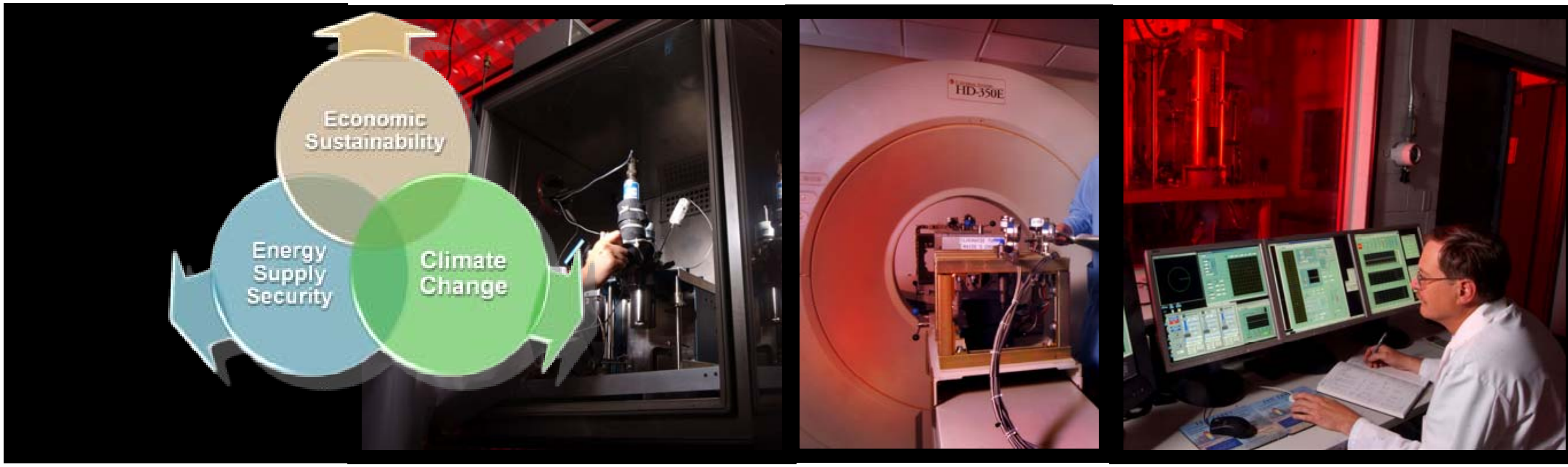
NATIONAL ENERGY TECHNOLOGY LABORATORY



NETL Lab / Experimental Efforts

Eilis J. Rosenbaum, NETL
Yongkoo Seol, NETL

Project Personnel

Robert P. Warzinski – Team Leader of Methane Hydrate Research (NETL)

Experimentalist, Chemistry – hydrate research 1993 to present

- Qualifications:
  - B.S. Chemistry, Waynesburg College, 1974
  - M.S. Chemistry, Duquesne University, 1976
  - E.I.T. Certification, 1992

Eilis J. Rosenbaum – Project Engineer (NETL)

Experimentalist, Chem. & Mech. Engineering – hydrate research 2001 to present

- Qualifications:
  - B.S., Chem. Eng., Geneva College, 2001
  - B.S.E., Mech. Eng., Geneva College, 2001
  - E.I.T. Certification, 2001
  - M.S. Chem. Eng., University of Pittsburgh, 2004
    - Thesis: “Thermal Properties and Characterization of Methane Hydrates”

Ronald Lynn – Engineering and Electrical Specialist (NETL – Parsons)

Experimentalist/Technical Specialist – hydrate research 1993 to present

- Qualifications:
  - Associate in Specialized Electronics Degree, Penn Technical Institute, 1973
  - Penn State/CCAC College courses, 1989 to 1991
  - E.I.T. Certification, 1992
  - Extensive experience with process instrumentation and design

Project Personnel

Dr. David Shaw – University Research Associate (ORISE Visiting Faculty)

Experimentalist, Mechanical Engineering – hydrate research 1992 to present

- Qualifications:
  - B.S.M.E., Geneva College, 1983
  - M.S., Mech. Eng., The Ohio State University, 1986
  - Ph.D., Mech. Eng., The Ohio State University, 1988
  - Professor of Mechanical Engineering, Geneva College, 1990 – present

Yongkoo Seol – Project Engineer (NETL)

Experimentalist, Geology / Physical Science – hydrate research 2005 to present

- Qualifications:
  - B.S., Seoul National University, Seoul, Korea, 1989
  - M.S., Hydrogeology, Western Michigan University, 1993
  - Ph.D., Soil Chemistry, Purdue University, 1998
  - Post Doctoral Researcher, Ohio State University, 1998-2001
  - Geological Scientist, Lawrence Berkeley National Lab., 2001-2007

Wu Zhang – Project Engineer (NETL - WVU)

Experimentalist, Chemical Engineering – hydrate research 1998 to present

- Qualifications:
  - B. E. Chemical Engineering, North-western Polytechnical University (NPU), China. 1982
  - M. E. Dept. of Chemical Engineering, NPU, and the Aviation Material Institute. 1986
  - Ph.D., Polymer Composites and Experimental Mechanics, NPU, 1993
  - Ph.D., Natural Gas Hydrates, The Dept. of Chemistry, King's College London, University of London. 1995-1998.
  - Postdoctoral Research Staff member, Lawrence Livermore National Laboratory (LLNL)

Presentation Outline

Projects to be Reviewed

1. Thermophysical Properties of Methane Hydrate (current)

2. Kinetic Study on Methane Hydrate Induction and Reformation (current and proposed)

3. Observation of Gas Migration and Hydrate Formation in Saturated Porous Media (proposed)

NATIONAL ENERGY TECHNOLOGY LABORATORY

Thermophysical Properties

Presented by: Eilis Rosenbaum

Programmatic Relevance

"The primary goal of the National Methane Hydrate R&D Program is to provide the knowledge and technologies to fully realize the potential of methane hydrates in supporting our nation's continued economic growth, energy security, and environmental protection. The program will achieve this goal by focusing on four key issues (NETL, 2007b):

- Understanding the role hydrates play in global processes such as climate and the carbon cycle.
- Investigating the impact of hydrates on seafloor stability and deep-sea life.
- Developing the tools and knowledge that will ensure the safety of drilling and producing deep-water oil and gas resources located below marine hydrate deposits.
- **Developing the knowledge and technology base to allow commercial production of methane from domestic hydrate deposits by the year 2015.** "

http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/rd-program/goals.htm
National Methane Hydrate Multi-Year R&D Program Plan, U.S. Department of Energy, Sep. 2006, pp 34-35.

Programmatic Relevance

Near-Term Goals (by 2010)

- "**Conduct field and laboratory studies to determine 1) the fundamental physical properties (flow capacity, mechanical strength, thermal conductivity, and others) of methane hydrate bearing sediments at different levels of hydrate saturation, and 2) how those physical properties might change during either intentional or natural hydrate dissociation.**"

Long-Term Goals (by 2015)

- "**Provide a comprehensive knowledge base and suite of analytical tools to support ongoing research into natural methane hydrates and their role in the global environment.**"

Technical Challenges

Laboratory Formed Compacted Hydrate

Naturally Occurring Hydrate

•Formed under gas-rich environment.*

•Likely cement sediment.*

•High purity, reproducible samples.*

•Many form from dissolved gas.**

•Likely do not cement grains.

•Highly variable composition and properties.

Waite et al, 2004; Winters et al., 2004

*** Buffet and Zatsepina, 2000*

Goals and Objectives

Project Objective:

– Provide high-quality thermal property data to benefit the development of models and methods for predicting the behavior of gas hydrates in their natural environment under production or climate change scenarios.

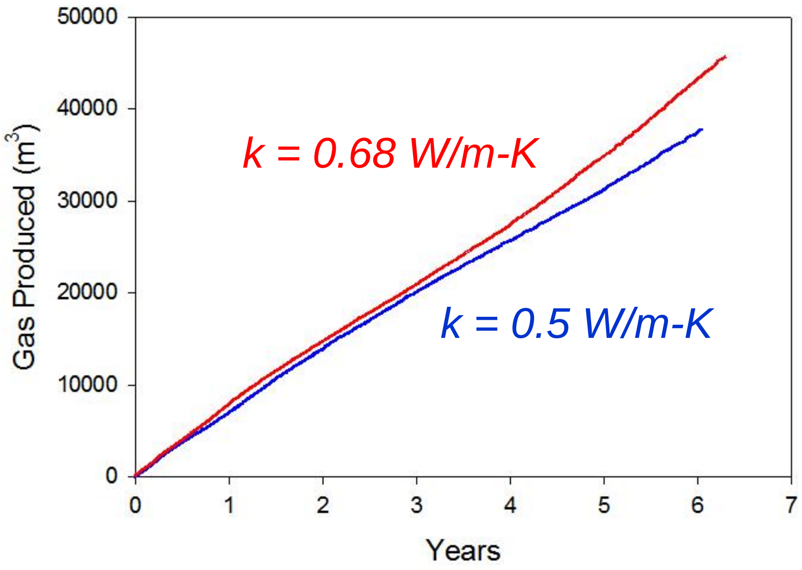
Near Term:

– Adapt NETL's laboratory approach for measurements
  - in vessels designed to be viewed in a CT Scanner;
  - and vessels designed to preserve hydrate-bearing cores under natural conditions.

