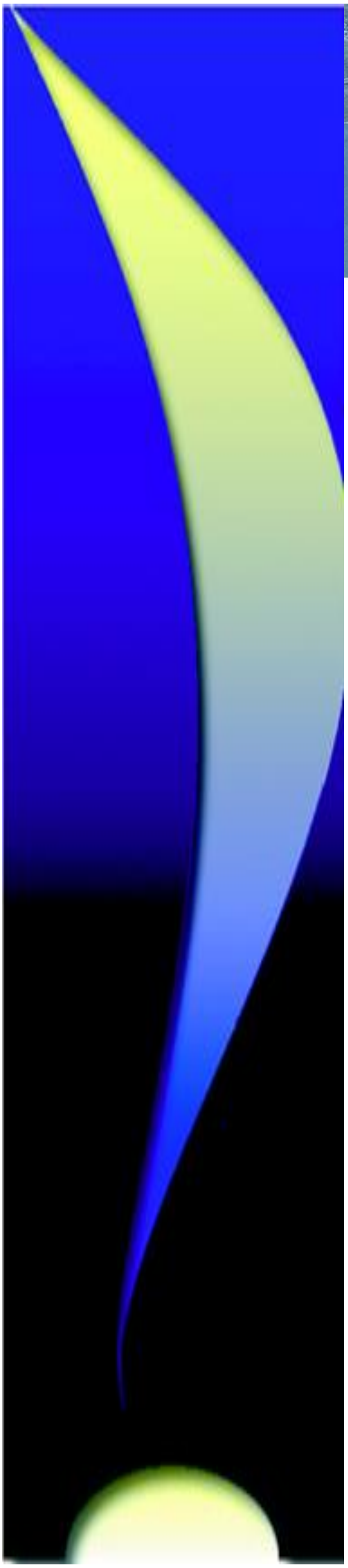

TEXAS A&M UNIVERSITY CORPUS CHRISTI

HOKKAIDO UNIVERSITY

UNIVERSITAS BERGENSIS

HNEI

AIST
NATIONAL INSTITUTE OF
ADVANCED INDUSTRIAL SCIENCE
AND TECHNOLOGY (AIST)

11th International Methane Hydrate Research and Development Workshop

Organizers

Dr. Richard Coffin, TAMU-CC
Dr. Bjørn Kvamme, University of Bergen
Dr. Stephen Masutani, University of Hawaii
Dr. Norio Tenma, AIST-Tokyo
Dr. Tsutomu Uchida, Hokkaido University

DISCLAIMER

This DRAFT document is an overview of presentations and discussions during the 11th International Methane Hydrate Research and Development Workshop in Corpus Christi, Texas during December 6-8, 2017. This provides information presented and an overview of discussion topics. We do not provide our interpretations of the presentations.

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KEYNOTE SPEAKER

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BREAKOUT SESSION REVIEWS

Overview

Texas A&M University - Corpus Christi held the 11th International Workshop on Methane Hydrate Research and Development, in Corpus Christi TX during December 6-8, 2017**.** The 1st International Workshop on Methane Hydrate R&D was held in March 2001 in Honolulu, Hawaii. Subsequent workshops have been held, on average, every 1.5 years in different countries including the U.S., Chile, Canada, U.K., Norway, New Zealand, Japan, and India. This workshop was created so hydrate researchers and stakeholders could freely exchange information and identify research priorities in an effort to promote collaboration field and laboratory international collaborations.

The main focuses of this workshop were:

1) Gas Hydrate Energy: exploration, production, and economics;

2) Methane and Climate Change: Arctic, Antarctic and regions in between;

3) Natural and anthropogenic warming contributions to coastal and industrial platform stability;

4) Carbon dioxide injection for methane acquisition and sequestration.

Plenary lectures, oral presentations and posters, and breakout sessions were held during the workshop.

The past ten workshops have been co-organized by Professors Bjørn Kvamme (University of Bergen), Tsutomu Uchida (Hokkaido University), Stephen Masutani (University of Hawaii), Dr. Norio Tenma, (AIST) and Richard Coffin (TAMU-CC). Participant countries at the conference, in addition to the U.S., typically includes Canada, the United Kingdom, Norway, New Zealand, Japan, India and Chile, among twenty others. Previous workshops have been held in the US, Japan, India, Canada, Chile, New Zealand, Scotland, and Norway. With this strong international focus topics addressed include new energy, climate change, and coastal and industrial platform stability. With this workshop held in Texas there is special interest because of the deposits of frozen methane under the Gulf of Mexico that have potential to increase the world's energy supply and contribute to long-term energy security. It is estimated that there are 7,000 trillion cubic feet of methane in the Gulf of Mexico in reservoirs near the seafloor.

Workshop Agenda

Tuesday, 5 December Registration and Mix and Mingle **OMNI 2nd Floor 4:00PM-8:00PM**		
Wednesday, 6 December		
TIME		
7:30AM-8:15AM Nueces B	**Breakfast**	
	SESSION	**SPEAKERS**
8:15AM-10:00AM Nueces A	**Introductions** **&** **Key Note Speakers** **Chair: Prof. Bjørn Kvamme**	• **8:15 – 8:30, Overview:** Prof. Richard Coffin, TAMU-CC • **8:30 – 8:40, Welcome to TAMU-CC:** President Kelly M. Quintanilla, TAMU-CC • **8:40 – 8:50, College of Science and Engineering:** Dean Frank Pezold, CSE TAMU-CC • **8:50 – 9:00, 10th IMHRD Overview:** Prof. Stephen Masutani University of Hawaii, HNEI • **9:00 – 10:00, Key Note Speaker:** Dr. Marianne Walck VP Emeritus Sandia National Laboratory “Energy Research and Development: View from the DOE National Laboratories”
10:00AM-10:20AM Foyer	**Coffee Break**	
10:20PM-12:20PM Nueces A	**National Reviews** **Chair: Prof. Tsutomu Uchida**	• **10:20 – 11:05, United States**: Mr. Jared Ciferno, US Department of Energy – National Energy Technology Laboratory, “An Overview of US DOE Gas Hydrate Research and Development” • **11:05 – 12:20, China:** Dr. Zhou Shouwei and Dr. Li Qingping – China National Offshore Oil Corporation – “Achievement Report of solid-state fluidization production test of Deep-sea Natural Gas Hydrate in China” Prof. Wang Guorong, Southwest Petroleum University – “Non Diagenesis Nature Gas Hydrate Production by Solid Fluidization”

1:20PM – 3:10PM Nueces A	**Research Presentations** **Chair:** **Prof. Richard Coffin**	• **1:20 – 1:50** Prof. Bjørn Kvamme, University of Bergen – “Modeling CH4/CO2 exchange on reservoir scale” • **1:50 – 2:10** Dr. Kelly Rose, NETL Albany, DOE – “A Methodology for Evaluating Offshore Carbon Storage Potential” • **2:10 – 2:30** Assoc. Prof. Geir Ersland, University of Bergen – “Pore-to-Core Imaging of Hydrate Formation and Dissociation Patterns” • **2:30 – 2:50** Prof. Yoshihiro Konno, University of Tokyo – “Enhancement of Gas Hydrate Reservoir Performance by Deep Depressurization below the Quadruple Point” • **2:50 – 3:10** Mr. Zhenyuan Yin, National University of Singapore – “Calibration and validation of a numerical model against experimental data of methane hydrate formation and dissociation in a sandy porous medium”
3:10PM-4:10PM Foyer	**Poster Session and Coffee Break**	
BREAKOUT SESSIONS		
4:10PM-5:40PM Nueces A	**Chair:** **Prof. Bjørn Kvamme** **Rapporteur:** **Prof. Na Wei**	Laboratory Experimentation: 1) Limitations on experimentation relative to the environment. 2) Mineral/hydrate/ Fluid interactions focus on porous non steady stat conditions
4:10PM-5:40PM Laguna Madre	**Chair:** **Prof. Joo Yong Lee** **Rapporteur:** **Mr. Zhenyuan Yin**	Gas Hydrate Related Modelling: Load Predictions, Coastal - Platform Stability, Environmental Safety
6:30PM	**Bus to Aquarium**	
7:00PM	**Corpus Christi Aquarium Cocktails and Dinner**	

Thursday, 7 December

TIME		SESSION CHAIR
7:30AM-8:15AM Nueces B	**Breakfast**	
8:15AM-9:45AM Nueces A	**National Reviews**	• **8:15 – 9:00, Japan:** Dr. Norio Tenma AIST, Tokyo, Japan “Recent Status of Methane Hydrate R&D Program in Japan” • **9:00 – 9:45, Korea:** Dr. Joo Yong Lee KIGAM, South Korea “The National Report on Gas Hydrate R&D Program in Korea”
9:45AM-10:55AM Nueces A	**Research Presentations** **Chair:** **Dr. Norio Tenma**	• **9:45 – 10:15** Prof. Jurgen Mienert, University of Tromsø – “4D Seismics and Ocean Observatories in Arctic Gas Hydrate Research” • **10:15 – 10:35** Dr. Xin Lu, China National Offshore Oil Corporation – “Experimental study on the effective thermal conductivity of pressure-tight sampling corer natural gas hydrate samples of South China Sea” CANCELLED • **10:35 – 10:55** Prof. Na Wei, Southwest Petroleum University – “The first solid fluidization exploitation experimental system of marine natural gas hydrate in the world”
10:55AM-11:10AM Foyer	**Coffee**	

11:10AM-12:30PM Nueces A	**Research Presentations** **Chair:** **Prof. Stephen Masutani**	- **11:10 – 11:30** Prof. Bjørn Kvamme, University of Bergen – ” Natural gas hydrates - a substantial non-equilibrium challenge” - **11:30 – 11:50** Prof. Subbarao Yelisetti – Texas A&M University Kingsville – “Gas hydrate role in coastal slope failure” - **11:50 – 12:10** Prof. Lin Zhong, Southwest Petroleum University “Technology Status of Mining Guide Device of Natural Gas Hydrate in Seabed Shallow Layer” - **12:10 – 12:30** Prof. Yang Tang, Southwest Petroleum University “Feasibility Research on a Purification Technology of Natural Gas-hydrate Slurry by Sand Removal based on Hydrocyclone Separation”
12:30PM – 1:30 PM Nueces B	**Lunch**	
1:30PM-3:10PM Nueces A	**Research Presentations** **Chair:** **Prof. Stephen Masutani**	- **1:30 – 1:50** Prof. Richard Coffin, Texas A&M University – Corpus Christi – “Geochemical Assessment of Coastal Gas Hydrate Loading off the Coast of New Zealand” - **1:50 – 2:10** Prof. Brandi Reese, Texas A&M University – Corpus Christi – “Organic matter mineralization pathways in Baltic Sea Basin sediments revealed through DNA and RNA sequencing” - **2:10 – 2:30** Prof. Joseph Smith, US Naval Academy – “Factors Influencing Spatial Variability in Late Summer Methane Fluxes from the North Slope of Alaska” - **2:30 – 2:50** Prof. Lin Zhang, Texas A&M University – Corpus Christi – “Examining the relationship between trophic status and methane production pathways in Alaskan peatlands using stable isotopes and molecular techniques” - **2:50 – 3:10** Prof. Hussain Abdulla, Texas A&M University – Corpus Christi – “Accumulation of deaminated peptides in anoxic sediment of Santa Barbara Basin”
3:10PM-4:10PM Foyer	**Poster Session and Coffee**	
BREAKOUT SESSIONS		

4:10PM-5:40PM Nueces A	**Chair:** **Prof. Subbarao Yelisetti** **Rapporteur:** **Ms. Hao Yu**	Gas Hydrate Deep Drilling: Technology, Recent Data
4:10PM-5:40PM Laguna Madre	**Chair:** **Dr. Kelly Rose** **Rapporteur:** **Dr. Xin Lu**	Carbon Sequestration Related to Gas Hydrate Mining: Platform Stability, Environmental Safety vs. Impact, CO2 Residence Time
6:40PM	**Bus to TAMU-CC**	
7:00PM	**TAMU-CC Cocktails and Dinner**	

Friday, 8 December

TIME		
7:30AM-8:30AM Nueces B	**Breakfast**	
	BREAKOUT SESSIONS	
8:30AM-10:00AM Nueces A	**Chair:** **Prof. Richard Coffin** **Rapporteur:** **Mr. Sajjad Abdullajintakam**	Initial Site Assessment: Seismic and Geochemical Evaluation, Recent Data (Positive and Negative), Additional Approaches.
8:30AM-10:00AM Laguna Madre	**Chair:** **Prof. Brandi Reese** **Rapporteur:** **Prof. Joseph Smith**	Biogeochemical Assessments of Gas Hydrate Loading and Monitoring Environmental Health
10:00AM–11:00AM Foyer	**Coffee Break**	
11:00AM-12:00PM Nueces A	**Chair:** **Prof. Tsutomu Uchida** **Rapporteur:** **Ms. Jenna Cooper**	Summary of Sessions
12:00PM-1:00PM Nueces A	**Chair:** **Prof. Richard Coffin** **Rapporteur:** **Prof. Bjørn Kvamme**	Closing Remarks

Abstracts and Presentations

INTRODUCTIONS AND REVIEWS

Dr. Richard Coffin PENS, TAMU-CC   Meeting Introduction and Overview

11th International Methane Hydrate Research and Development Workshop

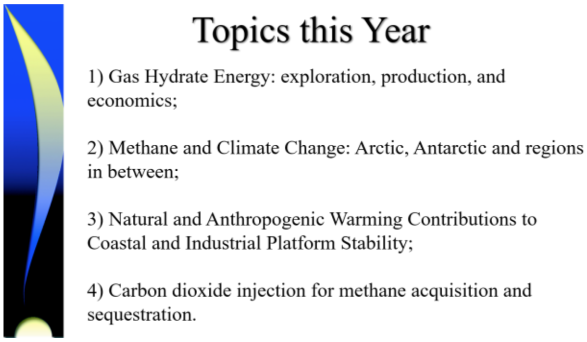
Welcome

Organizers

Dr. Richard Coffin, TAMU-CC
Dr. Bjørn Kvamme, University of Bergen
Dr. Stephen Masutani, University of Hawaii
Dr. Norio Tenma, AIST-Tokyo
Dr. Tsutomu Uchida, Hokkaido University

Local Development: Mrs. Alessandra Garcia

Workshops and Attendees



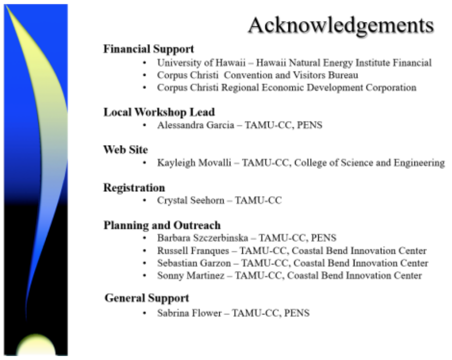
Topics this Year

1) Gas Hydrate Energy: exploration, production, and economics;

2) Methane and Climate Change: Arctic, Antarctic and regions in between;

3) Natural and Anthropogenic Warming Contributions to Coastal and Industrial Platform Stability;

4) Carbon dioxide injection for methane acquisition and sequestration.



