

**Energy for the Future –
CO2 Sequestration in Hydrates with
Associated Methane Gas Production**

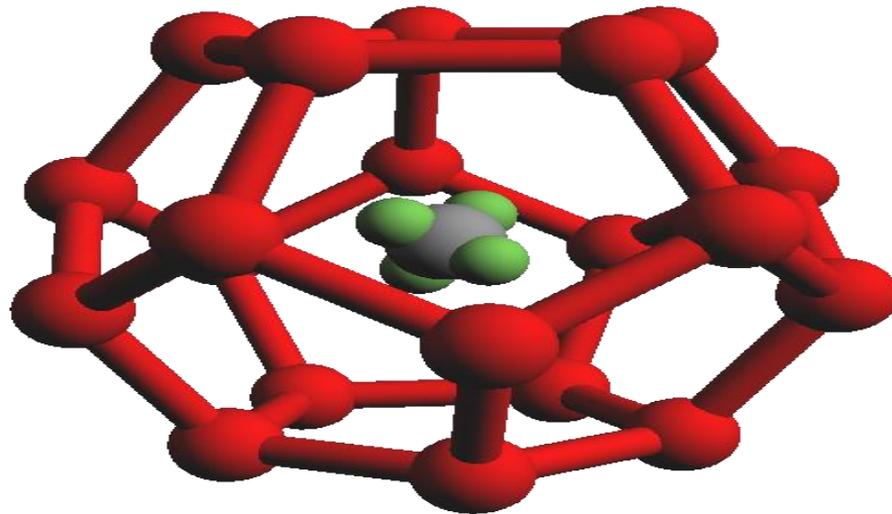
by

**Prof. Arne Graue
Dept. of Physics and Technology
University of Bergen, NORWAY**

Whole Value Chain CCUS Student Week, Oct. 15th - 19th, 2018, Golden, CO, USA.

GAS HYDRATES

- Solid state of gas and water where the water molecules form a cavity that encapsulates the guest molecule.



What is natural gas hydrate?

- Methane and other small non-polar (or slightly polar) molecules immersed in water will induce organisation of the water structure that maximizes the entropy.
- Above certain pressures, and below certain temperatures, this results in a phase transition over to a solid like structure.

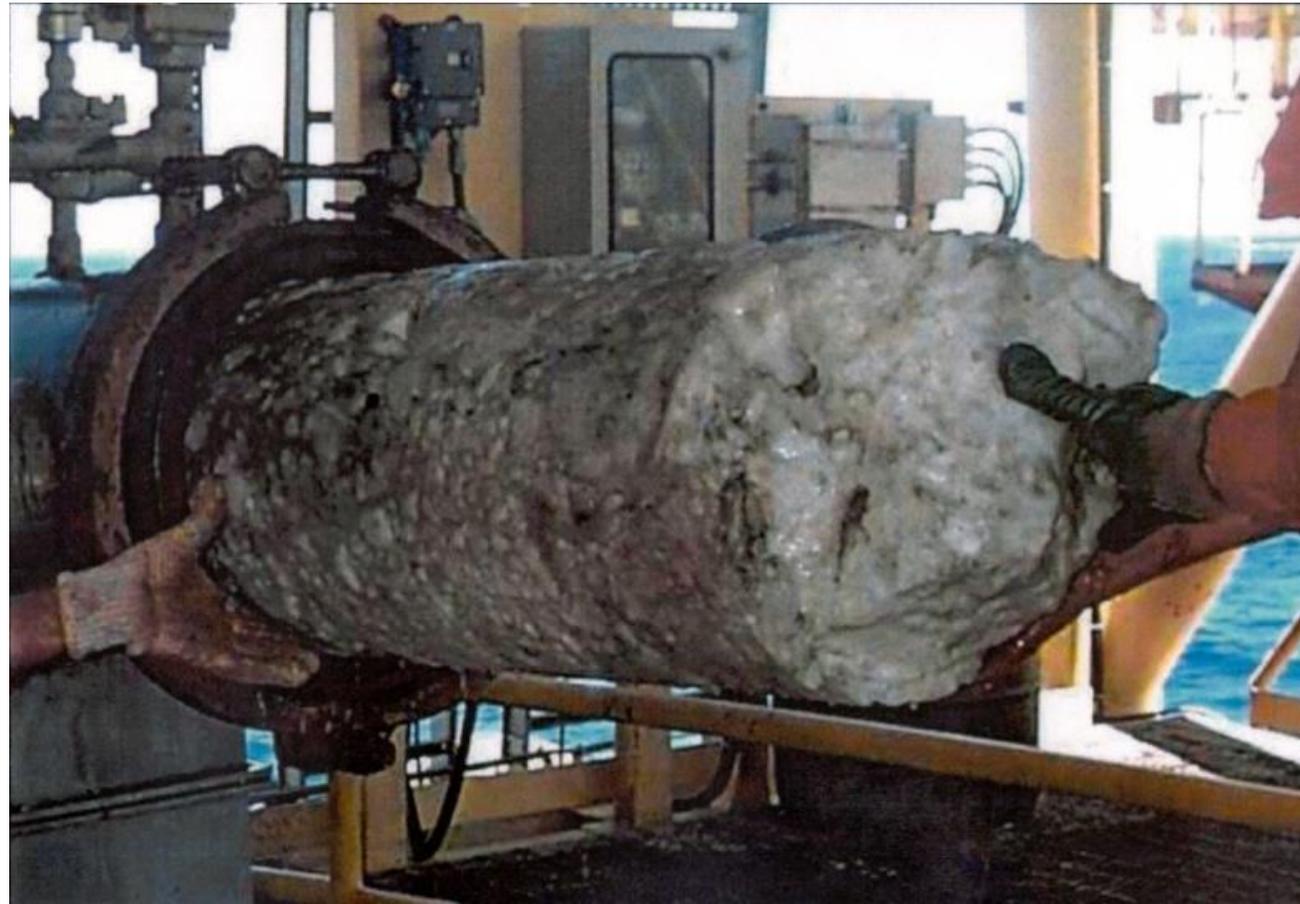
The glass to the right contains water at 0 C

The pipe to the left contains hydrate at 5 C



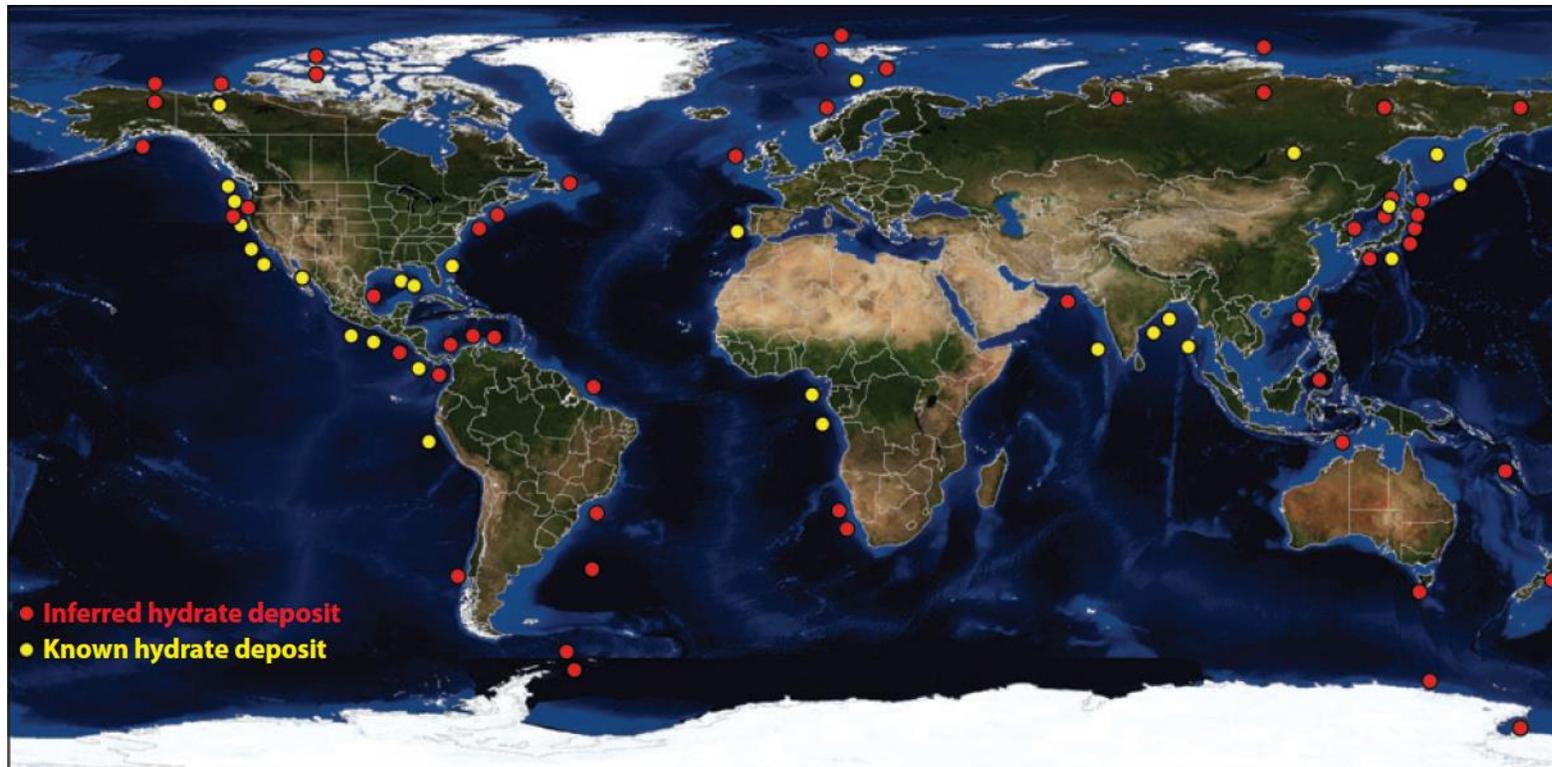
Why are hydrates of interest?

- Initial interest as a curiosity
- Plugging of production and transportation pipelines



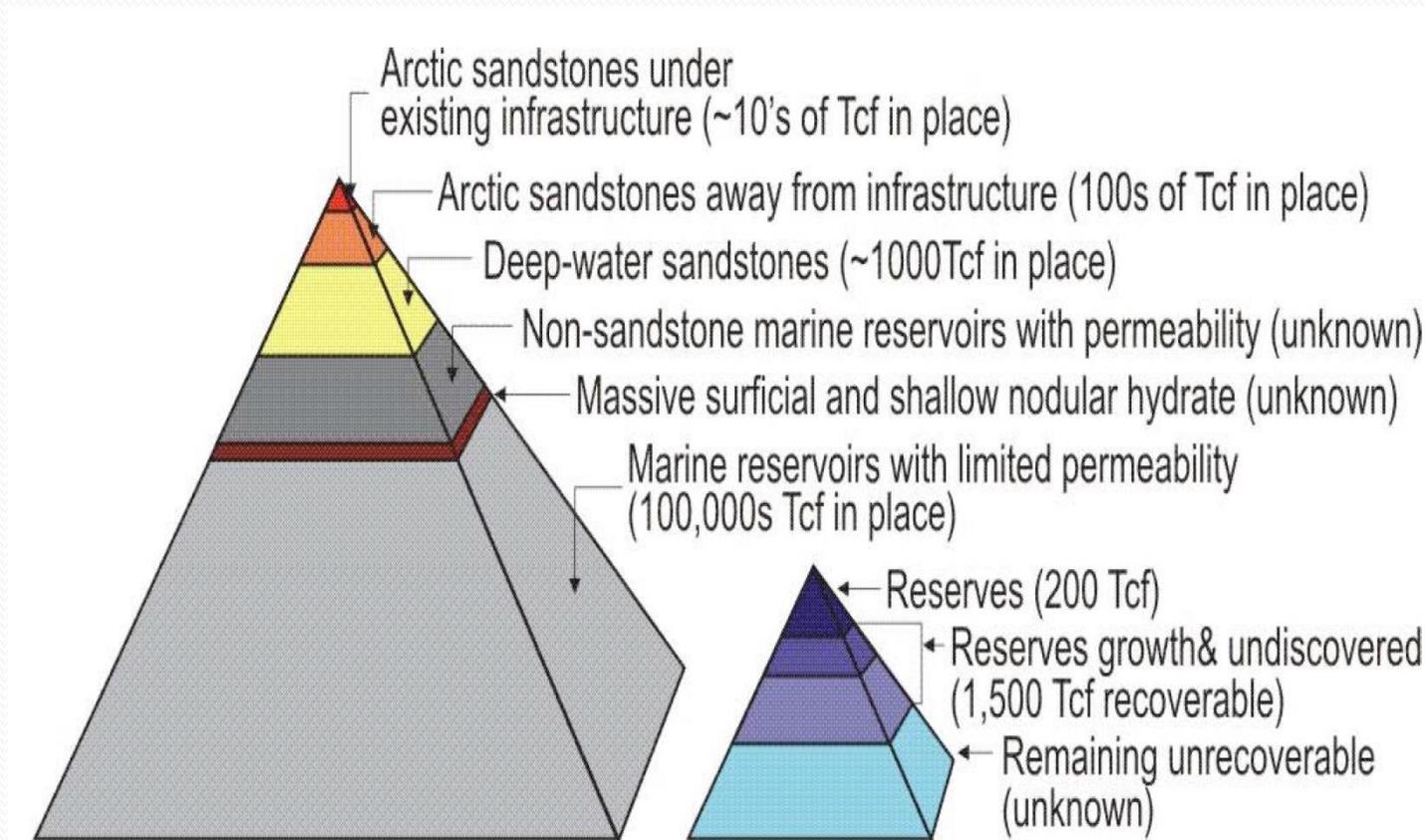
Renewed interest

- Significant amount of energy
 - Permafrost regions
 - Marine environments (high water column)



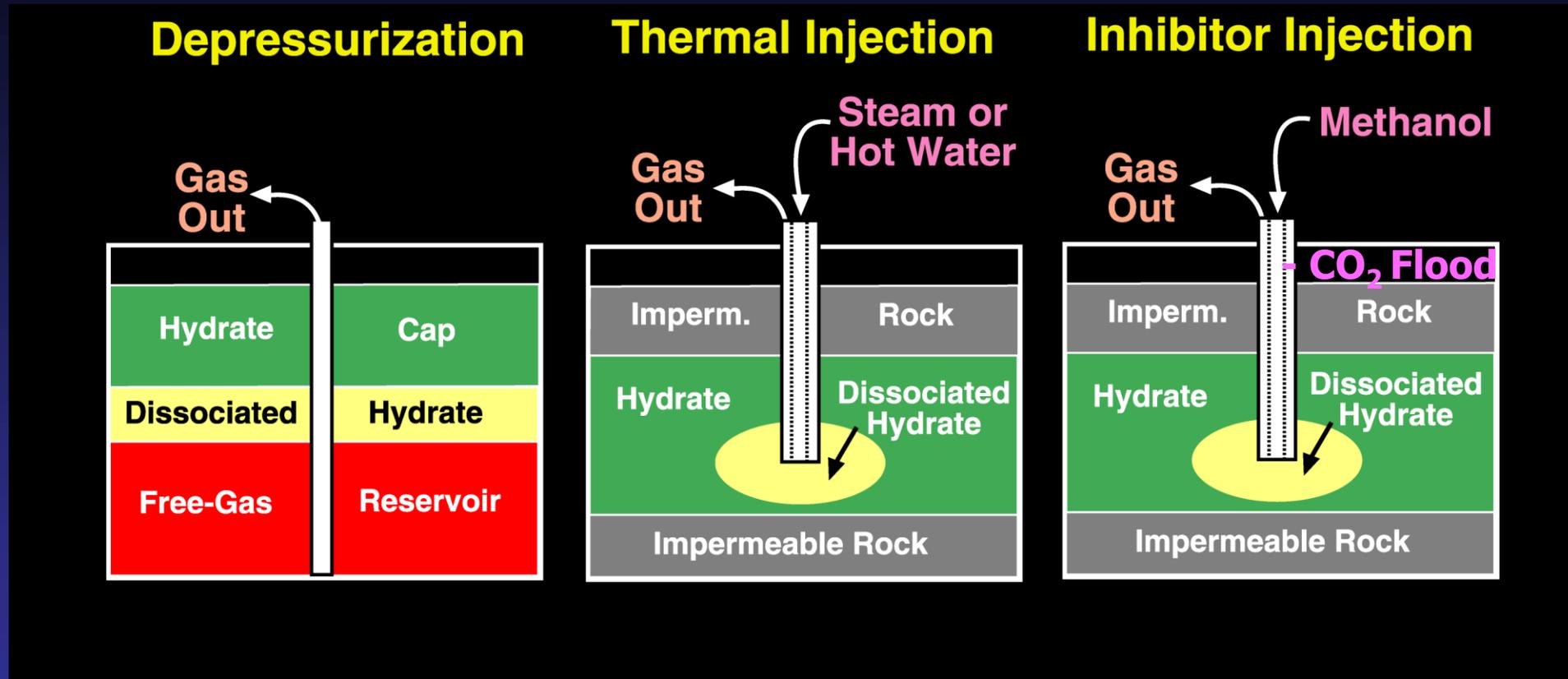
Hydrate as Energy Resource

Ref.: *Fire in the Ice*, U.S. Department of Energy • Office of Fossil Energy • National Energy Technology Laboratory



Gas Hydrates Resource Pyramid (left). To the right is an example gas resources pyramid for all non-gas-hydrate resources.

Gas Hydrate Production Methods



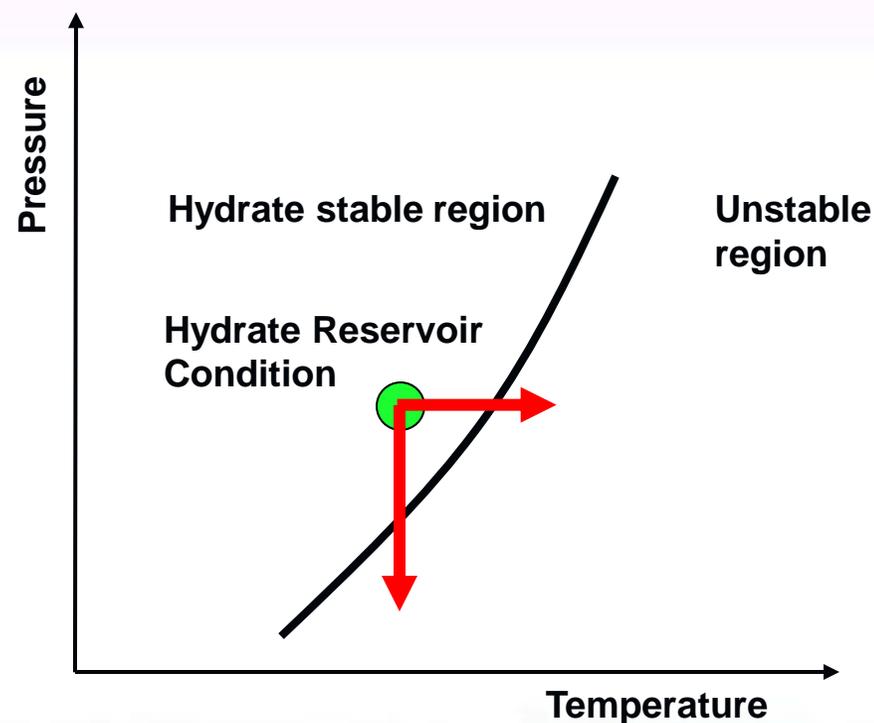
Modified from "GAS HYDRATES OF NORTHERN ALASKA", January 2005
Evaluation of Alaska North Slope Gas Hydrate Energy Resources: A Cooperative Energy Resource Assessment Project
US Bureau of Land Management, US Geological Survey, & State of Alaska Division of Geological and Geophysical Surveys
Bob Fisk, USBLM, Anchorage, Alaska, Tim Collett, USGS, Denver, Colorado & Jim Clough, DGGS, Fairbanks, Alaska

Depressurization: PROS AND CONS

- Pros
 - All of the methane is accessible for production by depressurization; at sufficient low pressures
- Cons
 - Large pressure drop may be needed to initiate hydrate dissociation
 - Water production may represent an economic challenge and an environmental issue
 - Hydrate melts; causing possible unstable formation

GAS HYDRATE PRODUCTION METHODS

- Move the gas hydrate outside its stability region
 - Depressurization
 - Thermal stimulation
 - Hydrate inhibitors
- **CO₂ exchange**



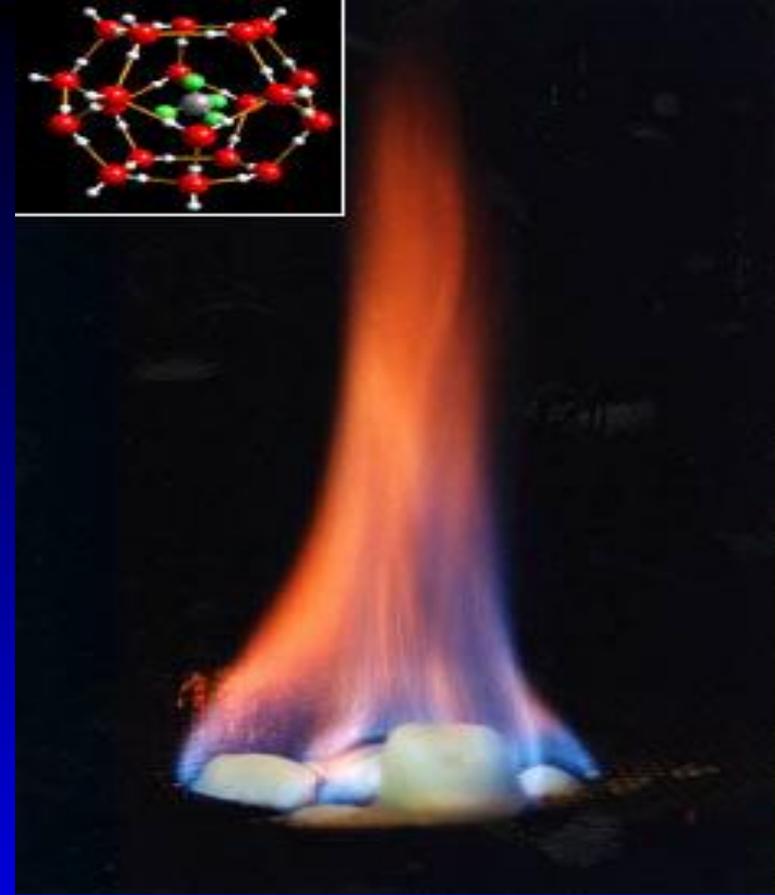
CO₂ Exchange: Project Motivation

- **The amount of energy bound in hydrates may be more than twice the world's total energy resources in conventional hydrocarbon reservoirs; i.e. oil-, gas- and coal reserves**
- **Simultaneous CO₂ Sequestration**
- **Win-win situation for gas production**
- **Need no hydrate melting or heat stimulation**
- **Spontaneous process**
- **No associated water production**
- **Formation integrity**

**CO₂ storage in hydrates
with associated methane
gas production**

Challenge:

**Determine exchange mechanisms during potential
sequestration of CO₂ to produce methane from hydrates**



Three component Phase Field Theory

$$F = \int d\mathbf{r} \left\{ \frac{\varepsilon^2 T}{2} (\nabla \phi)^2 + \sum_{i,j=1}^3 \frac{\varepsilon_{i,j}^2 T}{4} (c_i \nabla c_j - c_j \nabla c_i)^2 + f_{bulk}(\phi, c_1, c_2, c_3, T) \right\}$$

$$f_{bulk} = wTg(\phi) + [1 - p(\phi)]f_S(c_1, c_2, c_3, T) + p(\phi)f_L(c_1, c_2, c_3, T)$$

$$\dot{\phi} = -M_\phi \frac{\delta F}{\delta \phi} + \zeta_\phi$$

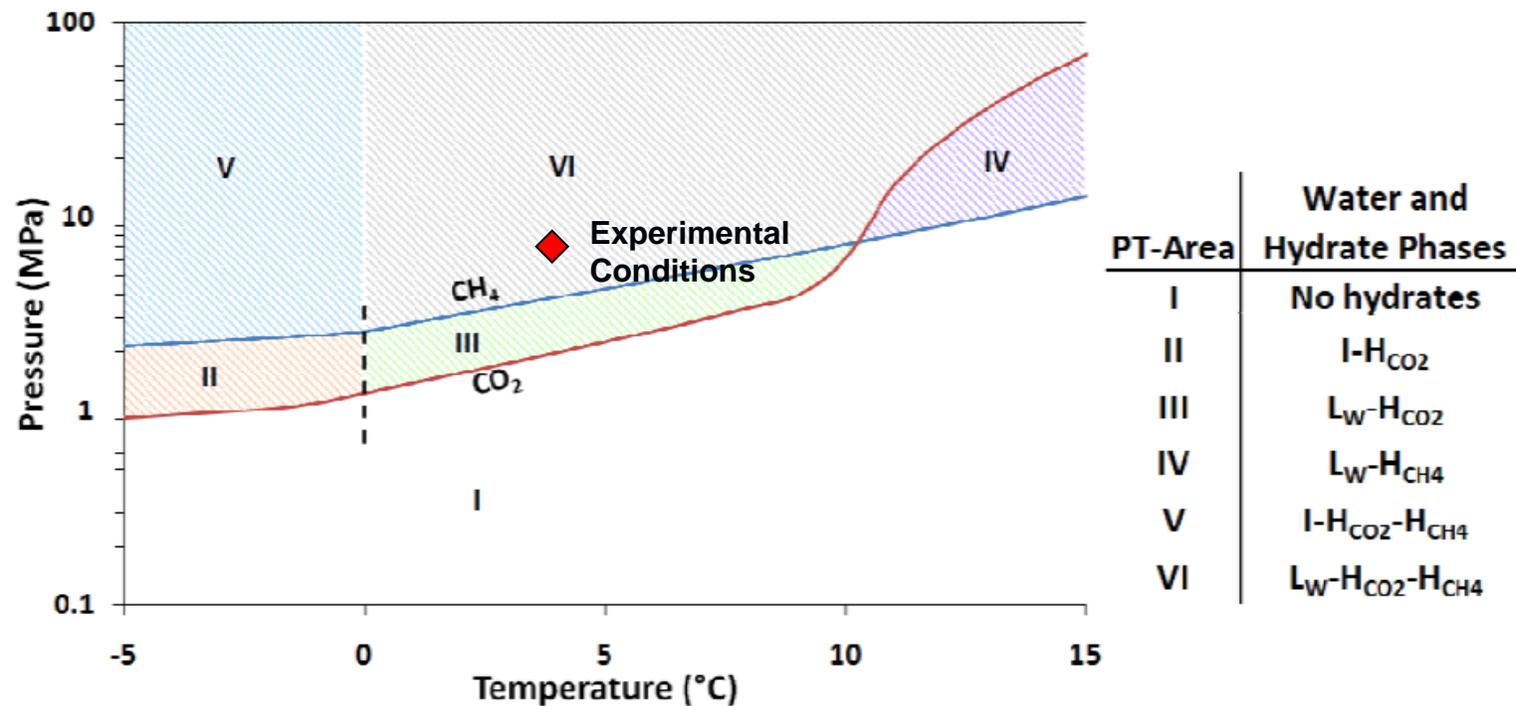
$$\sum_{i=1}^3 c_i = 1$$

$$\dot{c}_i = \nabla M_{c_i}(c_1, c_2, c_3) \nabla \left(\frac{\delta F}{\delta c_i} - \zeta_i \right)$$