Long Term:

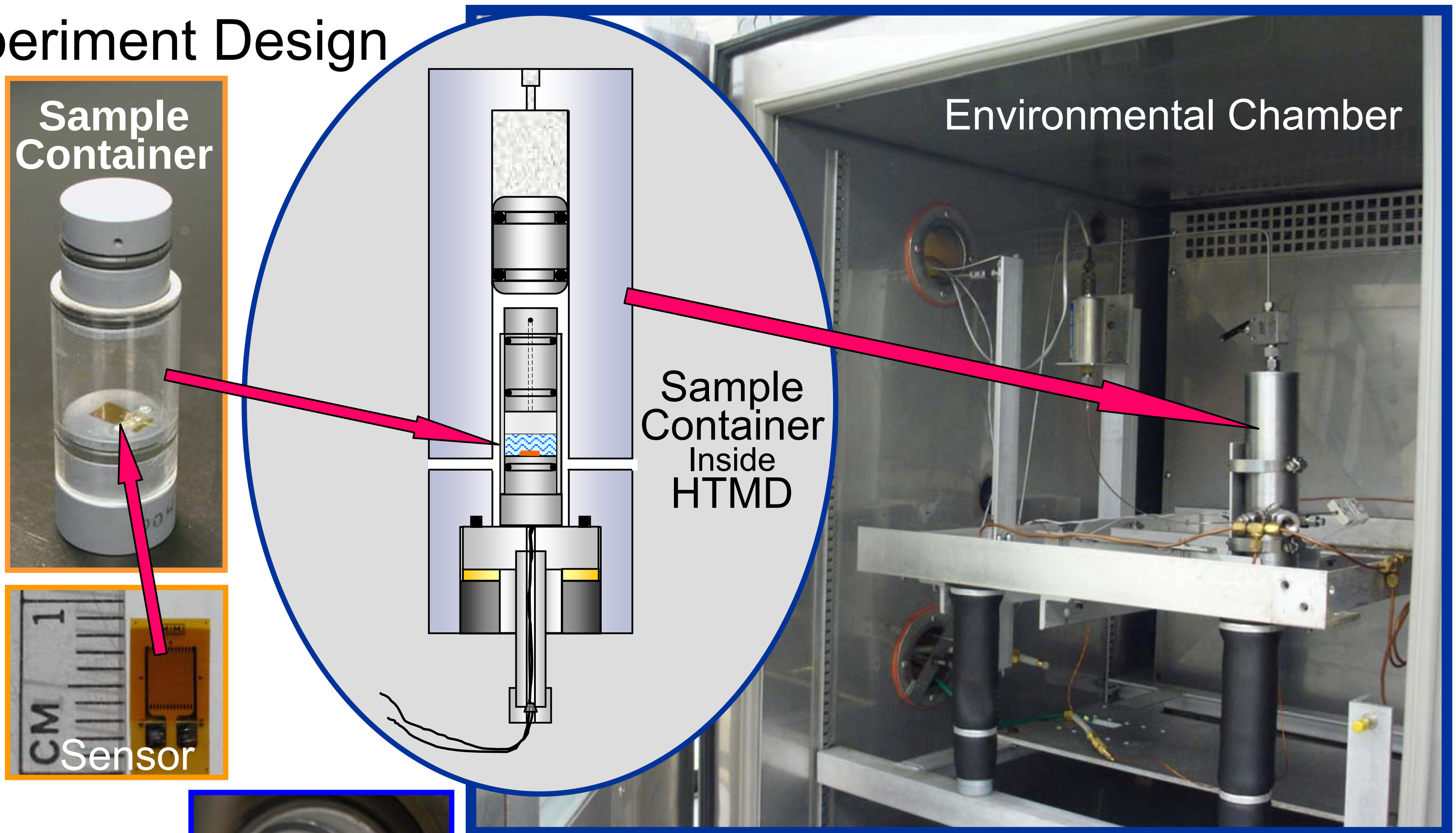
– Develop tools for in situ measurement.

Production Scenario Simulation



NETL’s Scientific Approach

Experiment Design



Compacted Methane Hydrate

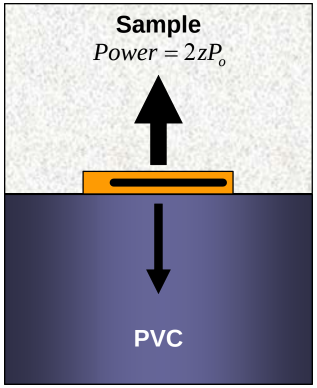
NETL's Scientific Approach

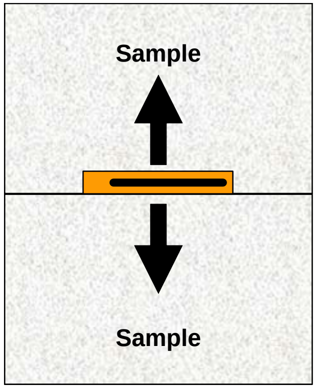
Innovative One-Sided Measurement

- Measurement reflects properties of sample and sensor support (PVC).
- Reproducible conductivity values obtained by using an energy partitioning method.
- Diffusivity sensitive to differing time scales.
- Diffusivity requires more rigorous approach – finite difference model.
- FD model is being developed for analysis of experiment data to determine the diffusivity.