Acknowledgements

Financial Support
- University of Hawaii – Hawaii Natural Energy Institute Financial
- Corpus Christi Convention and Visitors Bureau
- Corpus Christi Regional Economic Development Corporation

Local Workshop Lead
- Alessandra Garcia – TAMU-CC, PENS

Web Site
- Kayleigh Movalli – TAMU-CC, College of Science and Engineering

Registration
- Crystal Seehorn – TAMU-CC

Planning and Outreach
- Barbara Szczerbinska – TAMU-CC, PENS
- Russell Franques – TAMU-CC, Coastal Bend Innovation Center
- Sebastian Garzon – TAMU-CC, Coastal Bend Innovation Center
- Sonny Martinez – TAMU-CC, Coastal Bend Innovation Center

General Support
- Sabrina Flower – TAMU-CC, PENS

10th Workshop Overview

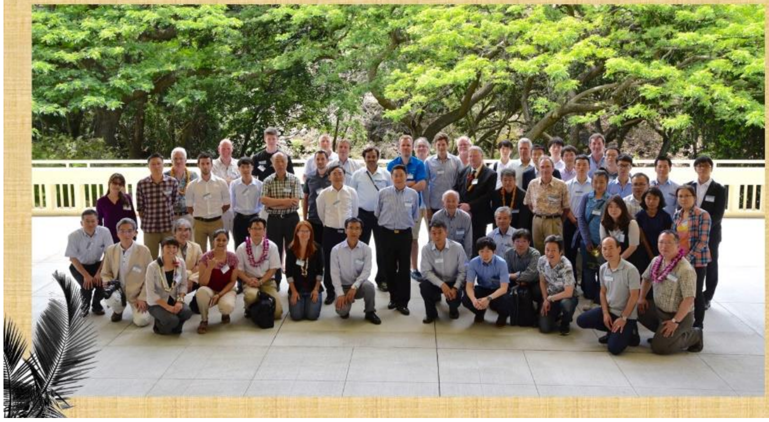
Fiery Ice 2016
15-17 June 2016, Honolulu Hawaii

Summary

- Workshop theme was "15 Years of Progress and Future Directions"
- Highlighted accomplishments and changes in hydrate science and engineering since the first workshop in 2001, and identified directions for the future
- 60 participants from the U.S., Japan, China, Germany, India, New Zealand, Norway, and the Republic of Korea
- 7 national reports, 5 breakout sessions, and 20 oral and 25 poster presentations

Summary (continued)

- National reports described the present status of gas hydrate research in the U.S., China, Korea, Japan, Norway, New Zealand, and Germany
- Five breakout session topics were: 1) Fundamental laboratory and modeling studies, 2) Exploration and resource assessment, 3) Reservoir and production modeling, 4) The path forward: key areas for future R&D, and 5) The impact of cheap fossil fuels on methane hydrate R&D
- 12 peer-reviewed papers published in special issue of *Energies*



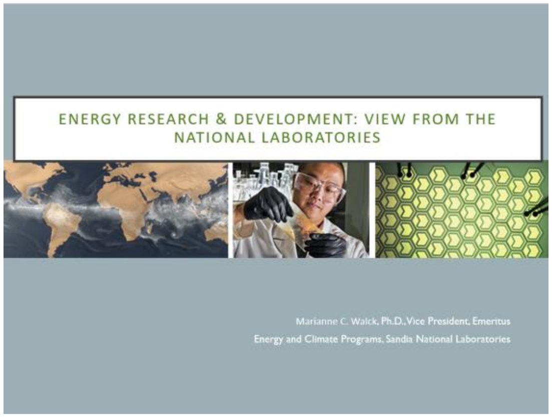
KEYNOTE SPEAKER

Energy Research and Development: View from the National Laboratories

Marianne C Walck, PhD
Vice President Emeritus
Sandia National Laboratories Energy and Climate Programs

The United States consistently delivers a reliable supply of abundant, inexpensive energy to consumers, and while carbon-intensity has declined over time, many challenges remain. More than 80% of US energy is still derived from carbon-based subsurface sources: oil, gas, and coal. Recent advances in producing hydrocarbons directly from shale have dramatically reduced natural gas prices, resulting in a marked increase of natural gas usage in electricity production, and a corresponding decrease in coal use. Renewable energy sources for electricity generation and transportation are increasing, but remain a small part of the overall energy equation. Low-carbon electricity from nuclear power faces an uncertain future due to low natural gas prices, high capital costs, and the need for a clear path for nuclear waste storage and disposal. The changing climate and challenges in water supply and quality provide additional complexity for the future energy system.

The presentation discusses numerous challenges that face the future of electric power and transportation in the nation, and how collaborative research and development conducted in the US Department of Energy national laboratory system provides technologies for efficient and effective energy generation, use, and storage. Specific examples include carbon sequestration, nanotechnologies, batteries, combustion modeling, earth system simulation, biomass deconstruction, wave energy conversion, and solar receivers.



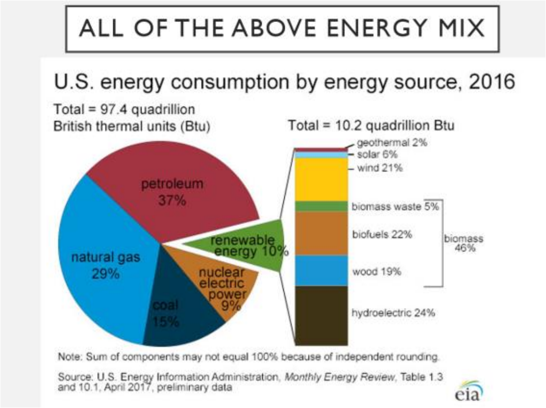
ENERGY RESEARCH & DEVELOPMENT: VIEW FROM THE NATIONAL LABORATORIES

Marianne C. Walck, Ph.D., Vice President, Emeritus
Energy and Climate Programs, Sandia National Laboratories

CLEAN ENERGY & CLIMATE SUSTAINABILITY: DEFINING CHALLENGES OF OUR TIME

We want energy to be:

- ✓ Affordable
  - Low cost per unit of energy
  - Price Volatility: stable or fluctuating
- ✓ Available
  - Access substantial resources
- ✓ Reliable
  - Baseload or intermittent
  - Safe: natural/human causes
  - Secure
- ✓ Sustainable
  - Clean: reduce emissions
  - Dense: land footprint
  - Minimize Water Use

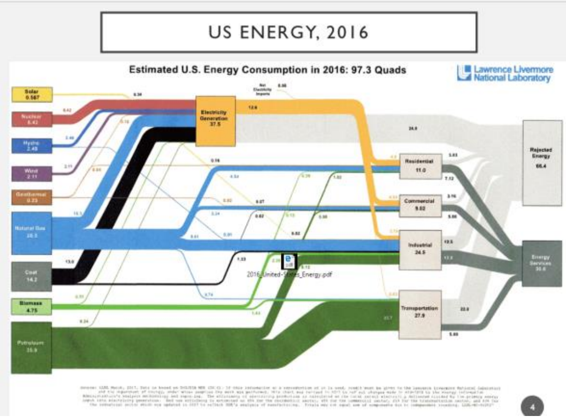


ALL OF THE ABOVE ENERGY MIX

U.S. energy consumption by energy source, 2016

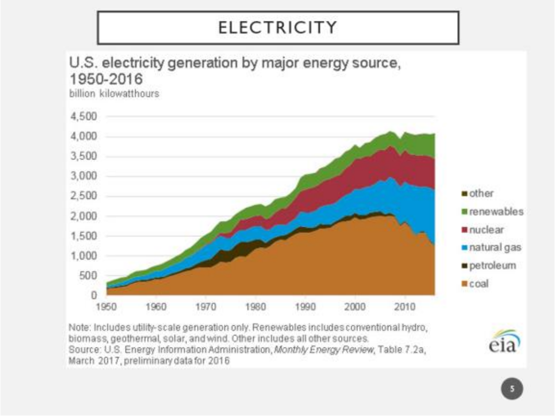
Note: Sum of components may not equal 100% because of independent rounding.

Source: U.S. Energy Information Administration, *Monthly Energy Review*, Table 1.3 and 10.1, April 2017, preliminary data



US ENERGY, 2016

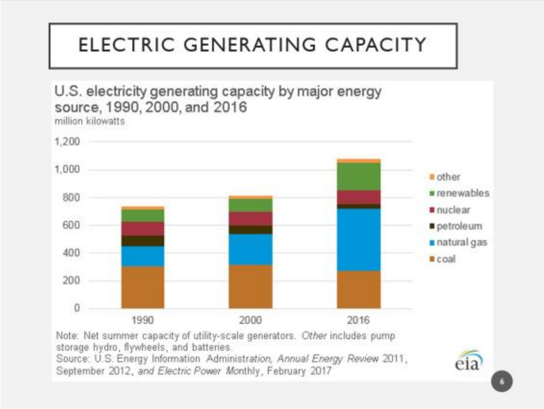
Estimated U.S. Energy Consumption in 2016: 97.3 Quads



ELECTRICITY

U.S. electricity generation by major energy source, 1950-2016

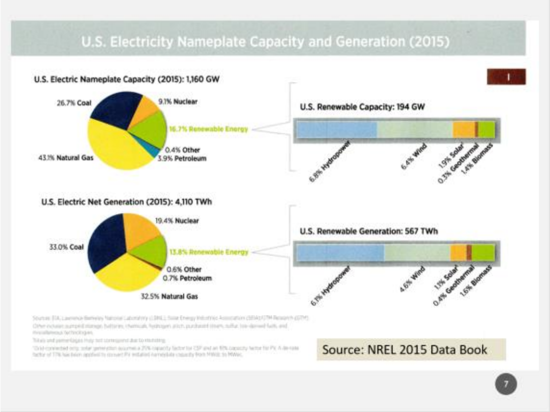
Note: Includes utility-scale generation only. Renewables includes conventional hydro, biomass, geothermal, solar, and wind. Other includes all other sources.
Source: U.S. Energy Information Administration, *Monthly Energy Review*, Table 7.2a, March 2017, preliminary data for 2016



ELECTRIC GENERATING CAPACITY

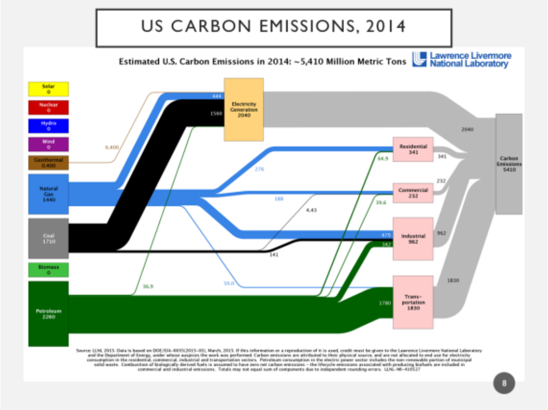
U.S. electricity generating capacity by major energy source, 1990, 2000, and 2016

Note: Net summer capacity of utility-scale generators. *Other* includes pump storage hydro, flywheels, and batteries.
Source: U.S. Energy Information Administration, *Annual Energy Review* 2011, September 2012, and *Electric Power Monthly*, February 2017



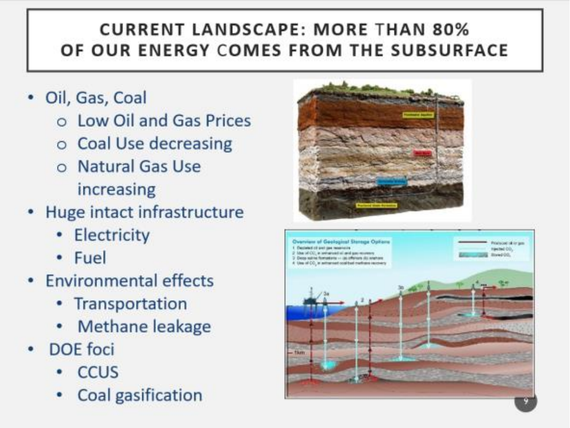
U.S. Electricity Nameplate Capacity and Generation (2015)

Source: NREL 2015 Data Book



US CARBON EMISSIONS, 2014

Estimated U.S. Carbon Emissions in 2014: ~5,410 Million Metric Tons

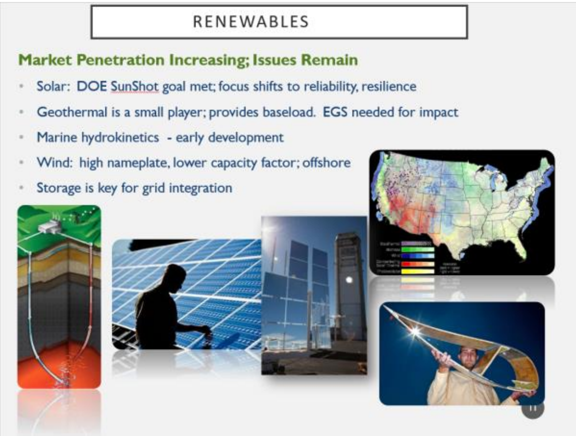


CURRENT LANDSCAPE: MORE THAN 80% OF OUR ENERGY COMES FROM THE SUBSURFACE

- Oil, Gas, Coal
  - Low Oil and Gas Prices
  - Coal Use decreasing
  - Natural Gas Use increasing
- Huge intact infrastructure
  - Electricity
  - Fuel
- Environmental effects
  - Transportation
  - Methane leakage
- DOE foci
  - CCUS
  - Coal gasification

NUCLEAR ENERGY

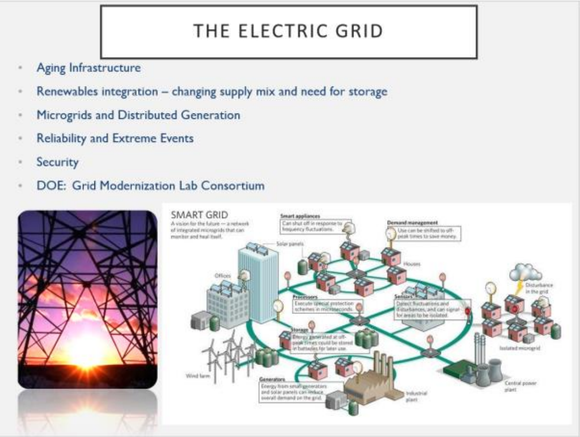
- Low-carbon, baseload power with high capacity factor
  - (> 90%, 2014-2016)
- ~20% of US electricity; 99 operating plants
- 6 completed US reactor closures since 2013, 2 under construction
- Dozens of new units planned or under construction worldwide: China, India, Middle East
- Europe, Korea, Japan reducing plans for future nuclear
- Why is nuclear not expanding in the US?
  - Economics (High capital cost, low natural gas prices),
  - Waste disposal
- DOE focus
  - New reactor and fuel types
  - Waste storage/disposal