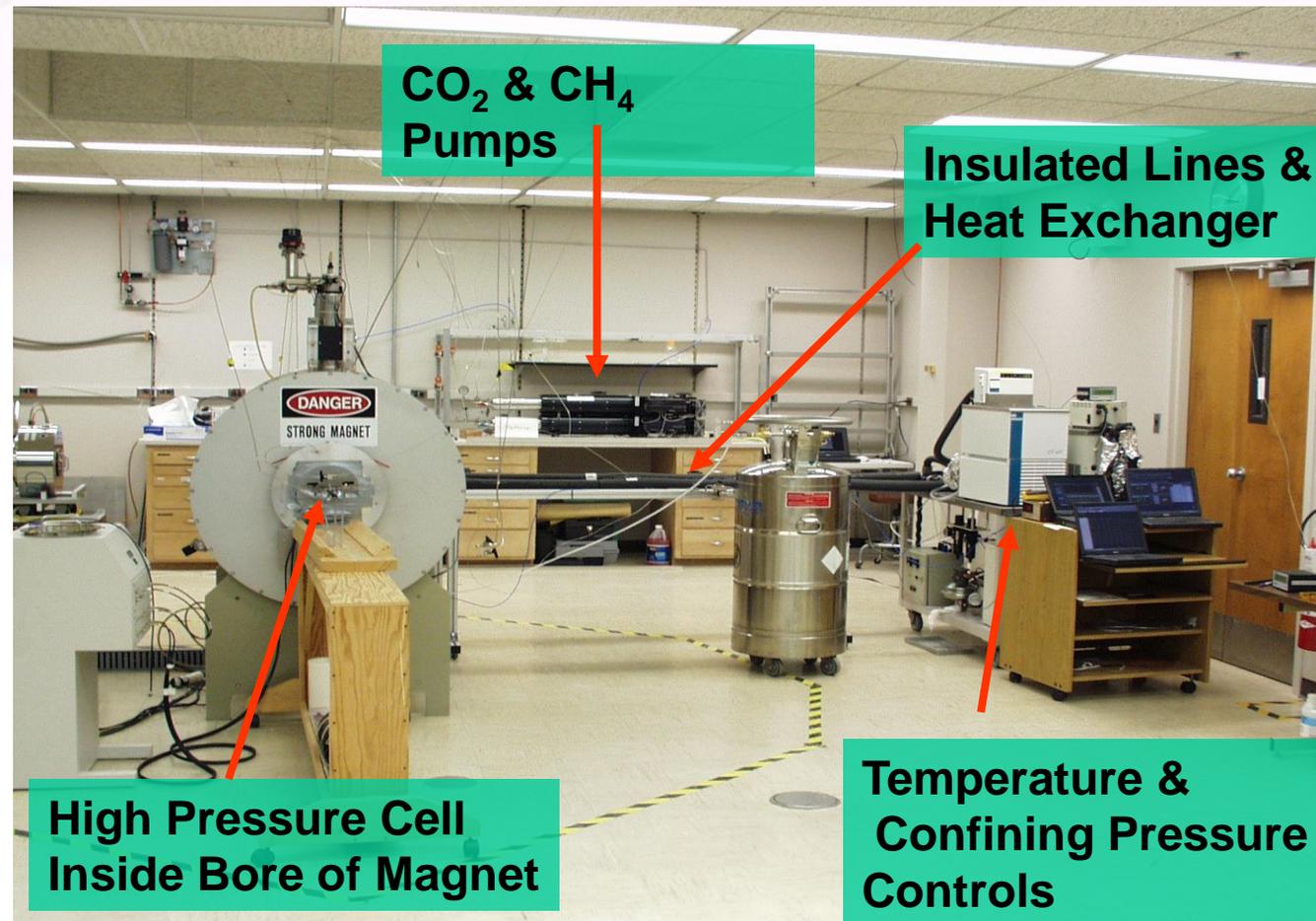
Parameters ε and w can be fixed from the interface thickness and interface free energy. ε_{ij} set equal to ε

CH₄ PRODUCTION INDUCED BY CO₂ INJECTION

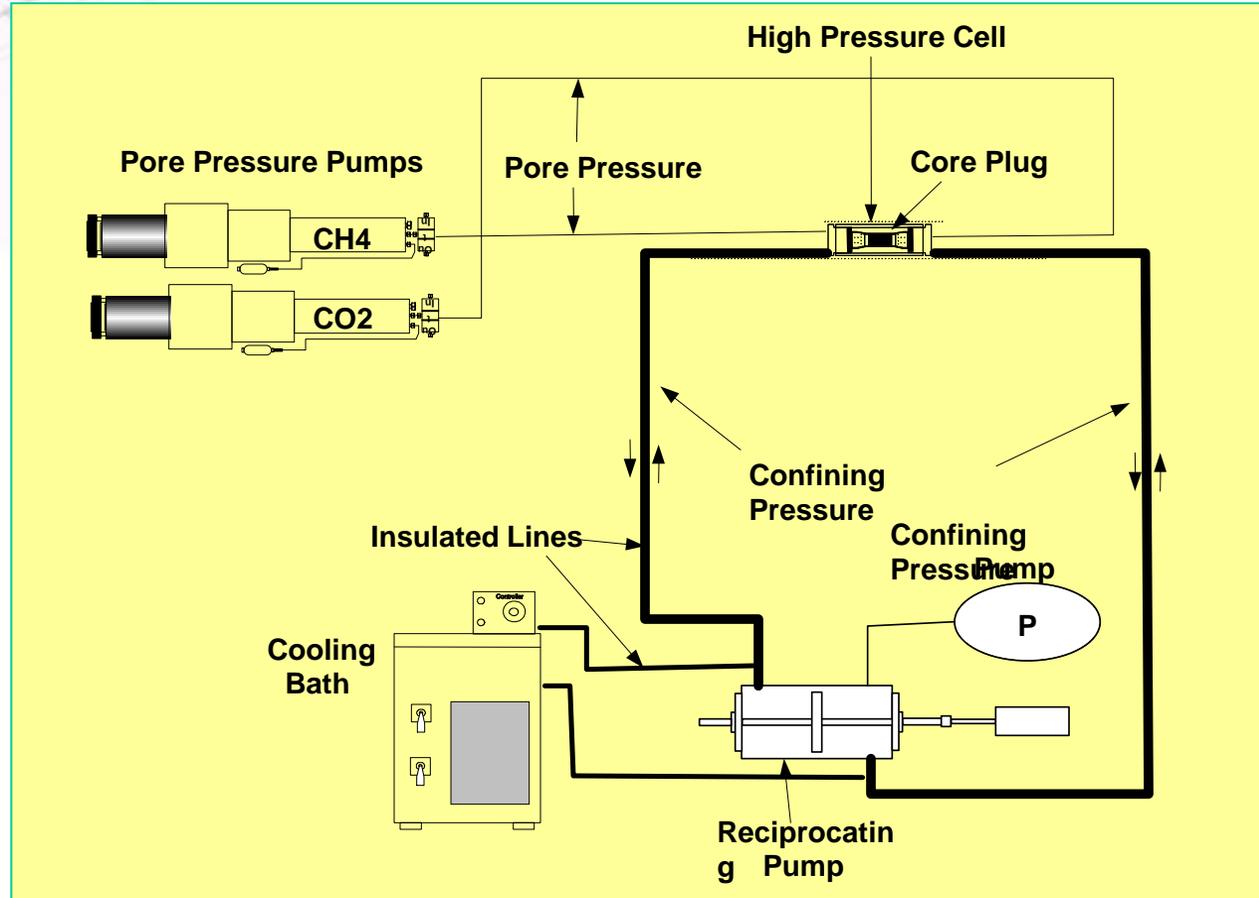
- Provides thermodynamically more stable gas hydrate than CH₄



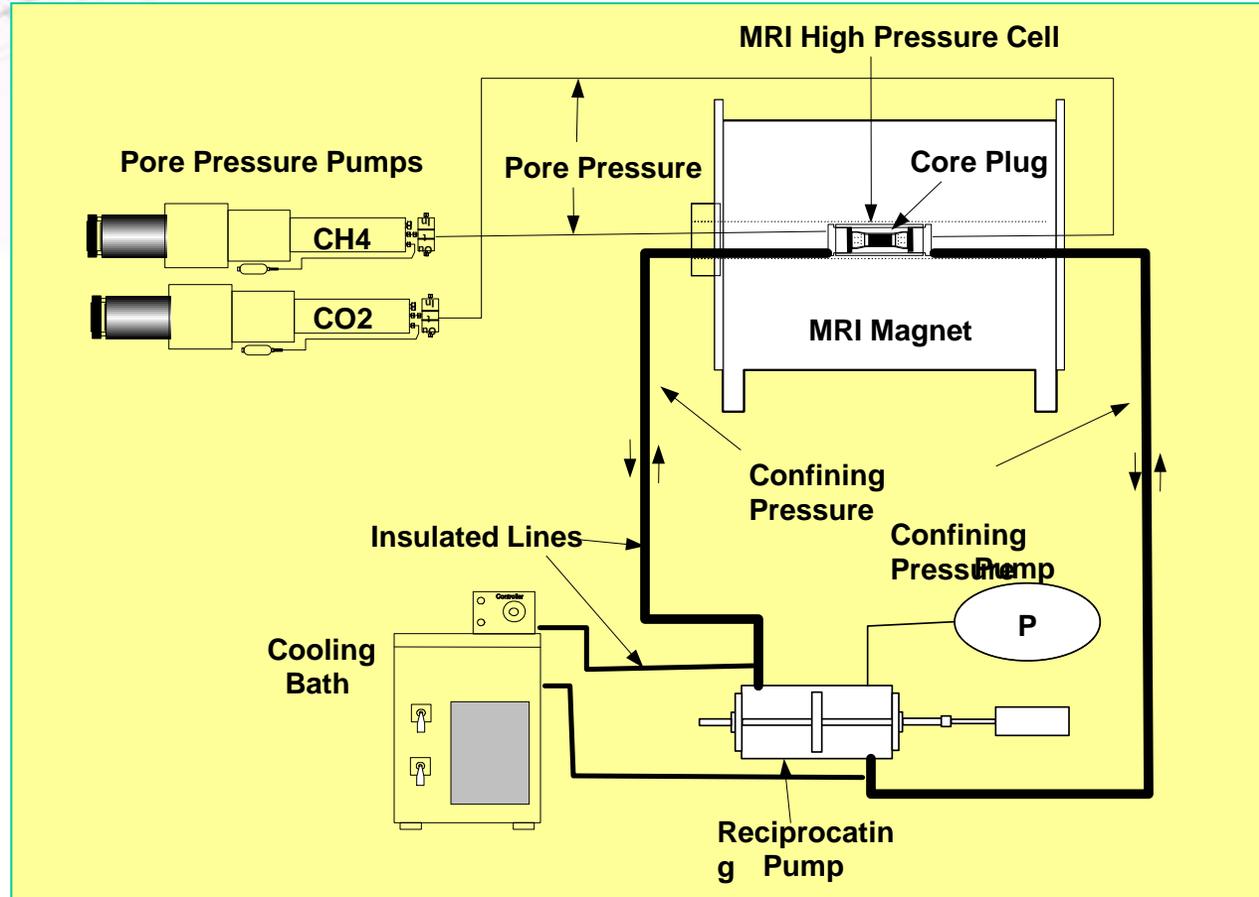
Experimental Setup



Experimental Setup



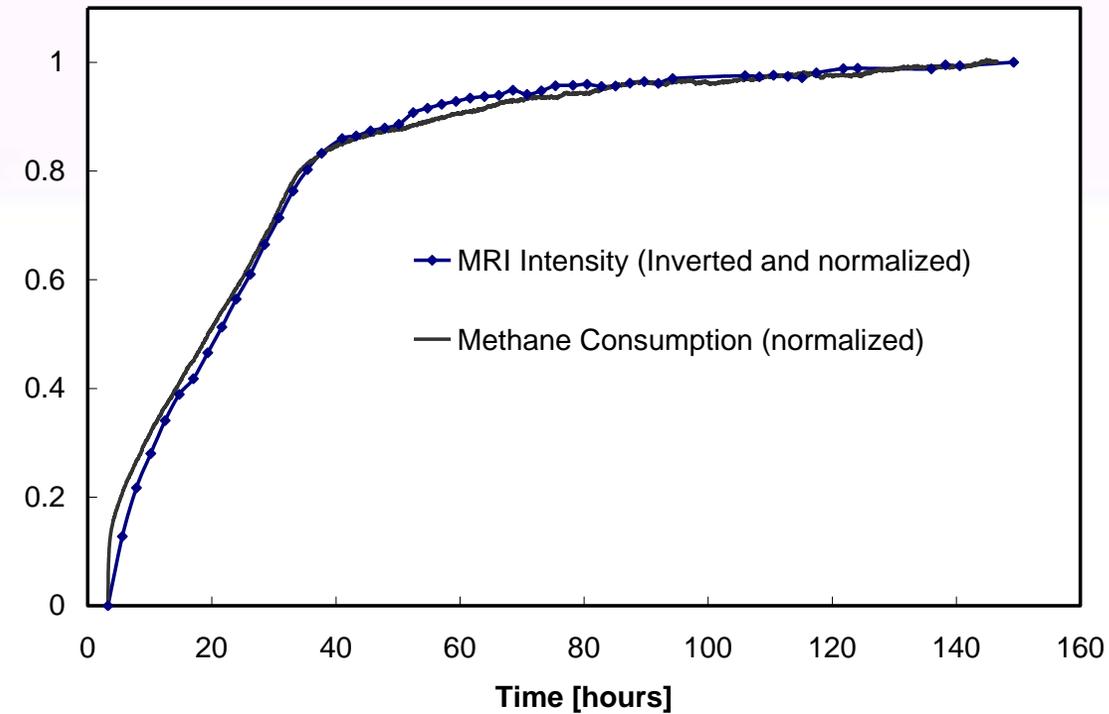
Experimental Setup



Monitor P-V-T and MRI Intensity

During Hydrate Formation

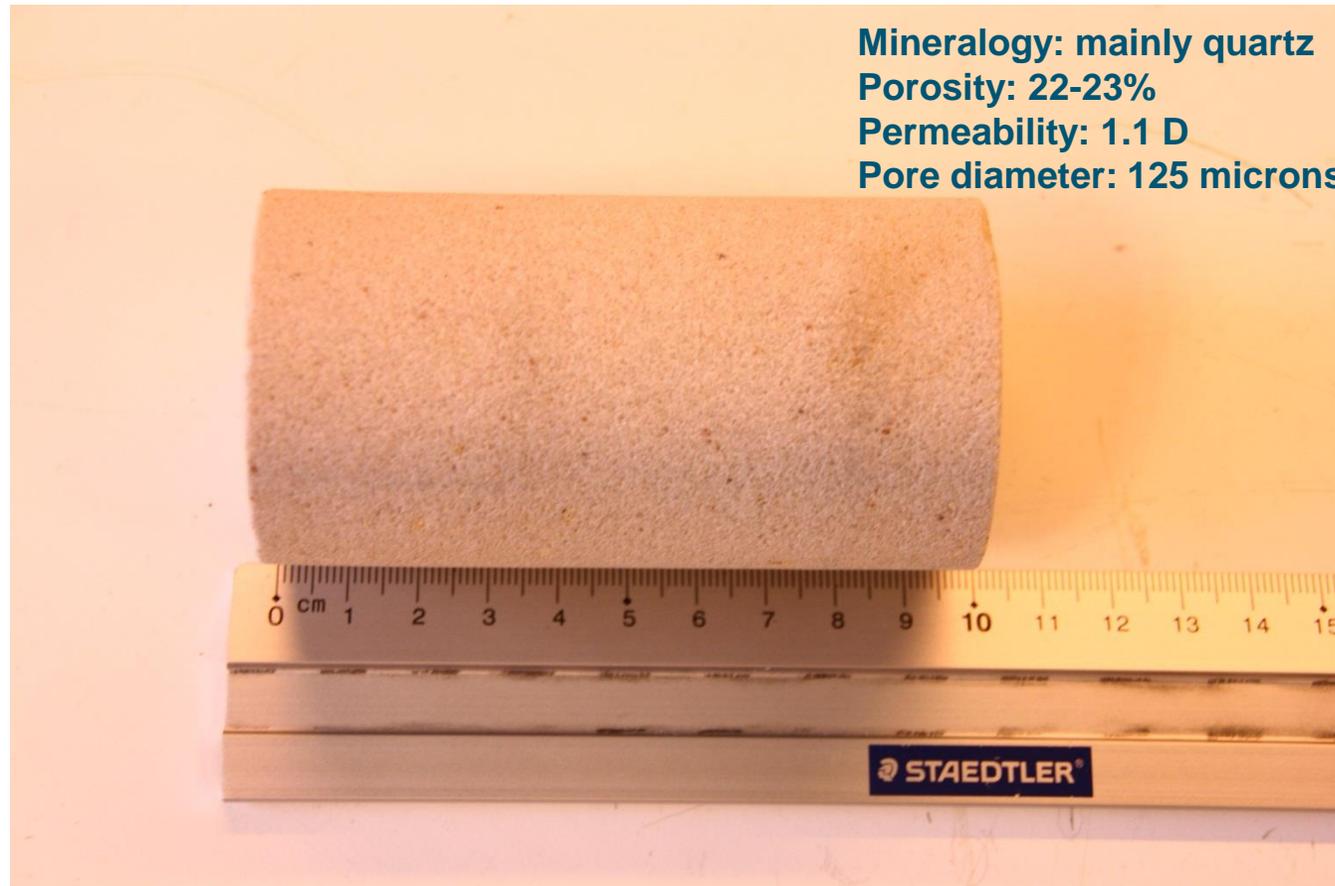
Volumetrics and MRI Results



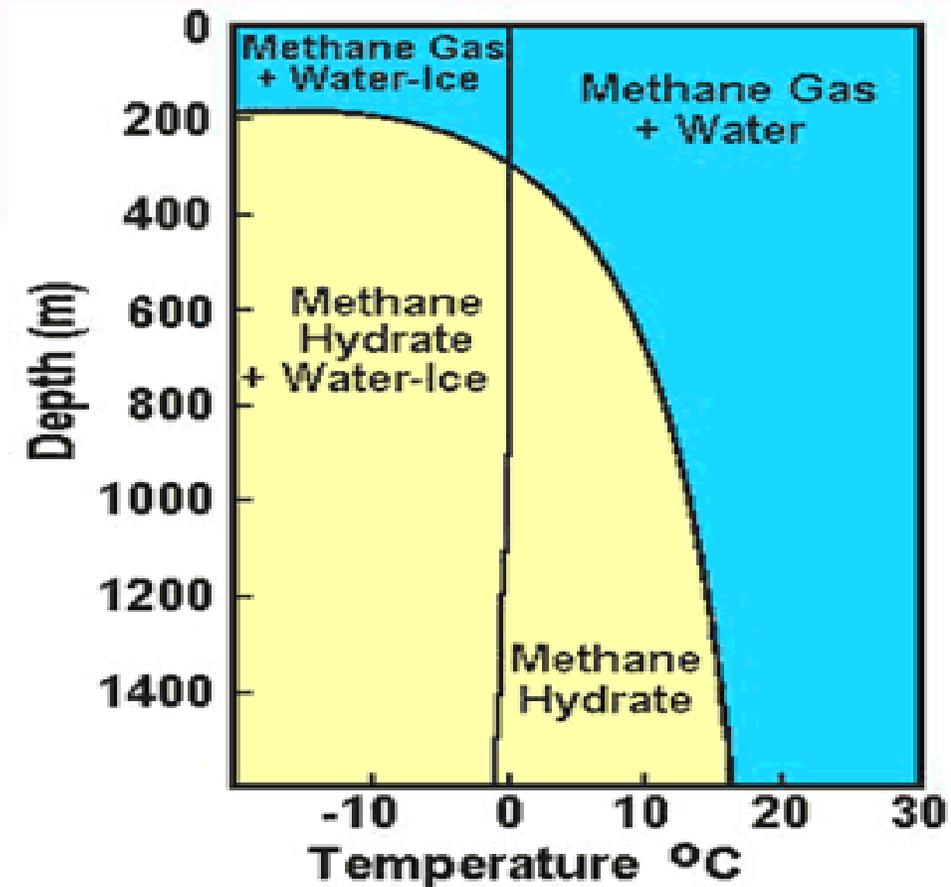
MRI Intensity in Core and CH₄ Volume Consumption

CONDITIONS OF A HYDRATE RESERVOIR

- Hydrate reservoirs are often found in porous media
 - Sedimentary rock



Conditions for Methane Hydrate Formation/Dissociation

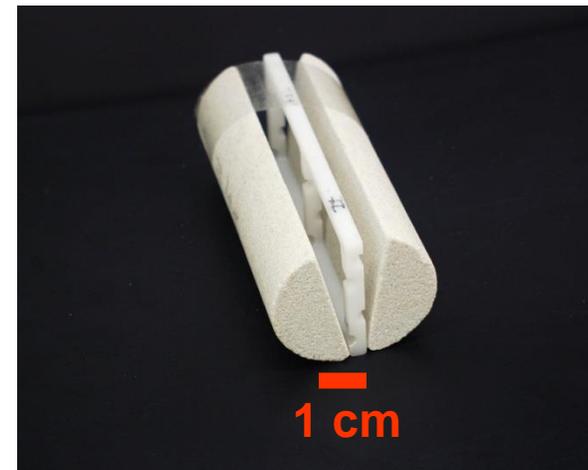
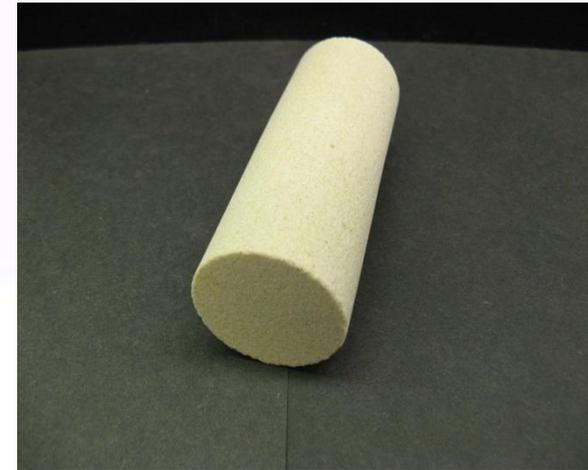


Core Sample Design

Bentheim Sandstone

20-25% porosity, ~ 1.1 D Perm

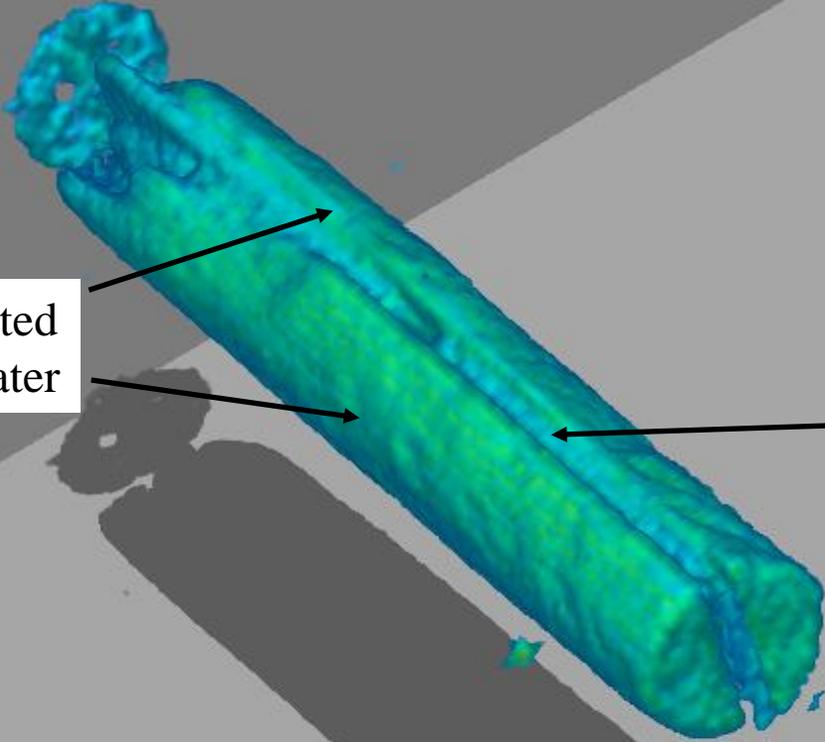
- Whole Core
- Longitudinal Cut With Machined Spacer to Simulate Open Fracture.



