_g}{P_w + \frac{2\Gamma}{R_{th}}\cos\theta} + \frac{18\chi}{16+18\chi}\frac{\rho_h}{\rho_w}$$

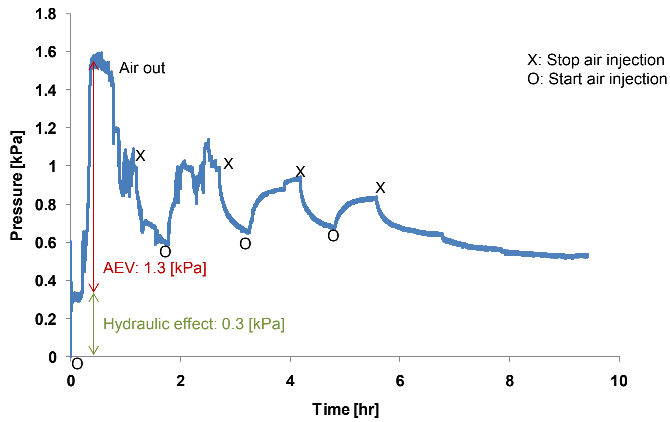


Key #3: Gas driven fractures

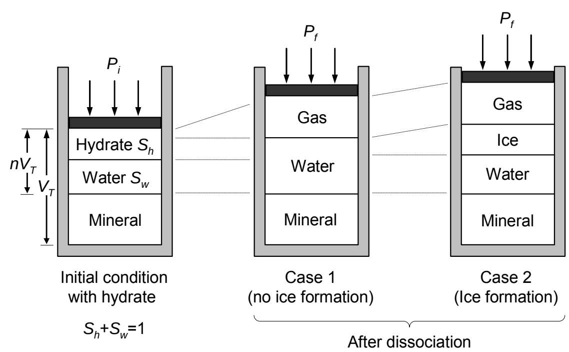


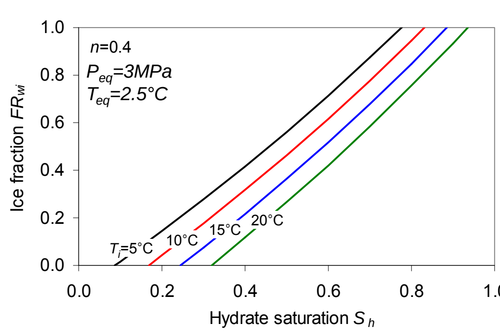
Key #4: Migration in layered sediments



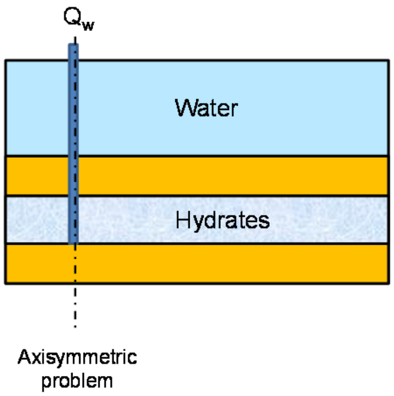


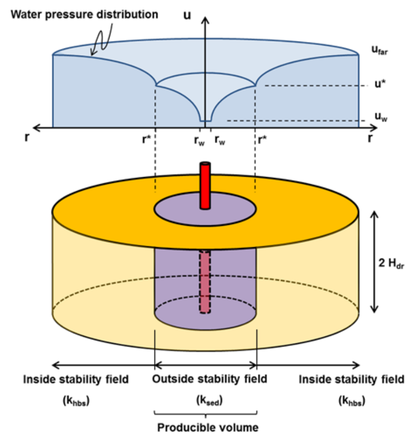
Key #5: Heat Source



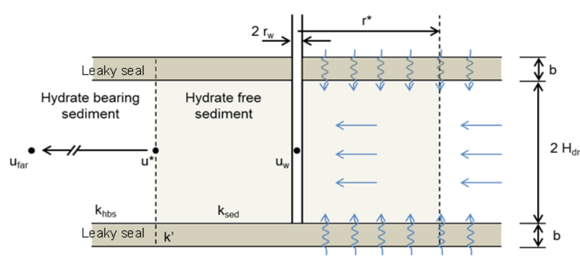


But … #1: Limited Volume of Influence

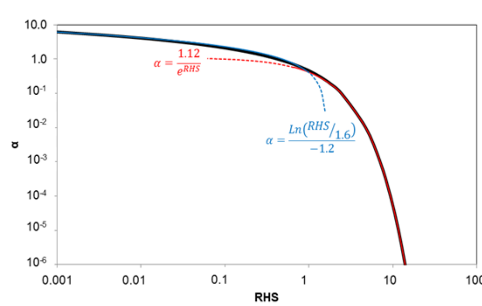




But … #1: Limited Volume of Influence



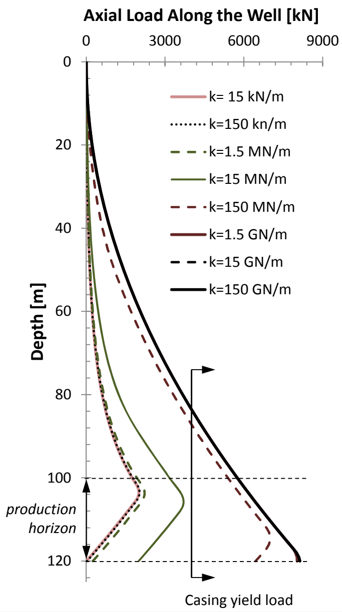
$$K_0\left(\sqrt{\frac{k'}{k_{hbs}}\frac{2\,r^{*2}}{H\,b}}\right)=K_0\left(\sqrt{\frac{k'}{k_{sed}}\frac{2\,r_w^2}{H\,b}}\right)\frac{k_{hbs}\,(u_{far}-u^*)}{k_{sed}\,(u^*-u_w)}$$