RENEWABLES

Market Penetration Increasing; Issues Remain

- Solar: DOE SunShot goal met; focus shifts to reliability, resilience
- Geothermal is a small player; provides baseload. EGS needed for impact
- Marine hydrokinetics - early development
- Wind: high nameplate, lower capacity factor; offshore
- Storage is key for grid integration

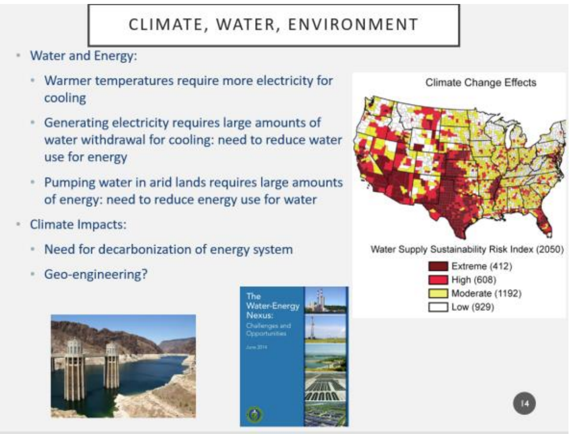


THE ELECTRIC GRID

- Aging Infrastructure
- Renewables integration – changing supply mix and need for storage
- Microgrids and Distributed Generation
- Reliability and Extreme Events
- Security
- DOE: Grid Modernization Lab Consortium

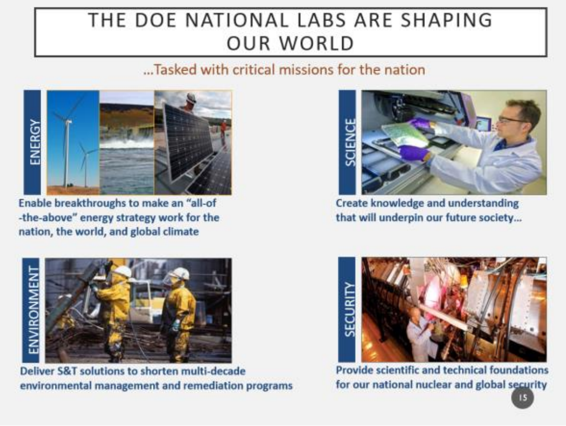
TRANSPORTATION OPTIONS

- Natural gas: more likely for heavy duty vehicles
- Hydrogen Fuel Cells
- Electric
- Biofuels



CLIMATE, WATER, ENVIRONMENT

- Water and Energy:
  - Warmer temperatures require more electricity for cooling
  - Generating electricity requires large amounts of water withdrawal for cooling: need to reduce water use for energy
  - Pumping water in arid lands requires large amounts of energy: need to reduce energy use for water
- Climate Impacts:
  - Need for decarbonization of energy system
  - Geo-engineering?



THE DOE NATIONAL LABS ARE SHAPING OUR WORLD

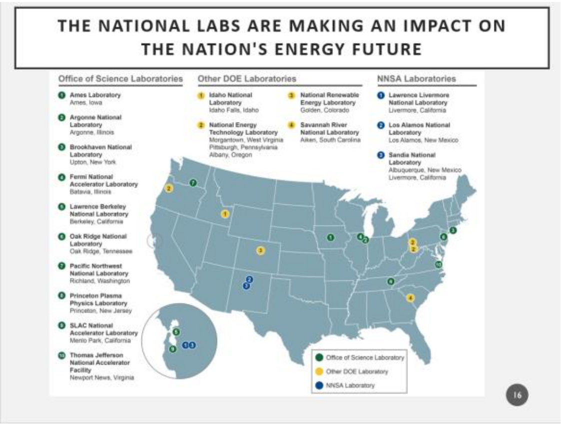
...Tasked with critical missions for the nation

Enable breakthroughs to make an "all-of -the-above" energy strategy work for the nation, the world, and global climate

Create knowledge and understanding that will underpin our future society...

Deliver S&T solutions to shorten multi-decade environmental management and remediation programs

Provide scientific and technical foundations for our national nuclear and global security



THE NATIONAL LABS ARE MAKING AN IMPACT ON THE NATION'S ENERGY FUTURE

Office of Science Laboratories

1. **Ames Laboratory** Ames, Iowa
2. **Argonne National Laboratory** Argonne, Illinois
3. **Brookhaven National Laboratory** Upton, New York
4. **Fermi National Accelerator Laboratory** Batavia, Illinois
5. **Lawrence Berkeley National Laboratory** Berkeley, California
6. **Oak Ridge National Laboratory** Oak Ridge, Tennessee
7. **Pacific Northwest National Laboratory** Richland, Washington
8. **Princeton Plasma Physics Laboratory** Princeton, New Jersey
9. **SLAC National Accelerator Laboratory** Menlo Park, California
10. **Thomas Jefferson National Accelerator Facility** Newport News, Virginia

Other DOE Laboratories

1. **Idaho National Laboratory** Idaho Falls, Idaho
2. **National Energy Technology Laboratory** Morgantown, West Virginia; Pittsburgh, Pennsylvania; Albany, Oregon
3. **National Renewable Energy Laboratory** Golden, Colorado
4. **Savannah River National Laboratory** Aiken, South Carolina

NNSA Laboratories

1. **Lawrence Livermore National Laboratory** Livermore, California
2. **Los Alamos National Laboratory** Los Alamos, New Mexico
3. **Sandia National Laboratory** Albuquerque, New Mexico; Livermore, California

WHAT CAN/SHOULD A NATIONAL LAB DO?

DOE mission in energy (2015 QTR) :

- Secure and Resilient
- Economically Competitive
- Environmentally Responsible

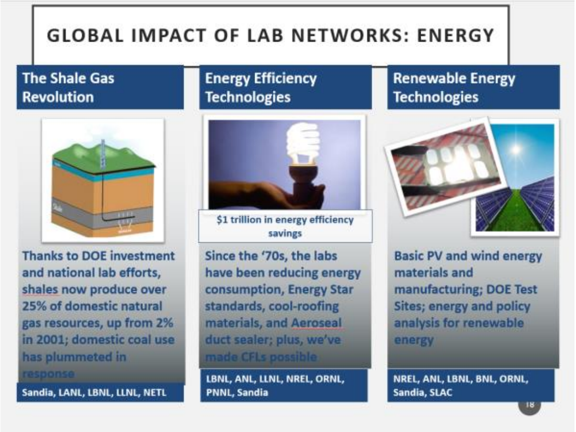
Lab Elements:

- Foundational Research
- New Technologies
- Integrate to understand systems behavior
- Reduce key technical uncertainties
- Provide unbiased technical information
- Broad multidisciplinary capability

QTR

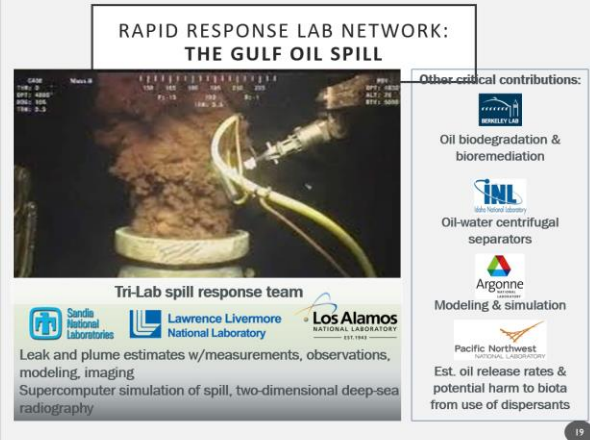
QUADRENNIAL TECHNOLOGY REVIEW
AN ASSESSMENT OF ENERGY TECHNOLOGIES AND RESEARCH OPPORTUNITIES

SEP



GLOBAL IMPACT OF LAB NETWORKS: ENERGY

The Shale Gas Revolution	Energy Efficiency Technologies	Renewable Energy Technologies
	$1 trillion in energy efficiency savings	
Thanks to DOE investment and national lab efforts, shales now produce over 25% of domestic natural gas resources, up from 2% in 2001; domestic coal use has plummeted in response	Since the '70s, the labs have been reducing energy consumption, Energy Star standards, cool-roofing materials, and Aeroseal duct sealer; plus, we've made CFLs possible	Basic PV and wind energy materials and manufacturing; DOE Test Sites; energy and policy analysis for renewable energy
Sandia, LANL, LBNL, LLNL, NETL	LBNL, ANL, LLNL, NREL, ORNL, PNNL, Sandia	NREL, ANL, LBNL, BNL, ORNL, Sandia, SLAC



RAPID RESPONSE LAB NETWORK: THE GULF OIL SPILL

Tri-Lab spill response team

Sandia National Laboratories
Lawrence Livermore National Laboratory
Los Alamos NATIONAL LABORATORY EST. 1943

Leak and plume estimates w/measurements, observations, modeling, imaging
Supercomputer simulation of spill, two-dimensional deep-sea radiography

Other critical contributions:

BERKELEY LAB
Oil biodegradation & bioremediation

INL Idaho National Laboratory
Oil-water centrifugal separators

Argonne NATIONAL LABORATORY
Modeling & simulation

Pacific Northwest NATIONAL LABORATORY
Est. oil release rates & potential harm to biota from use of dispersants

MULTI-LAB CROSS-CUTTING DOE INITIATIVES

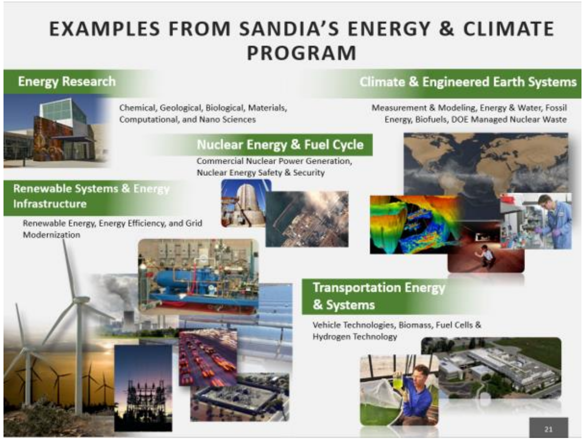
GRID MODERNIZATION LABORATORY CONSORTIUM U.S. Department of Energy

- Grid Modernization Initiative
- Subsurface Crosscut
- Energy –Water Nexus
- Advanced Computing Tech Team
- Supercritical CO_2 Tech Team
- Clean Manufacturing Initiative

Knowledge informs our ability to adapt to change.

Energy Efficiency and Renewable Energy Crosscut Programs

- Co-Optimization of Fuels and Engines
- Hydrogen @Scale (transportation and storage)



EXAMPLES FROM SANDIA'S ENERGY & CLIMATE PROGRAM

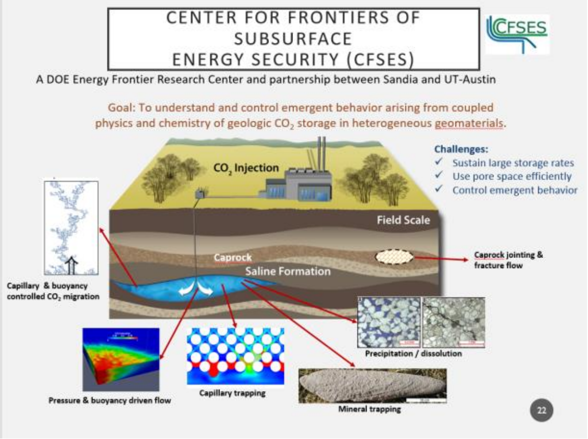
Energy Research
Chemical, Geological, Biological, Materials, Computational, and Nano Sciences

Climate & Engineered Earth Systems
Measurement & Modeling, Energy & Water, Fossil Energy, Biofuels, DOE Managed Nuclear Waste

Nuclear Energy & Fuel Cycle
Commercial Nuclear Power Generation, Nuclear Energy Safety & Security

Renewable Systems & Energy Infrastructure
Renewable Energy, Energy Efficiency, and Grid Modernization

Transportation Energy & Systems
Vehicle Technologies, Biomass, Fuel Cells & Hydrogen Technology



CENTER FOR FRONTIERS OF SUBSURFACE ENERGY SECURITY (CFSES)

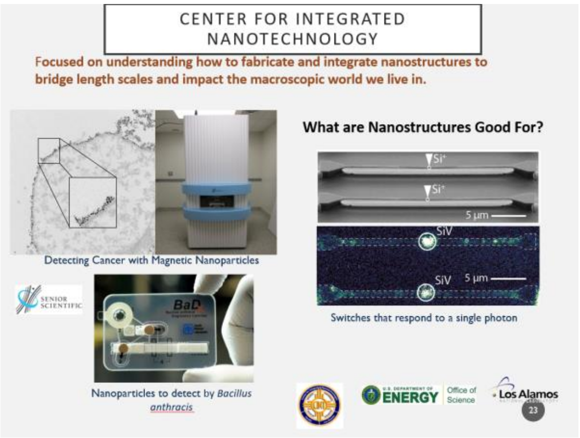
CFSES

A DOE Energy Frontier Research Center and partnership between Sandia and UT-Austin

Goal: To understand and control emergent behavior arising from coupled physics and chemistry of geologic CO_2 storage in heterogeneous geomaterials.

Challenges:
✓ Sustain large storage rates
✓ Use pore space efficiently
✓ Control emergent behavior

CO_2 Injection
Field Scale
Caprock
Saline Formation
Caprock jointing & fracture flow
Capillary & buoyancy controlled CO_2 migration
Pressure & buoyancy driven flow
Capillary trapping
Precipitation / dissolution
Mineral trapping



CENTER FOR INTEGRATED NANOTECHNOLOGY

Focused on understanding how to fabricate and integrate nanostructures to bridge length scales and impact the macroscopic world we live in.

Detecting Cancer with Magnetic Nanoparticles

SENIOR SCIENTIFIC

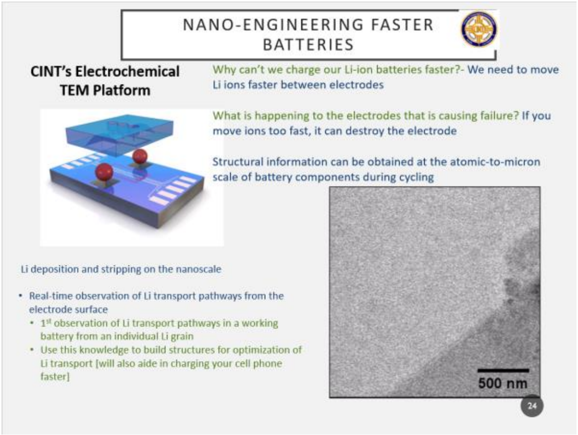
Nanoparticles to detect by *Bacillus anthracis*

What are Nanostructures Good For?