Sample – BH-01

Sample halves saturated
With methane and water

Middle space saturated
With methane

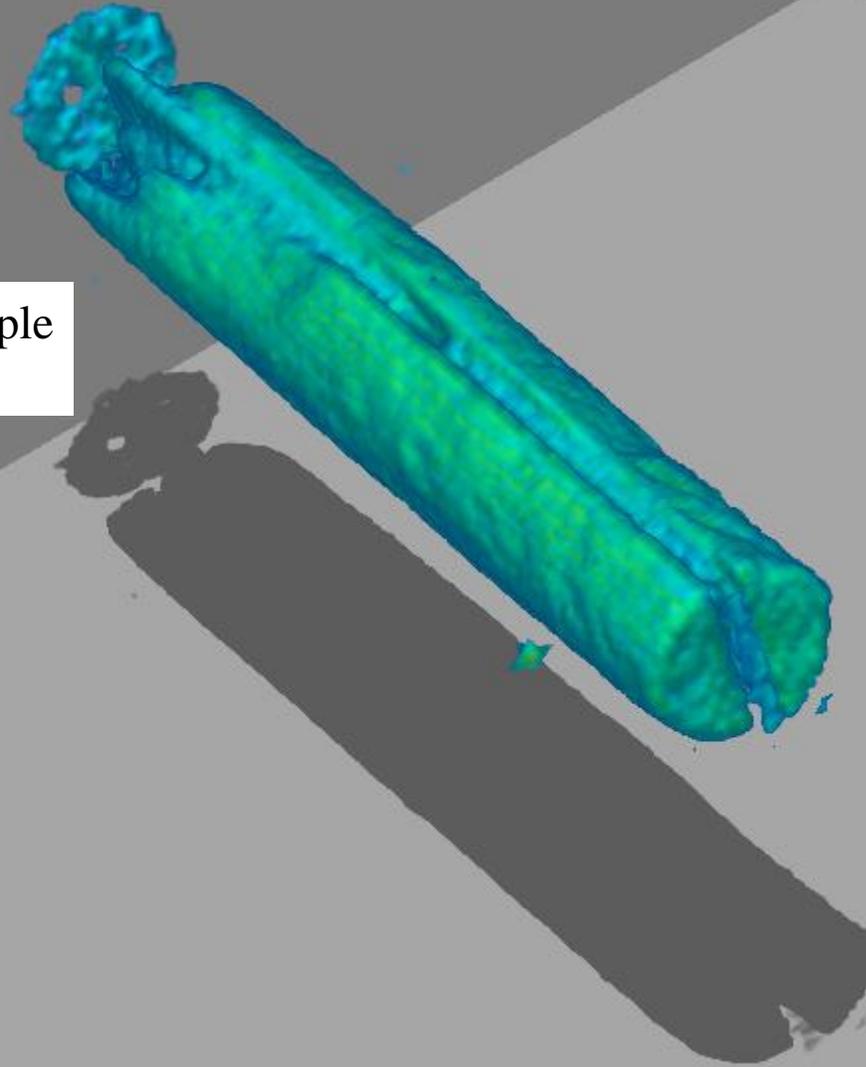


Sample – BH-01

Run – 17-39

Time – 0min

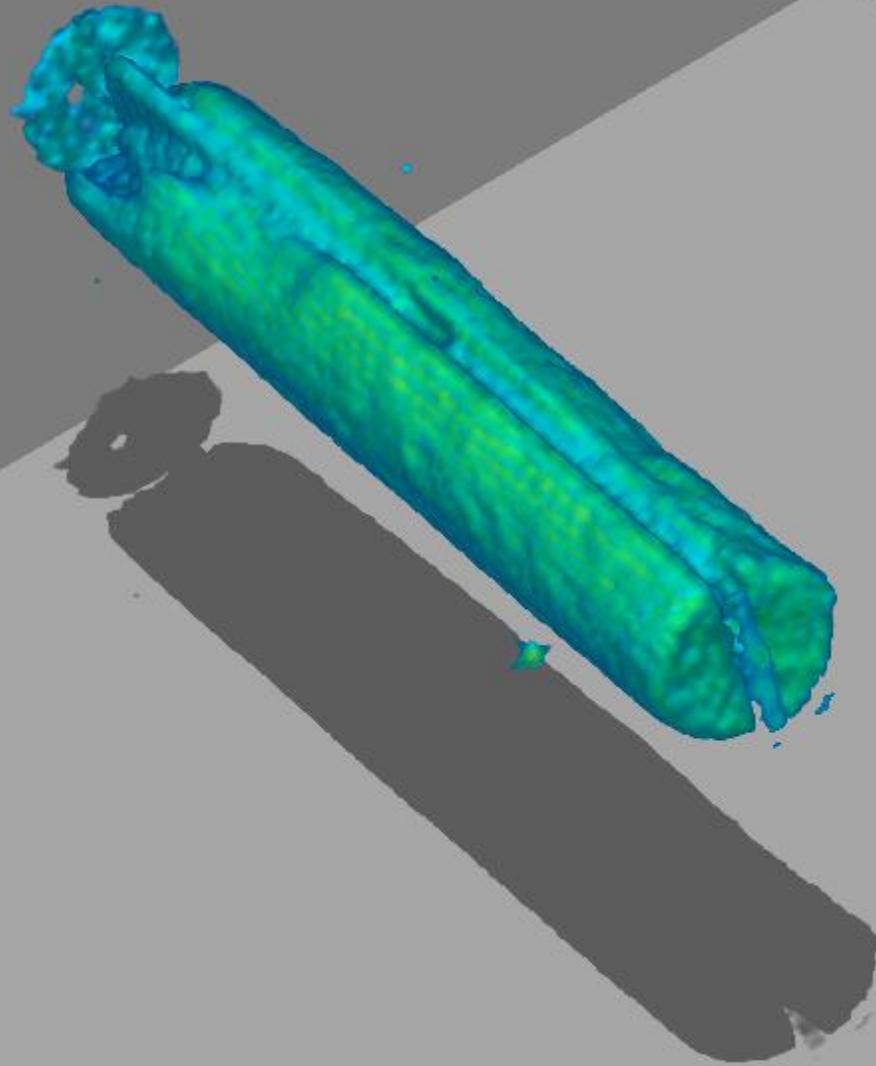
Started cooling sample
To 4° C



Sample – BH-01

Run – 18-01

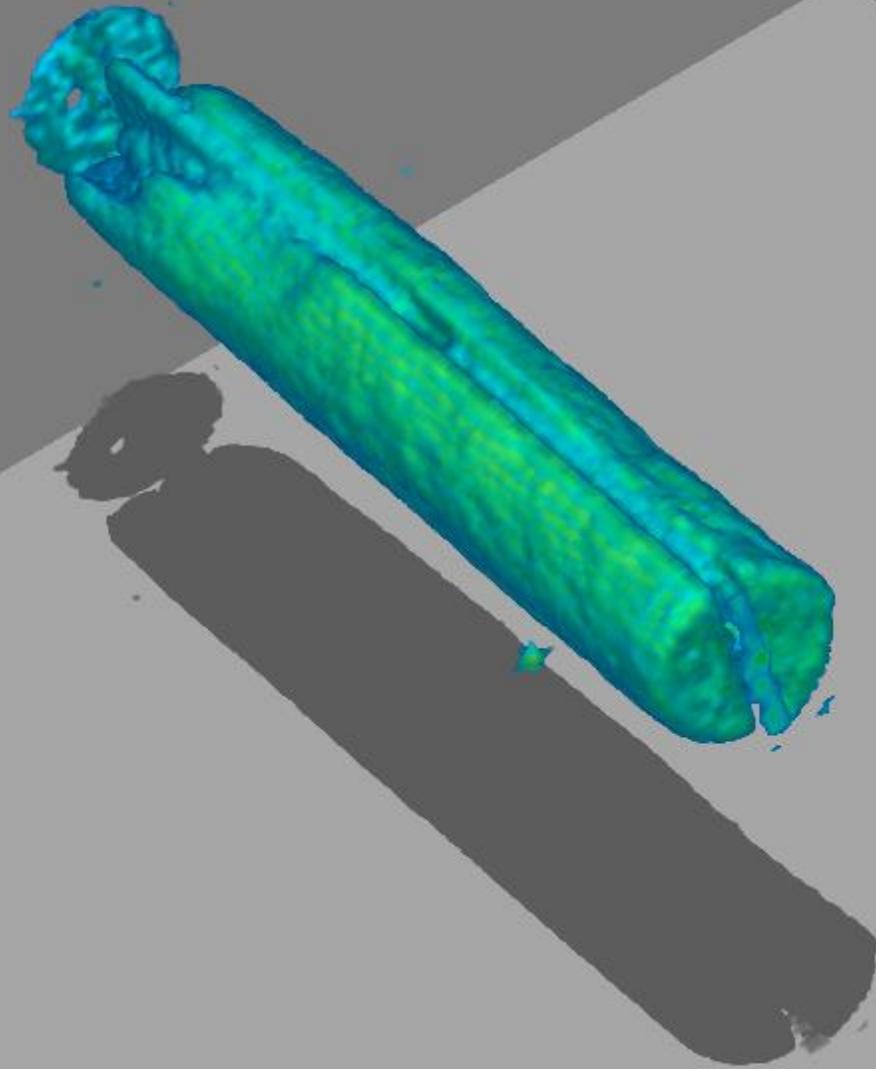
Time – 55min



Sample – BH-01

Run – 18-03

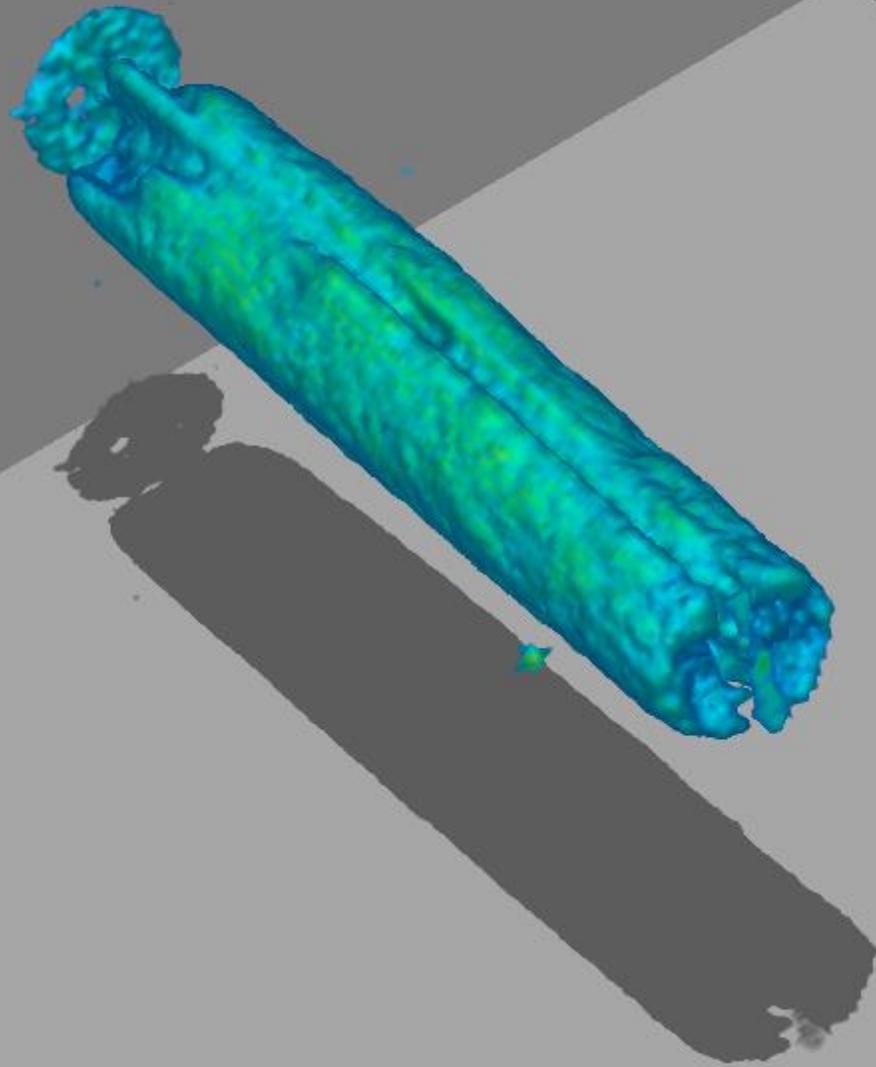
Time – 2hr 45min



Sample – BH-01

Run – 18-05

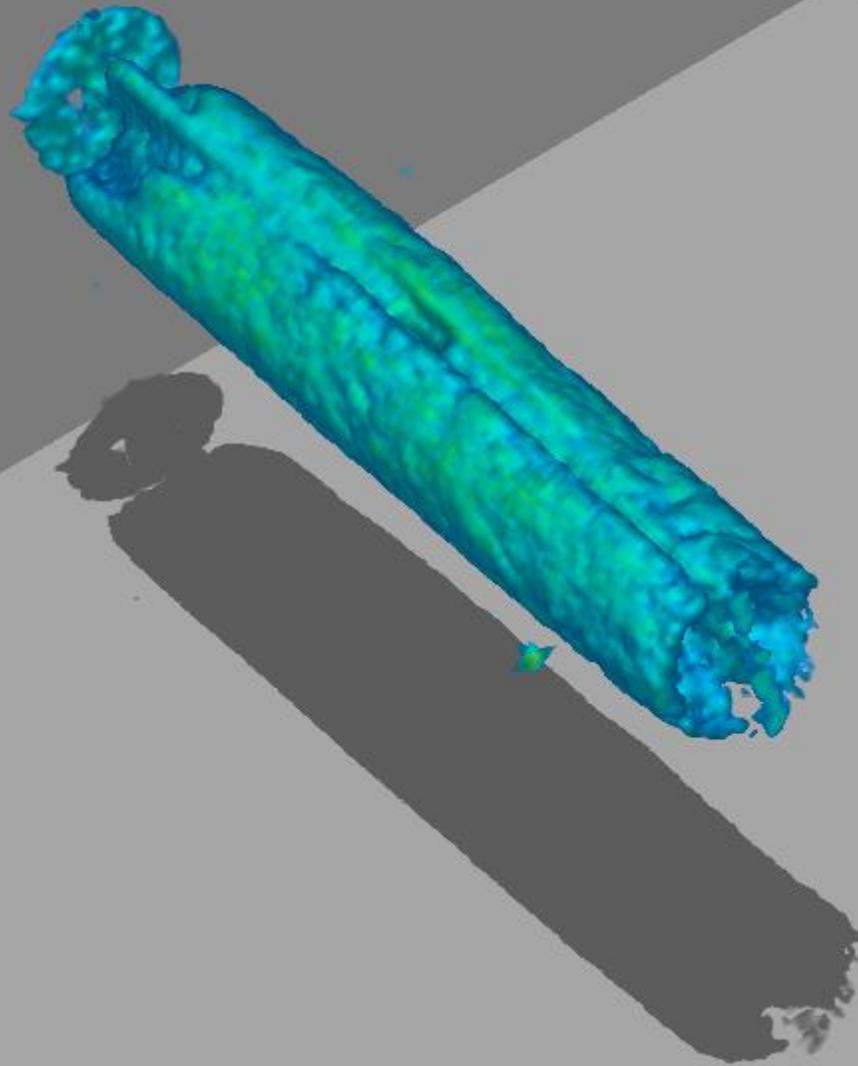
Time – 4hr 35min



Sample – BH-01

Run – 18-06

Time – 5hr 30min

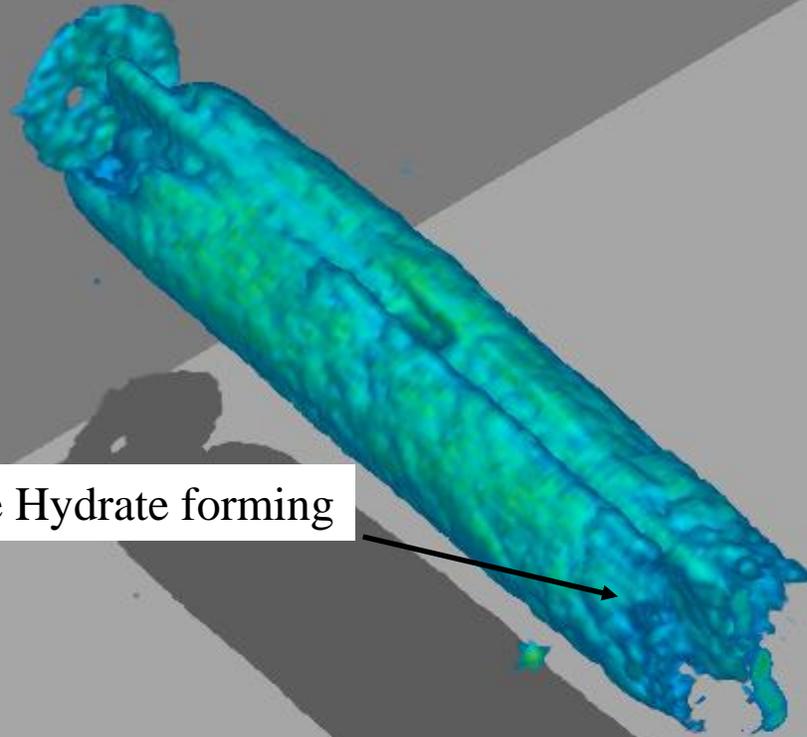


Sample – BH-01

Run – 18-07

Time – 6hr 25min

Methane Hydrate forming

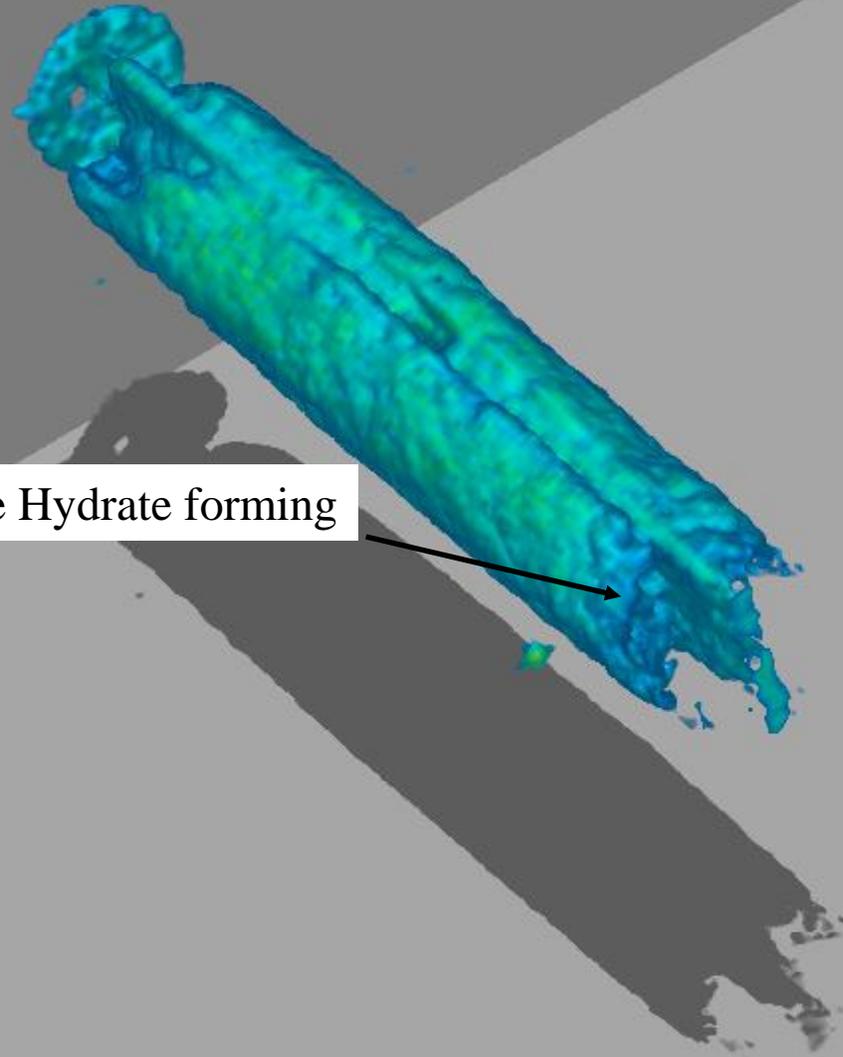


Sample – BH-01

Run – 18-08

Time – 7hr 20min

Methane Hydrate forming

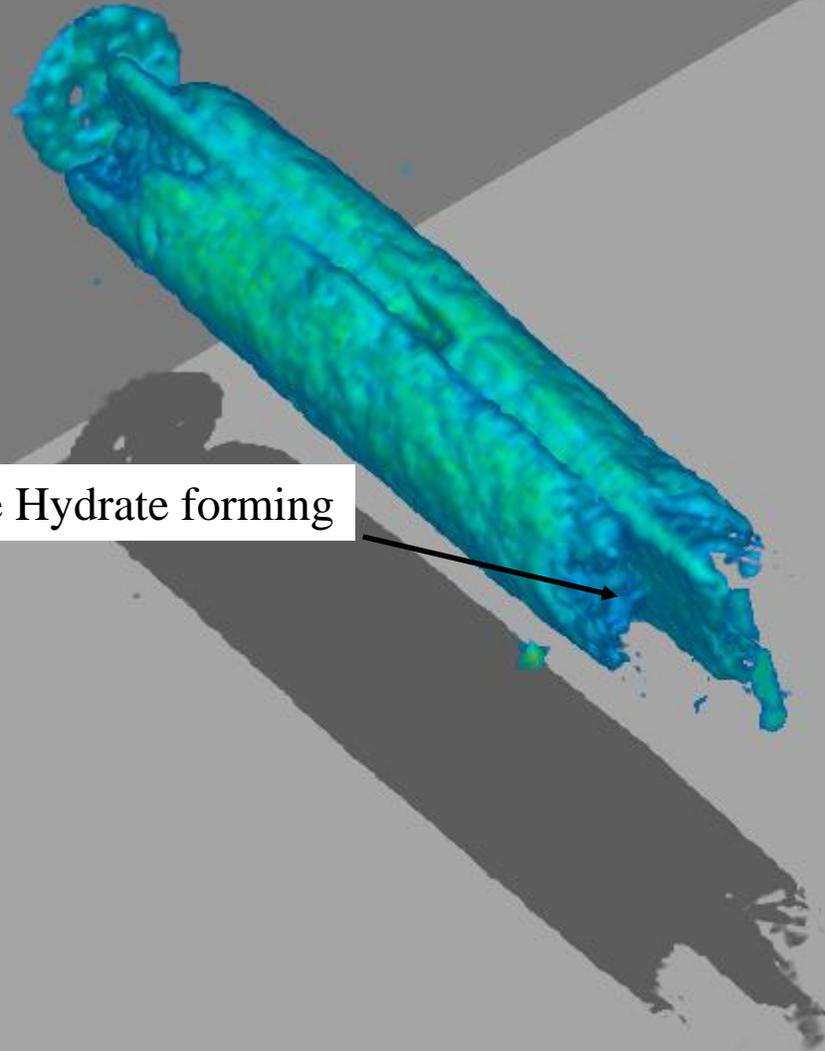


Sample – BH-01

Run – 18-09

Time – 8hr 15min

Methane Hydrate forming

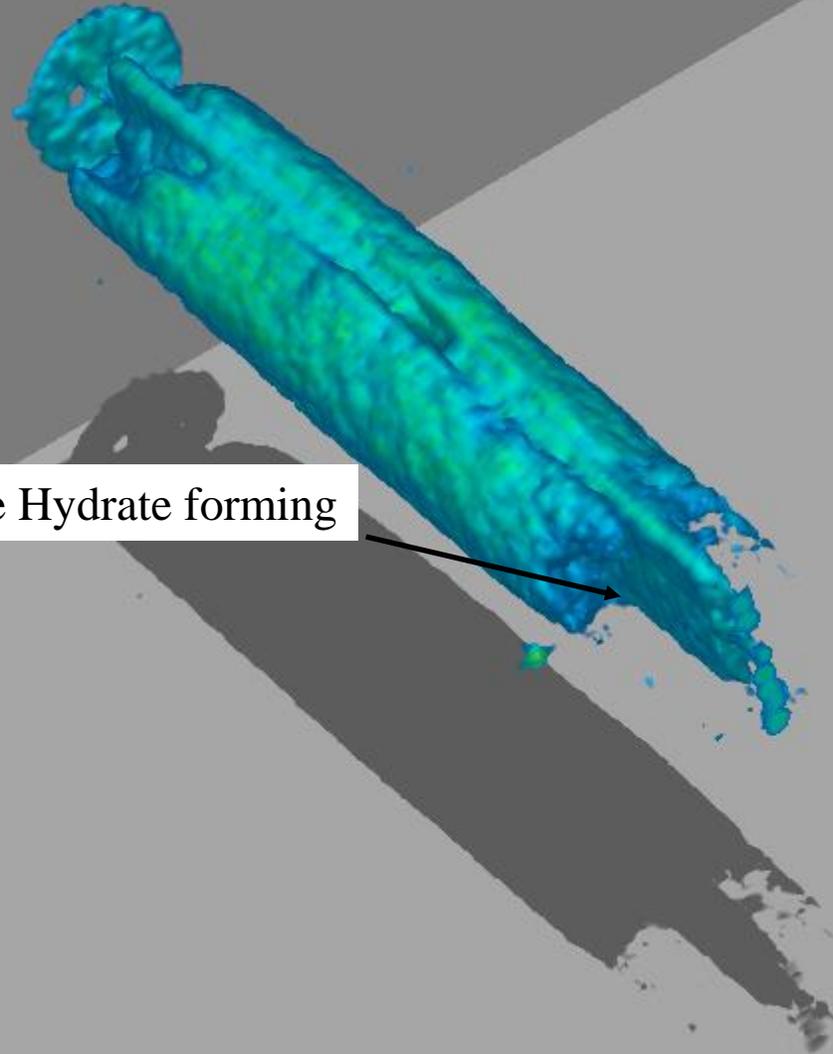


Sample – BH-01

Run – 18-10

Time – 9hr 10min

Methane Hydrate forming

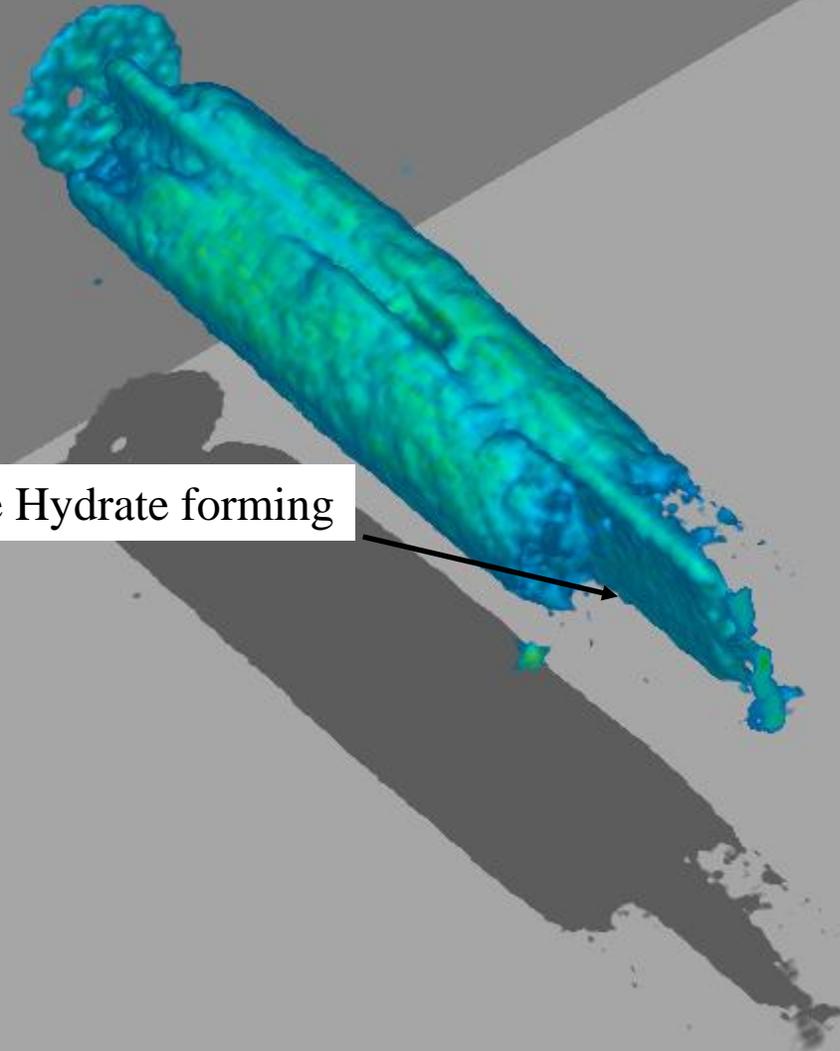


Sample – BH-01

Run – 18-11

Time – 10hr 05min

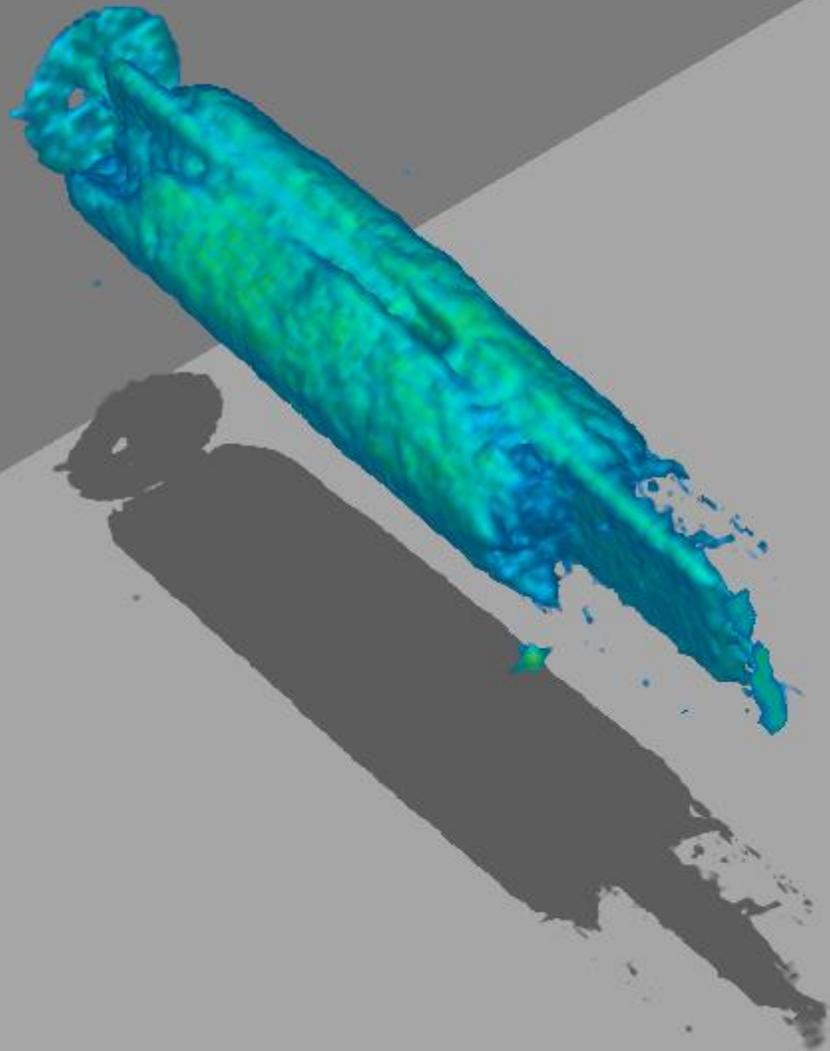
Methane Hydrate forming



Sample – BH-01

Run – 18-12