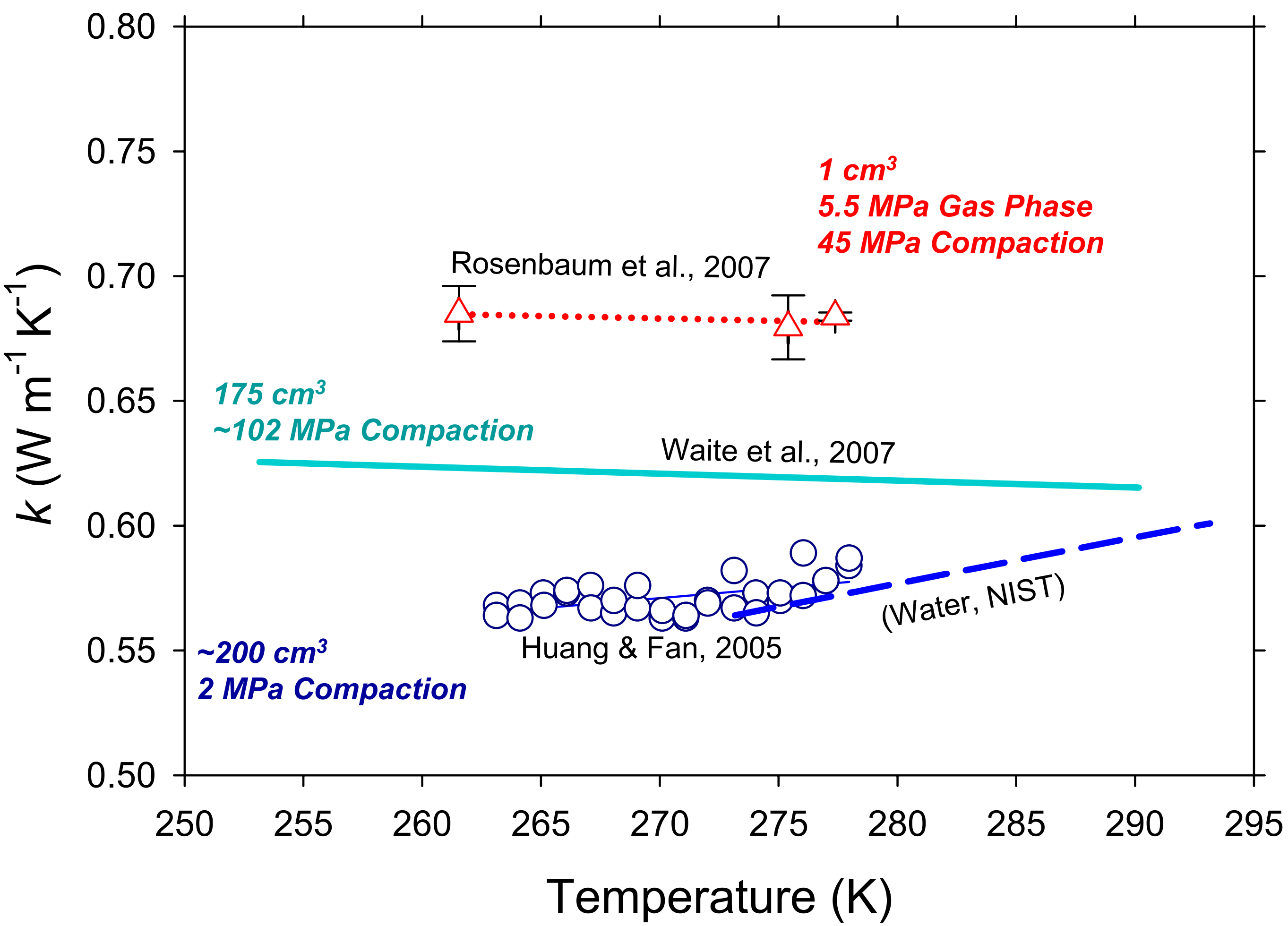
1 Sided Measurement

2 Sided Measurement

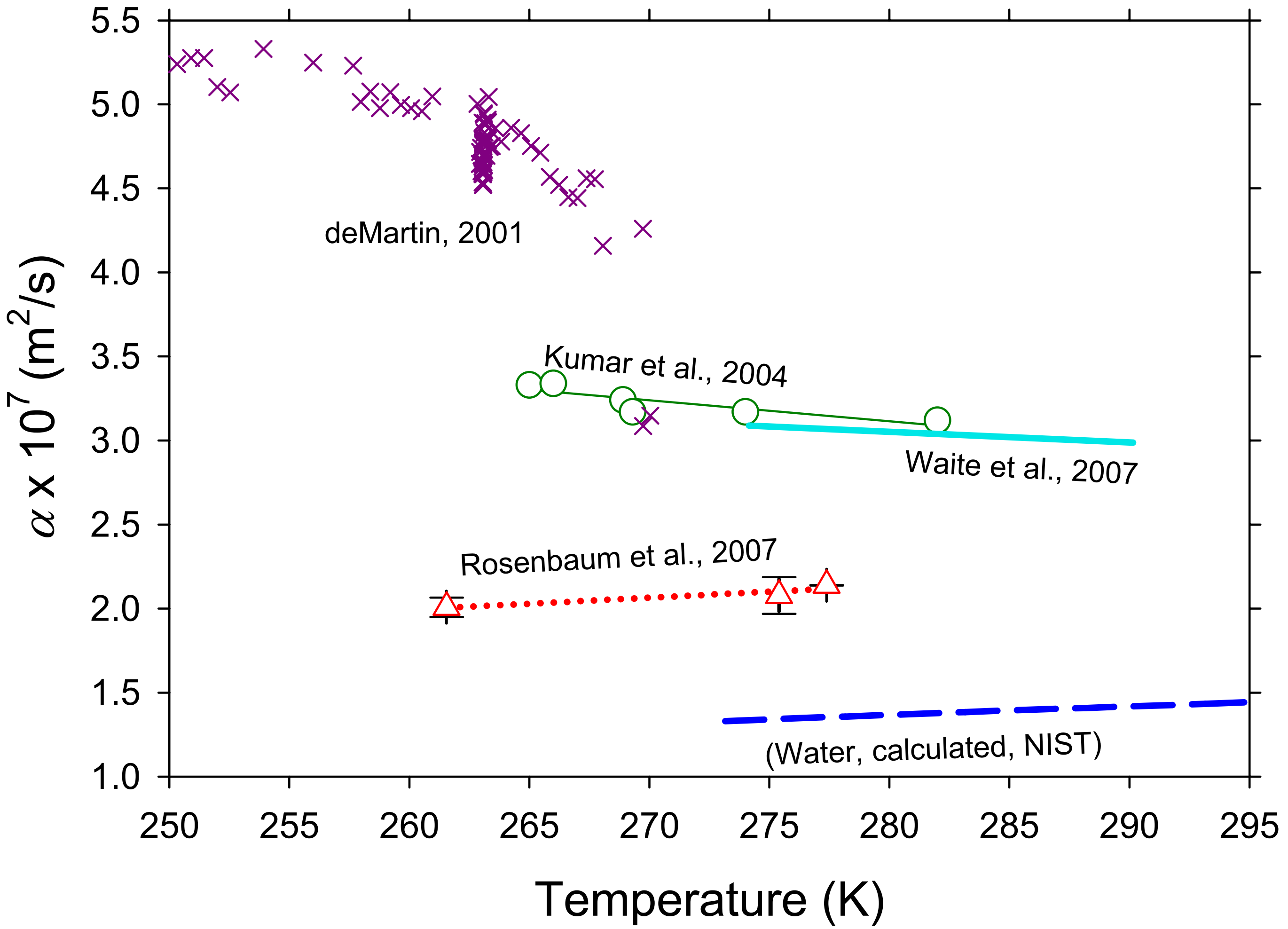




Thermal Conductivity – Experimental Data



Thermal Diffusivity - Experimental

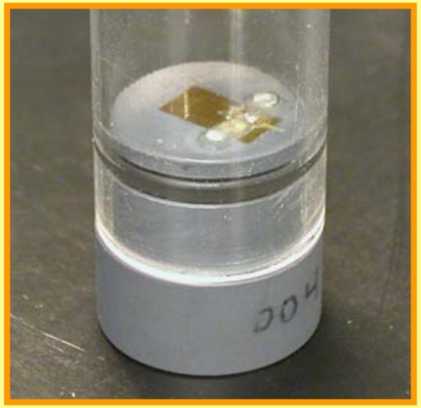


Near Future Research Activities

- **Fully adapt technique for incorporation into devices designed to preserve natural hydrate-bearing cores.**
  - Current design enables mobility.
- **Incorporate into NETL's vessels designed for CT Scanning.**
- **Test configurations for development of in situ measurement device.**

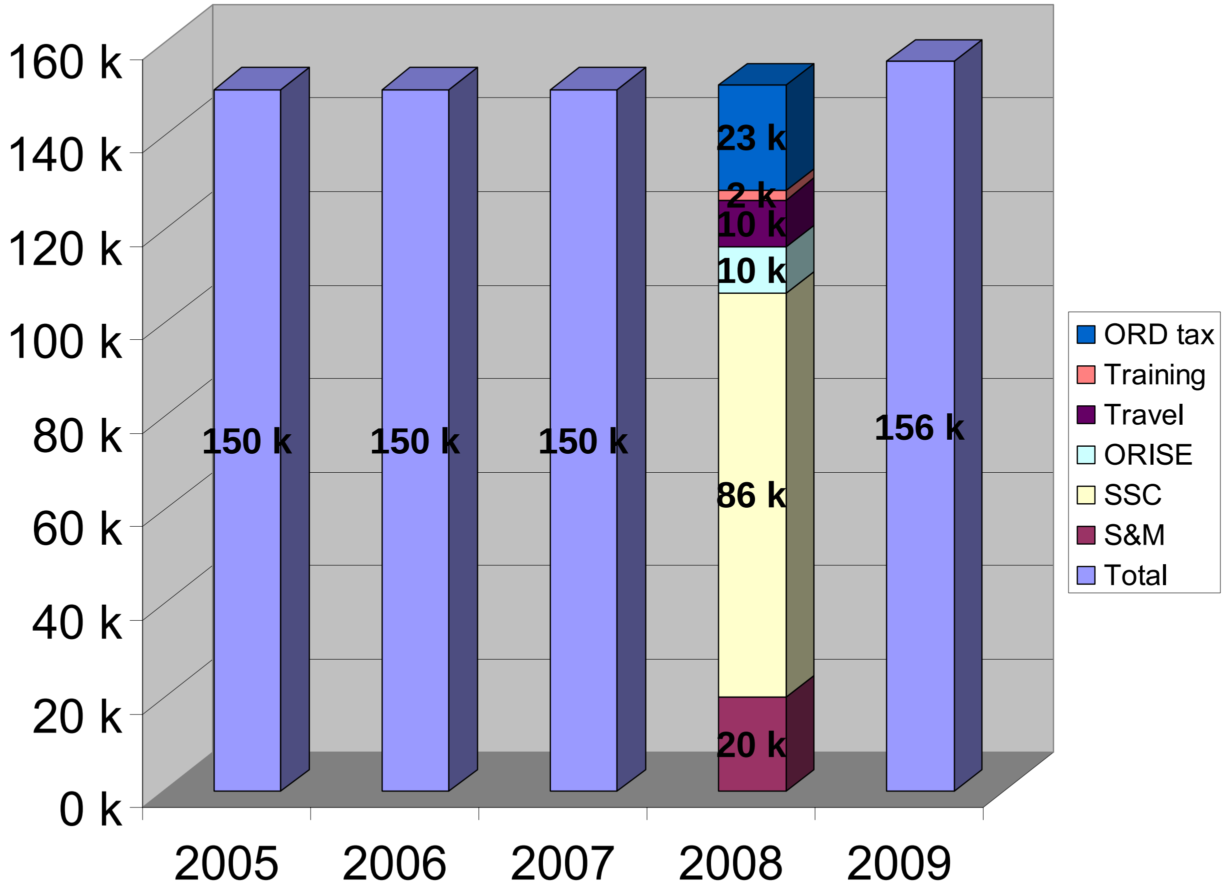
Measurement Components

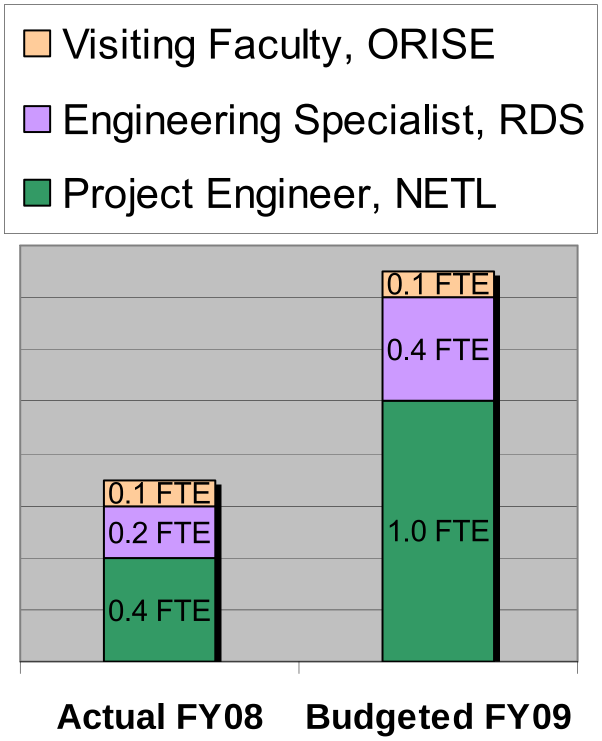
Keithley Source Meter
Programmed to be a constant power source



Sensor on support material

Budget and Staffing





Publications

D.W. Shaw E.J. Rosenbaum, D.A. Clark, R.P. Warzinski; "Modified Transient Plane Source Probe for Measurement of Thermal Conductivity and Thermal Diffusivity in confined Samples," in preparation. Target: Rev. Sci. Inst., 2009.