Si⁺
Si⁺
5 µm
SiV
SiV
5 µm

Switches that respond to a single photon

U.S. DEPARTMENT OF ENERGY Office of Science
Los Alamos



NANO-ENGINEERING FASTER BATTERIES

CINT's Electrochemical TEM Platform

Why can't we charge our Li-ion batteries faster?- We need to move Li ions faster between electrodes

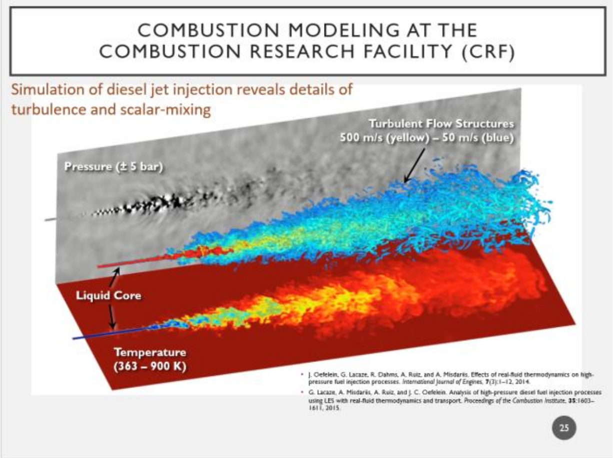
What is happening to the electrodes that is causing failure? If you move ions too fast, it can destroy the electrode

Structural information can be obtained at the atomic-to-micron scale of battery components during cycling

Li deposition and stripping on the nanoscale

- Real-time observation of Li transport pathways from the electrode surface
  - 1st observation of Li transport pathways in a working battery from an individual Li grain
  - Use this knowledge to build structures for optimization of Li transport [will also aide in charging your cell phone faster]

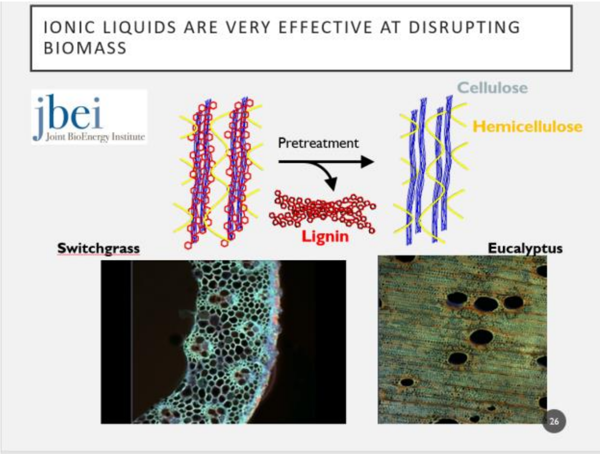
500 nm



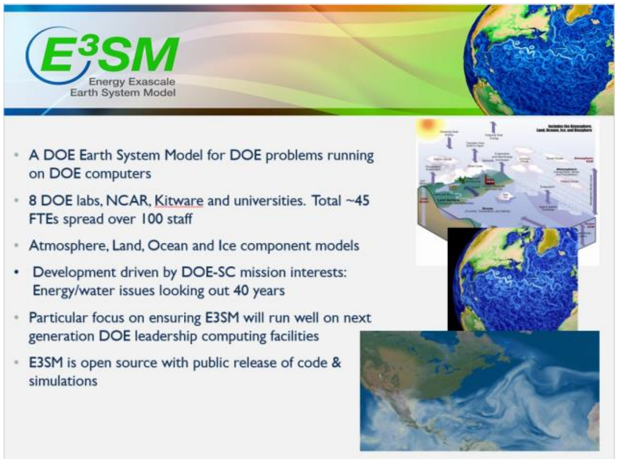
COMBUSTION MODELING AT THE COMBUSTION RESEARCH FACILITY (CRF)

Simulation of diesel jet injection reveals details of turbulence and scalar-mixing

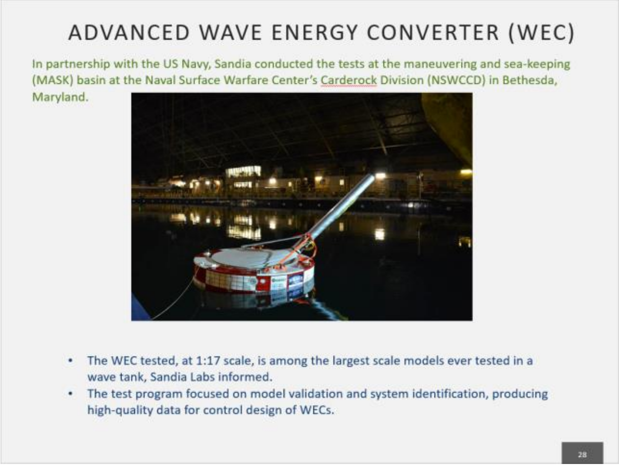
- J. Oefelein, G. Lacaze, R. Dahms, A. Ruiz, and A. Misdariis. Effects of real-fluid thermodynamics on high-pressure fuel injection processes. *International Journal of Engines*, **7**(3):1–12, 2014.
- G. Lacaze, A. Misdariis, A. Ruiz, and J. C. Oefelein. Analysis of high-pressure diesel fuel injection processes using LES with real-fluid thermodynamics and transport. *Proceedings of the Combustion Institute*, **35**:1603–1611, 2015.



IONIC LIQUIDS ARE VERY EFFECTIVE AT DISRUPTING BIOMASS



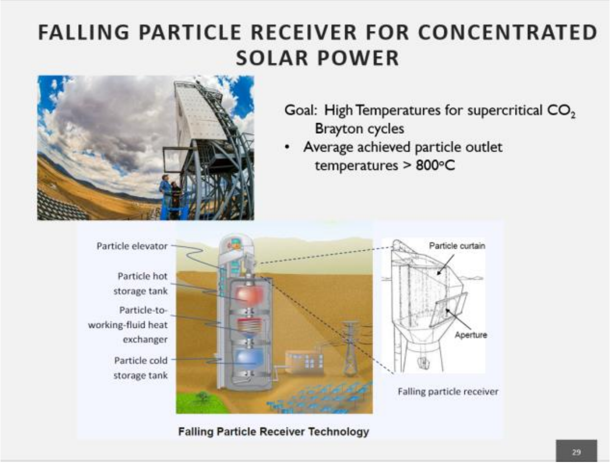
- A DOE Earth System Model for DOE problems running on DOE computers
- 8 DOE labs, NCAR, Kitware and universities. Total ~45 FTEs spread over 100 staff
- Atmosphere, Land, Ocean and Ice component models
- Development driven by DOE-SC mission interests: Energy/water issues looking out 40 years
- Particular focus on ensuring E3SM will run well on next generation DOE leadership computing facilities
- E3SM is open source with public release of code & simulations



ADVANCED WAVE ENERGY CONVERTER (WEC)

In partnership with the US Navy, Sandia conducted the tests at the maneuvering and sea-keeping (MASK) basin at the Naval Surface Warfare Center's Carderock Division (NSWCCD) in Bethesda, Maryland.

- The WEC tested, at 1:17 scale, is among the largest scale models ever tested in a wave tank, Sandia Labs informed.
- The test program focused on model validation and system identification, producing high-quality data for control design of WECs.

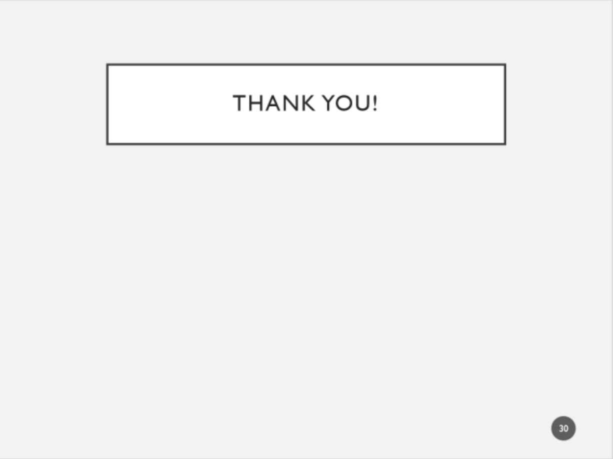


FALLING PARTICLE RECEIVER FOR CONCENTRATED SOLAR POWER

Goal: High Temperatures for supercritical CO_2 Brayton cycles

- Average achieved particle outlet temperatures > 800°C

Falling Particle Receiver Technology



THANK YOU!

NATIONAL REVIEWS

TEXAS A&M UNIVERSITY CORPUS CHRISTI

HOKKAIDO UNIVERSITY

UNIVERSITAS BERGENSIS

HNEI

AIST
NATIONAL INSTITUTE OF
ADVANCED INDUSTRIAL SCIENCE
AND TECHNOLOGY (AIST)

Methane Hydrates as a Potential Natural Gas Energy Resource: DOE's Research and Development Strategy for Success

Jared Ciferno (National Energy Technology Laboratory; jared.ciferno@netl.doe.gov)

Summary/Conclusions

A portfolio of research projects is delivering new findings focused on developing a better understanding of the nature and occurrence of gas hydrates within the United States, the technologies that can achieve production of natural gas from gas hydrates and the role of gas hydrates in environmental and safety-related dynamics. The Department of Energy's (DOE) National Energy Technology Laboratory (NETL) Gas Hydrates R&D Program includes recently completed and ongoing research projects. These projects are building on a history of important research efforts that have helped to more accurately quantify the global gas hydrate resource, test practical methods for identifying hydrate in the subsurface, understand the physical processes at work during hydrate formation and dissociation, and model gas production from gas hydrate accumulations in arctic and deepwater marine shelf environments.

Background

Methane hydrate represents a potentially vast natural gas resource for the United States and the world. Once thought to be rare in nature, gas hydrates are now known to occur in great abundance in association with arctic permafrost and in the shallow sediments of the deep-water continental shelves. The most recent estimates of gas hydrate abundance suggest that they contain more organic carbon than all of the world's oil, gas, and coal combined.

In 1982, the United States launched a national R&D program dedicated to the study of naturally occurring methane hydrate. During the first phase of this program, from 1982-1992, the United States carried out research on the physical and chemical properties of methane hydrate, and the United States Geological Survey (USGS) focused on characterizing sub-permafrost hydrate trends on the North Slope of Alaska.

Renewed interest in methane hydrate as a potential energy source resulted in the DOE Methane Hydrates R&D Program, a reinvigorated national program in the U.S. that was launched in 1998 and continues to the present day. Since 2009, more than 50 different projects under have received funding under this program of roughly $160 million, including both government and non-government costs. The bulk of the funding supports field and laboratory programs conducted through partnerships with industry and academia and supported by work conducted with DOE's national laboratories and collaborating federal agencies.

Aims

The mission of the NETL-managed DOE Methane Hydrates R&D Program is to collaborate nationally and internationally to advance the scientific understanding of naturally occurring gas hydrates. This discussion will review the technical, economic, and environmental challenges associated with natural gas production via methane hydrates and DOE's role in addressing these challenges.

Methods

DOE's research program relies on partnerships among national labs, federal agencies such as the USGS, academic research universities, technology providers, and natural gas producers to implement cost shared projects to address research needs identified by consensus. Primary R&D needs in recent years have been (1) to provide an accurate assessment of the nature and occurrence of gas hydrates within the United States; (2) to identify, refine, and demonstrate technologies that can achieve production of natural gas from gas hydrates in an economically-viable and environmentally-responsible manner; and (3) to determine and effectively communicate the role of gas hydrates in environmental and safety-related dynamics, chiefly in the natural sequestration and cycling of carbon over a range of time scales, including potential short-term responses to global climate change, and in natural and operational geohazards.

Over the past fifteen or so years, the DOE Methane Hydrates R&D Program has been based on near-term (2020) and longer-term (2025–2030) goals for these three focus areas. Near-term goals representing intermediate steps toward the long-term goals are discussed in the following sections. Specific efforts currently underway to answer the identified science and technology questions include (1) development of tools for reliable marine gas hydrate sampling and analysis; (2) integrated geologic/geophysical characterization methodologies to enable pre-drill assessments of natural gas hydrate systems; (3) development of exploration technologies; (4) development of production technologies; (5) determination of gas hydrate's implications for long-term global carbon cycling and potential near-term feedbacks to ongoing climate change; and (6) development and demonstration of effective numerical simulation tools to enable the effective design and interpretation of field data related to both production and environmental implications.

Selected Results (to date, research is ongoing)

Key accomplishments of the research program to date include:

- Characterization of potential testing sites on the Alaska North Slope, including drilling and evaluation at the Ignik Sikumi test site in 2011, and a three-month production trial of CO_2–CH_4 exchange technology in early 2012.
- Confirmation of the ability to reliably detect and characterize gas hydrate accumulations prior to drilling.
- Confirmation of the occurrence of resource-quality gas hydrate accumulations in the Gulf of Mexico.
- Acquisition of data in Alaska that enabled the first quantification of technically-recoverable resource volumes from gas hydrates.
- Development of new tools for measuring physical properties of gas hydrate-bearing sediment samples in the field.
- Expansion of numerical modeling capability to enable the first simulations of field-scale production, geomechanical stability of hydrate-bearing sediment, and gas hydrate-climate interaction.

During fiscal year (FY) 2016, six new R&D projects were awarded. University partners in these 6 projects are currently working with DOE to:

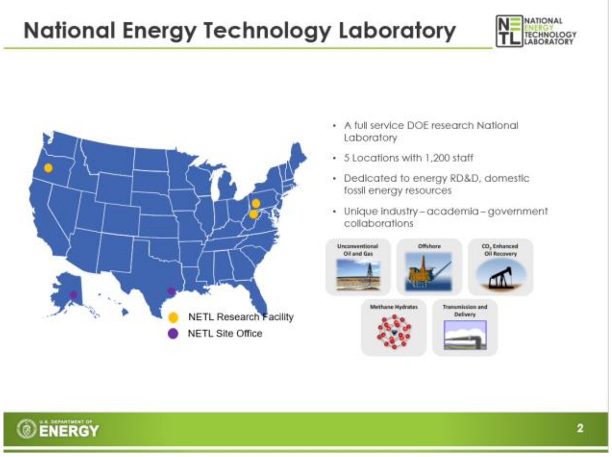
- Advance understanding of the environmental implications that methane leaking from dissociating gas hydrates could have on the ocean-atmosphere system.
- Conducting a laboratory investigation of the dynamic petrophysical attributes of gas hydrate-bearing sands in response to pressure reduction at the macro- and micro-scale.
- Conducting a laboratory evaluation of the migration of fine-grained particles during gas production from hydrate-bearing sediments.
- Studying the fate of methane in water columns where hydrate shells form around methane bubbles in a process called hydrate bubble armoring, helping to clarify hydrate's role in the global natural environment.
- Assessing controlled source electromagnetic (CSEM) technologies for locating marine hydrate deposits.
- Advancing the capabilities of a leading integrated model for hydrate system behavior, improving simulation capabilities useful in assessing and predicting production-related performance of hydrate deposits.