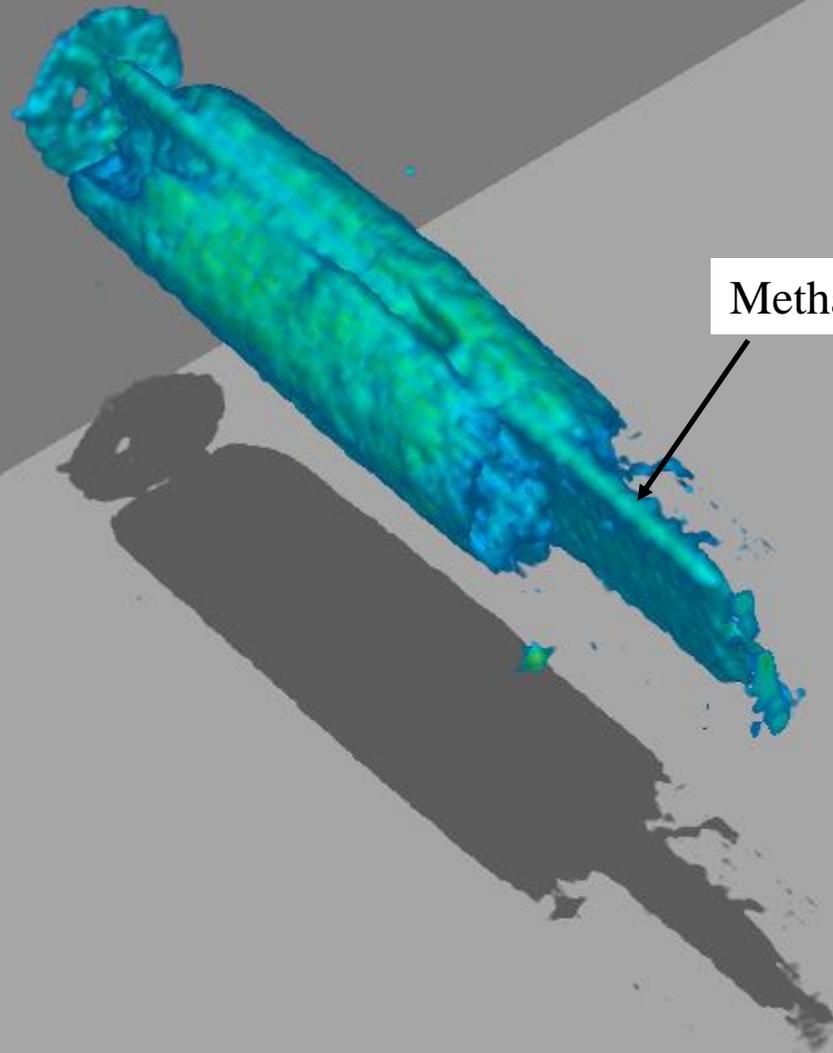
Time – 11hr 00min



Sample – BH-01

Run – 18-14

Time – 12hr 50min



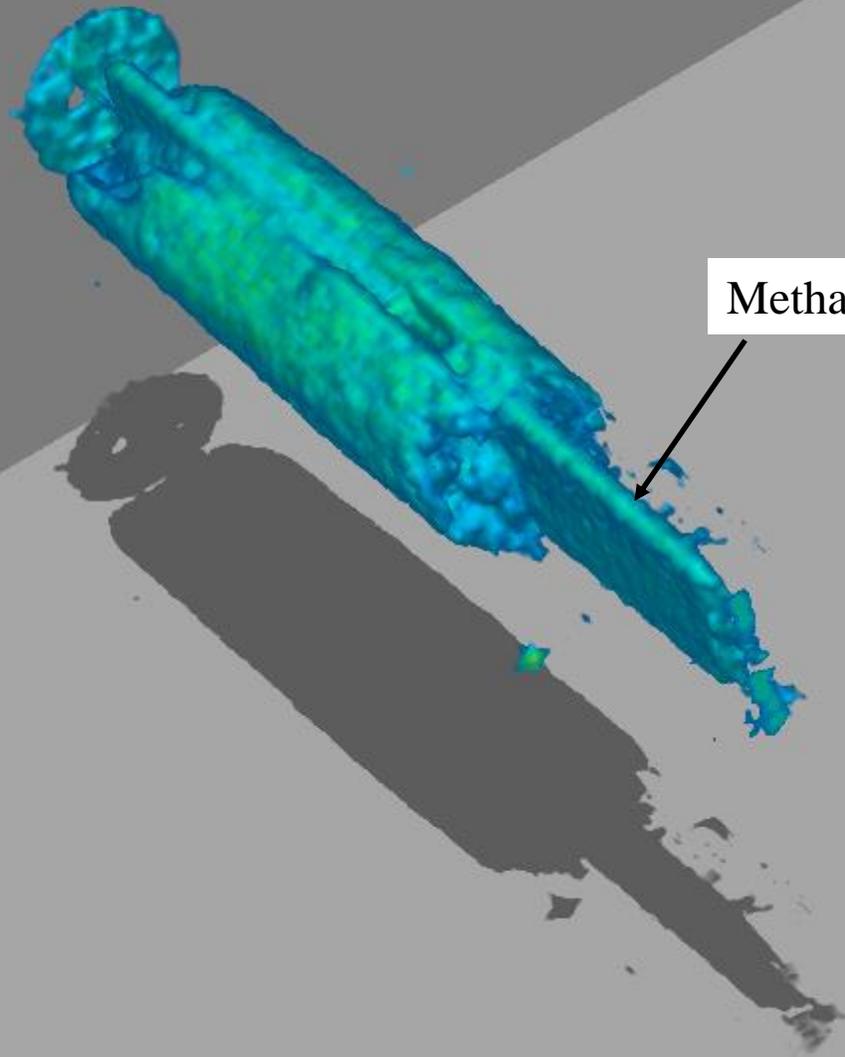
Methane in spacer



Sample – BH-01

Run – 18-16

Time – 14hr 40min

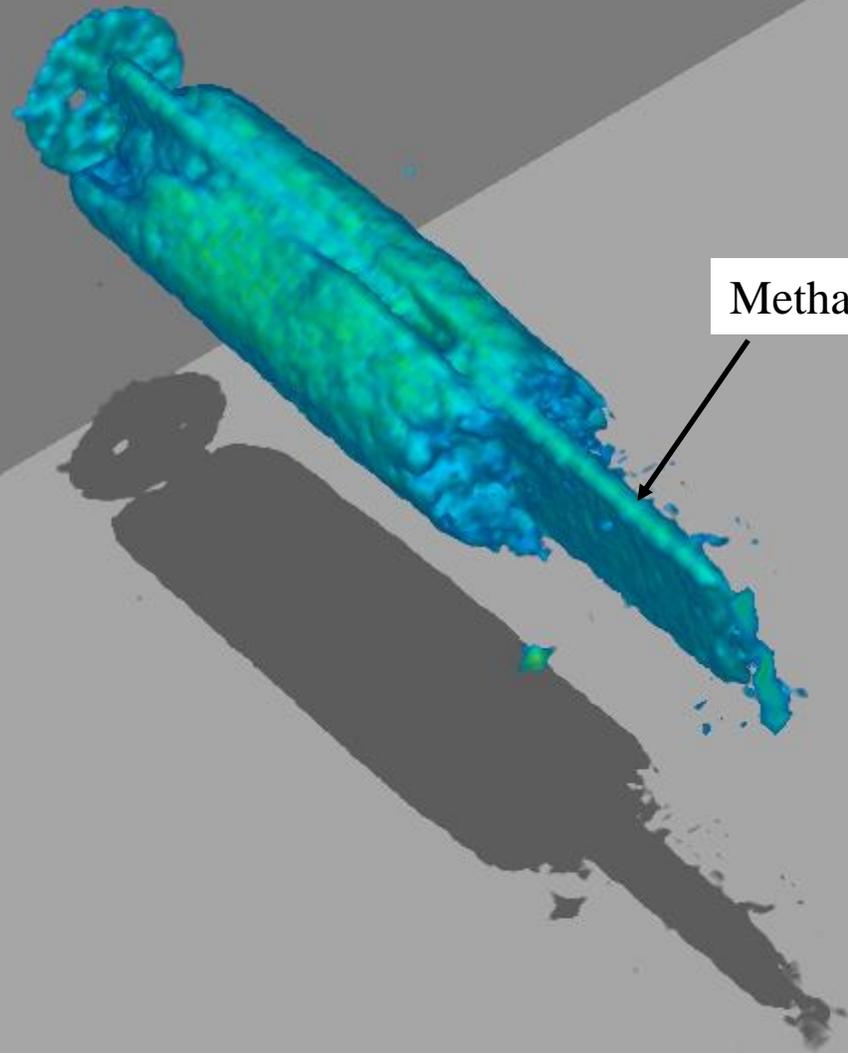


Methane in spacer

Sample – BH-01

Run – 18-17

Time – 15hr 35min



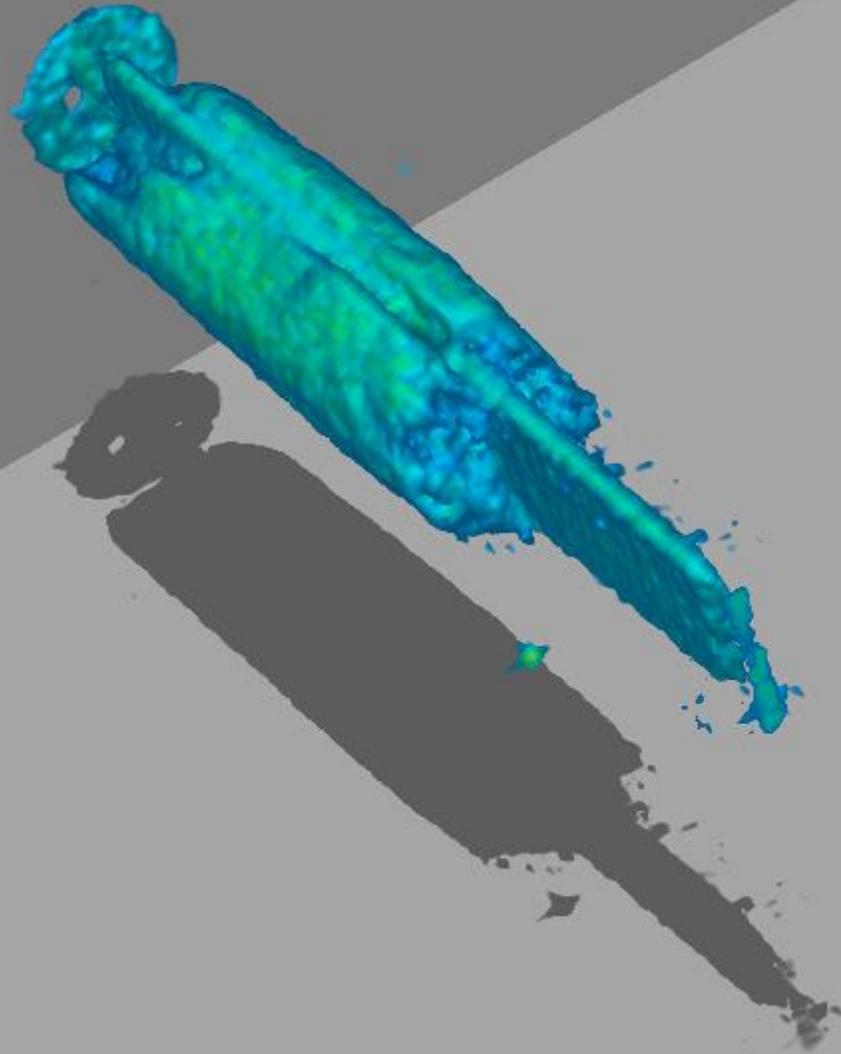
Methane in spacer



Sample – BH-01

Run – 18-19

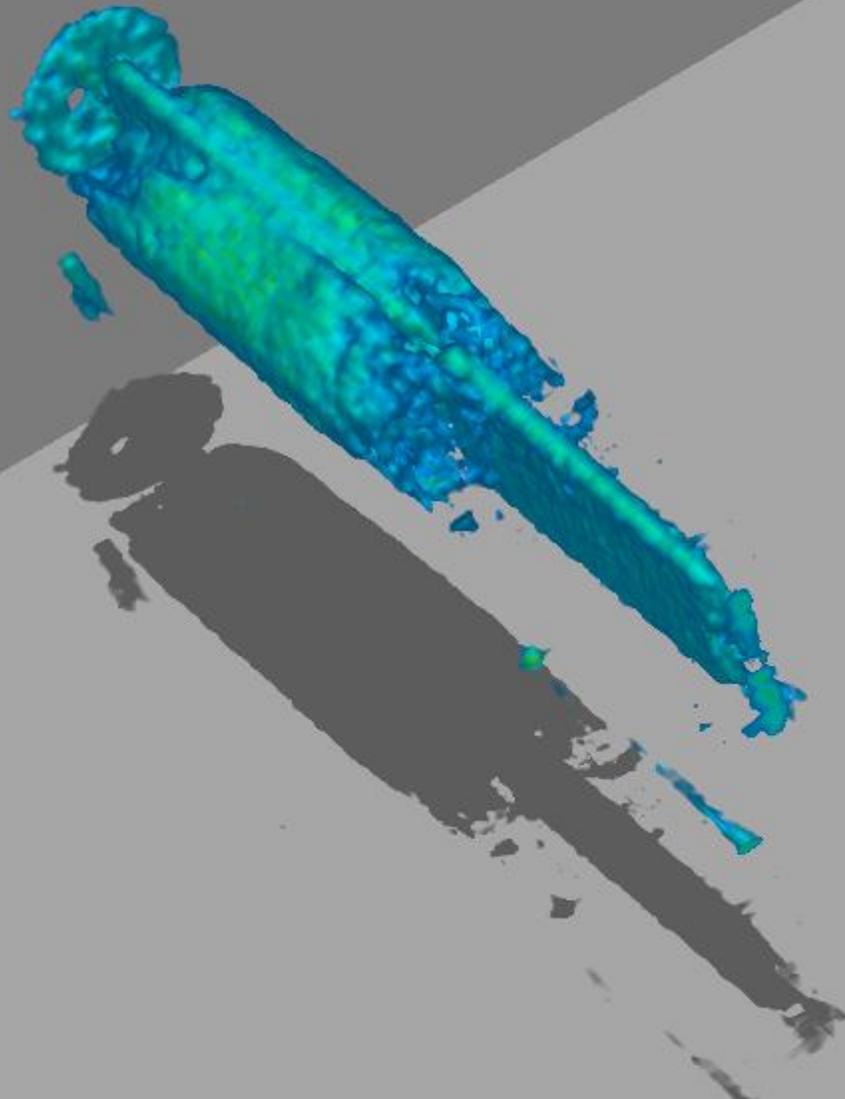
Time – 17hr 25min



Sample – BH-01

Run – 18-37

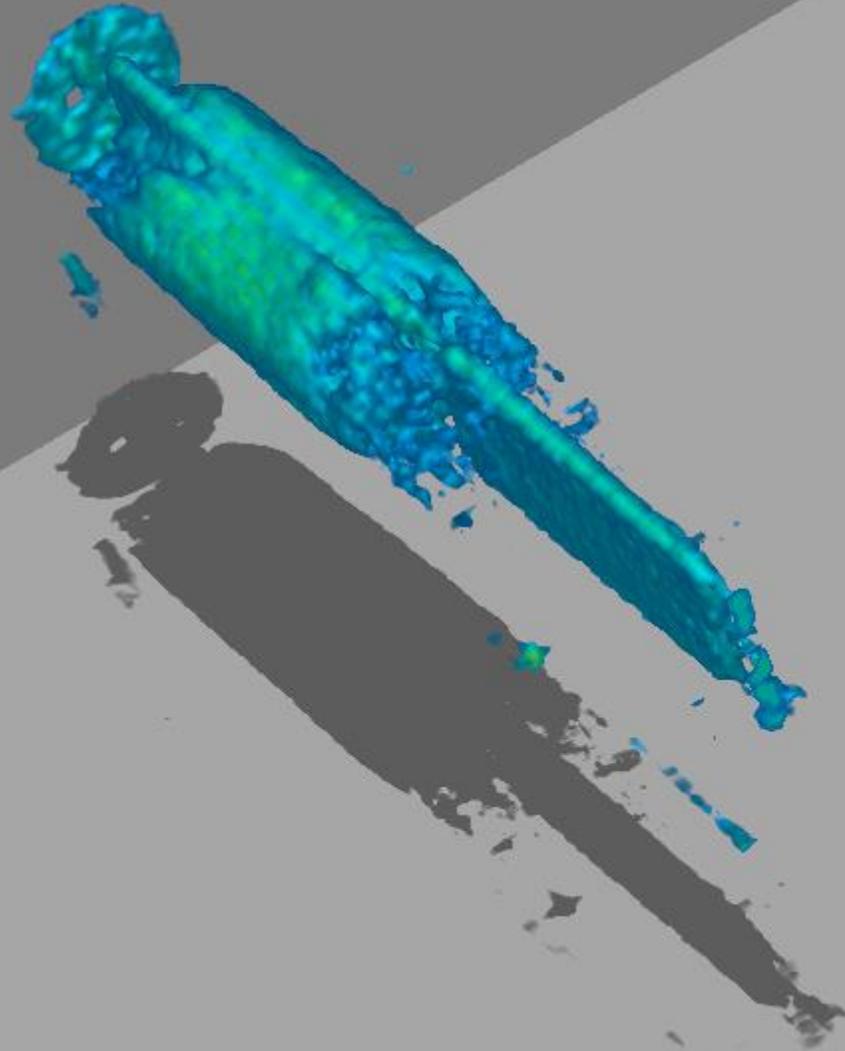
Time – 31hr 05min



Sample – BH-01

Run – 18-42

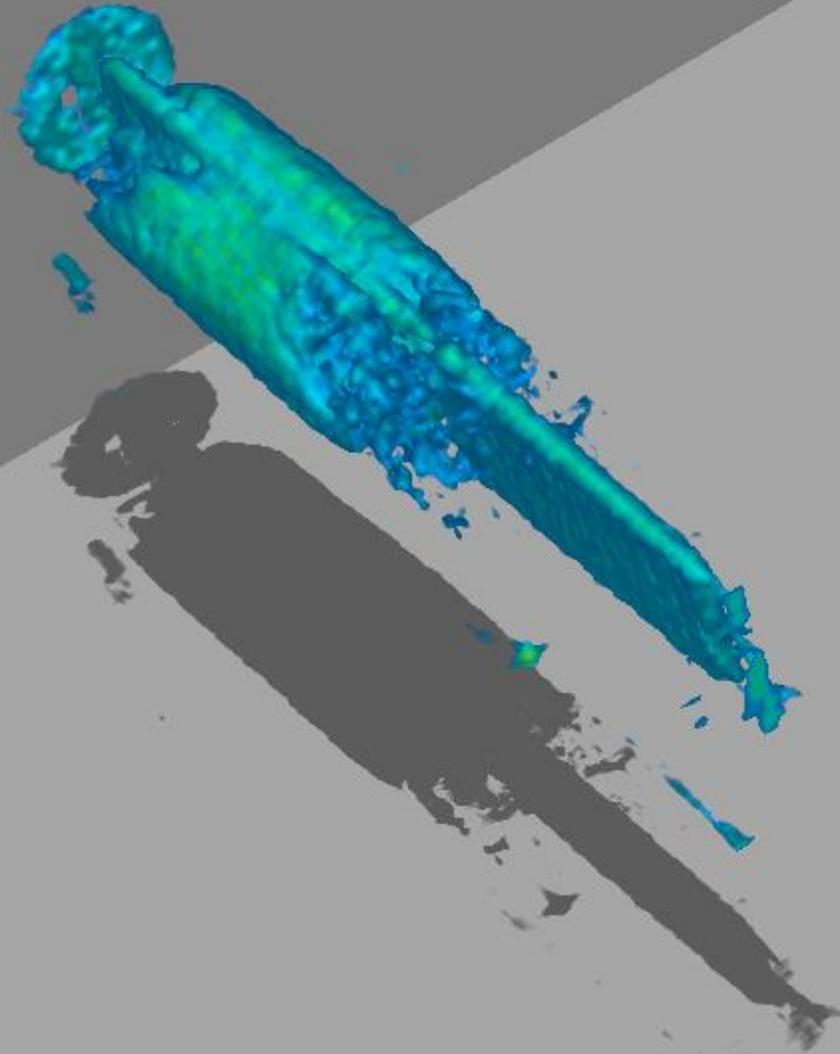
Time – 36hr 20min



Sample – BH-01

Run – 18-43

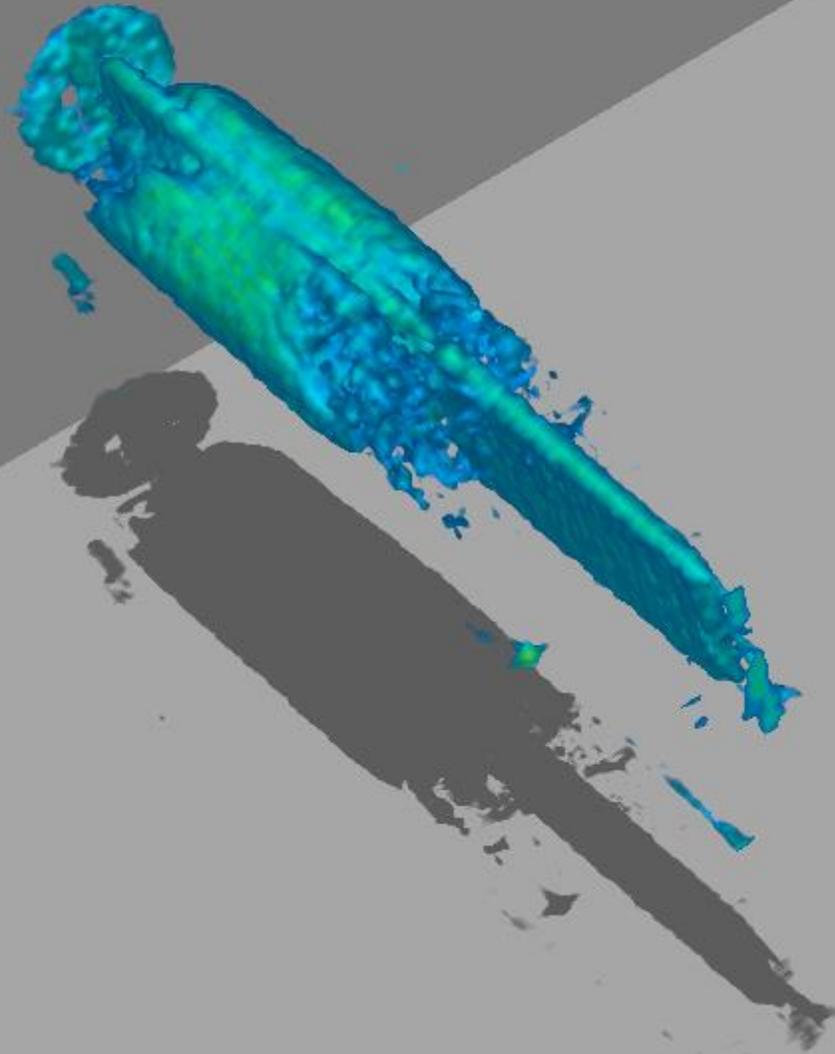
Time – 37hr 15min



Sample – BH-01

Run – 18-43

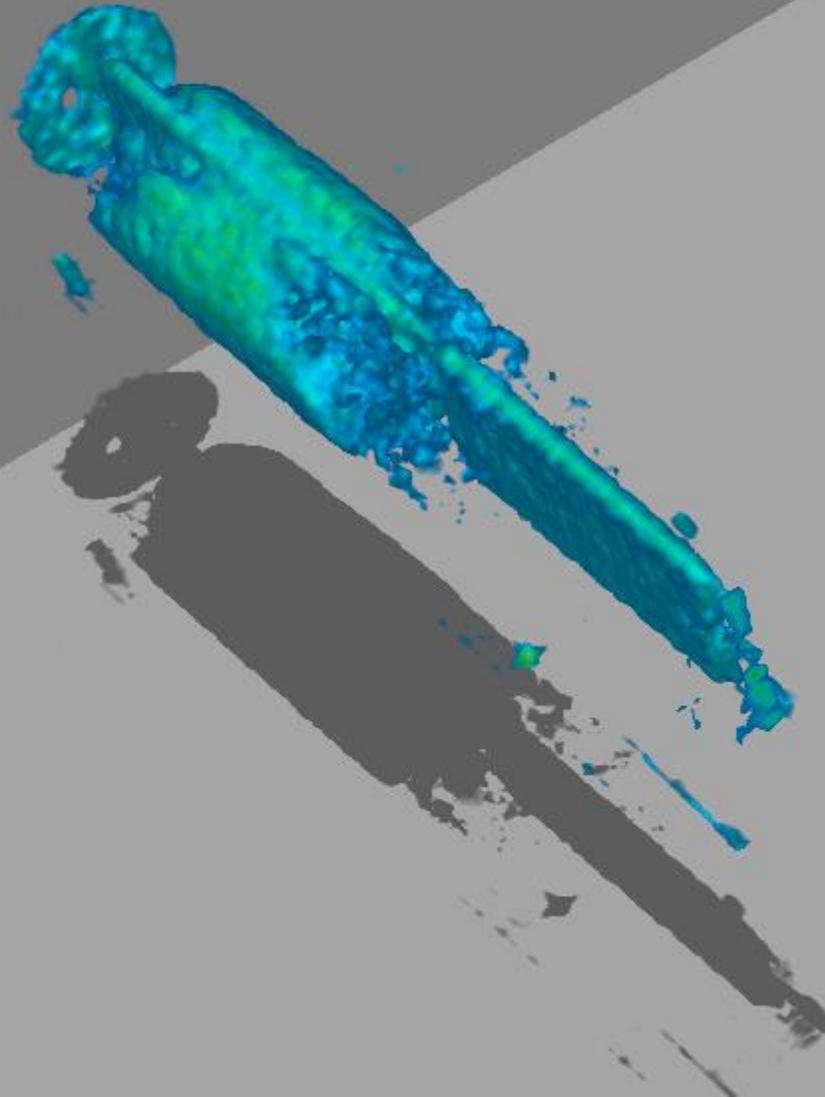
Time – 37hr 15min



Sample – BH-01

Run – 18-57

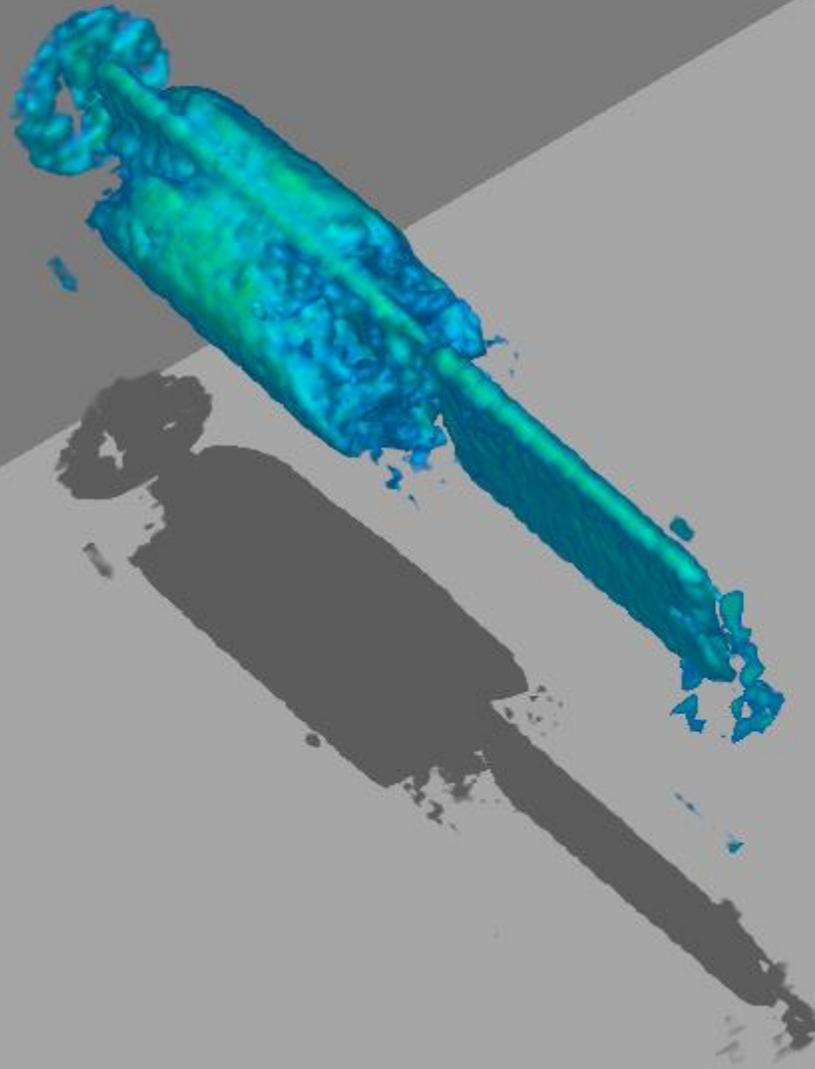
Time – 54hr 10min



Sample – BH-01

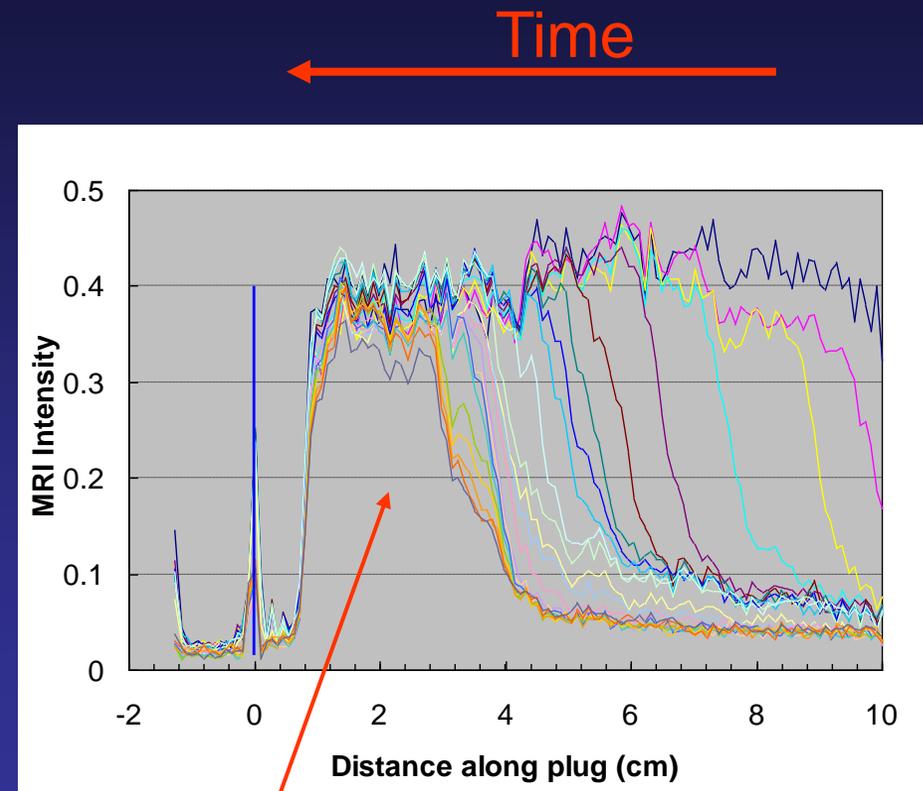
Run – 18-59

Time – 56hr 00min



Progress of Hydrate Front

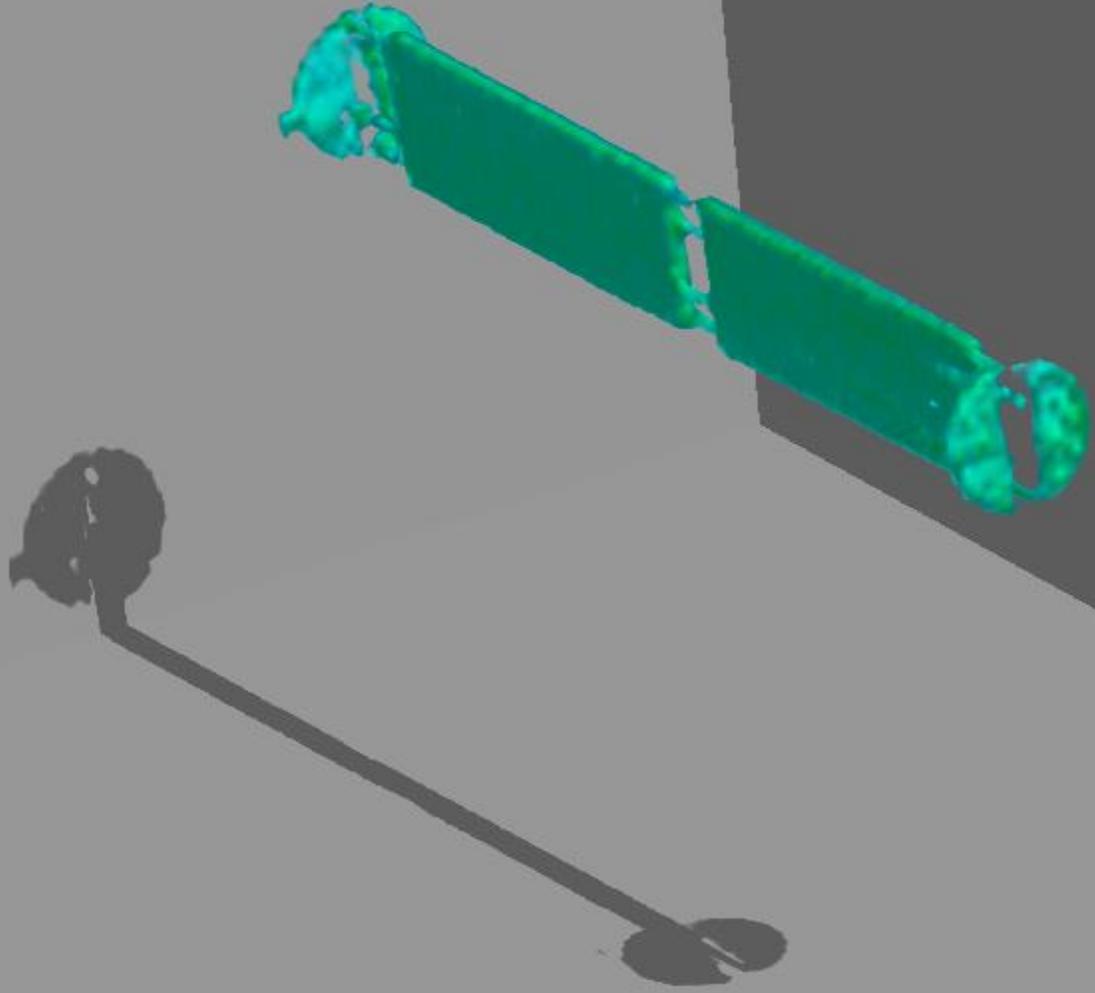
- Longitudinal Profile in Core – 5 mm from Fracture.
- Approximately 35 Hours, ~ Equal Time Increments.
- Hydrate Growth Slows with Time.