Warzinski, R.P., I.K. Gamwo, E.J. Rosenbaum, E.M. Myshakin, H. Jiang, K.D. Jordan, N.J. English, D.W. Shaw; "Thermal Properties of Methane Hydrate by Experiment and Modeling and Impacts upon Technology," Proceedings: 6th International Conference on Gas Hydrates, Vancouver, Canada; July, 2008.

Rosenbaum, E.J, N.J. English, J.K. Johnson, R.P. Warzinski; "Thermal Conductivity of Methane Hydrate from Experiment and Molecular Simulation," J. Phys. Chem. B, 112, 2007, 10207-10216.

Warzinski, R. P., R. J. Lynn, D. W. Shaw and E. J. Rosenbaum, "Thermal Property Measurements of Methane Hydrate Using a Transient Plane Source Technique," in press, AAPG Hedberg Conference publication on Gas Hydrates.

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Kinetic Study on Methane Hydrate Induction and Reformation in Porous Medium

Presented by: Yongkoo Seol

Programmatic Relevance

"The primary goal of the National Methane Hydrate R&D Program is to provide the knowledge and technologies to fully realize the potential of methane hydrates in supporting our nation's continued economic growth, energy security, and environmental protection. The program will achieve this goal by focusing on four key issues (NETL, 2007b):

- Understanding the role hydrates play in global processes such as climate and the carbon cycle.
- Investigating the impact of hydrates on seafloor stability and deep-sea life.
- Developing the tools and knowledge that will ensure the safety of drilling and producing deep-water oil and gas resources located below marine hydrate deposits.
- **Developing the knowledge and technology base to allow commercial production of methane from domestic hydrate deposits by the year 2015.** "

http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/rd-program/goals.htm
National Methane Hydrate Multi-Year R&D Program Plan, U.S. Department of Energy, Sep. 2006, pp 34-35.

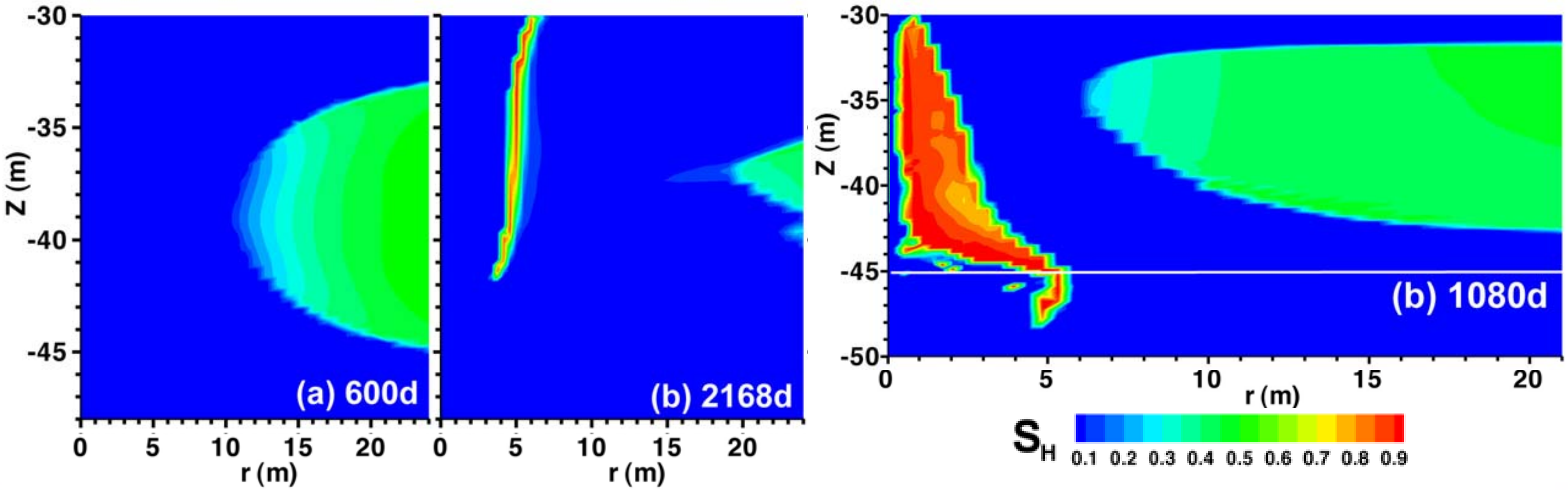
Programmatic Relevance

- **Future program decisions regarding production will rely heavily on the forecasts of numerical reservoir simulations.***
  - "It is, therefore, **imperative that laboratory measurements are comprehensive** and that they are rigorously reviewed to provide a robust foundation upon which reliable production models can be constructed."
- **The entire subject of prediction of gas production from hydrate deposits hinges on the availability of reliable models of hydrate dissociation.**
  - "This is probably the most important challenge facing the gas production effort"**

***National Methane Hydrate Multi-Year R&D Program Plan, U.S. Department of Energy, June 1999, pp 19-20.**
**** Moridis, G.J., Knowledge Gaps in the Study of Gas Production from Hydrate Deposits, 2004**

Current Status of the Problem

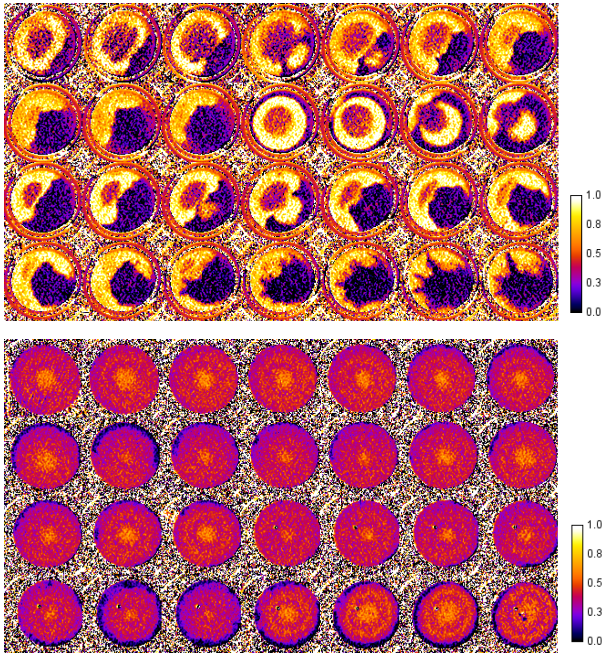
- **Predicted secondary hydrate formation (SHF) during gas production from hydrate reservoir**
  - by lowered temperature (Joule-Thompson effect and endothermic nature of hydrate dissociation)
  - by elevated pressure (production shutoff and local heterogeneity)
  - Modifications on production schemes to overcome SHF



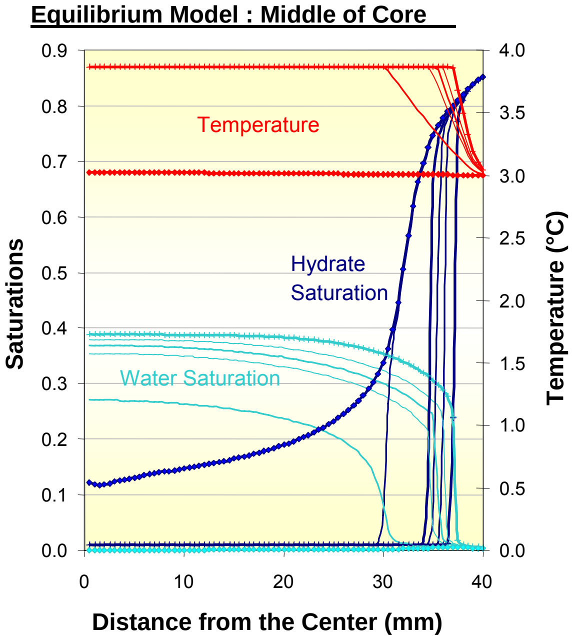
Current Status of the Problem

- **Is kinetics important?**
  - Current equilibrium can poorly reproduce hydrate formation pattern in a simple experimental column.