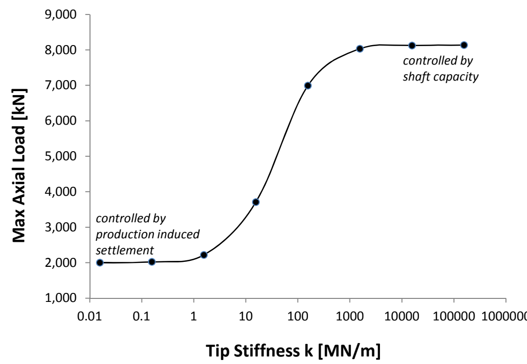


Embodied energy EE [J]

$$EE = \varepsilon\, n\, S_{hyd}\, V\, E_d\, \rho_{hyd}$$

But … #2: Sediment-Well Interaction





Goals – Objectives - Background

Natural HBF – Fine Grained (Analogues)

Underlying Physics

Devices

Hydrate Formation in the Lab

“Reservoir” Simulation

Physical Properties

Gas Production

Next – Team – Schedule

Coming up?

Experimental
Extend lense formation after injection
Formation in slurries: shallow accumulations

Numerical
Extend to real topologies

Production
Emphasis on shallow accumulations

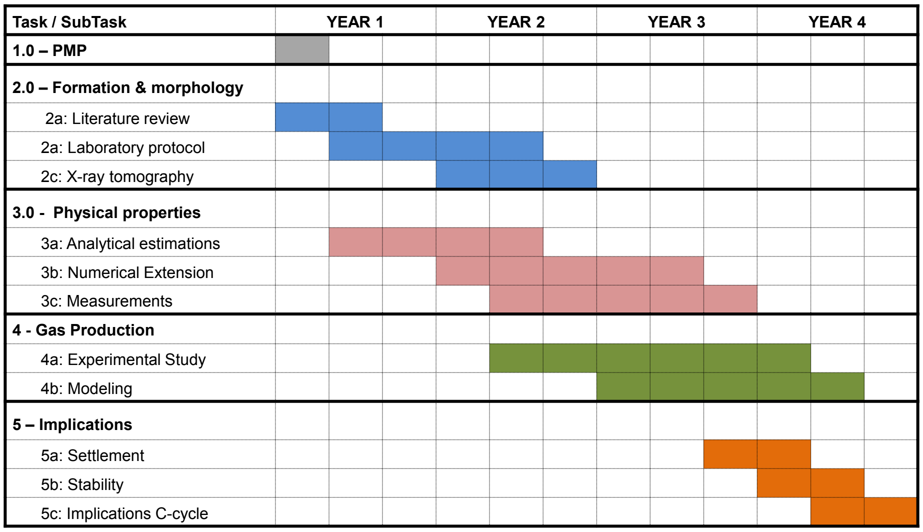
Team:

Liang Lei (4th year)
Seth Mallett (3rd year)
NN (1st year)

Sheng Dai

Marco Terzariol (Production – GT/KAUST)
Junbong Jang (Production – GT/KAUST)
Hosung Shin (Well-sediment – Ulsan U.)