Water-Filled Pores

0.0 hrs

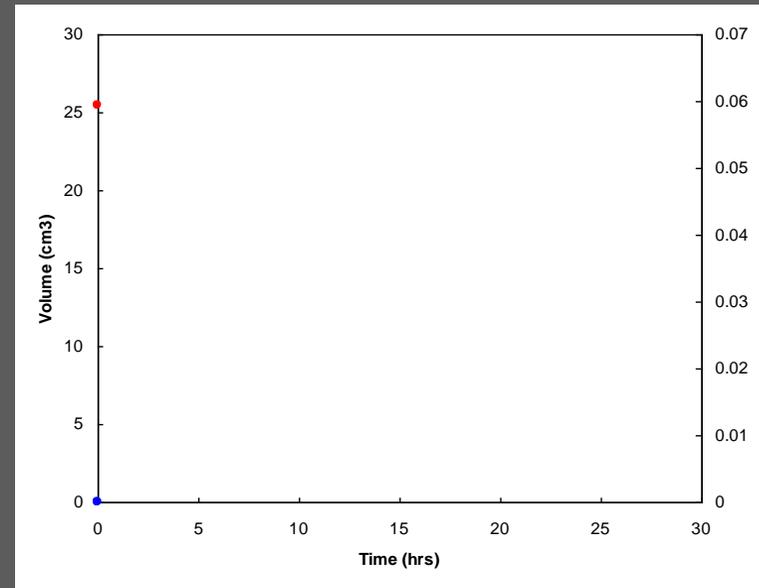
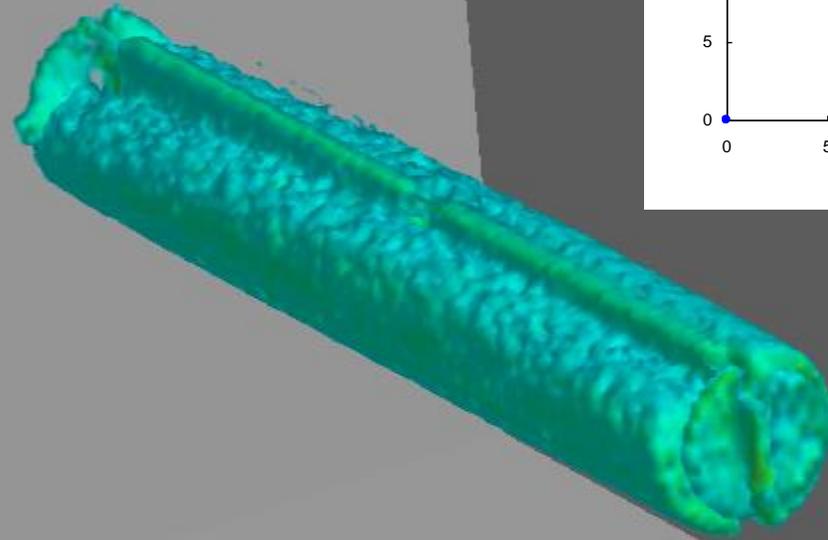
Methane in Spacer



33-07

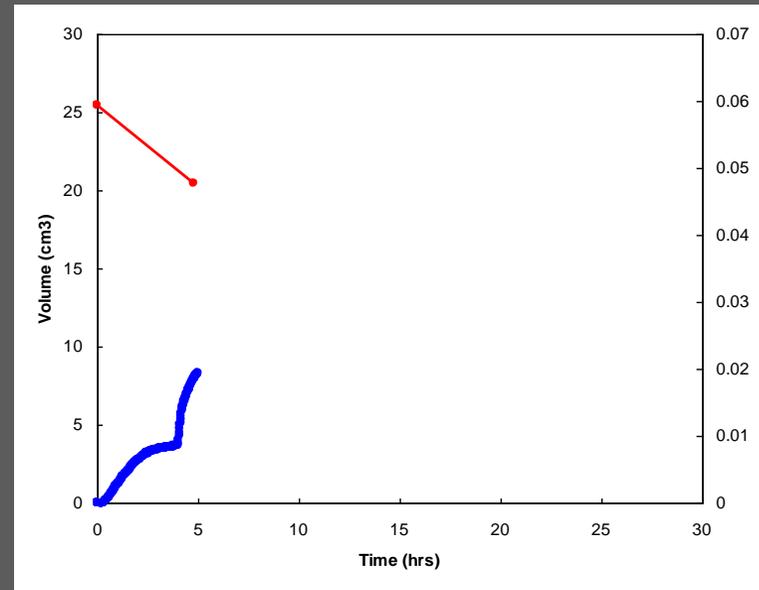
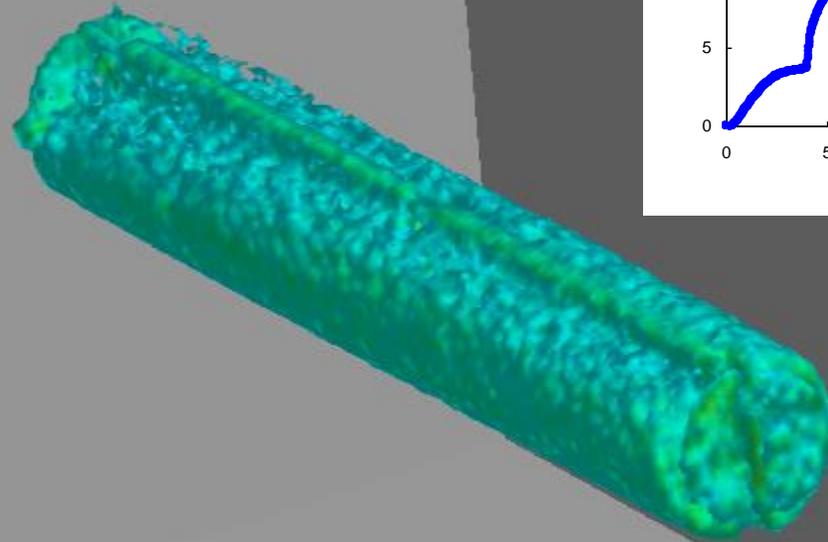
0.0 hrs

Sw=0.5 + Methane



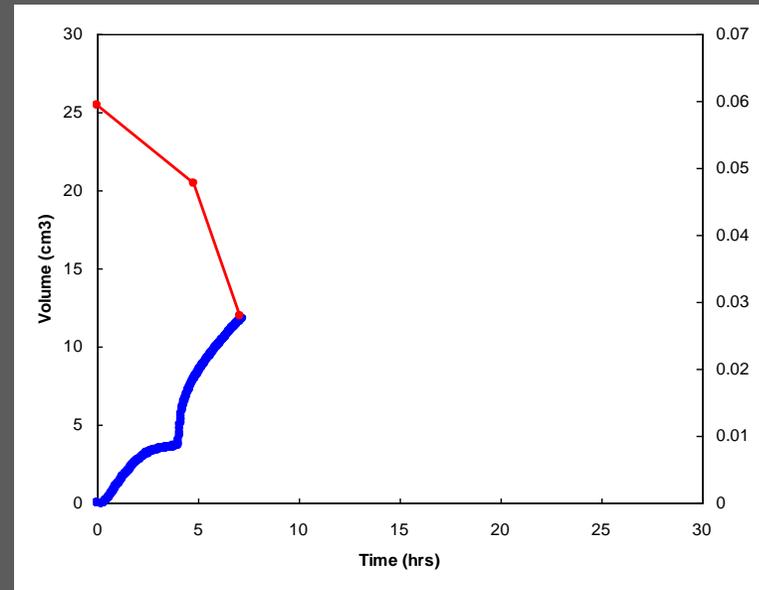
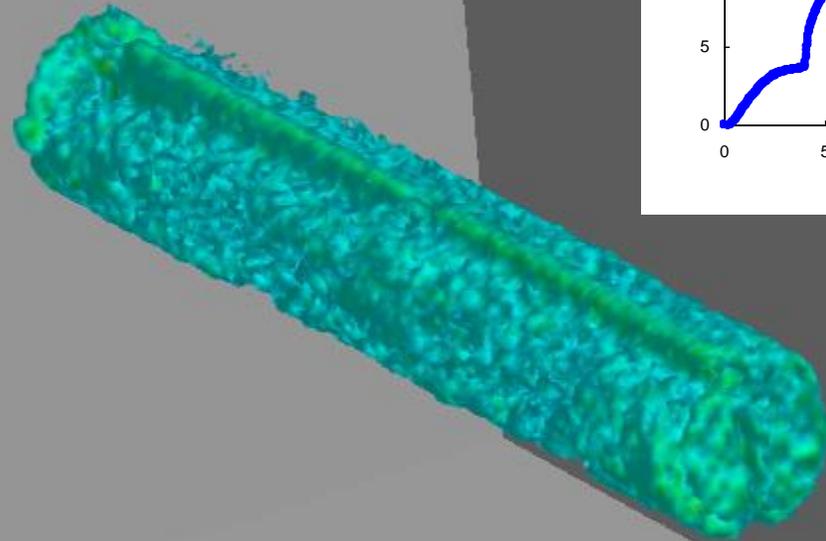
33a-01

5.0 hrs
Cooling Starts



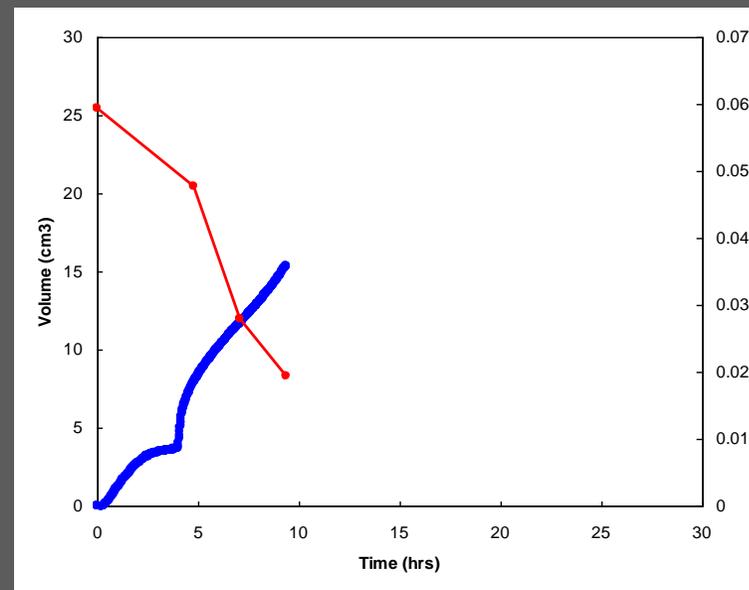
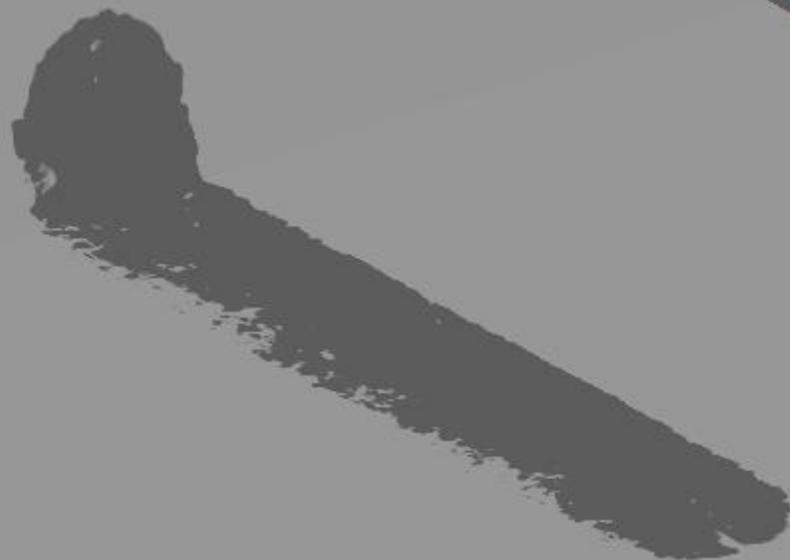
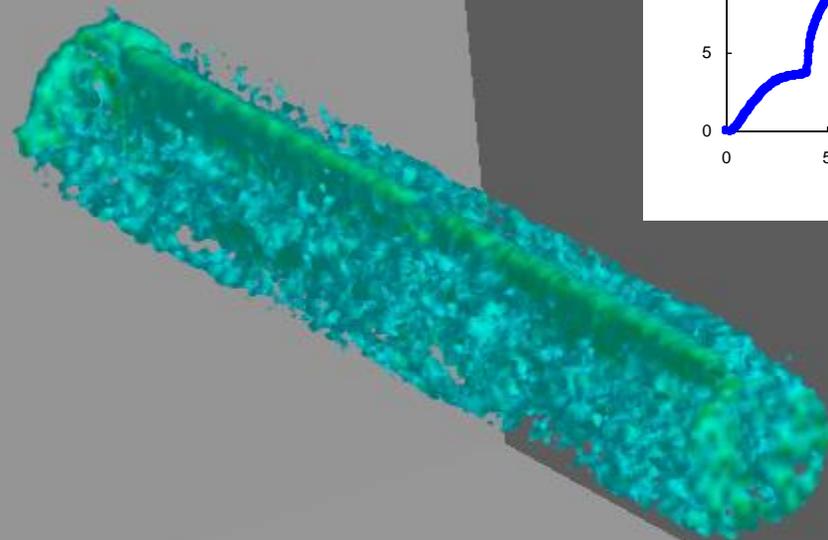
33c-01

7.2 hrs



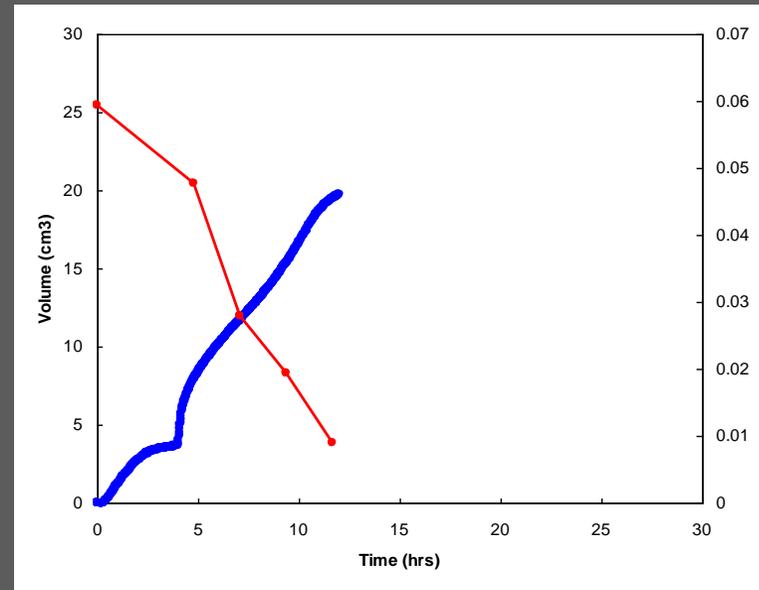
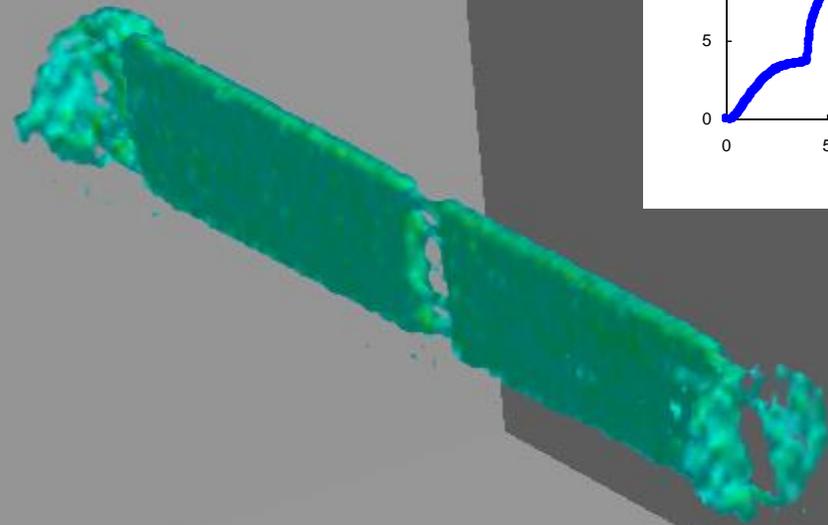
33c-02

9.4 hrs



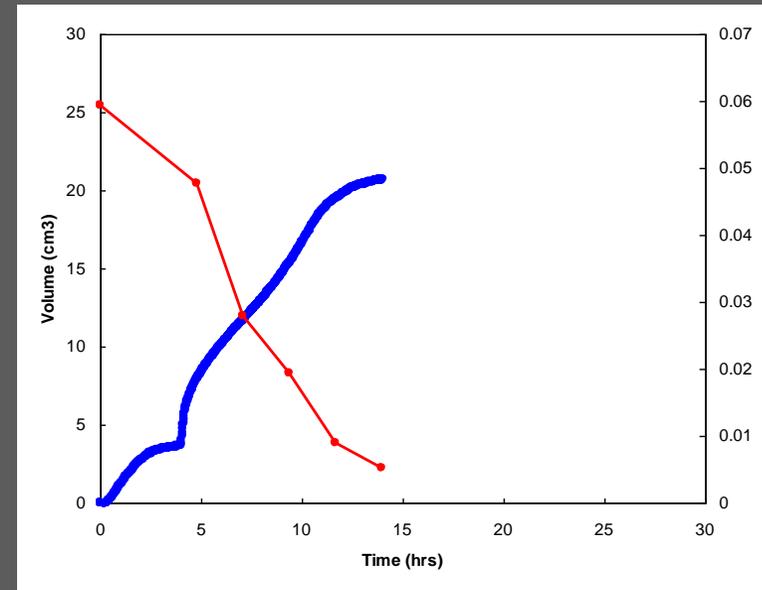
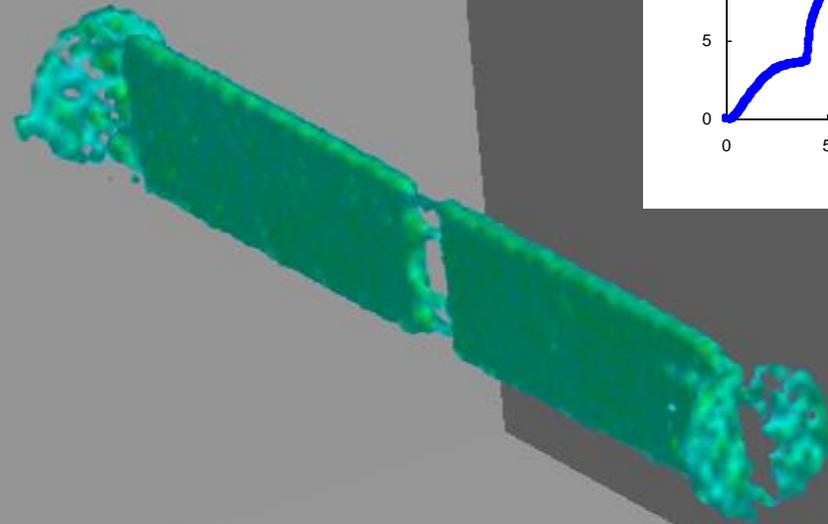
33c-03

12.0 hrs



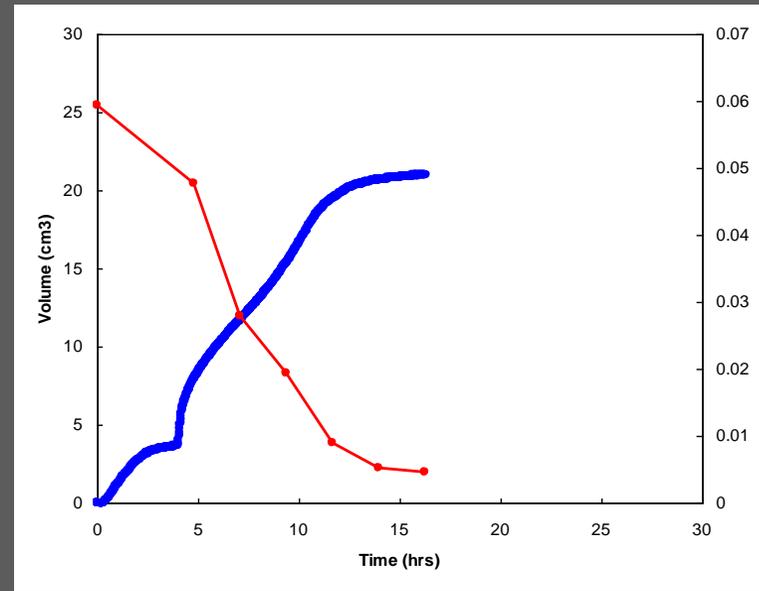
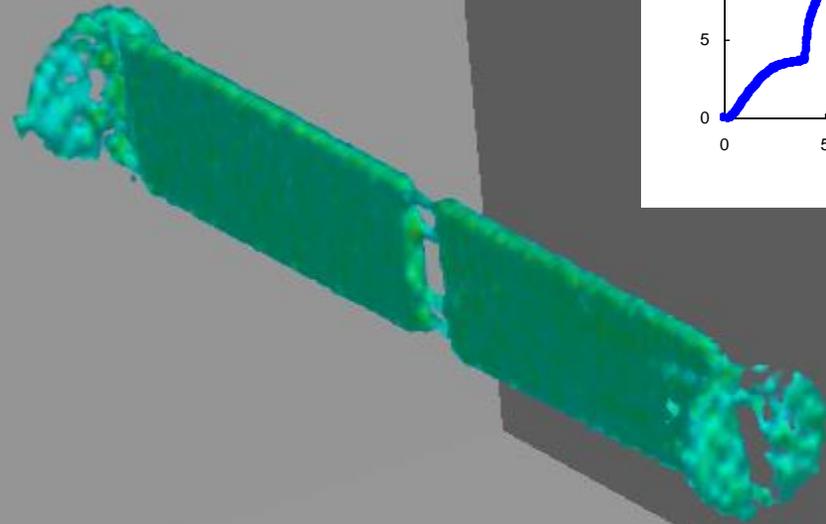
33c-04

14.0 hrs



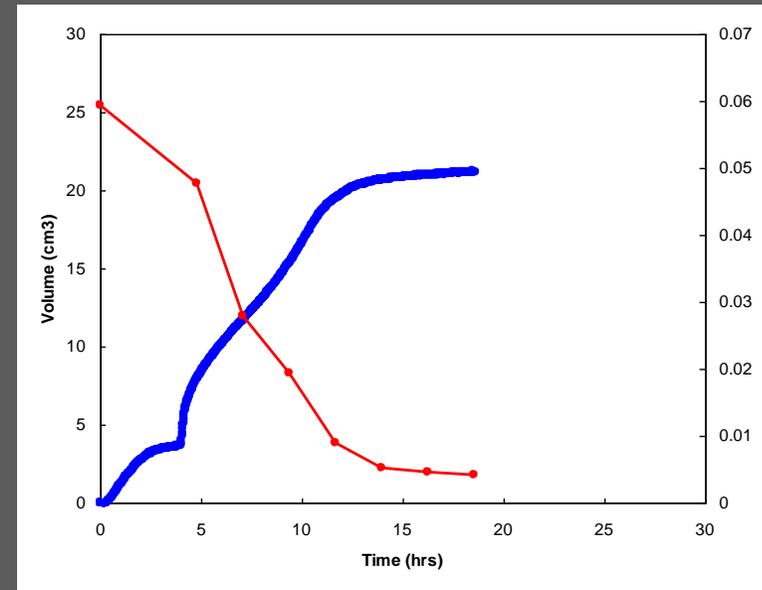
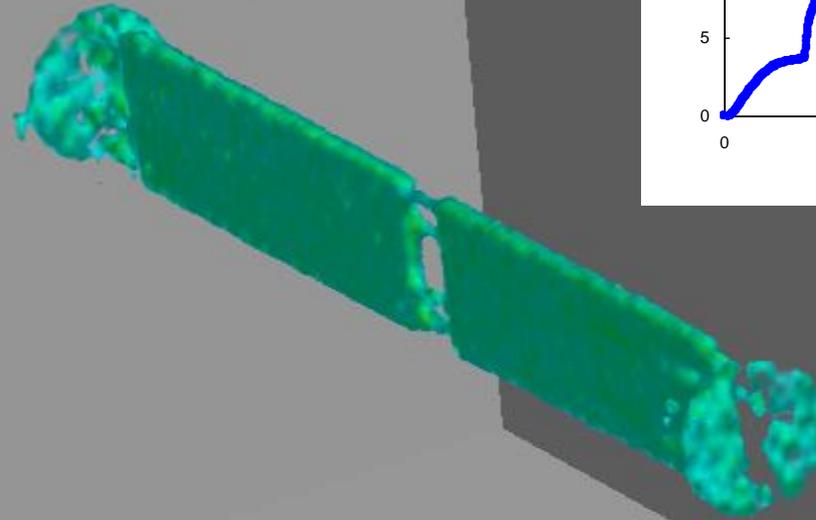
33c-05

16.3 hrs



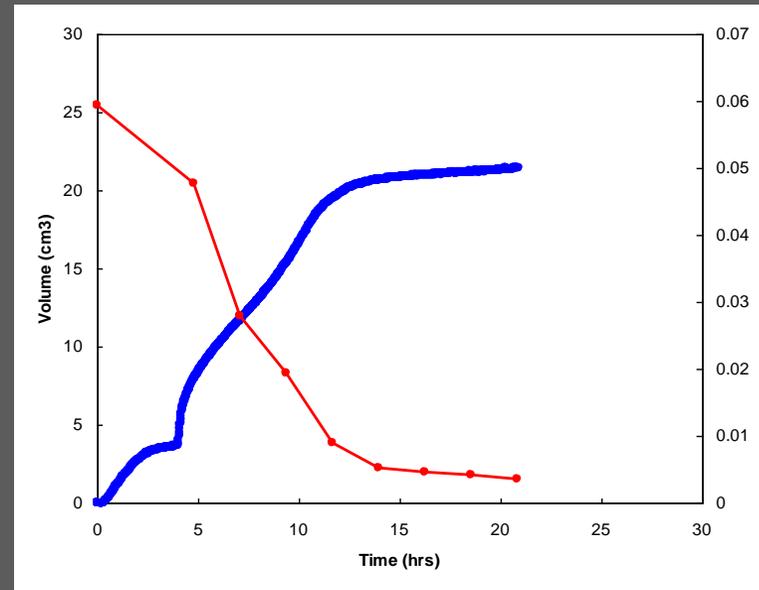
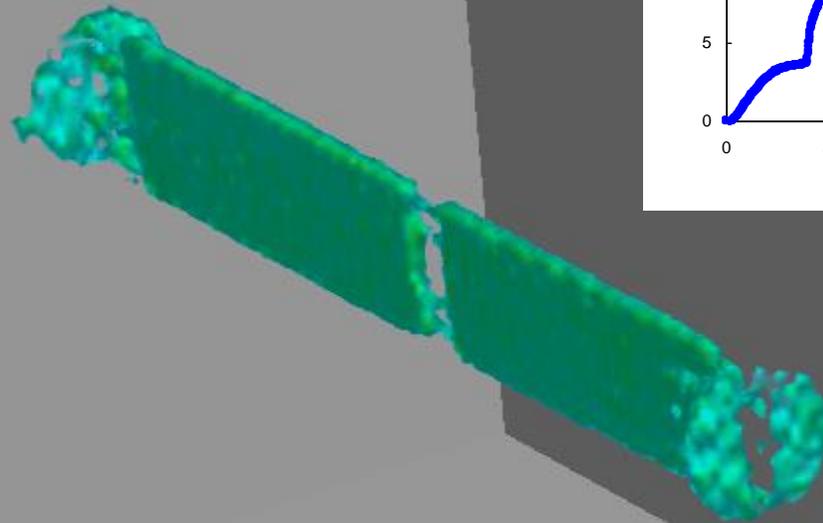
33c-06