CT Observation



Simulation*



Current Status of the Problem

- **Previous studies**
  - Induction delay time: Sloan and Fleyfel (1991); Skovborg et al. (1993); Barlow and Haymet (1993)
  - Kinetics of hydrate formation and dissociation in two-phase condition (agitated reactor): Vysniauskas and Bishnoi (1983, 1985); Kim et al. (1987); Englezos et al. (1987); Clarke and Bishnoi (2002)
  - Thermodynamics of hydrate formation: Munck et al. (1988)
  - Thermodynamics of hydrate formation in porous glass: Smith et al. (2006)
  - Hydrate formation rates in fixed surface area: Holder (1986)
  - Hydrate dissociation in porous media: Uchida et al. (2002, 2004); Klapproth et al. (2006)

Technical Challenges

- **Probabilistic nature of hydrate inductions**
- **Numerous key parameters:**
  - Porous Medium
    - Particle dimension, surface roughness, texture (particle size distribution, and sorting), composition (mineralogy), etc
  - Driving Forces
    - Types of Driving Forces
      - Lowered temperature at constant pressure (ΔT test)
      - Elevated pressure at constant temperature (ΔP test)
    - Magnitude of Driving Forces
  - Thermal History of Waters
    - Time gap between dissociation and reformation of hydrate

Technical Challenges

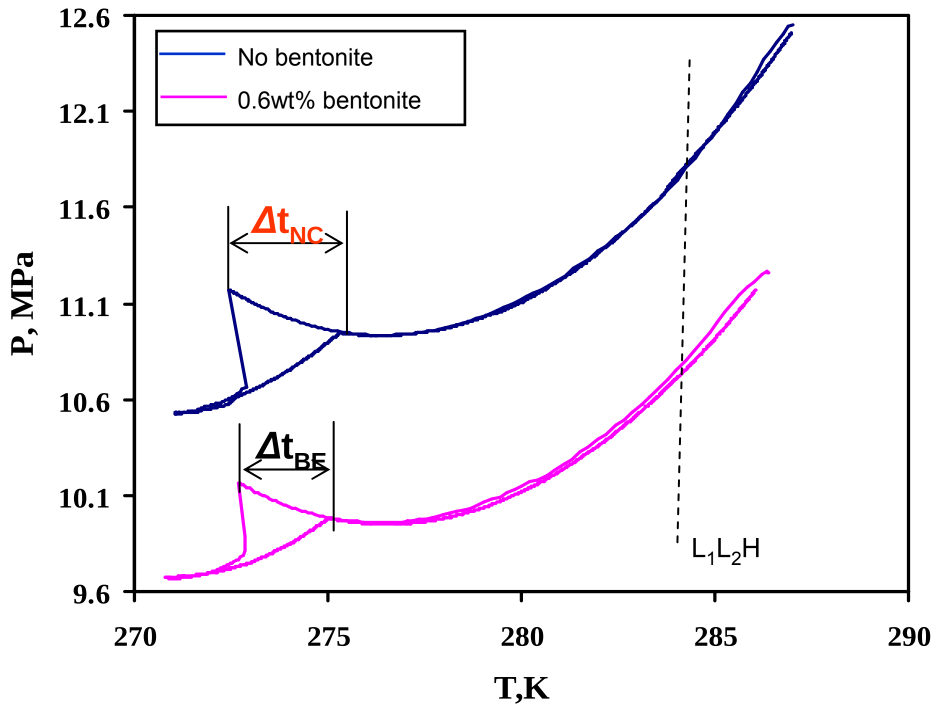
- **Separation of formation kinetics from heat and fluid conductivity**
  - Independent measurements for thermal conductivity and relative permeability of fluids are necessary
- **Discrepancy between natural and synthesized hydrates**
  - Hydrate occurrences (i.e. pore filling, cementing, or filming)
  - Phase saturations (water-gas system vs. dissolved gas system)
  - Heterogeneity in natural sediments: grain size distribution, surface roughness, compactness, etc.

Project Goals & Objectives

- **Goal**
  - Develop equipment and procedures to reliably and reproducibly form methane hydrate and measure hydrate formation induction time and gas consumption rates in various porous media of interest
- **Expected impacts**
  - Provide information useful for
    - Developing reliable kinetic models to be applied for numerical simulations of hydrate production
    - Predicting potential impacts of hydrate formation kinetics on production strategies for hydrates
    - Contributing to identify optimal models of hydrate formation for production simulation

Preliminary Studies

- **Determination of induction time (*Δt*) for hydrate formation from dissolved CO_2 in the presence of clay in a 100 cm^3 stirred autoclave.**



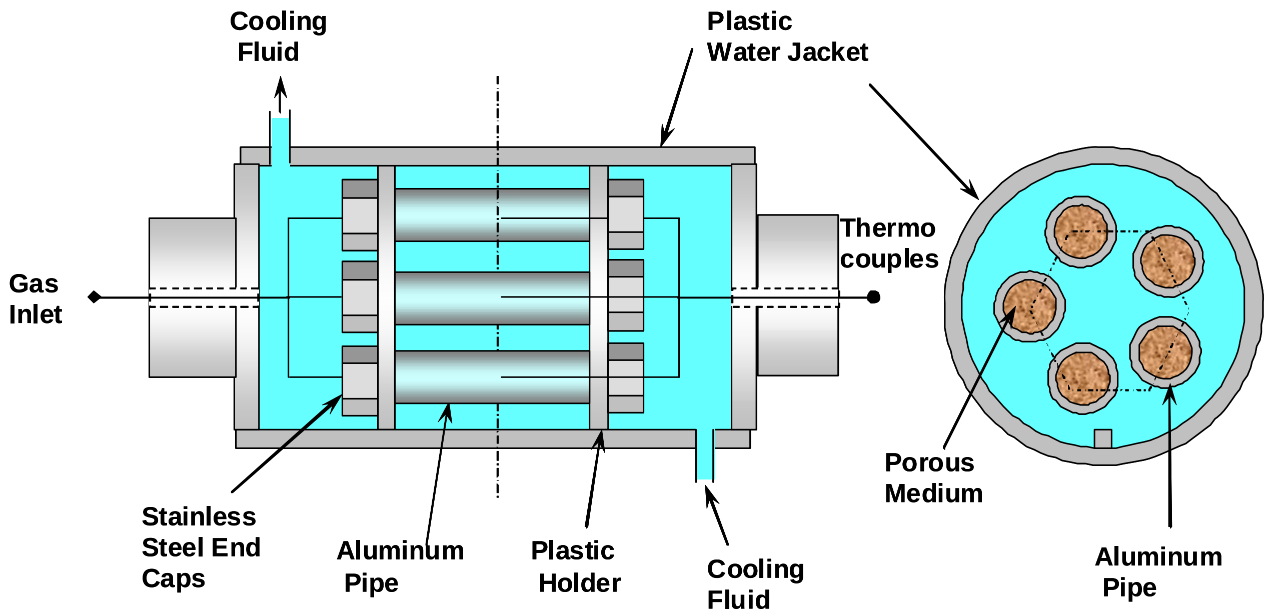
  - 0.6 wt% bentonite reduced induction time by 7 to 50%.

Approaches

- **Developing two-phase (water-gas) system with porous medium**
  - Reproducing secondary hydrate formation condition during hydrate production
  - Static system (no vortex): Diffusion dominated gas transfer for hydrate formation results in slower formation of hydrate.
  - Sediment grain surface: Greater interface area between gas and liquid enhances hydrate formation.
  - Unlimited gas supply

Approaches

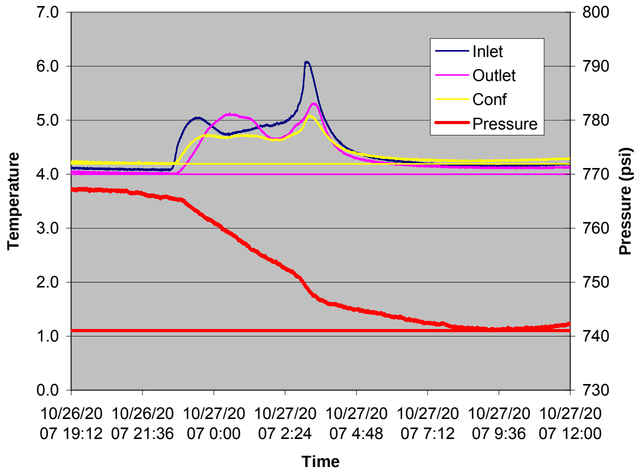
- **Multi-Pressure Vessel System (MPV)**

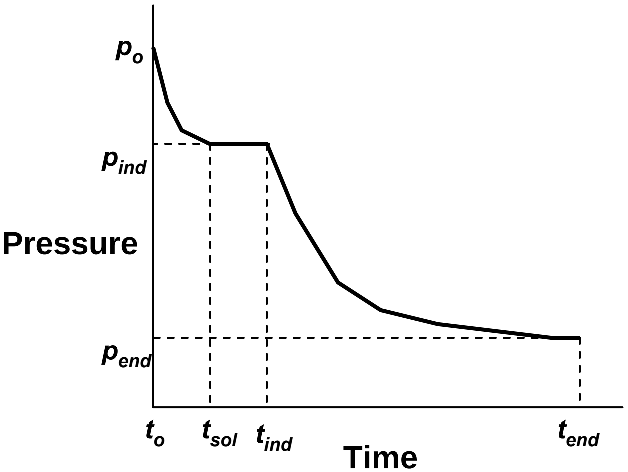


  - Advantages: X-ray transparent, quintuplicate
  - Disadvantages: Interference between vessels, no confining pressure, small sample cross sections