An Overview of US DOE Gas Hydrate Research and Development

11th International Methane Hydrate R&D Workshop

December 6, 2017

Jared Ciferno, Technology Manager, Oil & Gas



National Energy Technology Laboratory

- A full service DOE research National Laboratory
- 5 Locations with 1,200 staff
- Dedicated to energy RD&D, domestic fossil energy resources
- Unique industry – academia – government collaborations

DOE – NETL Hydrate Program

Program Mission

- Determine the potential for methane hydrates as an energy source,
- Determine environmental impacts associated with production and it's role in the global climate cycle.

Drivers/Stakeholders

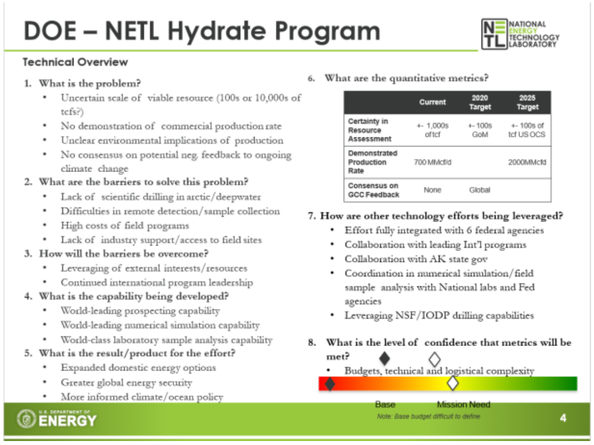
- Driver: Domestic & International Energy Security
- Driver: Global Climate Change
- Stakeholders: Interagency (BOEM, USGS, NSF, NOAA, DOI), International (Japan, S. Korea, India, Mexico), Industry, Academia

POCs

- FE-HQ Program Manager: Lou Capitanio
- Technology Manager: Jared Ciferno
- Senior Fellow(s): Grant Bromhal
- R&IC Technical Project Lead(s): Yongkoo Seol, Ray Boswell
- TD&IC Senior Project Managers: Rick Baker, Skip Pratt

BLUF

- A National Program led by DOE/NETL. Critical to understand and quantify the GLOBAL environmental impact



DOE – NETL Hydrate Program

Technical Overview

1. **What is the problem?**
   - Uncertain scale of viable resource (100s or 10,000s of tcfs?)
   - No demonstration of commercial production rate
   - Unclear environmental implications of production
   - No consensus on potential neg. feedback to ongoing climate change
2. **What are the barriers to solve this problem?**
   - Lack of scientific drilling in arctic/deepwater
   - Difficulties in remote detection/sample collection
   - High costs of field programs
   - Lack of industry support/access to field sites
3. **How will the barriers be overcome?**
   - Leveraging of external interests/resources
   - Continued international program leadership
4. **What is the capability being developed?**
   - World-leading prospecting capability
   - World-leading numerical simulation capability
   - World-class laboratory sample analysis capability
5. **What is the result/product for the effort?**
   - Expanded domestic energy options
   - Greater global energy security
   - More informed climate/ocean policy
6. What are the quantitative metrics?

	Current	2020 Target	2025 Target
Certainty in Resource Assessment	+- 1,000s of tcf	+- 100s GoM	+- 100s of tcf US OCS
Demonstrated Production Rate	700 MMcf/d		2000MMcfd
Consensus on GCC Feedback	None	Global	

7. **How are other technology efforts being leveraged?**
   - Effort fully integrated with 6 federal agencies
   - Collaboration with leading Int'l programs
   - Collaboration with AK state gov
   - Coordination in numerical simulation/field sample analysis with National labs and Fed agencies
   - Leveraging NSF/IODP drilling capabilities
8. **What is the level of confidence that metrics will be met?**
   - Budgets, technical and logistical complexity

Note: Base budget difficult to define

DOE – NETL Hydrate Program

Program Goals

Goals continually refined via

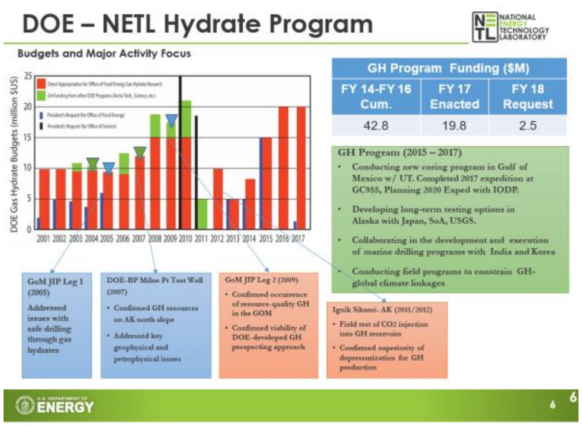
- Federal Advisory Committee (~ every 9 months)
- Interagency Technical Coordination Team (Bi-annual)
- National Academies Reviews (2005 & 2010)
- DOE QTR (2015)
- Secretary of Energy Advisory Board (2016)

NEAR-TERM GOALS (2020)

- Demonstrate long-term Technical Recoverability (Alaska)
- Confirm Gulf of Mexico Resource Assessment
- Continue International Collaborations

LONG-TERM GOALS (2025)

- Confirm scale of US resource base (+ Atlantic)
- Demonstrate Production Approach (Alaska + International)
- Consensus view on GH/Climate linkages via field programs + modeling



DOE – NETL Hydrate Program

Budgets and Major Activity Focus

GH Program Funding ($M)		
FY 14-FY 16 Cum.	FY 17 Enacted	FY 18 Request
42.8	19.8	2.5

GH Program (2015 – 2017)

- Conducting new coring program in Gulf of Mexico w/ UT. Completed 2017 expedition at GC955, Planning 2020 Exped with IODP.
- Developing long-term testing options in Alaska with Japan, SoA, USGS.
- Collaborating in the development and execution of marine drilling programs with India and Korea
- Conducting field programs to constrain GH-global climate linkages

GoM JIP Leg 1 (2005)

Addressed issues with safe drilling through gas hydrates

DOE-BP Milne Pt Test Well (2007)

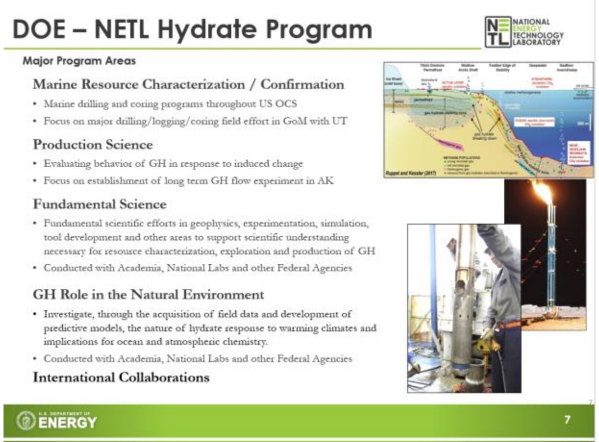
- Confirmed GH resources on AK north slope
- Addressed key geophysical and petrophysical issues

GoM JIP Leg 2 (2009)

- Confirmed occurrence of resource-quality GH in the GOM
- Confirmed viability of DOE-developed GH prospecting approach

Ignik Sikumi- AK (2011/2012)

- Field test of CO2 injection into GH reservoirs
- Confirmed superiority of depressurization for GH production



DOE – NETL Hydrate Program

Major Program Areas

Marine Resource Characterization / Confirmation

- Marine drilling and coring programs throughout US OCS
- Focus on major drilling/logging/coring field effort in GoM with UT

Production Science

- Evaluating behavior of GH in response to induced change
- Focus on establishment of long term GH flow experiment in AK

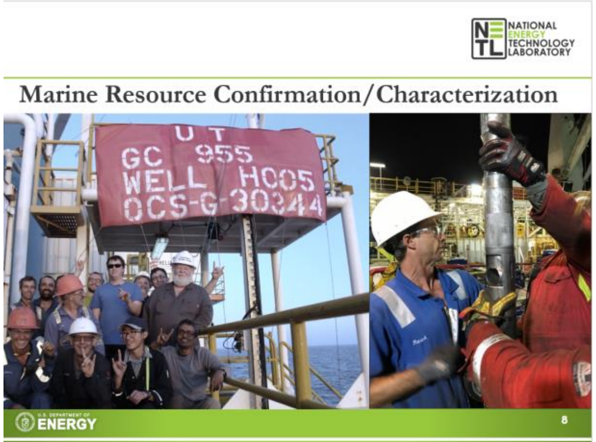
Fundamental Science

- Fundamental scientific efforts in geophysics, experimentation, simulation, tool development and other areas to support scientific understanding necessary for resource characterization, exploration and production of GH
- Conducted with Academia, National Labs and other Federal Agencies

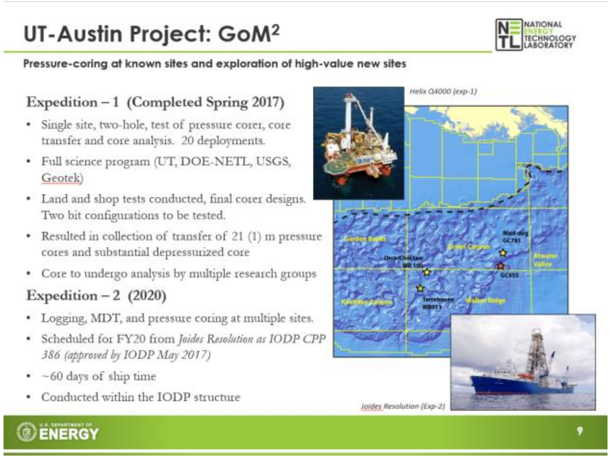
GH Role in the Natural Environment

- Investigate, through the acquisition of field data and development of predictive models, the nature of hydrate response to warming climates and implications for ocean and atmospheric chemistry.
- Conducted with Academia, National Labs and other Federal Agencies

International Collaborations



Marine Resource Confirmation/Characterization



UT-Austin Project: GoM²

Pressure-coring at known sites and exploration of high-value new sites

Expedition – 1 (Completed Spring 2017)

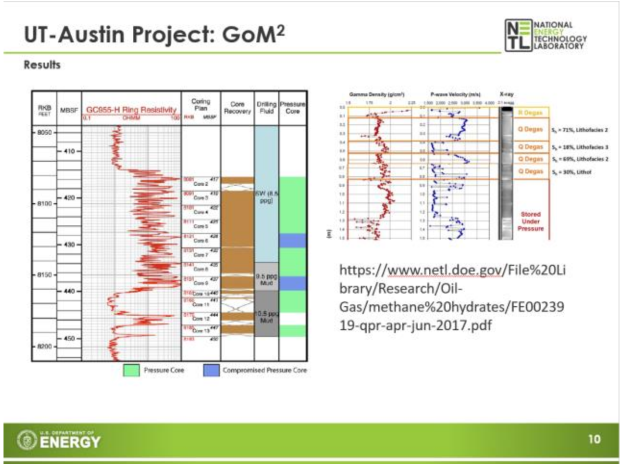
- Single site, two-hole, test of pressure corer, core transfer and core analysis. 20 deployments.
- Full science program (UT, DOE-NETL, USGS, Geotek)
- Land and shop tests conducted, final corer designs. Two bit configurations to be tested.
- Resulted in collection of transfer of 21 (1) m pressure cores and substantial depressurized core
- Core to undergo analysis by multiple research groups

Expedition – 2 (2020)

- Logging, MDT, and pressure coring at multiple sites.
- Scheduled for FY20 from *Joides Resolution as IODP CPP 386 (approved by IODP May 2017)*
- ~60 days of ship time
- Conducted within the IODP structure

Helix Q4000 (exp-1)

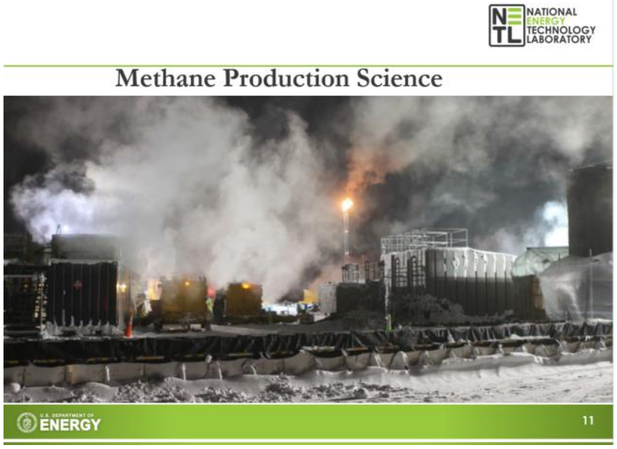
Joides Resolution (Exp-2)



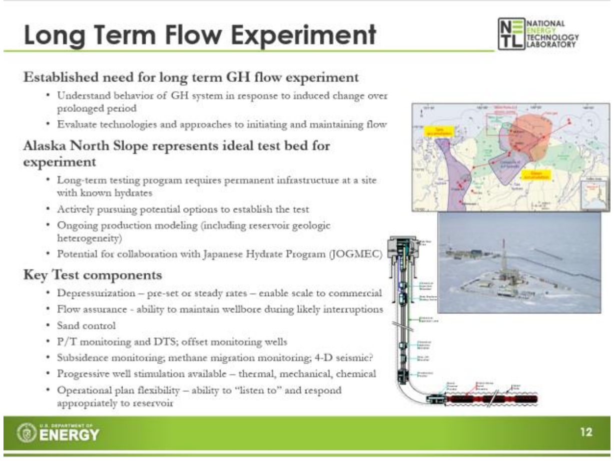
UT-Austin Project: GoM²

Results

https://www.netl.doe.gov/File%20Library/Research/Oil-Gas/methane%20hydrates/FE0023919-qpr-apr-jun-2017.pdf



Methane Production Science



Long Term Flow Experiment

Established need for long term GH flow experiment

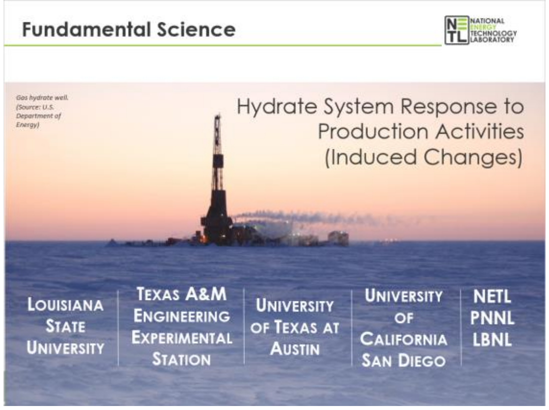
- Understand behavior of GH system in response to induced change over prolonged period
- Evaluate technologies and approaches to initiating and maintaining flow