18.6 hrs



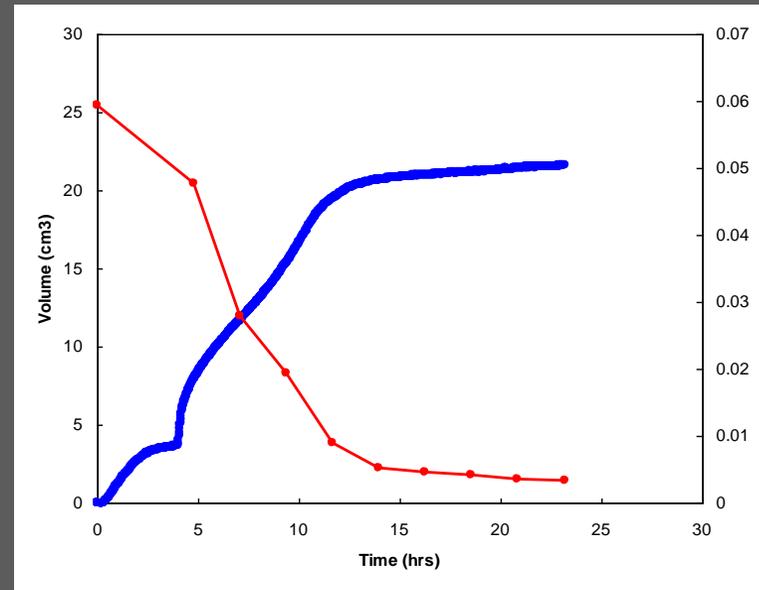
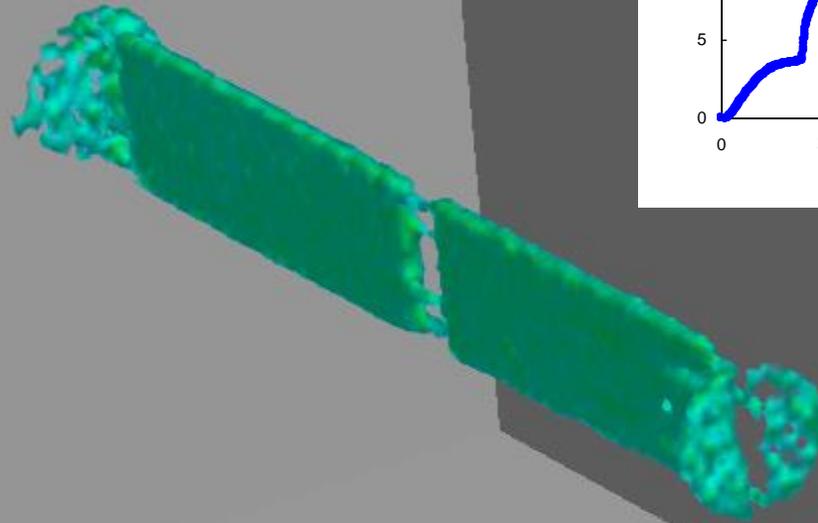
33c-07

20.9 hrs



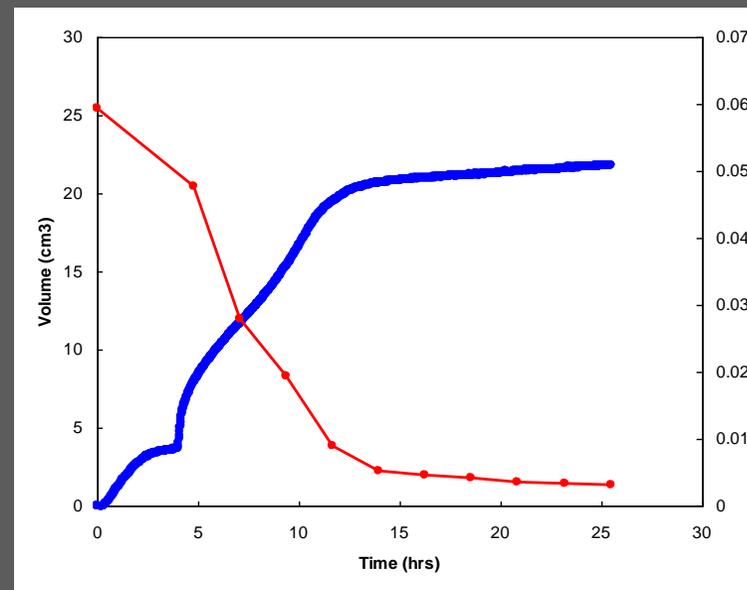
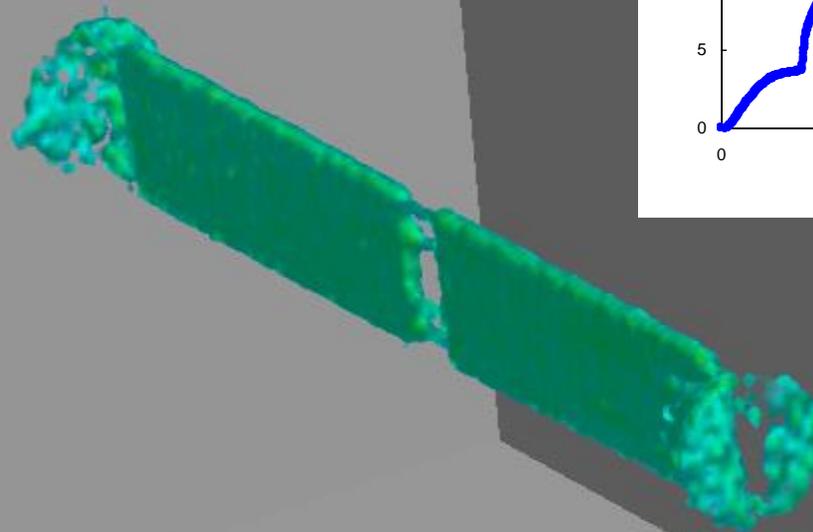
33c-08

23.2 hrs



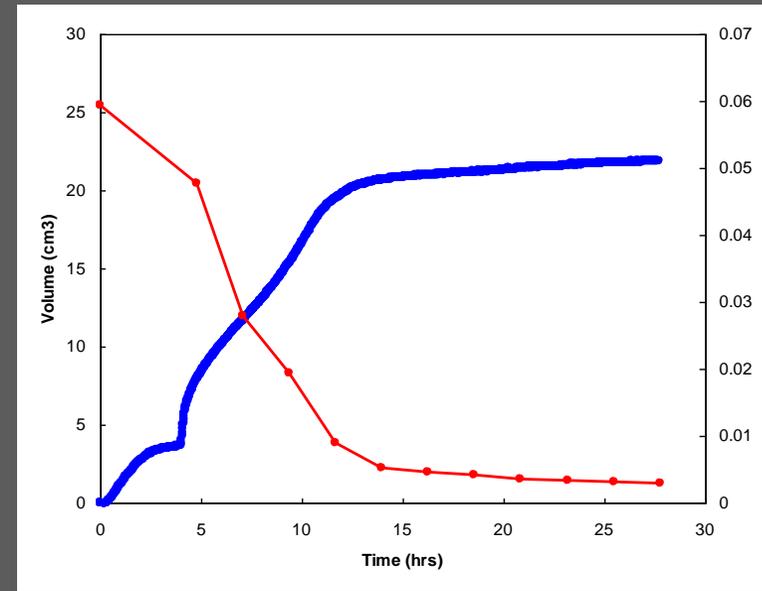
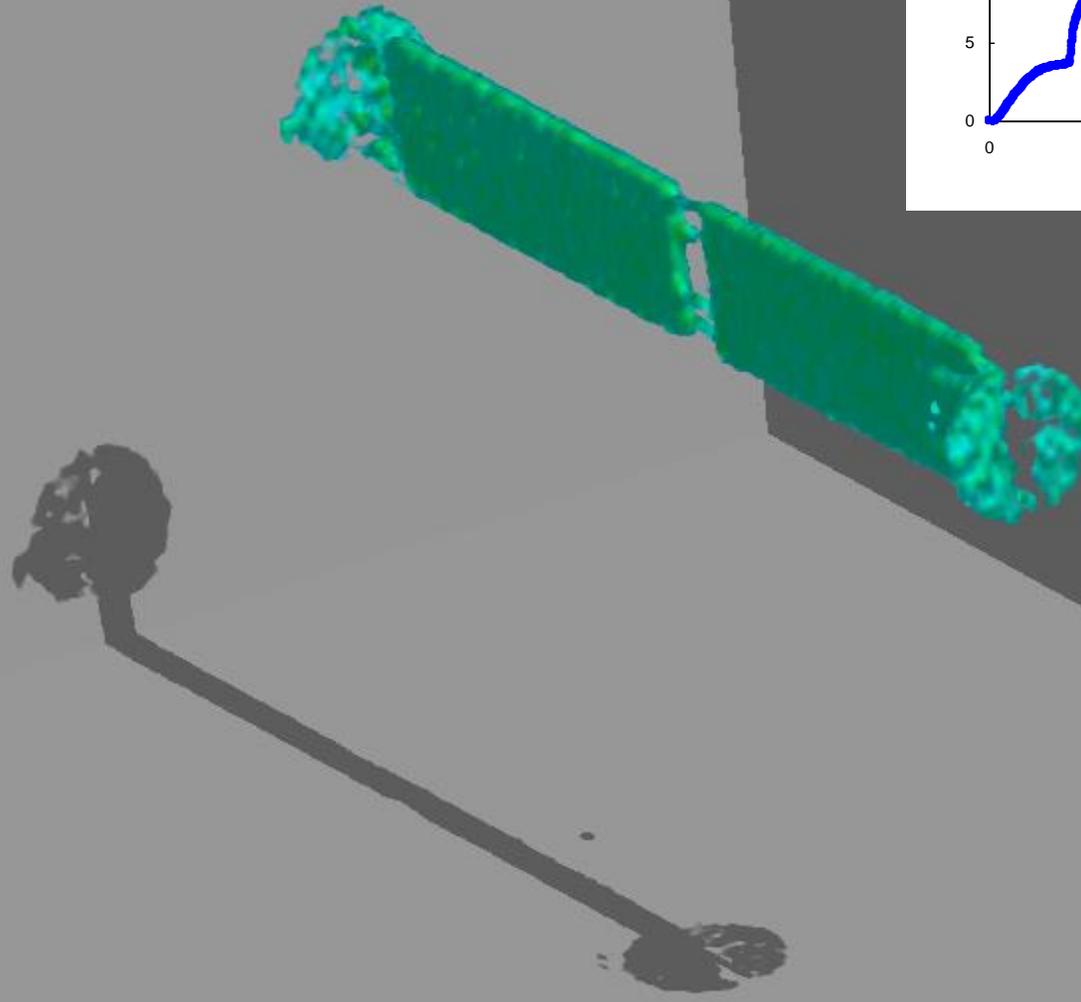
33c-09

25.5 hrs



33c-10

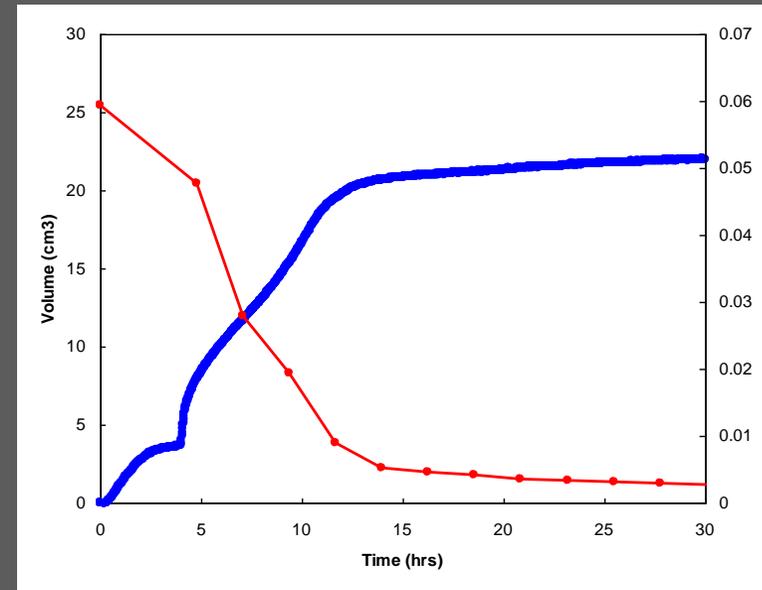
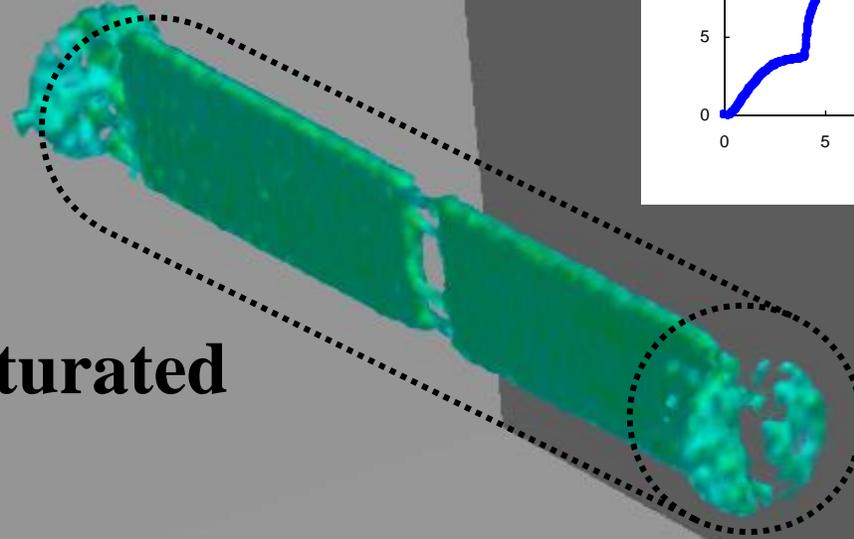
27.7 hrs



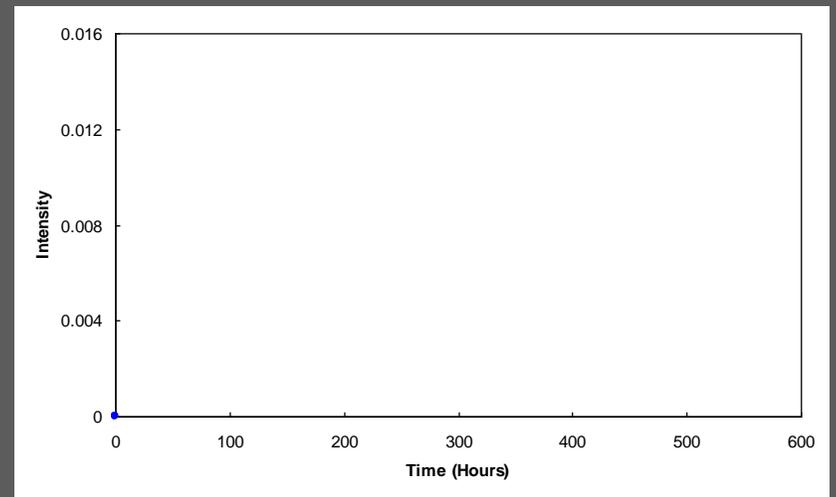
33c-11

30.0 hrs

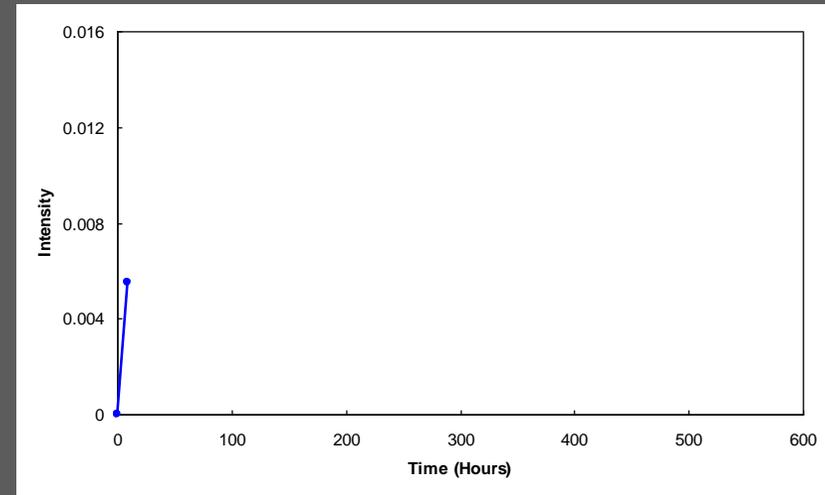
**Core Halves Saturated
with hydrate**



0.0 hrs

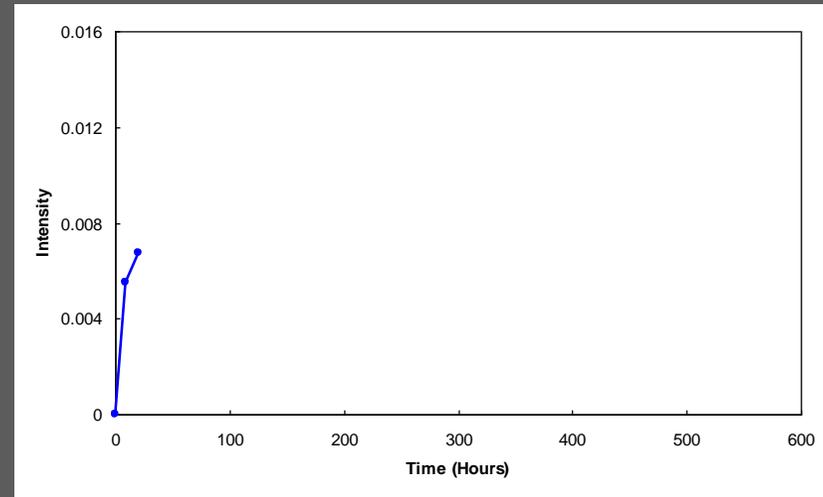


9.1 hrs



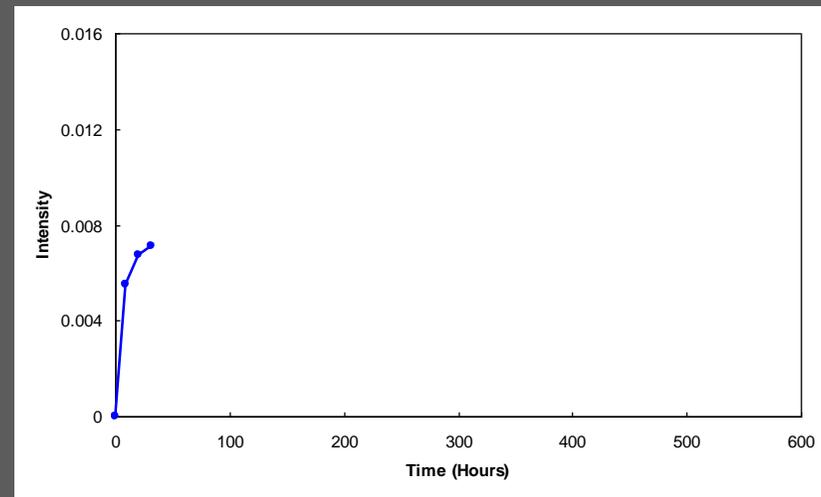
34b-01

20.6 hrs

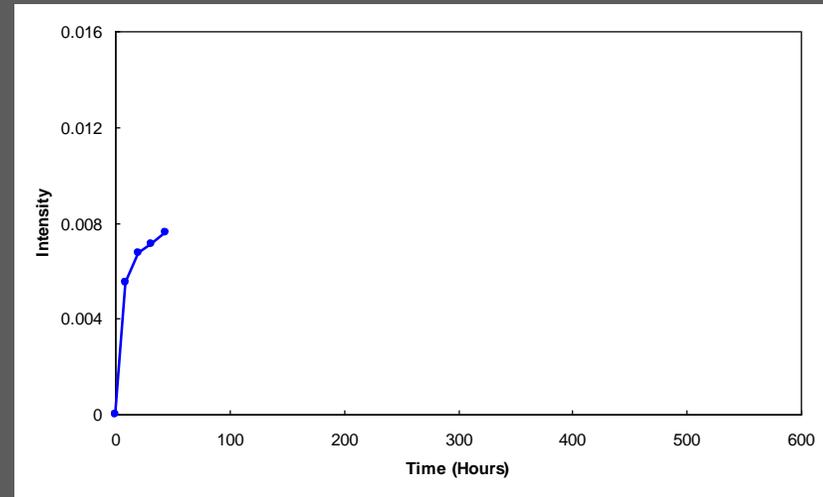


34b-02

32.0 hrs

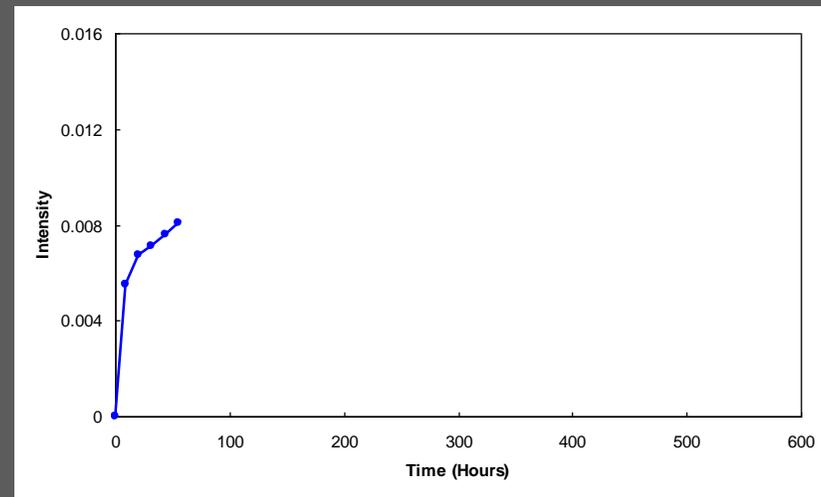


43.4 hrs



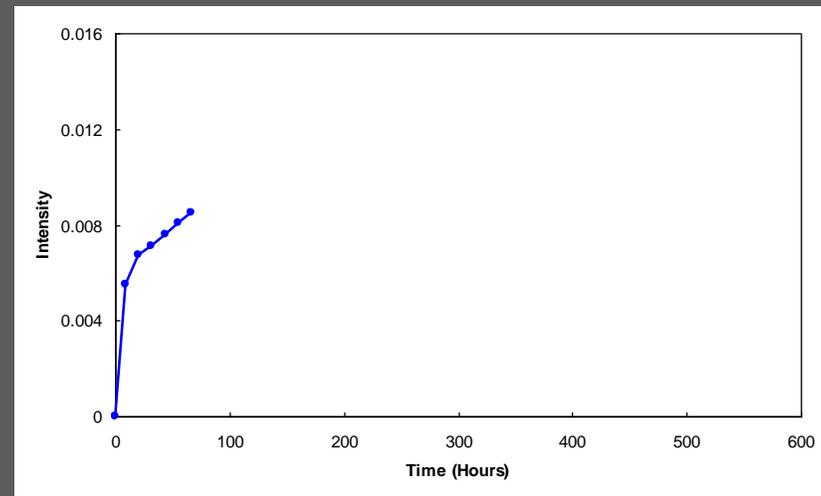
34b-04

54.9 hrs



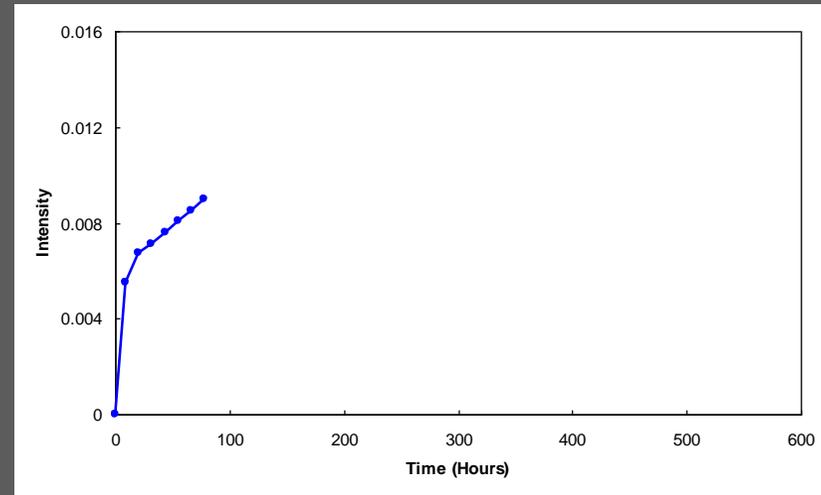
34b-05

66.3 hrs



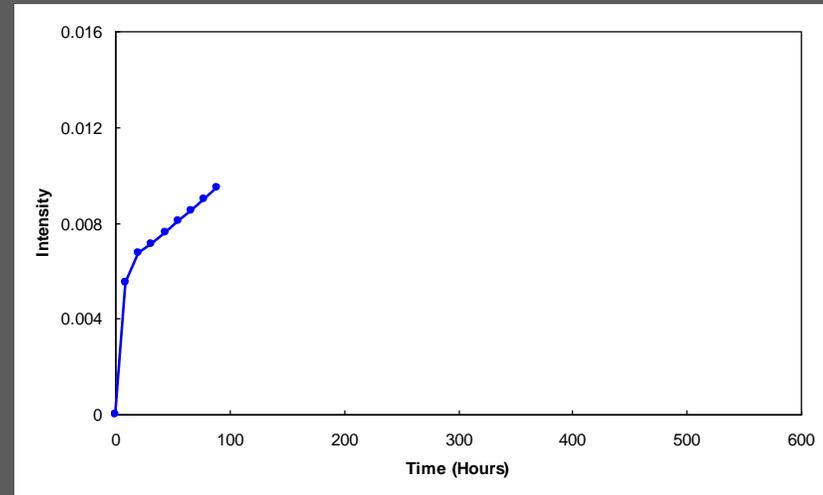
34b-06

77.8 hrs



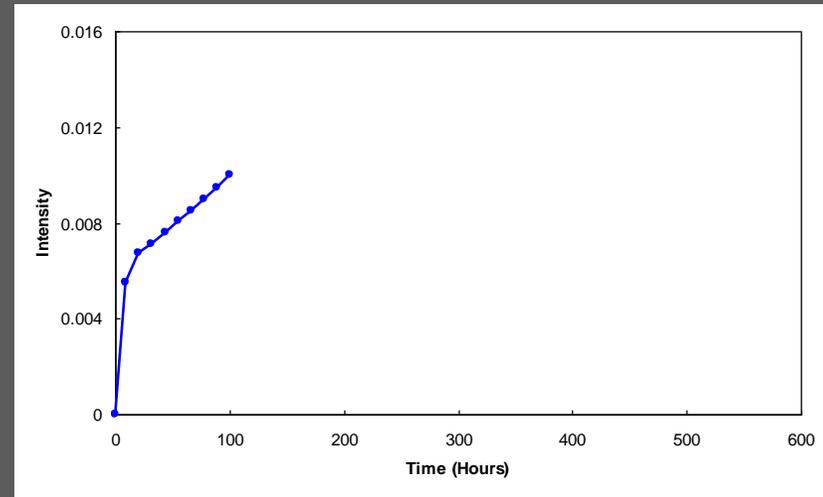
34b-07

89.2 hrs



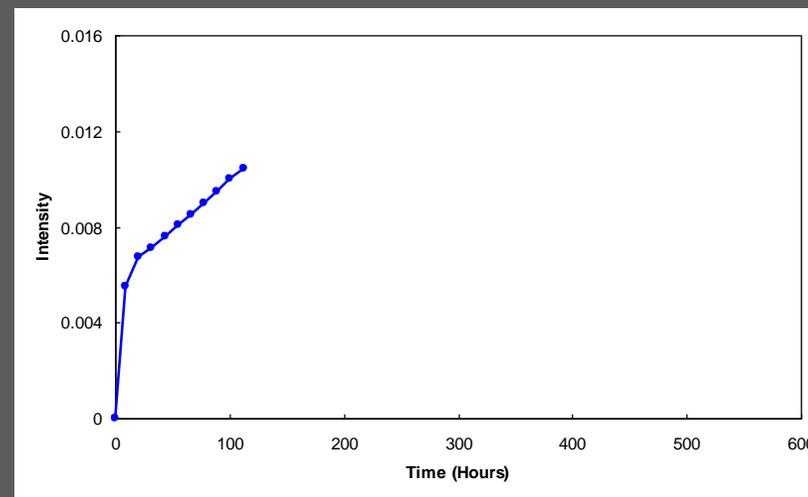
34b-08

100.6 hrs



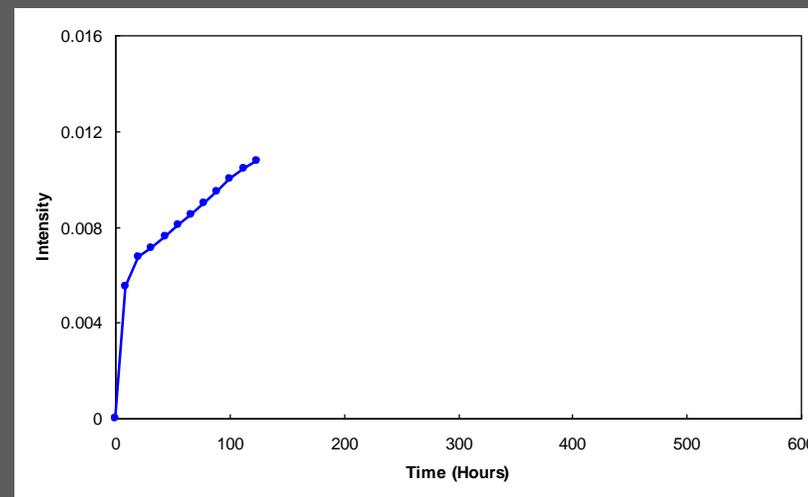
34b-09

112.1 hrs



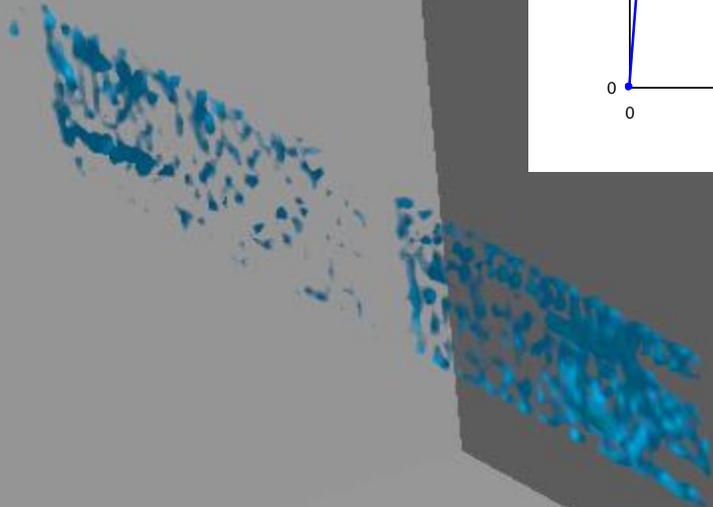
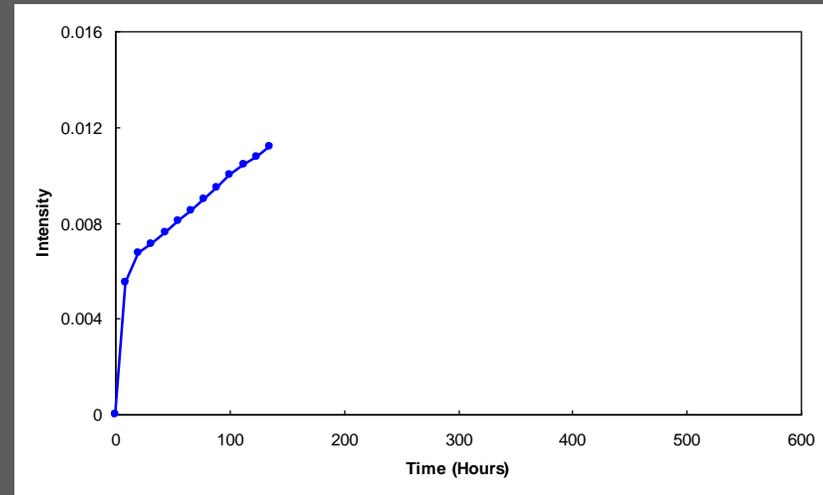
34b-10