Approaches

- **Volumetric gas consumption rates**





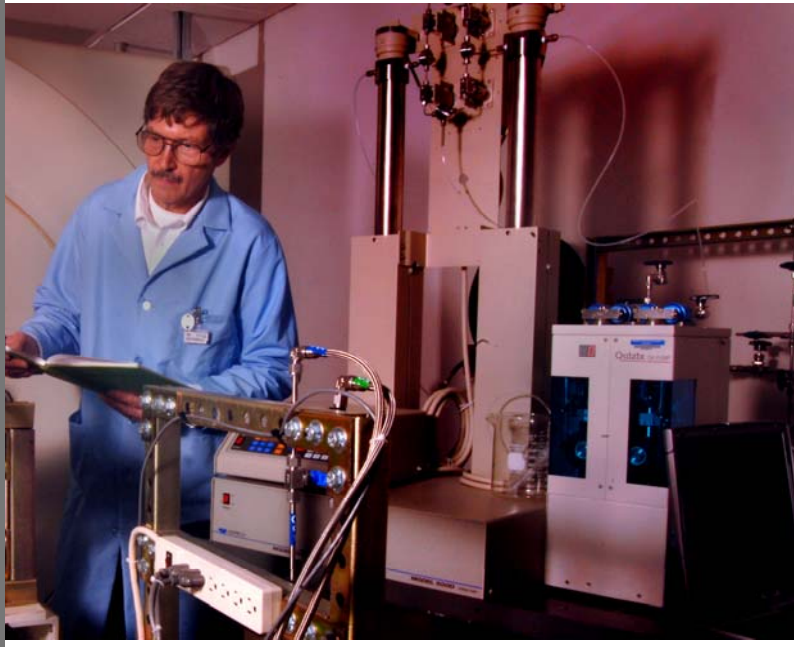
- **Empirical kinetic equations**
  - Example equation (Vysniauskas and Bishnoi 1983; Moridis et al. 2005)

$$r = \frac{\partial V_m}{\partial t} = K_o A F_A \exp\left(-\frac{\Delta E_a}{RT}\right)\exp\left(-\frac{a}{\Delta T^b}\right)\cdot p^{\gamma},$$

  - History matching for kinetic parameters

Approaches

- **Starting point:**
  - Simple initial conditions:
    - Constant temperature (3 °C),
    - Rapidly elevated pressure (800 psi),
    - Uniform size of glass bead (100 μm),
    - Relatively high initial water saturation (40%),
    - Fixed time interval between dissociation and reformation (24 hours)
  - Repeat the test to check reproducibility
  - Expand to include parameters: various porous media, P/T conditions, driving forces, and thermal history
- **Collaborations: Dr. Timothy Kneafsey, LBNL**



Observation of Gas Migration and Hydrate Formation in Saturated Porous Media

Presented by: Yongkoo Seol

Programmatic Relevance

- **Critical needs for laboratory work**
  - “To capture and understand the natural heterogeneities that may play a major role in controlling the behavior of natural deposits as environmental conditions changes”*
  - Given high priority in the near-term on determination of the model and distribution of hydrate in porous media

National Methane Hydrate Multi-Year R&D Program Plan, U.S. Department of Energy, Sep. 2006, pp 34-35.

Current Status of the Problem

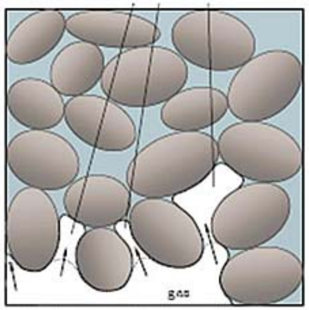
- **Fundamental observation at the sites at Hydrate Ridge, offshore Oregon and Blake Ridge, offshore South Carolina**
  - co-existence of methane hydrate, gas and brine within hydrate stability zone (HSZ)
  - Methane migration as a separate gas phase
- **Previous Studies*:**
  - Gas accumulations beneath HSZ may reach critical thickness to open fractures in sediments or activate pre-existing faults will serve as conduits for fast gas migration.
  - Competition between brine displacement and sediment fracturing determines extent of conversion of methane gas entering HZS to hydrate.

***Jain and Juanes (2008), Behseresht et al. (2008 a, b)**

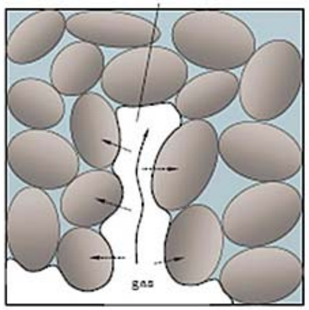
Current Status of the Problem

- **Previous Studies***
  - Coarse-grained sediments favor capillary invasion
  - fracturing dominates in fine-grained media.

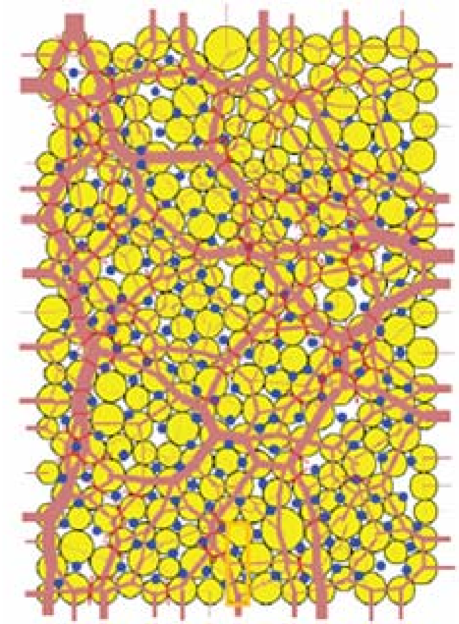
capillary pressure



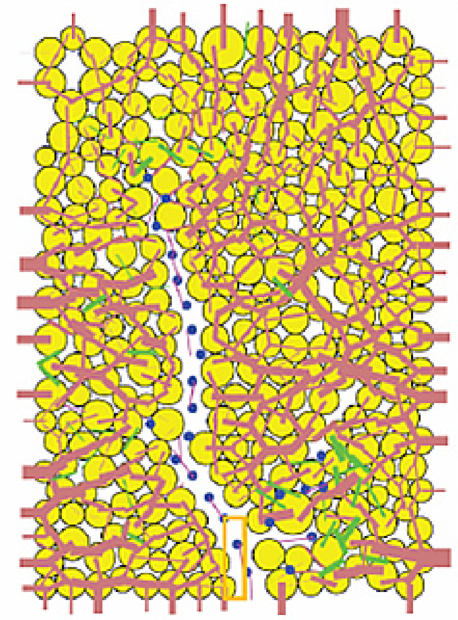
fracture opening



r_{min} = 1 mm



r_{min} = 1 μm



***Jain and Juanes (2008)**

Project Goals & Objectives

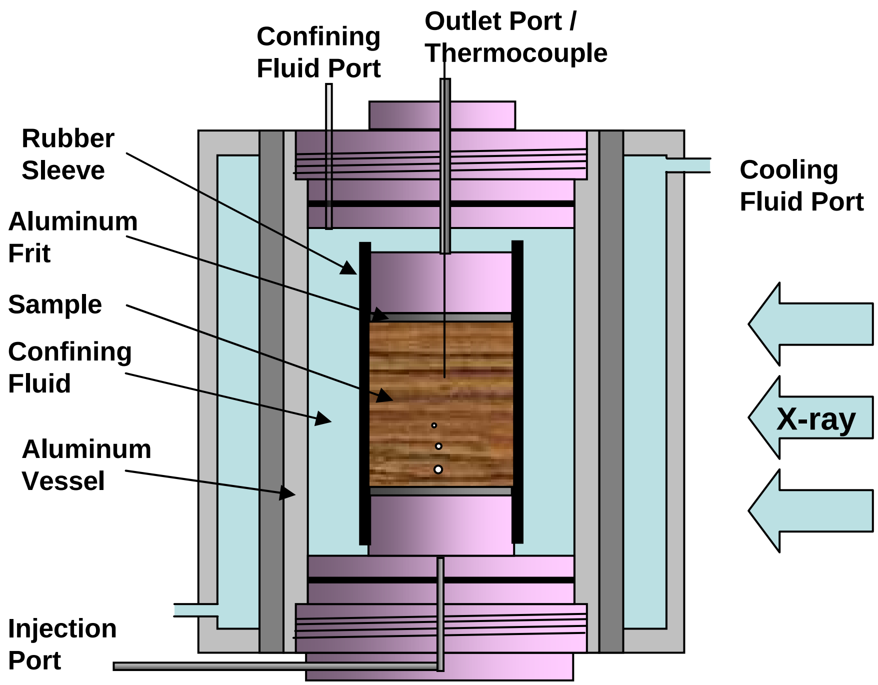
- **Goal**
  - Develop equipment and procedures to visualize hydrate formation modes in different sediments and to experimentally validate the model prediction and natural observations on lateral and vertical variability in hydrate saturation
- **Expected outcome**
  - Provide understanding on
    - Relations between hydrate accumulation patterns and sediment grain sizes and/or layer configurations in the HSZ
  - Contribute useful information
    - Better estimate the hydrate mass in varied sediments
    - Developing production strategies for hydrates

Technical Challenges

- **Experimental setup reproducing natural conditions for sediments in hydrate stability zone**
  - Heterogeneity in natural sediments: grain size distribution, surface roughness, compactness, etc.
  - Simplifying layer configurations representing natural setup
  - Vertical orientation of core samples for buoyancy driven gas migration
  - Identifying pressure and temperature condition
- **Challenging visualization requiring high resolutions:**
  - Identification of hydrate formation from water saturation due to similar density between water and hydrate
  - Visualization of fine cracks or fissures potentially in fine sediments