Alaska North Slope represents ideal test bed for experiment

- Long-term testing program requires permanent infrastructure at a site with known hydrates
- Actively pursuing potential options to establish the test
- Ongoing production modeling (including reservoir geologic heterogeneity)
- Potential for collaboration with Japanese Hydrate Program (JOGMEC)

Key Test components

- Depressurization – pre-set or steady rates – enable scale to commercial
- Flow assurance - ability to maintain wellbore during likely interruptions
- Sand control
- P/T monitoring and DTS; offset monitoring wells
- Subsidence monitoring; methane migration monitoring; 4-D seismic?
- Progressive well stimulation available – thermal, mechanical, chemical
- Operational plan flexibility – ability to "listen to" and respond appropriately to reservoir

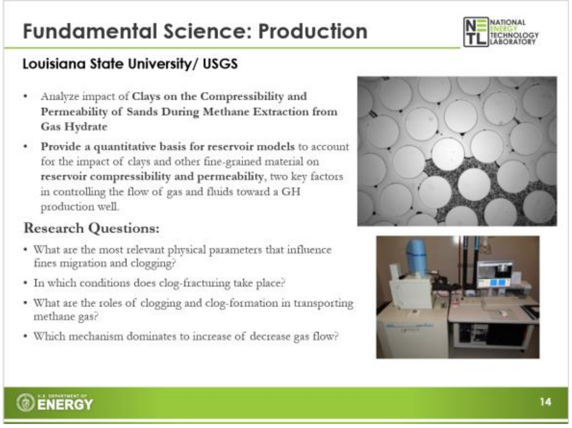


Fundamental Science

Gas hydrate well. (Source: U.S. Department of Energy)

Hydrate System Response to Production Activities (Induced Changes)

- LOUISIANA STATE UNIVERSITY
- TEXAS A&M ENGINEERING EXPERIMENTAL STATION
- UNIVERSITY OF TEXAS AT AUSTIN
- UNIVERSITY OF CALIFORNIA SAN DIEGO
- NETL PNNL LBNL



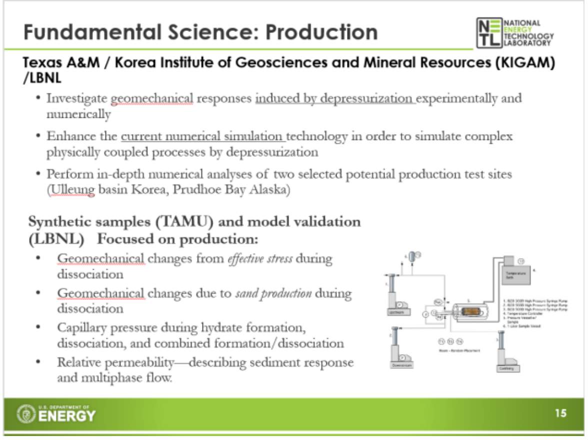
Fundamental Science: Production

Louisiana State University/ USGS

- Analyze impact of **Clays on the Compressibility and Permeability of Sands During Methane Extraction from Gas Hydrate**
- **Provide a quantitative basis for reservoir models** to account for the impact of clays and other fine-grained material on **reservoir compressibility and permeability**, two key factors in controlling the flow of gas and fluids toward a GH production well.

Research Questions:

- What are the most relevant physical parameters that influence fines migration and clogging?
- In which conditions does clog-fracturing take place?
- What are the roles of clogging and clog-formation in transporting methane gas?
- Which mechanism dominates to increase of decrease gas flow?



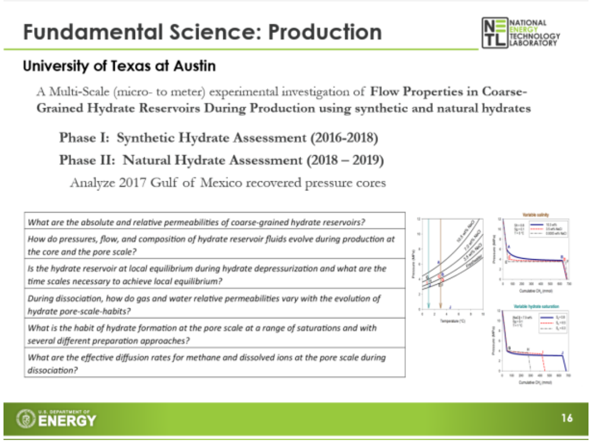
Fundamental Science: Production

Texas A&M / Korea Institute of Geosciences and Mineral Resources (KIGAM) /LBNL

- Investigate geomechanical responses induced by depressurization experimentally and numerically
- Enhance the current numerical simulation technology in order to simulate complex physically coupled processes by depressurization
- Perform in-depth numerical analyses of two selected potential production test sites (Ulleung basin Korea, Prudhoe Bay Alaska)

Synthetic samples (TAMU) and model validation (LBNL) Focused on production:

- Geomechanical changes from *effective stress* during dissociation
- Geomechanical changes due to *sand production* during dissociation
- Capillary pressure during hydrate formation, dissociation, and combined formation/dissociation
- Relative permeability—describing sediment response and multiphase flow.



Fundamental Science: Production

University of Texas at Austin

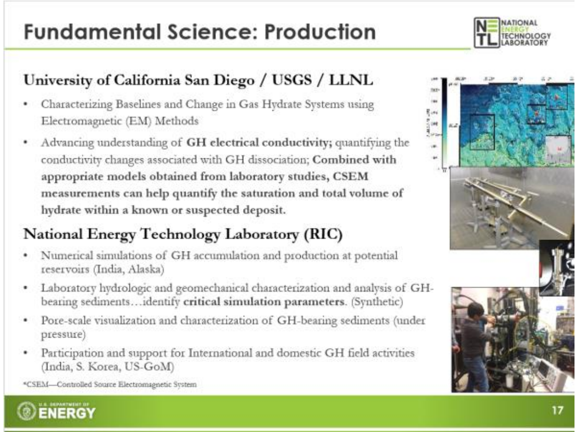
A Multi-Scale (micro- to meter) experimental investigation of **Flow Properties in Coarse-Grained Hydrate Reservoirs During Production using synthetic and natural hydrates**

Phase I: Synthetic Hydrate Assessment (2016-2018)

Phase II: Natural Hydrate Assessment (2018 – 2019)

Analyze 2017 Gulf of Mexico recovered pressure cores

What are the absolute and relative permeabilities of coarse-grained hydrate reservoirs?
How do pressures, flow, and composition of hydrate reservoir fluids evolve during production at the core and the pore scale?
Is the hydrate reservoir at local equilibrium during hydrate depressurization and what are the time scales necessary to achieve local equilibrium?
During dissociation, how do gas and water relative permeabilities vary with the evolution of hydrate pore-scale-habits?
What is the habit of hydrate formation at the pore scale at a range of saturations and with several different preparation approaches?
What are the effective diffusion rates for methane and dissolved ions at the pore scale during dissociation?



Fundamental Science: Production

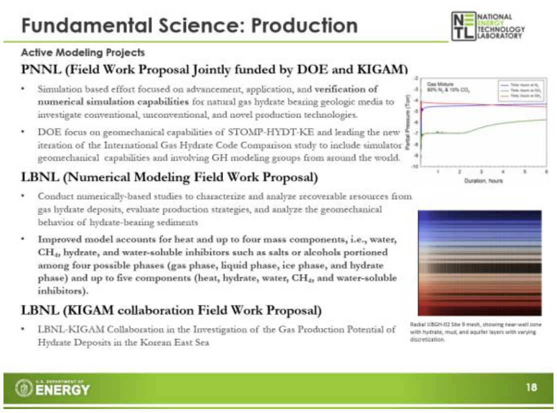
University of California San Diego / USGS / LLNL

- Characterizing Baselines and Change in Gas Hydrate Systems using Electromagnetic (EM) Methods
- Advancing understanding of **GH electrical conductivity;** quantifying the conductivity changes associated with GH dissociation; **Combined with appropriate models obtained from laboratory studies, CSEM measurements can help quantify the saturation and total volume of hydrate within a known or suspected deposit.**

National Energy Technology Laboratory (RIC)

- Numerical simulations of GH accumulation and production at potential reservoirs (India, Alaska)
- Laboratory hydrologic and geomechanical characterization and analysis of GH-bearing sediments…identify **critical simulation parameters**. (Synthetic)
- Pore-scale visualization and characterization of GH-bearing sediments (under pressure)
- Participation and support for International and domestic GH field activities (India, S. Korea, US-GoM)

*CSEM—Controlled Source Electromagnetic System



Fundamental Science: Production

Active Modeling Projects

PNNL (Field Work Proposal Jointly funded by DOE and KIGAM)

- Simulation based effort focused on advancement, application, and **verification of numerical simulation capabilities** for natural gas hydrate bearing geologic media to investigate conventional, unconventional, and novel production technologies.
- DOE focus on geomechanical capabilities of STOMP-HYDT-KE and leading the new iteration of the International Gas Hydrate Code Comparison study to include simulator geomechanical capabilities and involving GH modeling groups from around the world.

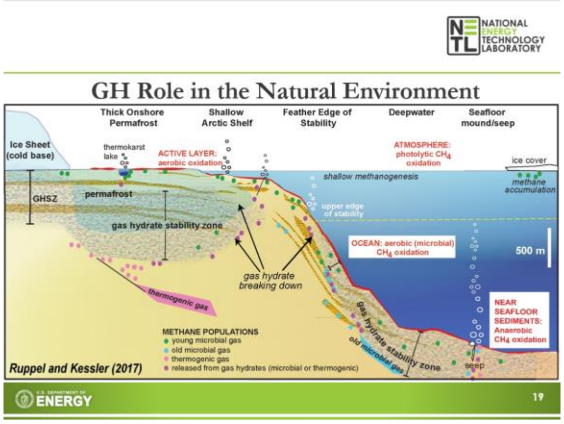
LBNL (Numerical Modeling Field Work Proposal)

- Conduct numerically-based studies to characterize and analyze recoverable resources from gas hydrate deposits, evaluate production strategies, and analyze the geomechanical behavior of hydrate-bearing sediments
- **Improved model accounts for heat and up to four mass components, i.e., water, CH_4, hydrate, and water-soluble inhibitors such as salts or alcohols portioned among four possible phases (gas phase, liquid phase, ice phase, and hydrate phase) and up to five components (heat, hydrate, water, CH_4, and water-soluble inhibitors).**

LBNL (KIGAM collaboration Field Work Proposal)

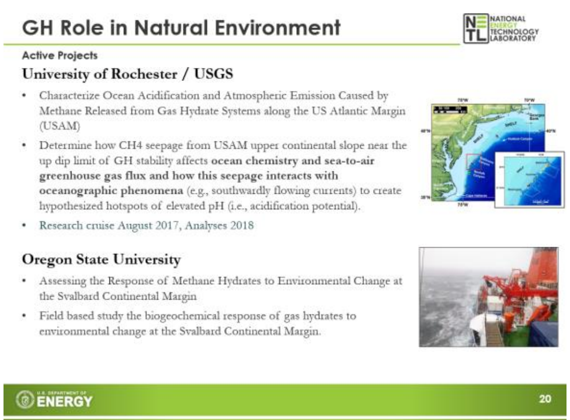
- LBNL-KIGAM Collaboration in the Investigation of the Gas Production Potential of Hydrate Deposits in the Korean East Sea

Radial UBGH-02 Site 9 mesh, showing near-well zone with hydrate, mud, and aquifer layers with varying discretization.



GH Role in the Natural Environment

Ruppel and Kessler (2017)



GH Role in Natural Environment

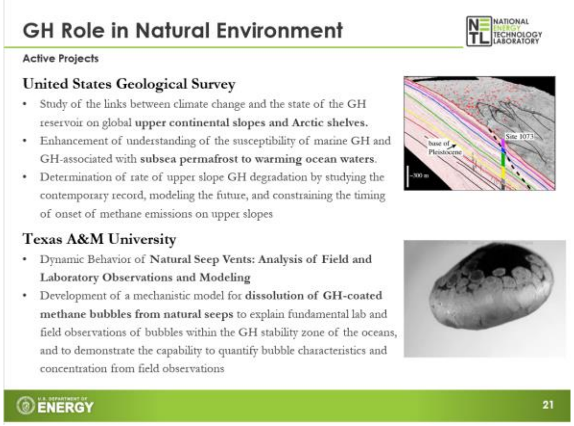
Active Projects

University of Rochester / USGS

- Characterize Ocean Acidification and Atmospheric Emission Caused by Methane Released from Gas Hydrate Systems along the US Atlantic Margin (USAM)
- Determine how CH4 seepage from USAM upper continental slope near the up dip limit of GH stability affects **ocean chemistry and sea-to-air greenhouse gas flux and how this seepage interacts with oceanographic phenomena** (e.g., southwardly flowing currents) to create hypothesized hotspots of elevated pH (i.e., acidification potential).
- Research cruise August 2017, Analyses 2018

Oregon State University

- Assessing the Response of Methane Hydrates to Environmental Change at the Svalbard Continental Margin
- Field based study the biogeochemical response of gas hydrates to environmental change at the Svalbard Continental Margin.