123.5 hrs



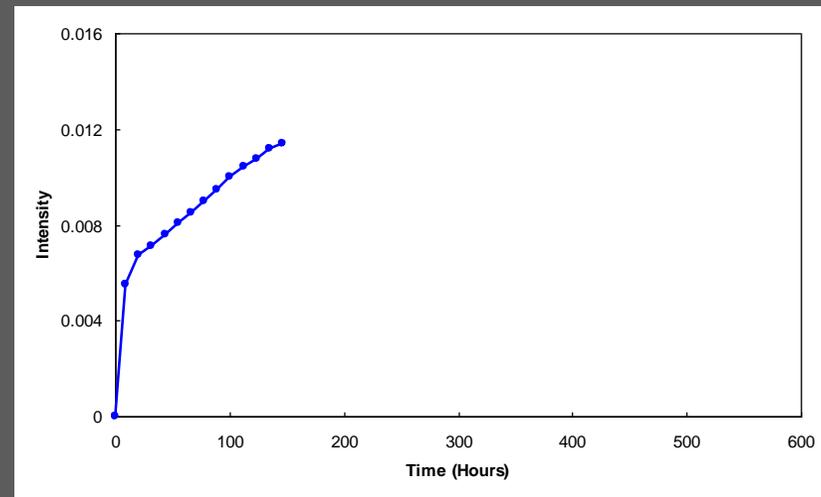
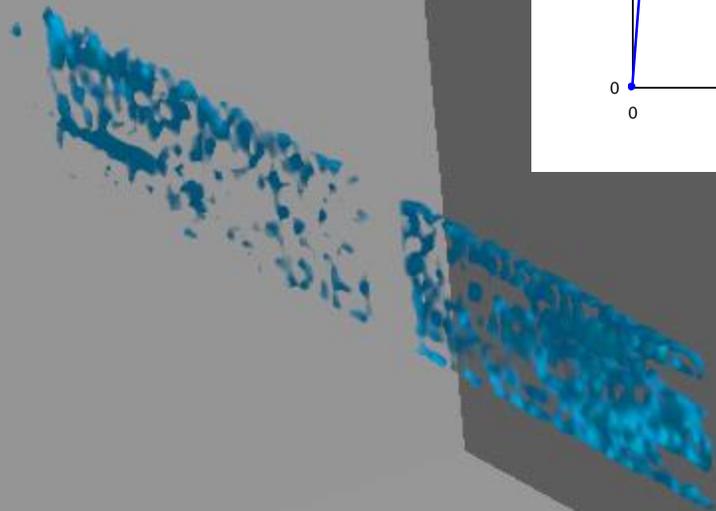
34b-11

135.0 hrs



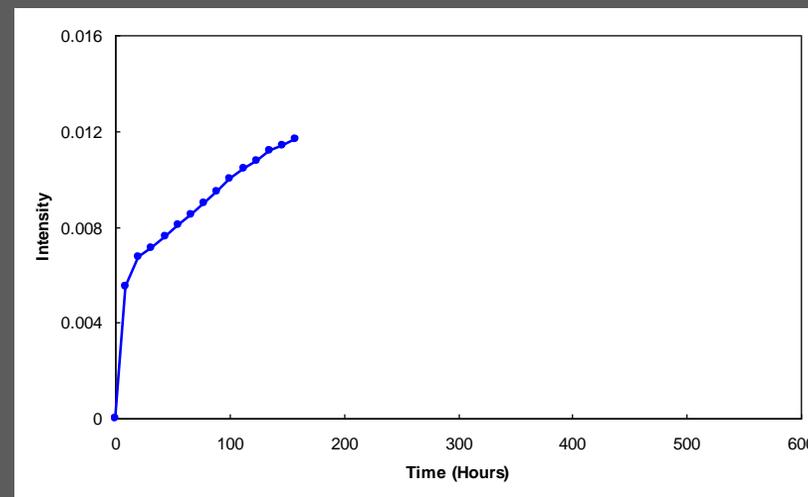
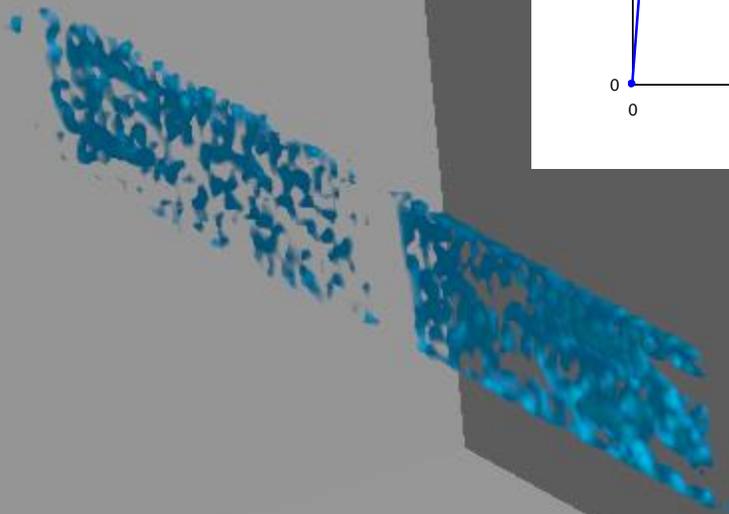
34b-12

146.4 hrs



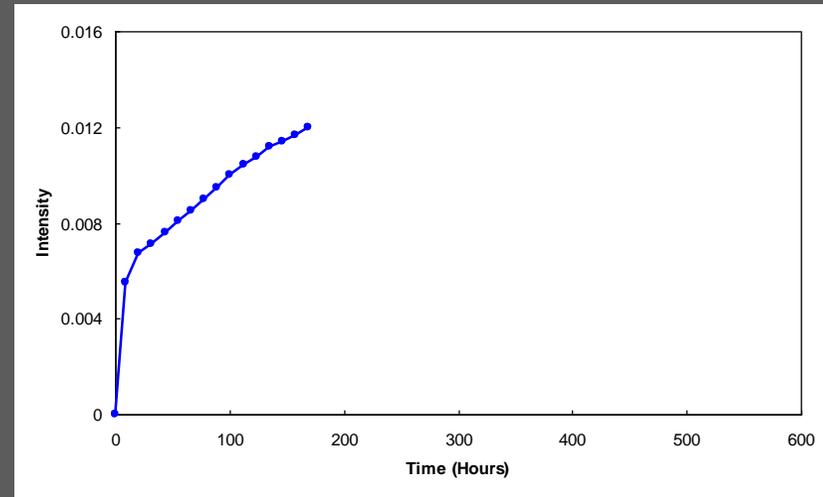
34b-13

157.8 hrs



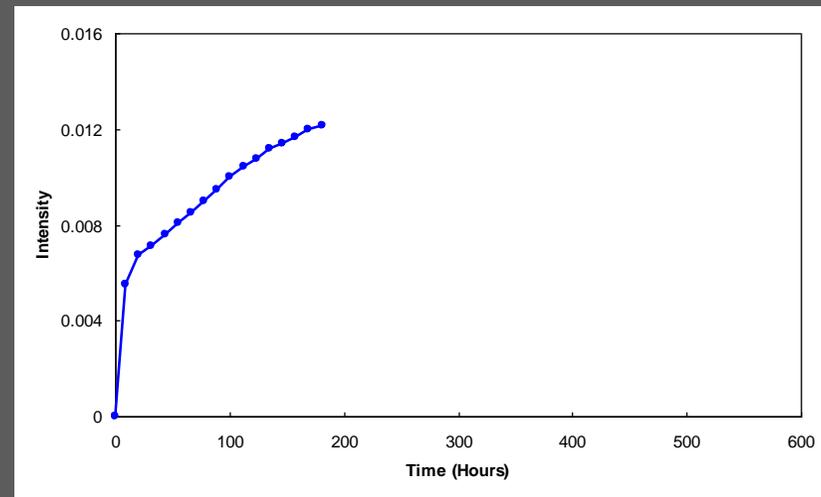
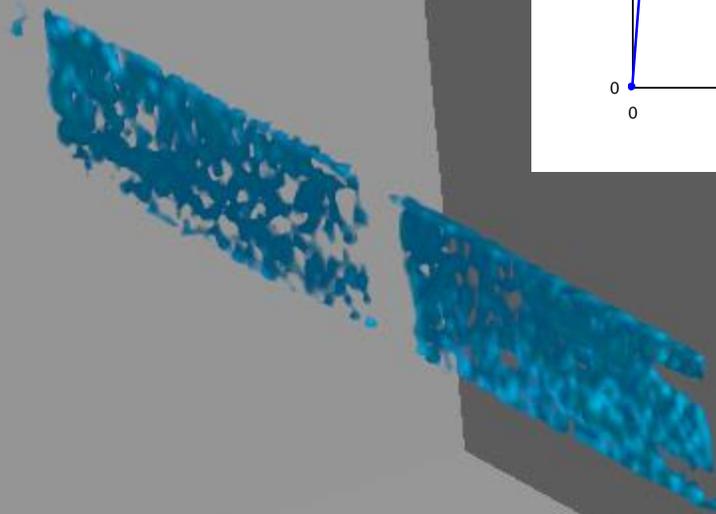
34b-14

169.3 hrs



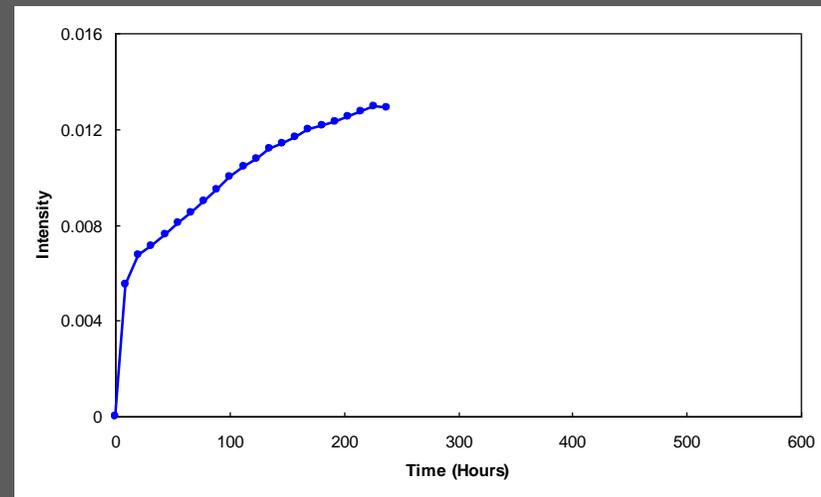
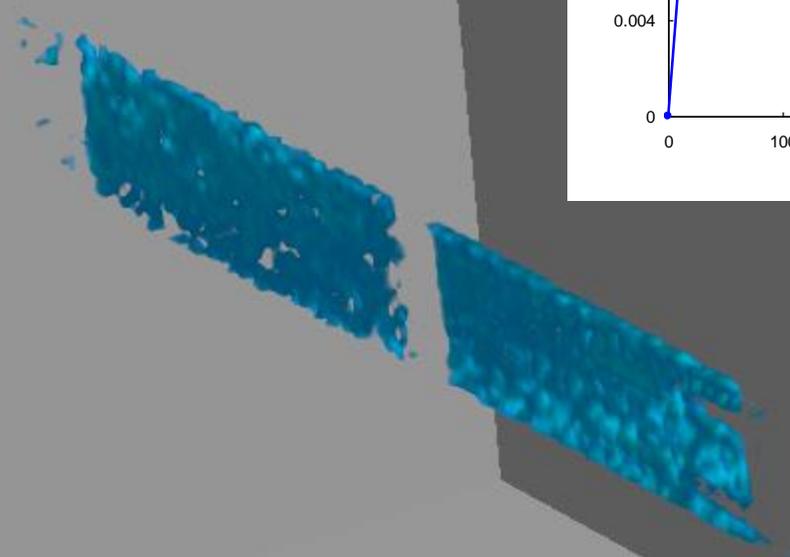
34b-15

180.7 hrs

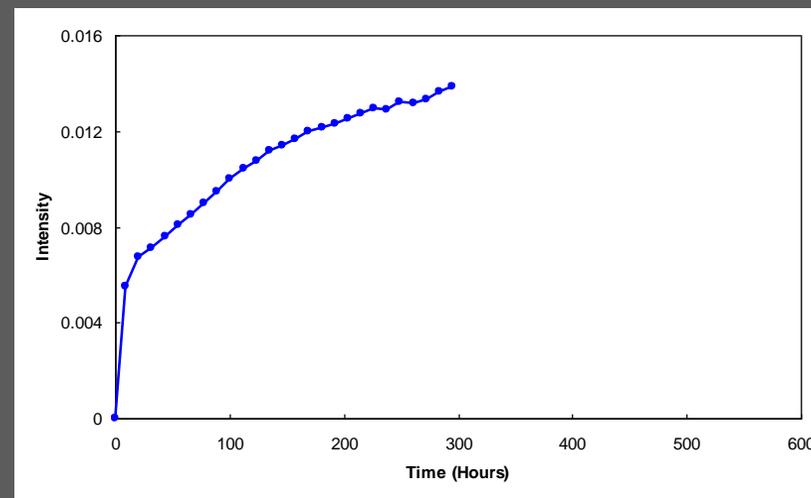
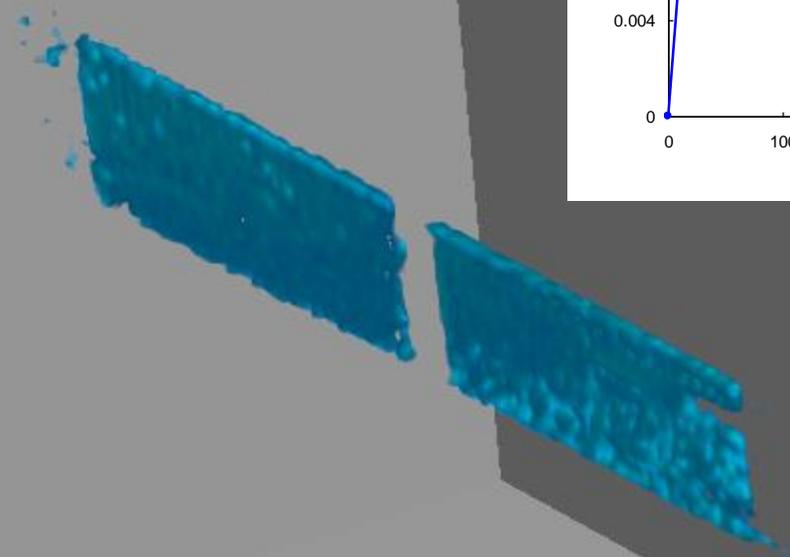


34b-20

237.9 hrs

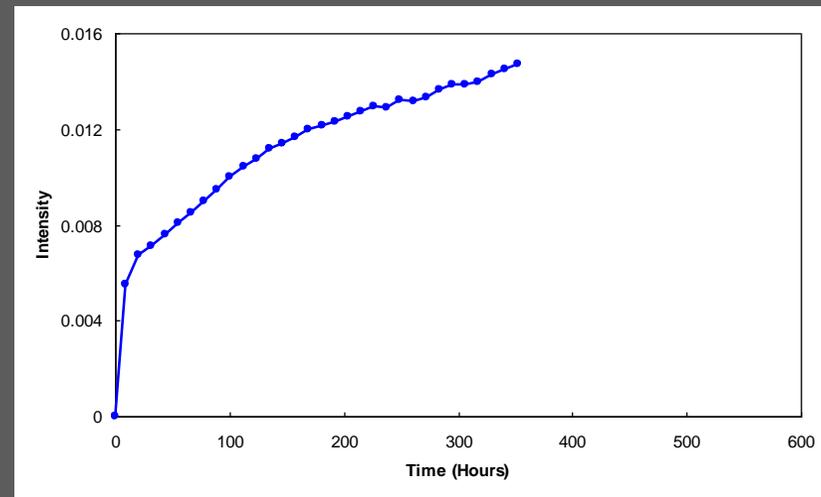
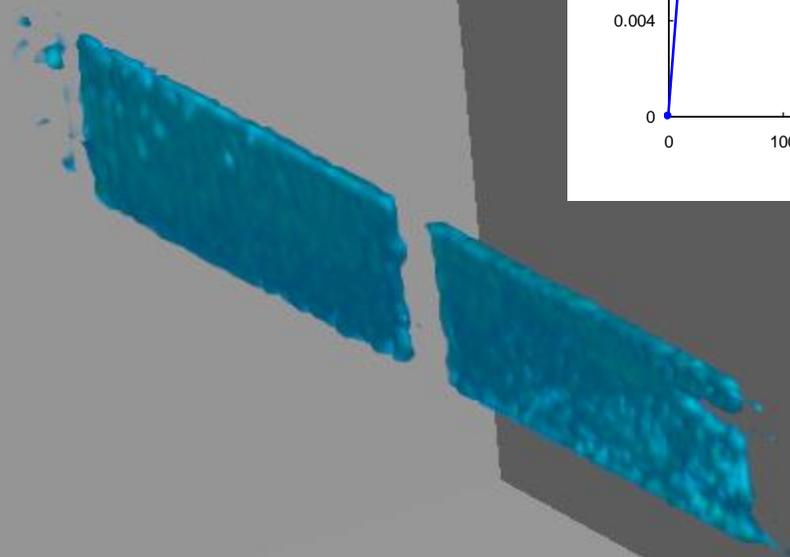


295.1 hrs

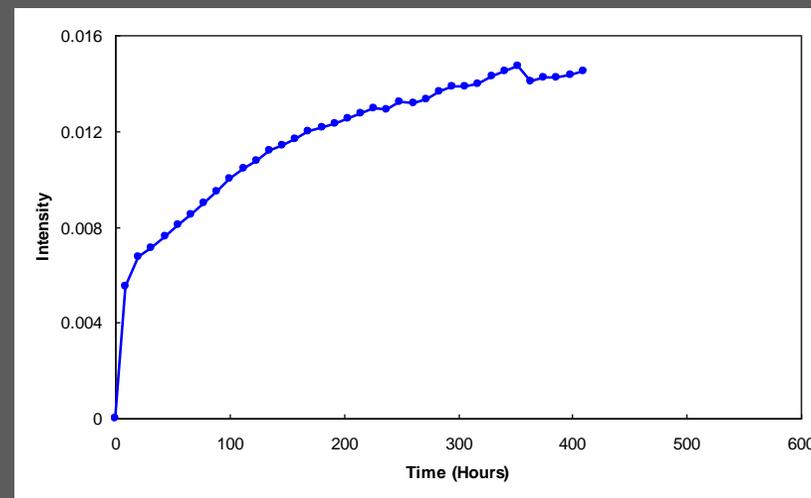
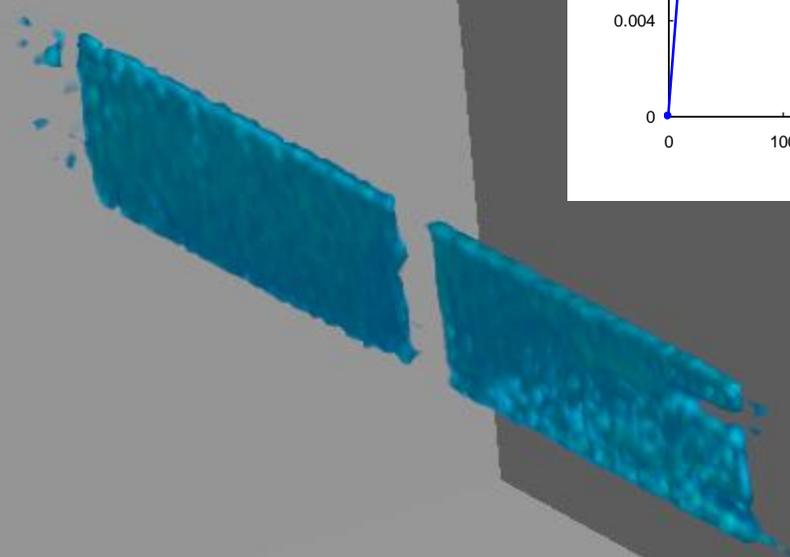


34b-30

352.3 hrs

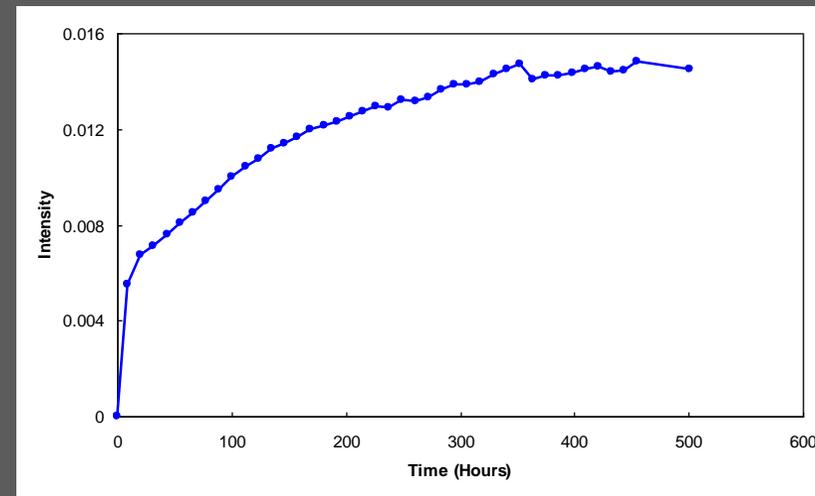
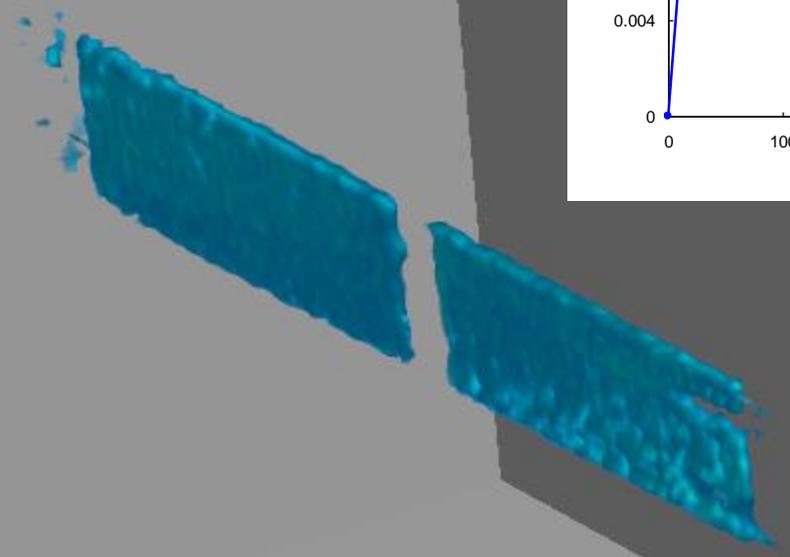


409.5 hrs



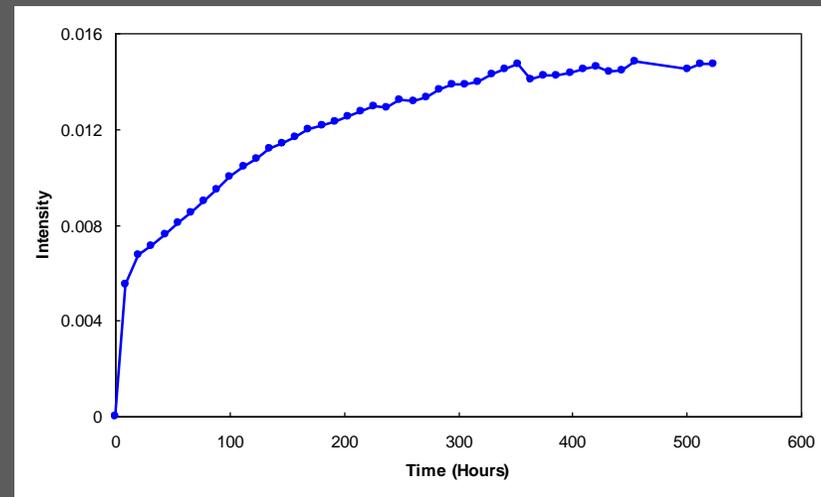
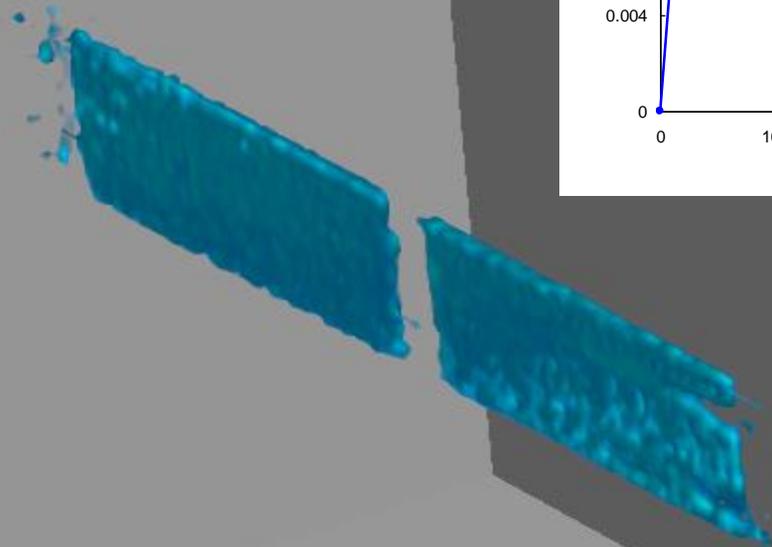
34b-40