Approaches

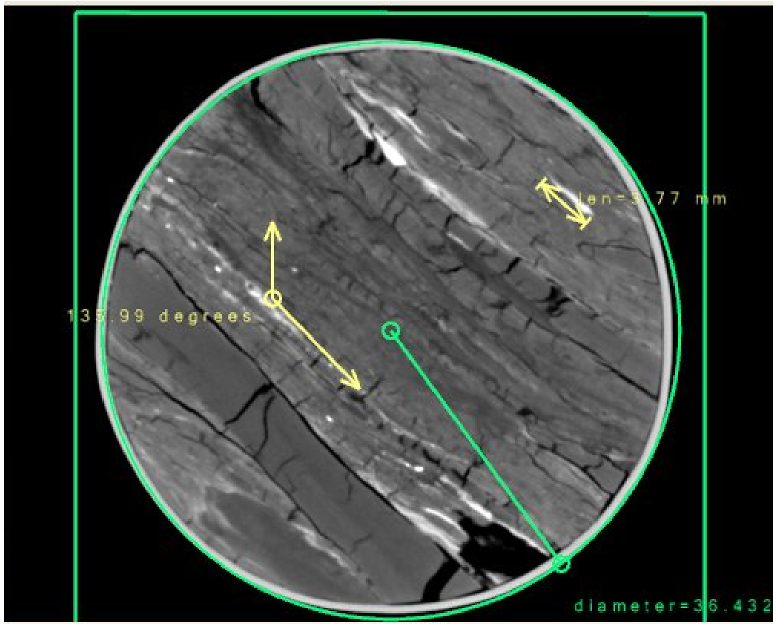
- **Vertical Pressure Vessel System (VPV)**

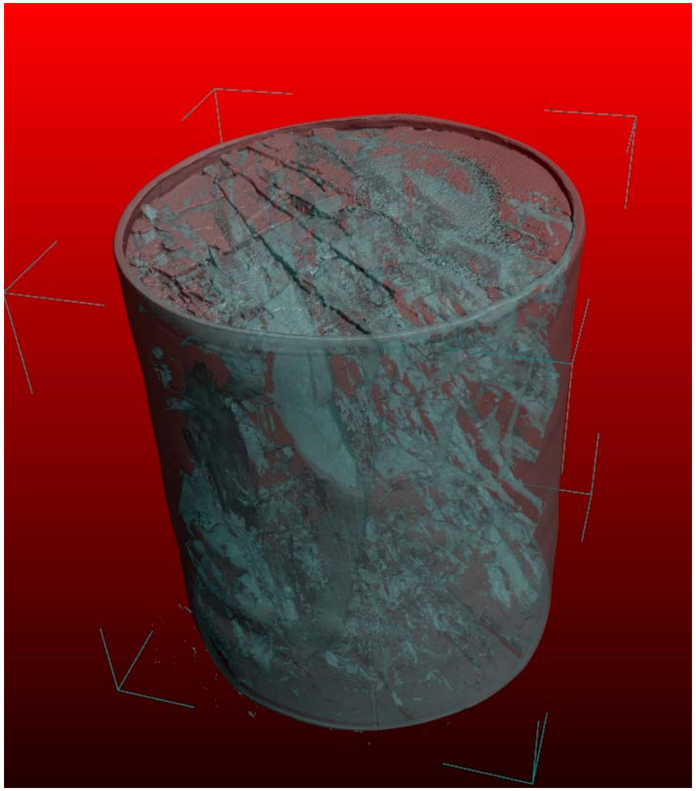


  - Accommodates vertical alignment of sample cores, tri-axial confining pressures, uniform gas phase boundary, and controlled temperature

Approaches

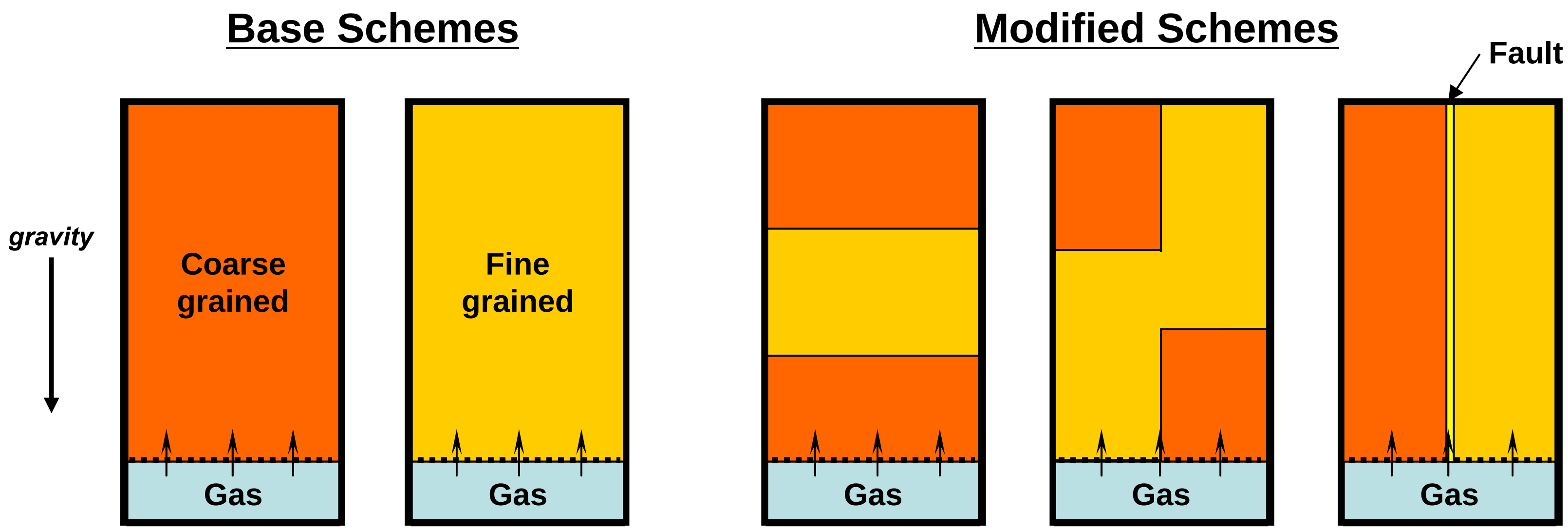
- **Volume CT with dual source**
  - Pixel size in object: 5 µm to 1 mm
  - Voltages: 225 and 320 kV
  - Flexible object turntable





Approaches

- **Conceptual layer configurations**



  – Show basic patterns of hydrate accumulations

  – Show impacts of layer stratification normal or parallel to gas migration and the presence of fast fluid conduits