GH Role in Natural Environment

Active Projects

United States Geological Survey

- Study of the links between climate change and the state of the GH reservoir on global **upper continental slopes and Arctic shelves.**
- Enhancement of understanding of the susceptibility of marine GH and GH-associated with **subsea permafrost to warming ocean waters**.
- Determination of rate of upper slope GH degradation by studying the contemporary record, modeling the future, and constraining the timing of onset of methane emissions on upper slopes

Texas A&M University

- Dynamic Behavior of **Natural Seep Vents: Analysis of Field and Laboratory Observations and Modeling**
- Development of a mechanistic model for **dissolution of GH-coated methane bubbles from natural seeps** to explain fundamental lab and field observations of bubbles within the GH stability zone of the oceans, and to demonstrate the capability to quantify bubble characteristics and concentration from field observations

International Collaborations

International Collaborations

GH Science is an International Endeavor

India-US Collaboration

- Planning, Execution of NGHP-01 and NGHP-02
- Evaluation and publication of Scientific Results
- Evaluation of NGHP-02 pressure cores
- Site evaluation for NGHP-03
- Planning and Execution of NGHP-03

Japan-US Collaboration

- Joint evaluation of potential Alaska flow experiment sites
- Collaborative numerical simulation of potential AK flow experiments
- Participation in 2nd Int'l Code Comp. (LBNL-PNNL)
- Pressure Coring Technology
- India Pressure Core Evaluation

South Korea-US Collaboration

- Major USGS Support and DOE personnel contribution to UBGH-01 and UBGH-02
- NETL, USGS, LBNL support for UBGH-03 planning
- Joint Funding for Numerical Simulation Studies with LBNL and PNNL
- New Cooperative Agreement includes with Texas A&M includes KIGAM participation (leveraging unique large-scale reactors)

Other Informal US Collaborations

- New Zealand
- Europe (various)

Jared.ciferno@netl.doe.gov
412-386-5862
Jared.ciferno@netl.doe.gov

NETL
www.netl.doe.gov

Office of Fossil Energy
www.fe.doe.gov

National Energy Technology Laboratory

@NETL_News

2017' FIERY ICE

第十一届国际天然气水合物开发大会

11th INTERNATIONAL WORKSHOP ON METHANE HYDRATE RESEARCH AND DEVELOPMENT

中国深海天然气水合物固态流化试采作业成果

Performance of the solid fluidization well testing and production for natural gas hydrate in Chinese deep water

周守为 李清平
ZHOU Shouwei LI Qingping
CNOOC
2017.12.06

主要内容 Outlines

一、中国天然气水合物固态流化试采概况
General situation well testing and production for NGH in China

二、水合物试采视频播放 Video (4mins)

三、固态流化试采技术原理
Technical principle of solid fluidization

四、固态流化作业实施
Operation implementation of solid fluidization

五、固态流化试采成功的意义
The significance of success

一、中国天然气水合物固态流化试采概况

General situation well testing and production for NGH in China

深海天然气水合物试采技术及工程现状

Present situation of technology and Engineering

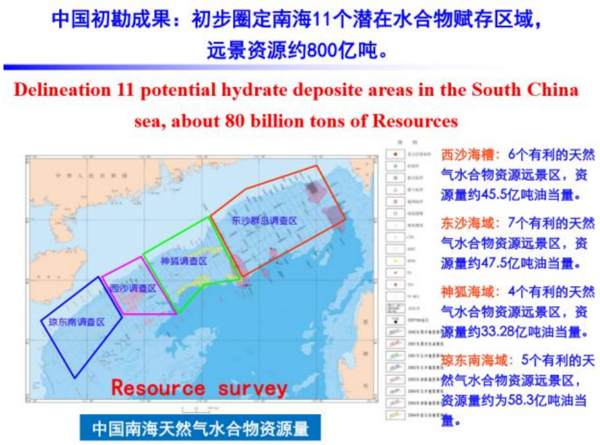
世界各国重视
So many countries have begun to attach importance

美 国 USA
制定了商业开采计划

日 本 Japan
- 钻探了30多口井
- 制定了商业开采计划
- 2013、2017年进行了3次海上试采

加拿大、印度、俄罗斯等国制定了开发计划

中 国 China
- 列入国家中长期科学技术发展规划
  National medium and long term science and technology development plan
- 国家863、973计划
  National Plan 863 and 973
- 南海资源调查专项
  South China Sea resources survey
- 国家重点研发计划
  National key research and development plan



中国初勘成果：初步圈定南海11个潜在水合物赋存区域，远景资源约800亿吨。

Delineation 11 potential hydrate deposite areas in the South China sea, about 80 billion tons of Resources

中国南海天然气水合物资源量

西沙海槽：6个有利的天然气水合物资源远景区，资源量约45.5亿吨油当量。

东沙海域：7个有利的天然气水合物资源远景区，资源量约47.5亿吨油当量。

神狐海域：4个有利的天然气水合物资源远景区，资源量约33.28亿吨油当量。

琼东南海域：5个有利的天然气水合物资源远景区，资源量约为58.3亿吨油当量。

Currently there are two teams in China conduct research and engineering for NGH.

中国目前有2支队伍，同时进行天然气水合物研究和海上试采。

中国地质调查局
China geological survey
- 天然气水合物资源勘查与试采工程(国家财政专项 National finance special)

参与单位：
1、广州海洋地质调查局
2、中石油海洋工程公司
3、探矿工程所
4、水环中心
5、中石油青海石油管理局
6、中集集团公司
7、北京大学

中国海洋石油总公司 CNOOC
- 国家863计划（详勘取样）
- 国家973计划
- 国家重点研发计划 （试采）

参与单位：
1、中海油研究总院
2、中海油深海公司
3、中海油田服务公司
4、西南石油大学
5、大连理工大学
6、航天科工宏华集团
7、中科院力学所
8、中科院广州能源所
9、中石化胜利油田
10、西华大学
11、中国石油大学（北京）
12、中国石油大学（华东）
13、华南理工大学
14、地调局探工所

2017年5月—中国海上天然气水合物试采进入爆发期

May, 2017 – Well testing and production for NGH in China sea was put into eruption

中国地质调查局宣布用“深水半潜式钻井平台+降压法”试采天然气水合物成功。2017. 5. 18

China geological survey announced:
- Deepwater Semi-submersible drilling platform
- Depressurization
- 2017.5.18

◆ 依托半潜式钻井平台、“降压法”试采
◆ 连续试气点火60天，平均日产5151m³
◆ 神狐海域，水深1266m, 天然气水合物层泥线下 203m–277m

- Water depth 1266m
- Reservoir depth 203m-277m

2017年5月25日，中海油利用“勘查船+固态流化法”试采天然气水合物成功

CNOOC / Deepwater drilling rigs and survey ships / Solid fluidization (2017.5.25)

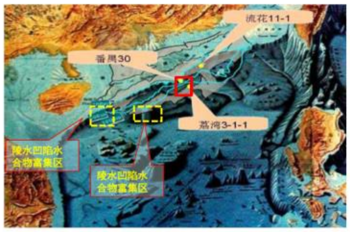
- ◆ 依托深水工程勘察船、“固态流化法”试采
- ◆ 点火测试获得气体81m³
- ◆ 荔湾海域，在水深1310m、水合物矿体埋深117m-196m

- ● Water depth 1266m
- ● Reservoir depth 117m-196m

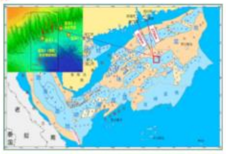
试采目标区

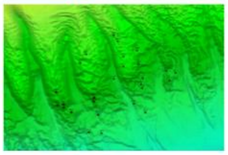
Optimization of target area

2015.9.16-20 :中海油依托自有技术和装备在南海深水油气区成功取样，所在区域水合物资源量约480亿方，为深水水合物和油气联合开发奠定了资源基础。
CNOOC obtained the hydrate samples in deep water gas field areas by self- developed technology and equipment



优选荔湾3海域
Lipan 3 area for optimization





Success of solid fluidization exploitation for the first time in the word with Deepwater engineering and survey ship

全球首次用深水勘查船试采水合物成功

深水半潜式钻井平台
Deepwater Semi-submersible drilling platform
日本试采 Japan
中国地质调查局试采
China geological survey

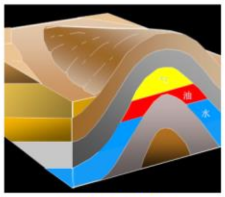
深水工程勘查船
Deepwater engineering and survey ships
中国海油试采
CNOOC

海洋水合物开发的挑战

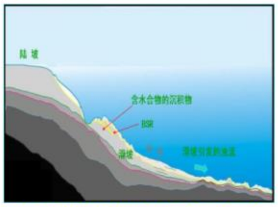
Challenges on Marine Hydrate Exploitation

无盖层 No closure cap

储层本质差别Essential distinction：水合物储层区别于常规油气藏，大多没有完整的圈闭构造和致密盖层



常规油气储层
Conventional oil field



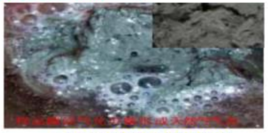
海域水合物储存区（无盖层）
No closure cap (NGH)

海洋水合物开发的挑战

Challenges on Marine Hydrate Exploitation

多为非成岩水合物 Non diagenesis NGH

东沙海域天然气水合物样品分解后的蜂窝状泥沙
Honeycomb sediment samples after decomposition



南海北部水合物样品分解
NGH dissociation in South China sea

东沙海域正在喷发的冷泉
Cold spring in Dongsha area

海洋水合物开发的挑战

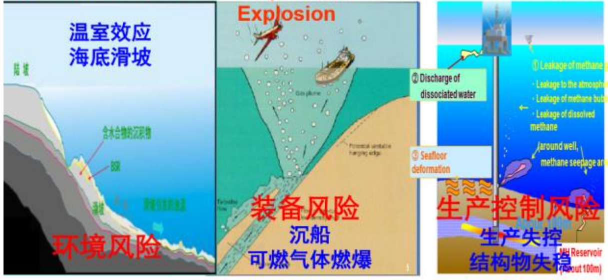
Challenges on Marine Hydrate Exploitation

大多数水合物没有封闭盖层，存在潜在地质风险和环境温室效应及生产控制和装备安全风险

Geological risk
Greenhouse effect

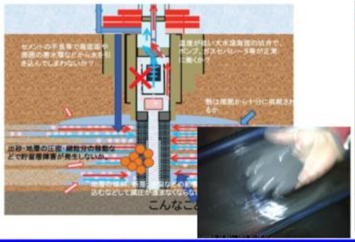
Equipment risk
Shipwrecks
Explosion

Production control risk



海洋水合物开发的挑战
Challenges on Marine Hydrate Exploitation

成岩水合物试采工艺面临的挑战
Challenge for diagenetic hydrate exploitation



挑战与问题
储层认识 开采方法储层适应性评价
井壁稳定 井涌分析 生产出砂 sand control 二次生成 second formation of NGH
砂漏 防砂困难
连续排采难 continue production

海上试采，亟需突破试采工艺、防砂、井眼稳定等技术瓶颈

深海天然气水合物绿色钻采技术策略的提出
The proposal of technical strategy

首次向世界提出深海非成岩水合物固态流化开采新理念和方法，受到世界同行的高度关注 。 （2014.11.10 第九届水合物开发大会 印度.海得拉巴市）

Introduced a new method of fluidified exploration of deep-water non-diagenetic hydrates solid to the world for the first time, receiving significant attention from the international academia. （2014.11.10 9th International Methane Hydrates R&D Workshop Hyderabad, India）

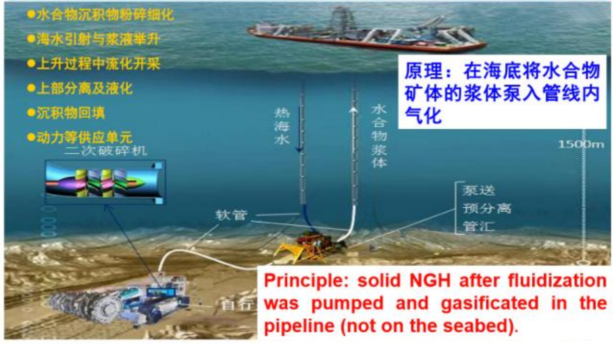
深海天然气水合物绿色钻采技术策略的提出
The proposal of technical strategy

进一步介绍中国深海天然气水合物勘探开发技术的进展，受到世界同行的高度关注。 （ 2016. 6. 10 第十届世界水合物开发大会 美国. 夏威夷）

The progress of exploration and development of deep-sea gas hydrate in China is introduced, receiving significant attention from the international academia. （ 2016. 6. 10 10th International Methane Hydrates R&D Workshop Hawaii, USA）

Technical principle of solid fluidization

海洋非成岩天然气水合物固态流化开采(工程化示意图)



原理：在海底将水合物矿体的浆体泵入管线内气化

Principle: solid NGH after fluidization was pumped and gasificated in the pipeline (not on the seabed).

- 在国家自然基金委、中国工程院大力支持下于2014年建立了世界上首个“海洋非成岩天然气水合物固态流化开采实验室”，位于西南石油大学（中国. 成都）。

The NGH lab in Chengdu has been built (The first “Solid fluidization exploitation” lab in the world) .

The lab was officially launched in early 2017, the experimental study supported the success of testing.

固态流化实验室已于2017年初正式投入实验，实验支持了水合物试采成功。

海洋天然气水合物开发研究计划
Research program for Marine NGH

- 2016年， 固态流化开采实验室建设完成（OK）
  Solid fluidization lab
- 2017年， 大尺度三维模拟器建设完成（Under construction）
  Large scale simulation facility
- 2018年， 海洋天然气水合物试采实施（1 year early）
  Marine NGH pilot production
- 2025年， 海洋天然气水合物与深海油气联合开发实验
  Marine NGH exploitation tests with oil and gas
- 2030年， 海洋天然气水合物商业性开发
  Marine NGH commercial development

Welcome to “Solid fluidization exploitation” lab

欢迎各国专家莅临“固态流化”开采实验室参观指导

Welcome to CHENGDU for "12th INTERNATIONAL WORKSHOP ON METHANE HYDRATE RESEARCH AND DEVELOPMENT "

欢迎各国专家莅临成都参加"第12届水合物开发国际论坛'

二、水合物试采视频播放

General situation of Chinese well testing and production for NGH

播放固态流化试采视频

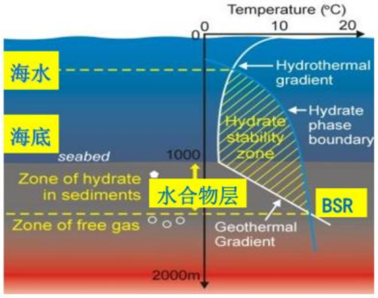
Video
(4mins)

Outlines

1. General situation well testing and production for NGH in China
2. Video (4mins)
3. Technical Principle of Solid Fluidization for non- diagenetic NGH in Deepwater Areas
4. Implementation of Solid Fluidization Engineering
5. The Significance of Success

3.Principle of SFE for non- diagenetic NGH

Where is hydrate?
90% NGH stored in continental slope areas



3.Principle of SFE for non- diagenetic NGH

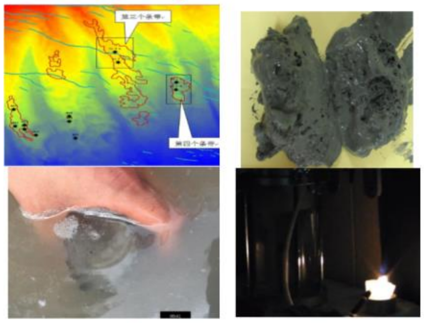
Each kind of NGH maybe has its own way to development method ?

Sandstone reservoir
Depressurization etc.

Non diagenetic
Silt? Sltpelite?
SFE

3.Principle of SFE for non- diagenetic NGH

What kinds of hydrate obtained in China Offshore?