501.0 hrs

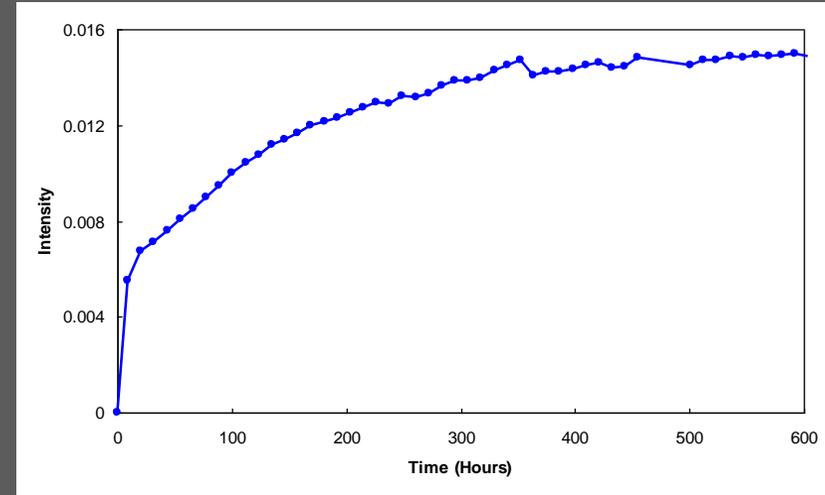
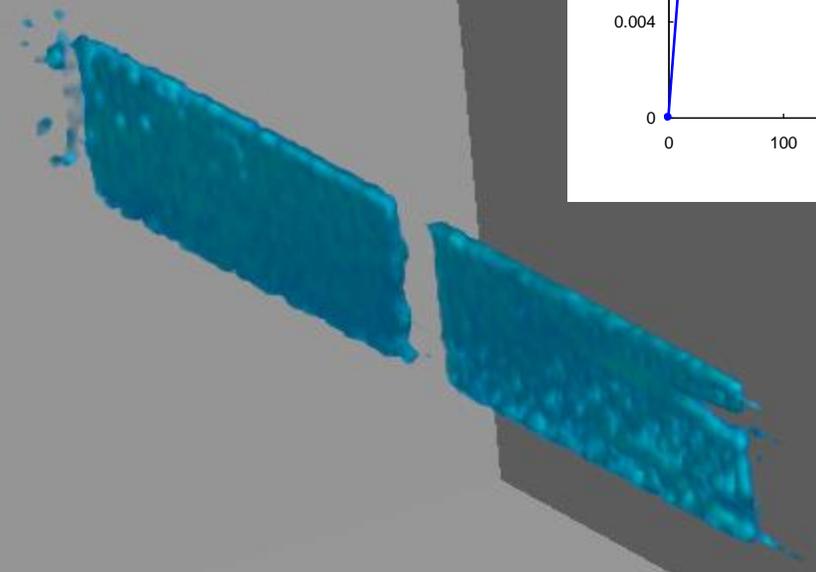


34b-45

523.8 hrs



603.9 hrs



Scientific Conclusions

- **MRI Provides Unique Dynamic Data of Hydrate Formation and Production Consistent with Conventional Results.**
- **CO₂ Exchange for CH₄ in Hydrates Is Rapid and Efficient.**
- **No Free Water Observed During Exchange Process.**
- **Sufficient Permeability Remains During Hydrate Formation and Subsequent Production.**

CO₂ Storage in Hydrate Reservoirs with Associated Spontaneous Natural Gas Production

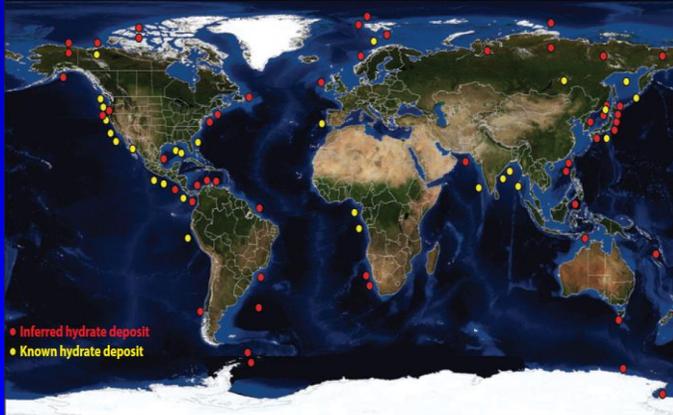
Arne Graue and Bjørn Kvamme, Dept. of Physics, University of Bergen, NORWAY
Funding: ConocoPhillips, Statoil and The Research Council of Norway



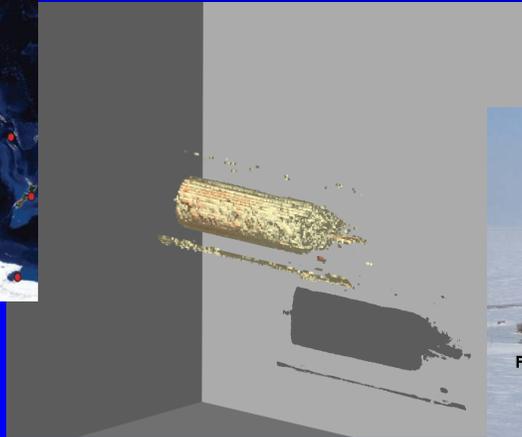
Objectives:

Experimentally and theoretically determine spontaneous methane production when hydrate is exposed to CO₂; with the purpose of CO₂ sequestration.

Methane hydrate reservoirs



In-Situ imaging (MRI) of hydrate formation



Methane production by CO₂ injection in field test in Alaska 2012



Alaska Field Injection Test 2011-2012

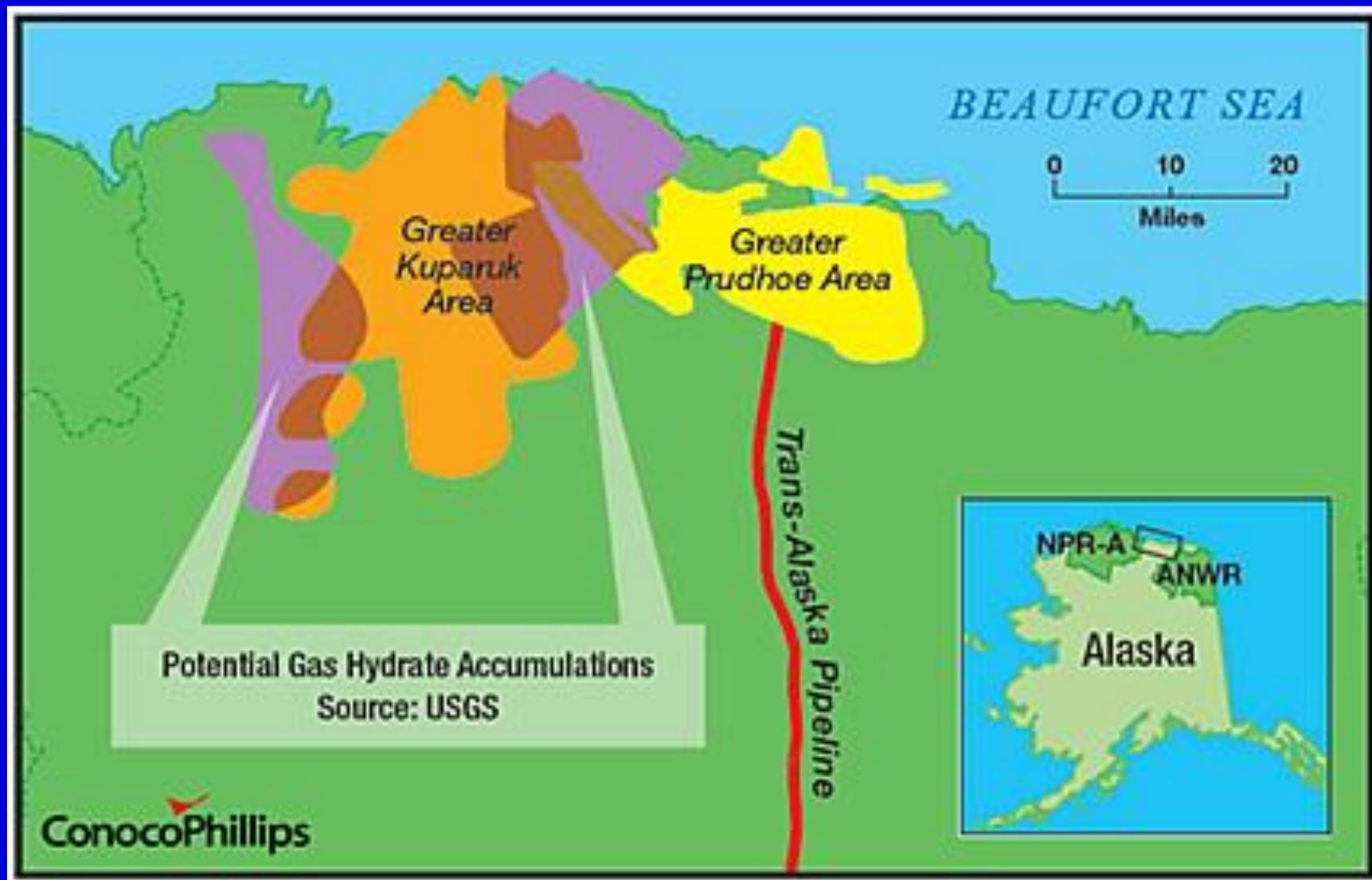
- **ConocoPhillips, USDOE and JOGMEC**
- **US\$ 11.6 mill funding from US DOE, total cost ca. US\$30mill**
- **CO₂ injection**

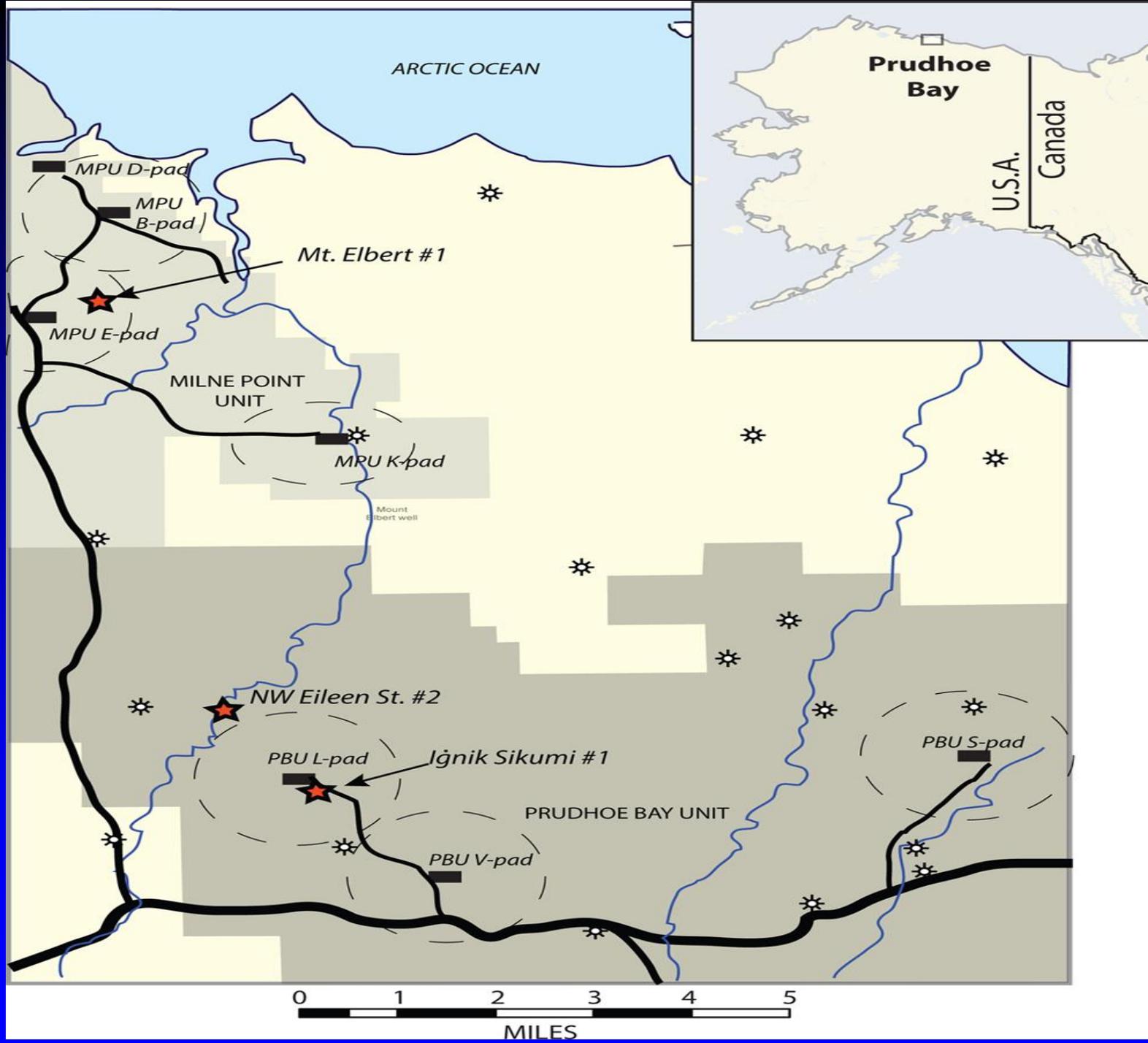
Summary of Field Test (Injection Test)

Schedule:

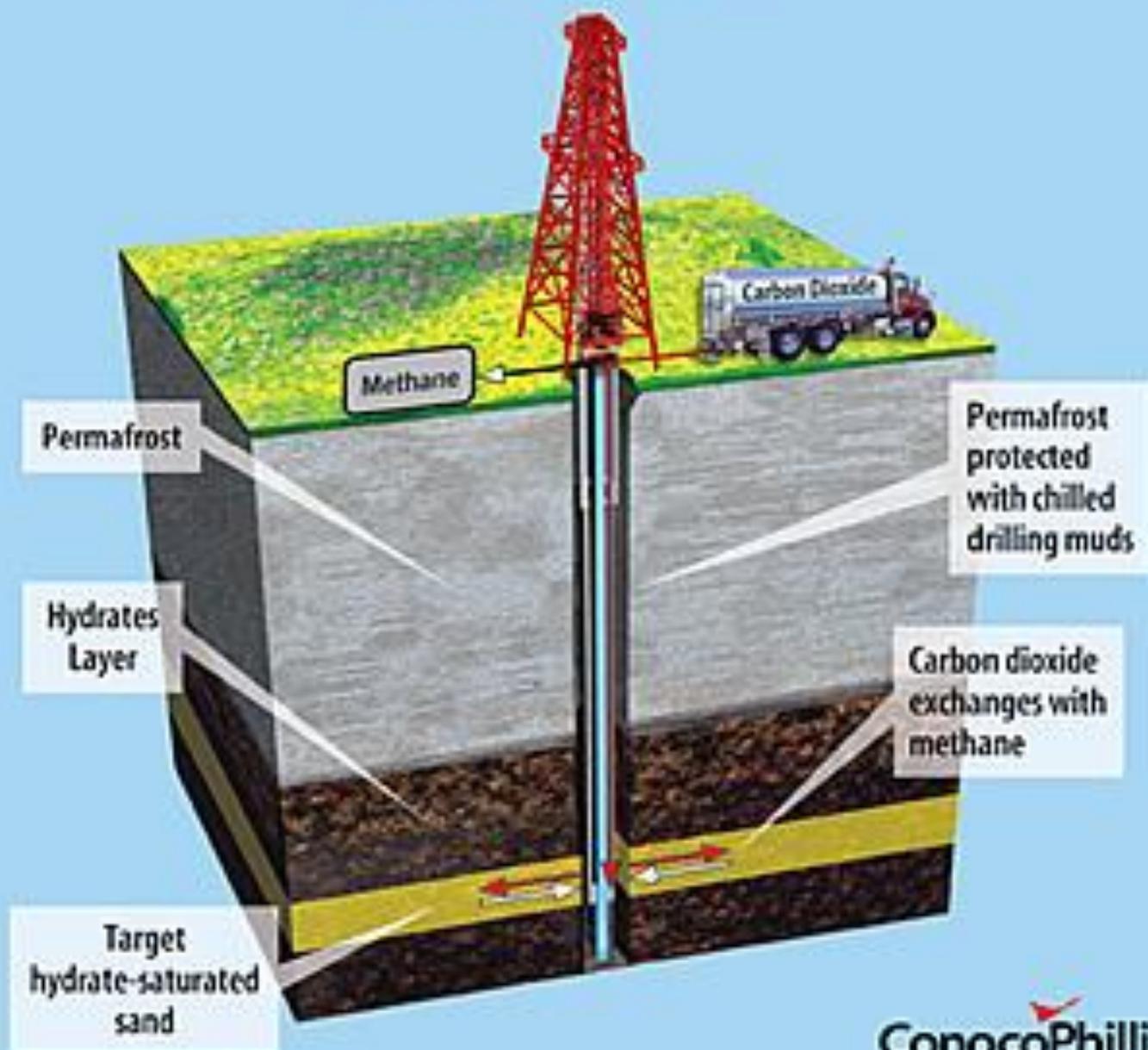
Apr. 2011: Drilling test well (Complete)
Nov. 2011: Finalizing parameters for the field test
Jan.-Apr. 2012: Field test

Location : Prudhoe Bay operating unit in Alaska, USA
Operator : ConocoPhillips Company (COP), through its wholly owned subsidiary, ConocoPhillips Alaska, Inc.
Investors : The United States Department of Energy (DOE)
JOGMEC; Japan Oil, Gas and Metals National Corp.





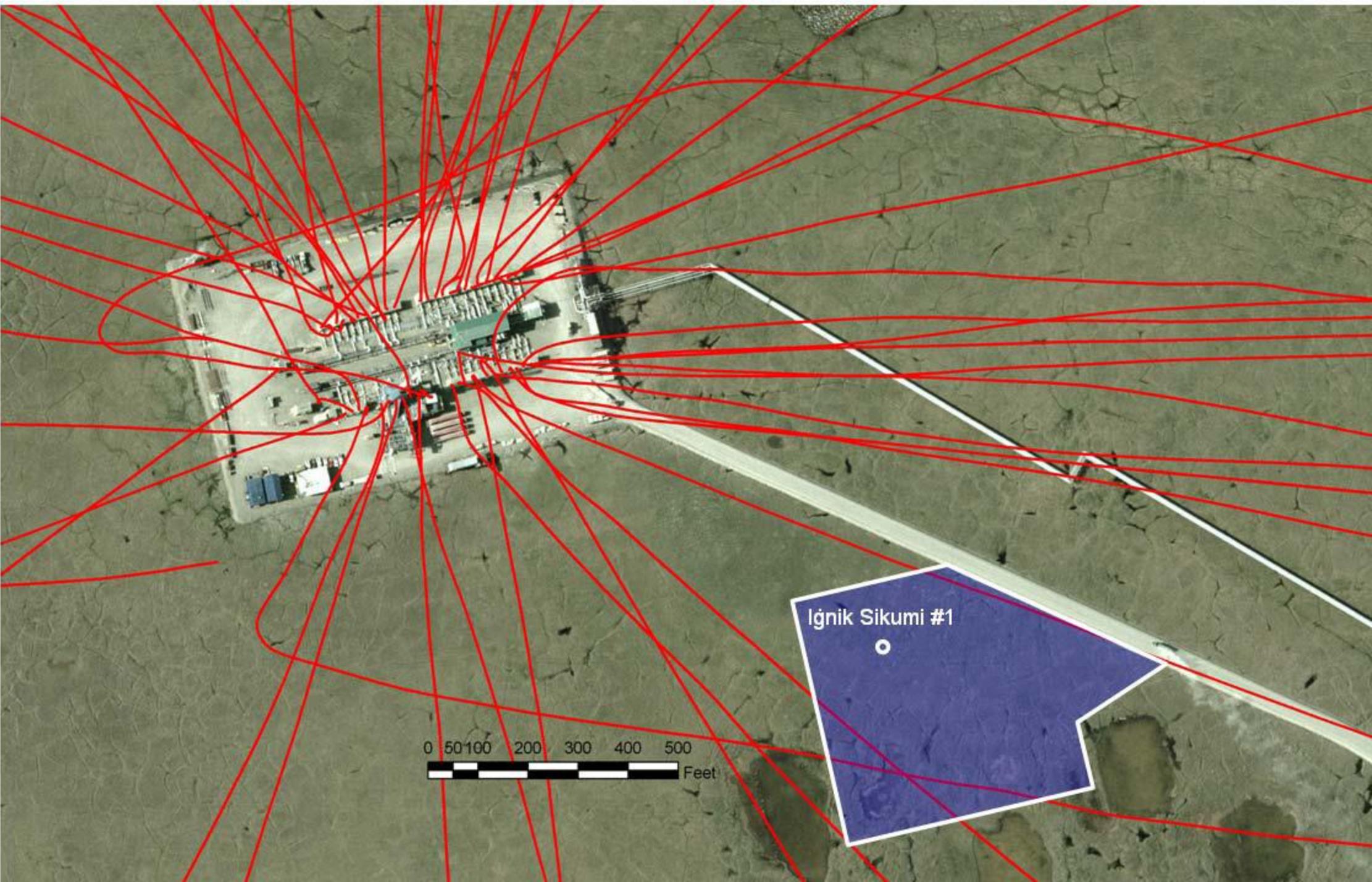
Methane Hydrates Well



Ignik Sikumi #1

Prudhoe Bay Unit L-pad



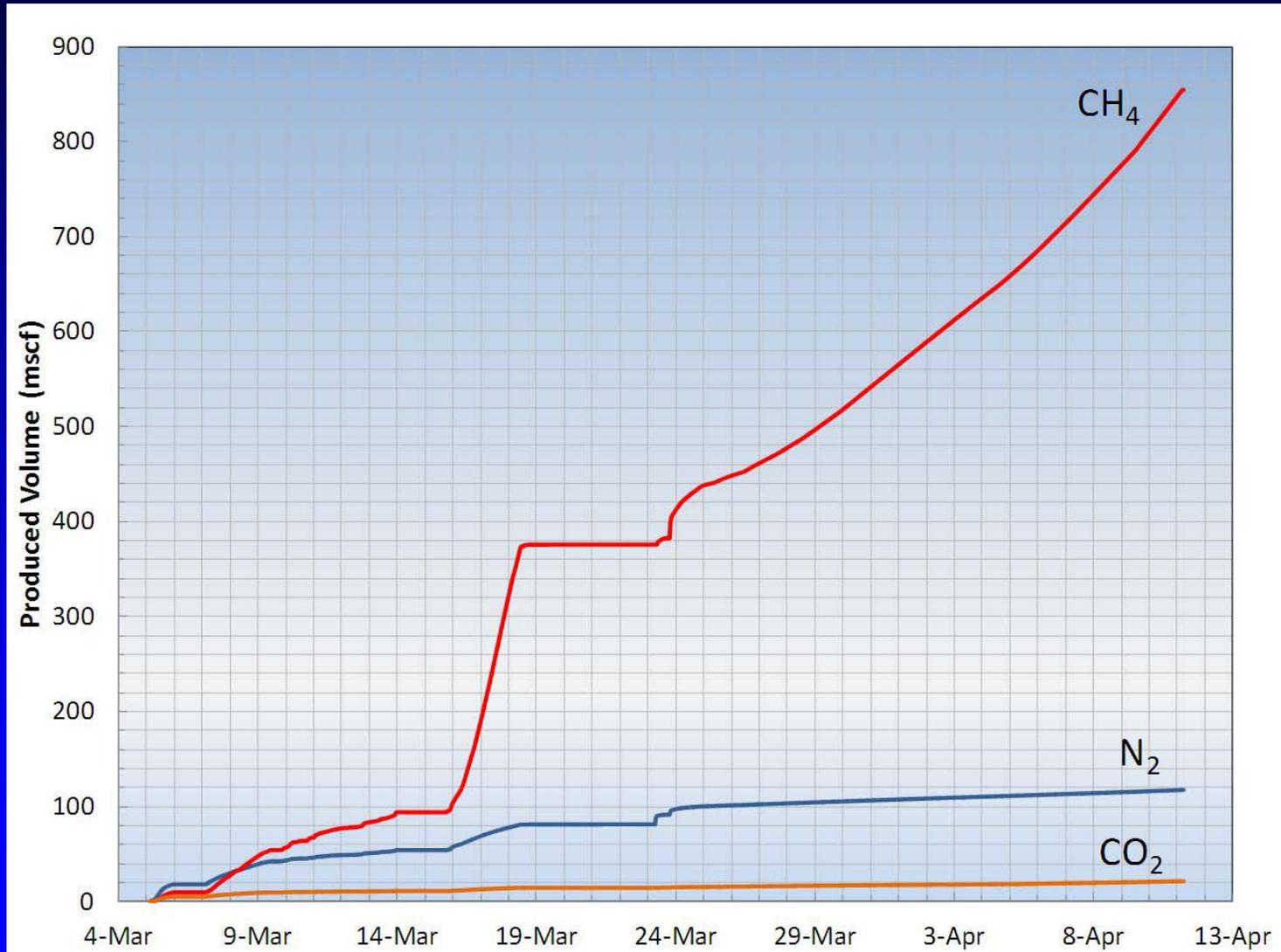


Iḡnik Sikumi #1

0 50 100 200 300 400 500 Feet



Gas Production from the Field Test



Ignik Sikumi #1 Flowback/Drawdown: Gas composition

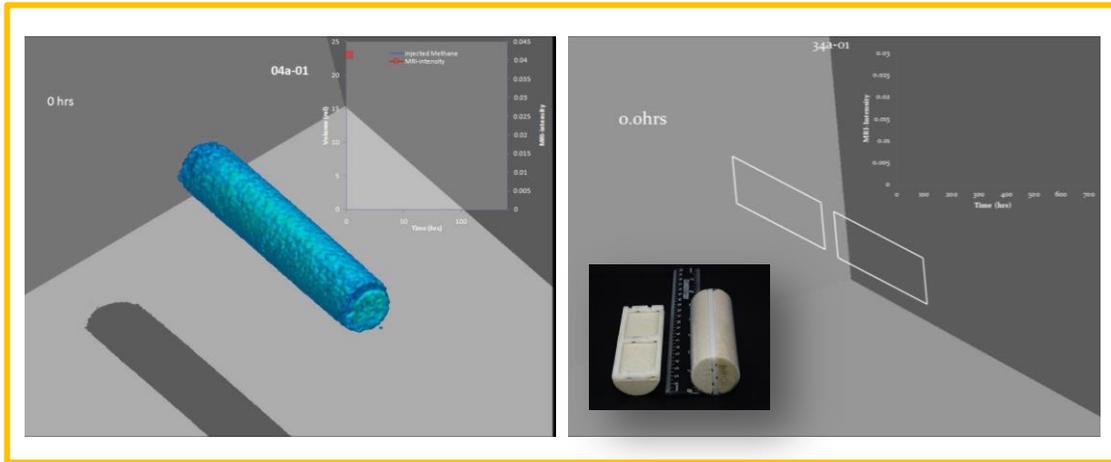
Conclusions on Industry Collaboration

- **Mutually beneficial**
- **Students exposed to experienced senior petroleum experts**
- **Access to advanced and expensive equipment**
- **Leveraged research**
- **Provides qualified candidates for Norway and the oil industry**
- **Recruitment of national students**

Energy for the Future Gas Production WITH CO₂ Storage in Hydrates

Energy bound in hydrates is more than combined energy in conventional oil, gas and coal reserves

UiB Laboratory Verification of Technology

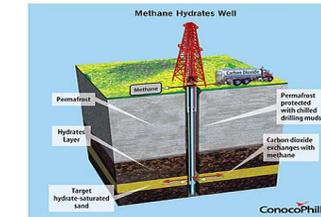


< 10 year
US \$30 mill

Field Verification of UiB Technology

“While this is just the beginning, this research could potentially yield significant new supplies of natural gas.”

U.S. Energy Secretary Steven Chu, May 2nd 2012



DOE, ConocoPhillips and JOGMEC at the Iġnik Sikumi test site, Alaska

What are Methane Hydrates?

Methane hydrates are ice-like structures with natural gas trapped inside, and are found both onshore and offshore along nearly every continental shelf in the world.

Excerpt from U.S. Energy Secretary Steven Chu’s statement

...to conduct a test of natural gas extraction from methane hydrate using a unique production technology, developed through laboratory collaboration between the University of Bergen, Norway... [D]emonstrated that this mixture could promote the production of natural gas. Ongoing analyses of the extensive datasets acquired at the field site will be needed to determine the efficiency of simultaneous CO₂ storage in the reservoirs.



Summary

Use of CO₂ as a commodity:

Business Case for CO₂ Storage:

- CO₂ EOR
- Integrated EOR (IEOR) with Foam: *Carbon Negative Oil Production*
- Exploitation of Hydrate Energy: *Carbon Neutral Gas Production*

Way Forward

New technologies ready for industrial scale implementation:

- Onshore in Permian Basin, USA (80% CO₂EOR, EOR target 137Bbbl)
- Offshore Opportunities: NCS, Middle East, Asia, Africa and Brazil
- International Whole Value Chain CCUS Collaboration Offshore

Thank you!