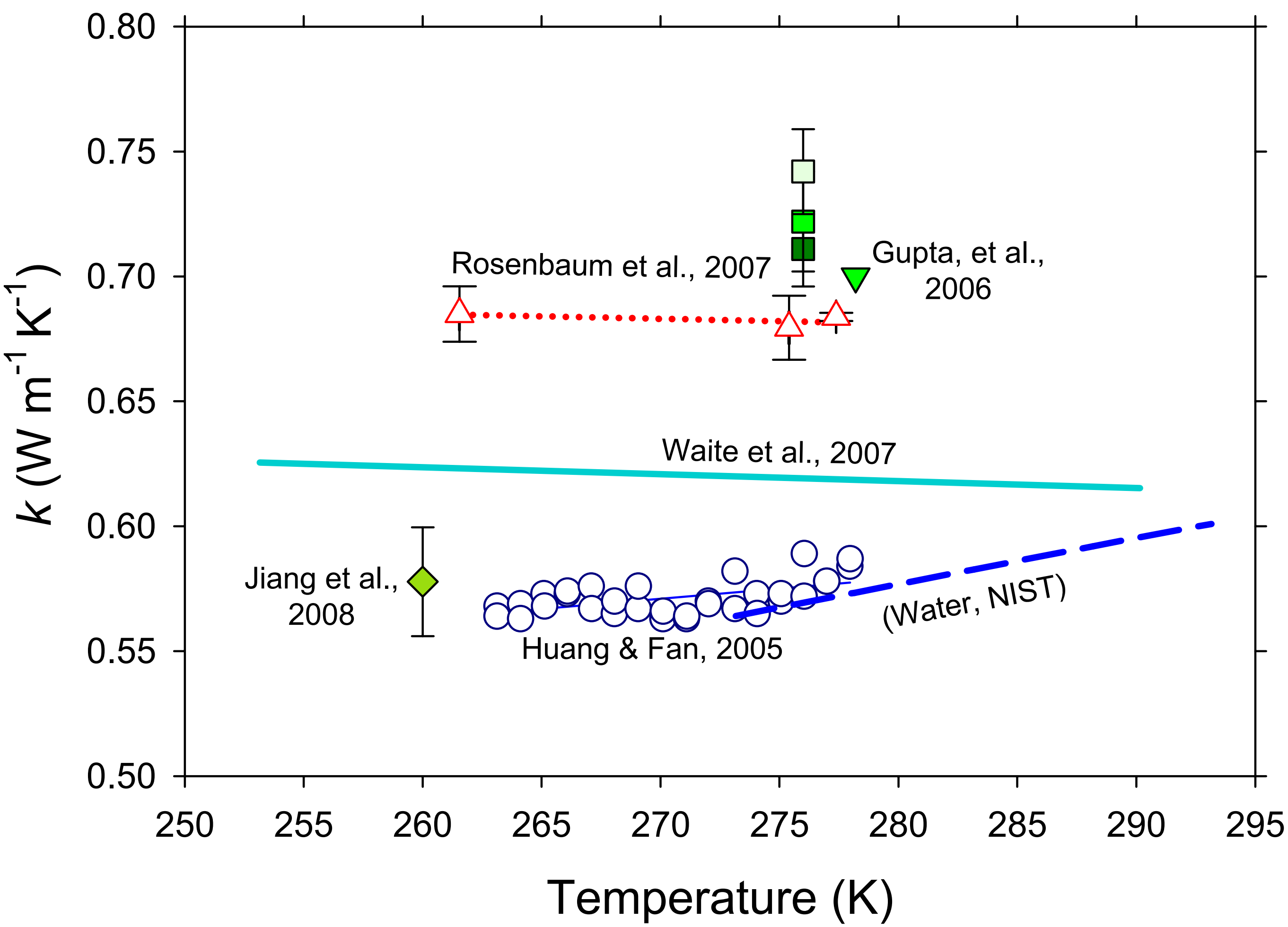
Timetable and Budget

#	Task	FY09	FY10	FY11
Hydrate Formation and Dissociation Kinetic Measurement				
1	Experiment Design and Setup			
2	Preliminary Formation/Dissociation Test			
3	Induction Time/Gas Consumption			
4	Data Analysis for Model Developments			
5	Inverse Modeling			
6	Result Reporting			
Gas Migration Observation				
1	Experiment Design and Setup			
2	Preliminary Test and CT Optimization			
3	Visualization of Gas Migration			
4	Data Analysis			
5	Result Reporting			
Total Budget		***$256K**		

*** Projected**

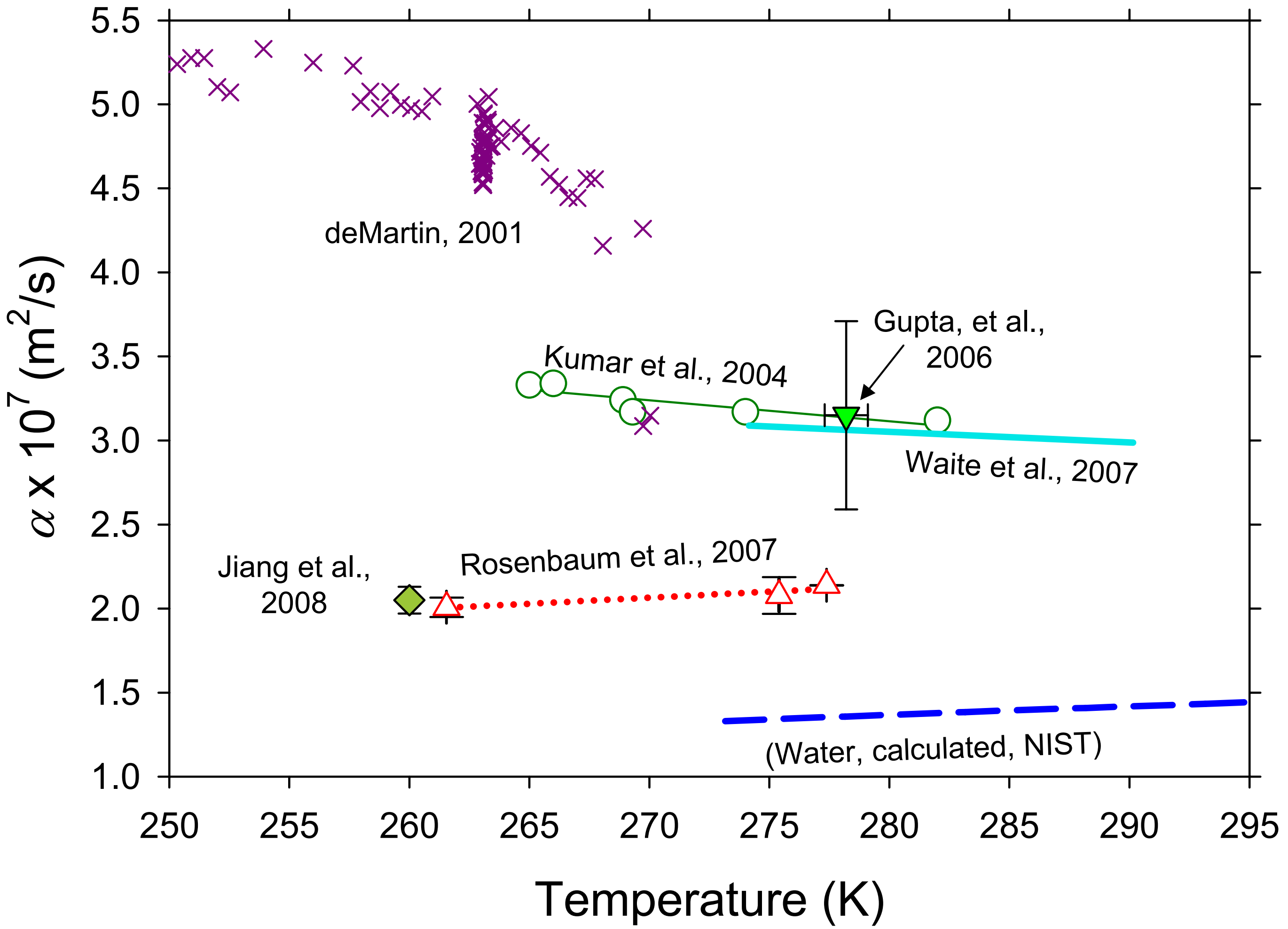
THANK YOU!

Thermal Conductivity – Modeling Data



- *k* for low-porosity methane hydrate = 0.65 to 0.70 W m^{-1} K^{-1}

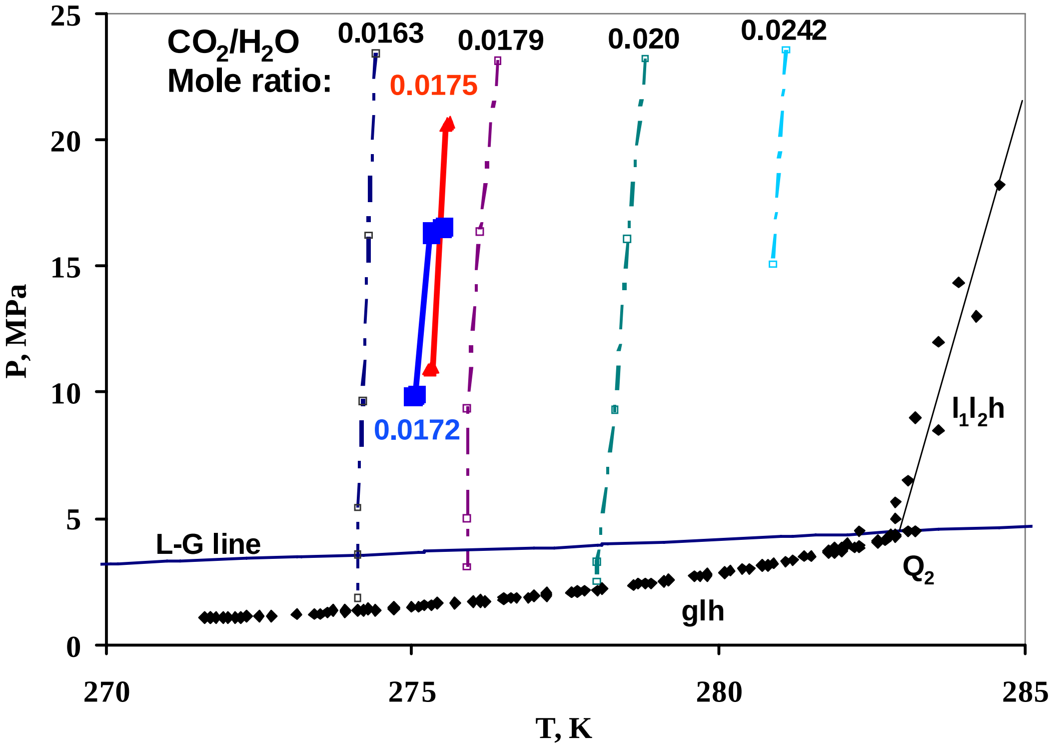
Thermal Diffusivity - Modeling



- At present, the correlation of Waite et al., should be used for α.

Preliminary Studies

- **Formation-dissociation of CO_2 hydrate**
  - Agitated autoclave without the framework of porous media
  - Added bentonite as a component of porous media



Zhang, Y., G. D. Holder, R.P. Warzinski, (2008) Ind. Eng. Chem. Res. 47: 459-469.

Preliminary Studies

- Induction time of CO_2 hydrate formation from liquid phase*

	No Clay	Bentonite 0.59%	% reduction
HP FC	0.74	0.69	7.14
LP FC	1.09	0.54	50.61
HP SC		2.68	
LP SC	2.71**	1.78	34.38

*all data are average of 4 repeating experiments except the one noted with **, which is the result of a single experiment.
FC, fast cooling, cooled down to -2.5ºC from 14ºC in about 4 hours;
SC, Slow cooling, 0.1ºC/h.