Schedule


Task / SubTask
YEAR 1
YEAR 2
YEAR 3
YEAR 4
1.0 – PMP
2.0 – Formation & morphology
2a: Literature review
2a: Laboratory protocol
2c: X-ray tomography
3.0 - Physical properties
3a: Analytical estimations
3b: Numerical Extension
3c: Measurements
4 - Gas Production
4a: Experimental Study
4b: Modeling
5 – Implications
5a: Settlement
5b: Stability
5c: Implications C-cycle

MILESTONE LOG

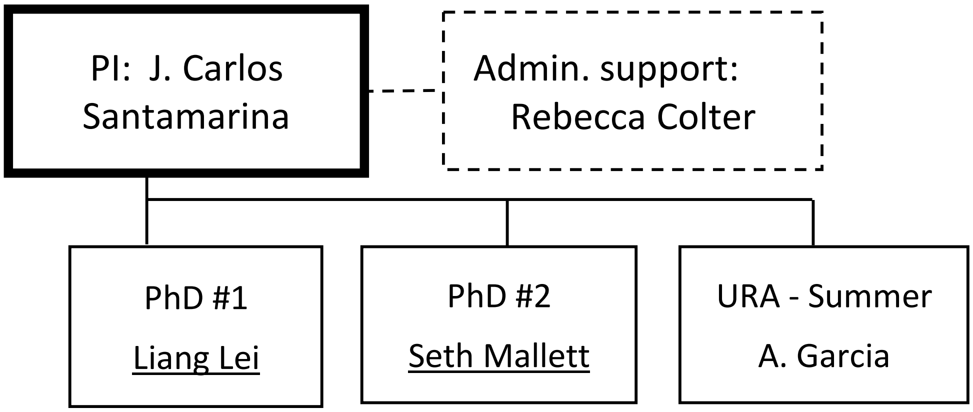
Milestone	Planed completion date	Actual completion date	Verification method	Comments
Literature review	5/2013	5/2013	Report	Completed first phase. Will continue throughout the project
Preliminary laboratory protocol	8/2013	8/2013	Report (with preliminary validation data)	this and previous reports
Cells for Micro-CT	8/2013	8/2013	Report (with first images)	this and previous reports
Compilation of CT images: segregated hydrate in clayey sediments	8/2014	In progress	Report (with images)	
Preliminary experimental studies on gas production	12/2014	12/2014	Report (with images)	Observed in experiments. Gas production engineering is conducted analytically/numerically
Analytical/numerical study of 2-media physical properties	5/2015	6/2015	Report (with analytical and numerical data)	
Experimental studies on gas production	12/2015		Report (with data)	Observed in experiments. Gas production engineering is conducted analytically/numerically
Early numerical results related to gas production	5/2016	In progress	Report	
Comprehensive results (includes Implications)	9/2016		Comprehensive Report	

PRODUCTS

- **Publications:** In progress
- **Presentations:** In progress
- **Website:** Publications and key presentations are included in http://pmrl.ce.gatech.edu/ (for academic purposes only)
- **Technologies or techniques:** X-ray tomographer and X-ray transparent pressure vessel
- **Inventions, patent applications, and/or licenses:** None at this point.
- **Other products:** None at this point.

PARTICIPANTS & OTHER COLLABORATING ORGANIZATIONS

Research Team: The current team is shown next. We anticipate including external collaborators as the project advances



IMPACT

While it is still too early to assess impact, we can already highlight preliminary success of exploring hydrate lenses morphology in real systems, and analogue studies using a high resolution tomographer.

CHANGES/PROBLEMS:

None at this point.

SPECIAL REPORTING REQUIREMENTS:

We are progressing towards all goals for this project.

BUDGETARY INFORMATION:

As of the end of this research period, expenditures are summarized in the following table.

Note: in our academic cycle, higher expenditures typically take place during the summer quarter.

Baseline Reporting Quarter DE-FE009897	Budget Period 3							
	Q1		Q2		Q3		Q4	
	10/1/14 - 12/31/14		1/1/15 - 3/31/15		4/1/15 - 6/30/15		7/1/15 - 9/30/15	
	Q1	Cumulative Total	Q2	Cumulative Total	Q3	Cumulative Total	Q4	Cumulative Total
Baseline Cost Plan								
Federal Share	40,059	341,026	40,059	381,086	40,059	421,145	40,059	461,204
Non-Federal Share	11,587	100,272	11,587	111,860	11,587	123,447	11,587	135,034
Total Planned	51,647	441,299	51,647	492,945	51,647	544,592	51,647	596,238
Actual Incurred Cost								
Federal Share	57,809	333,090	56,843	389,933	35,283	425,216		
Non-Federal Share	25,961	100,696	36,582	137,278	0	137,278		
Total Incurred Costs	83,770	433,786	93,425	527,211	35,283	562,494		
Variance								
Federal Share	17,749	-7,936	16,784	8,848	-4,776	4,071		
Non-Federal Share	14,374	424	24,995	25,419	-11,587	13,831		
Total Variance	32,123	-7,512	41,779	34,266	-16,364	17,903		

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