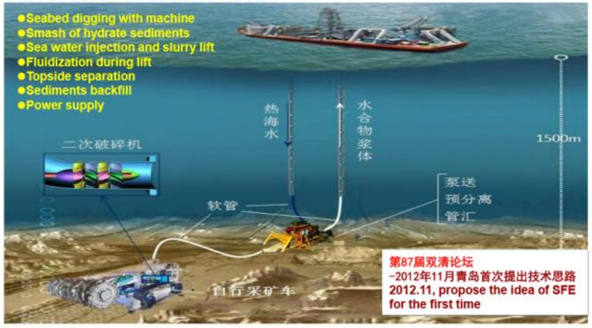
2015：
WD：700-2200m Bur ied :13-230M CH4:>99%
2013：
WD：600-2200m Bur ied:13-200m CH4:>99%
2007：
WD：1200m, Bur ied:199-300m CH4:>98%,

Slit? Siltpelite?

3.Principle of SFE for non- diagenetic NGH

NGH ON SEABED:Principle of solid fluidization exploitation(SFE)

Just like solid mineral resource



- Seabed digging with machine
- Smash of hydrate sediments
- Sea water injection and slurry lift
- Fluidization during lift
- Topside separation
- Sediments backfill
- Power supply

第87届双清论坛
-2012年11月青岛首次提出技术思路
2012.11, propose the idea of SFE for the first time

3.Principle of SFE for non- diagenetic NGH

Laboratory verification of SFE method

射流流化工具研发和验证

Tool developed and

室内实验验证
Experimental verification

工具本体/Tools

现场施工
Field experiment

3.Principle of SFE for non- diagenetic NGH

固态流化试采技术原理室内验证

Laboratory verification of SFE method

fluidization experiments

fluidization results of cement model

fluidization results of sand soil model

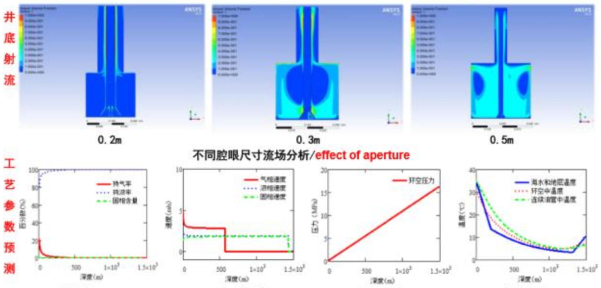
fluidization results of ice model

The experiments verify the feasibility of SFE method

3.Principle of SFE for non- diagenetic NGH

Design and analysis :

Effect of fluidization rate and range(hole diameter and depth)



不同腔眼尺寸流场分析/effect of aperture

相含量 content of different phase

各相速度 Speed of different phase

环空压力 Annulus pressure

井筒温度 Wellhole temperature

3.Principle of SFE for non- diagenetic NGH

固态流化试采方案设计和参数优化

Development scheme and parameter optimization of SFE

WD	1315m
NGH LAYER	1430m~1490m
Depth of Well	1490m
Surface T	26°C
Drilling fluid flow rate	500l/min
Density of Drilling fluid	1.03g/cm^3
Fluidization fluid	26℃
Sediment density	2.2g/cm^3

Outlines

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4、Implement of hydrate SFE

工程一体化方案设计：
Integrated engineering plan of hydrate SFE

工作任务：海上目标取钻探取样+固态流化试采
作业船：海洋石油708深水勘察船
工程量：先导测井孔、取样孔、海洋水合物试采

Task：sample drilling + hydrate SFE
Work ship：HYSY708
Engineering quantity：Logging hole、Sampling hole、Production test

先导孔：随钻测井
电阻率
声波
自然伽吗
井径、温度等

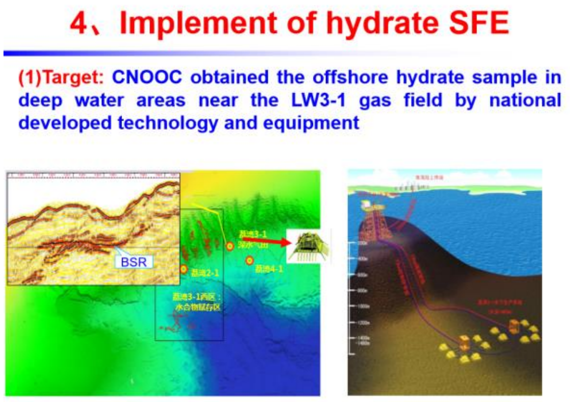
取样层位

取样孔：
压入活塞取样
超前伸缩活塞取样
射流搅簧式取样
液压捶击式
保温保压取样

测井层位

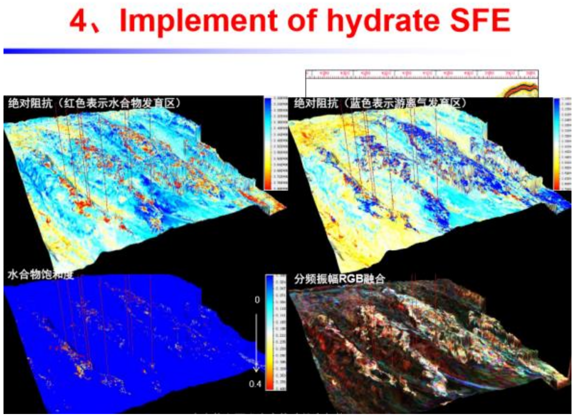
试采井：点火

方案：
深水勘察船固态流化试采



4、Implement of hydrate SFE

(1)Target: CNOOC obtained the offshore hydrate sample in deep water areas near the LW3-1 gas field by national developed technology and equipment

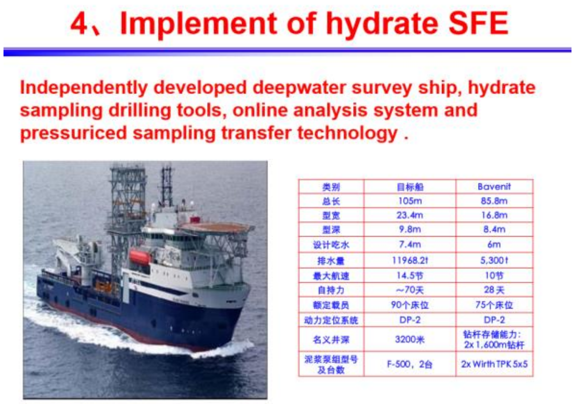


4、Implement of hydrate SFE

4、Implement of hydrate SFE

(3)Research and Manufacture the gas hydrate temperature-hold and pressure-tight Sampling corer

Design parameter:
工作水深：2000m
工具外径：102mm
（708钻具通径104mm）
岩心直径：≥30mm
岩心长度：1m
工作压力：20MPa



4、Implement of hydrate SFE

Independently developed deepwater survey ship, hydrate sampling drilling tools, online analysis system and pressuriced sampling transfer technology .

类别	目标船	Bavenit
总长	105m	85.8m
型宽	23.4m	16.8m
型深	9.8m	8.4m
设计吃水	7.4m	6m
排水量	11968.2t	5,300t
最大航速	14.5节	10节
自持力	~70天	28天
额定载员	90个床位	75个床位
动力定位系统	DP-2	DP-2
名义井深	3200米	钻杆存储能力： 2x 1,600m钻杆
泥浆泵组型号及台数	F-500，2台	2x Wirth TPK 5x5

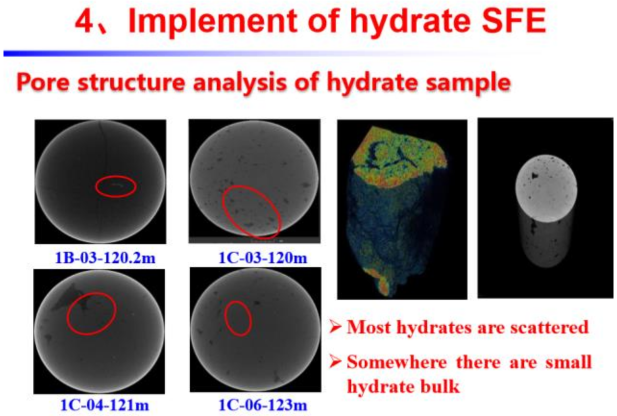
4、Implement of hydrate SFE

Obtain hydrate samples

4、Implement of hydrate SFE

Complete hydrate sample analysis

荔湾3-1西含水合物沉积物样品

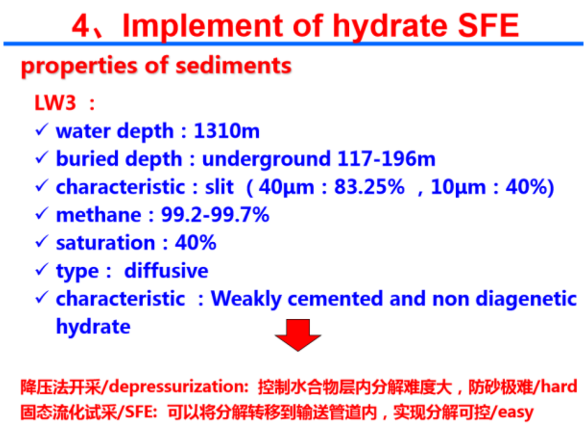


4、Implement of hydrate SFE

Pore structure analysis of hydrate sample

1B-03-120.2m
1C-03-120m
1C-04-121m
1C-06-123m

- Most hydrates are scattered
- Somewhere there are small hydrate bulk



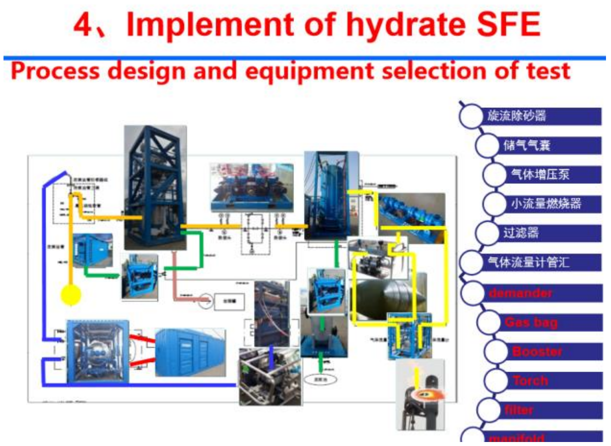
4、Implement of hydrate SFE

properties of sediments

LW3 ：

- ✓ **water depth : 1310m**
- ✓ **buried depth : underground 117-196m**
- ✓ **characteristic : slit （40μm : 83.25% ，10μm : 40%)**
- ✓ **methane : 99.2-99.7%**
- ✓ **saturation : 40%**
- ✓ **type： diffusive**
- ✓ **characteristic ：Weakly cemented and non diagenetic hydrate**

降压法开采/depressurization: 控制水合物层内分解难度大，防砂极难/hard
固态流化试采/SFE: 可以将分解转移到输送管道内，实现分解可控/easy



4、Implement of hydrate SFE

Process design and equipment selection of test

4、Implement of hydrate SFE

CNOOC Built the deep-water survey vessel and hydrate sampling tools

钻井装备及能力：满足要求
甲板、月池等：基本可满作业期间需求

Meet the requirements

4、Implement of hydrate SFE

试采装备:全部自有技术和装备
Production equipment: all belong to CNOOC

4、Implement of hydrate SFE

本次固态流化试采主要参数

- ●**孔隙度/porosity：0.43**
- ●**饱和度/saturation：0.40**
- ●**预测产气量:101m³**
- ●**采出气量/total gas production：81m³**

4、Implement of hydrate SFE

Outlines

1. General situation well testing and production for NGH in China
2. Video (4mins)
3. Technical Principle of Solid Fluidization for non- diagenetic NGH in Deepwater Areas
4. Implementation of Solid Fluidization Engineering
5. The Significance of Success

5、Significance of SFE method

(1) According to the Characteristic of shallow areas non diagenetic NGH, Stored in silt, weak cementation, CNOOC proposed gas hydrate solid fluidization exploitation technology for the first time.

(2) Developed a set of marine gas hydrate solid fluidization exploitation process and equipment, including drilling、fluidized, lift and gas liquid solid separation system, emergency relief, equipment and tools， can also use in other method。

5、Significance of SFE method

（3）Gas hydrate well test by of Solid Fluidization method was performed in Liwan 3 area, it was significant for the development of this kind of natural gas hydrate resources in the world.

（4）A set of technology including hydrate resources exploration, target evaluation, reservoir identification and hydrate detection has been developed by CNOOC. Based on the HYSY708 ship, gas hydrate samples were successfully obtained.

5、Significance of SFE method

Development of Natural gas hydrate safely is the leading area in the world，means more challenge、high technology and investment. We will continue to cooperate with researchers all over the world，try to find safety, cost-effective ways to development various kinds of NGH in future.

THANK YOU！

Non Diagenesis Nature Gas Hydrate Production by Solid Fluidization

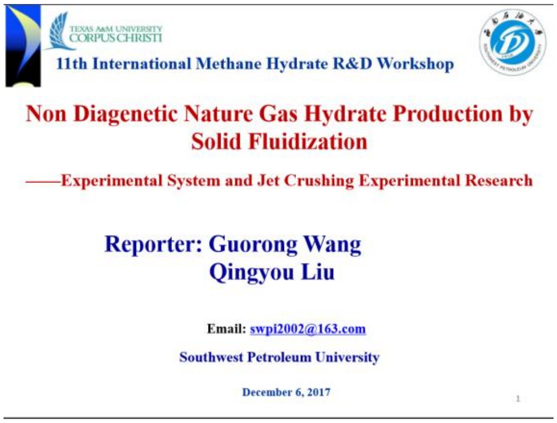
Wang Guorong[1] Wang Leizhen[1] Zhou Shouwei[3,5] Liu Qingyou[2,5]

Zhong Lin[1] Fu Qiang[4] Li Qingping[4] Hu Gang[1]

1College of Mechanical and Electrical Engineering, Southwest Petroleum University; 2. Key Laboratory for Fluid Machinery and Power Machinery of the Education Ministry of China, Xi Hua University, 610039; 3. China National Offshore Oil Corporation (CNOOC),Beijing,100010; 4.CNOOC Research Institute, Beijing,100027; 5. State Key Laboratory of Oil and Gas Reservoir Geology and Development Engineering, Southwest Petroleum University, Chengdu,610500

Abstract: For the characteristics of shallow deposit and weak cementing of China Marine non-diagenetic natural gas hydrate (NGH) storage, a new mining technology is proposed based on the ideas of solid-state fluidization exploitation of NGH, which includes continuous coiled tubing horizontal drilling in the hydrate deposits formation, pullback mining crushing NGH, fluidization collection of NGH solid particles, in-situ separation and backfill of downhole sediment. In order to carry out the experimental study of hydrate solid flow mining technology, a hydrate solid fluidized mining laboratory was established. The experimental system contains modules such as large samples preparation system，crushing and migrating system，multiphase piping system，monitor and control system, etc. The functions such as rapid preparation of large sample, evaluation the crushing efficient, safety transportation of methane hydrate, evaluation of the decomposition of methane hydrate, dynamic state change rule of slurry, simulation of safety law of well control can be realized. According to the requirements of the production testing, the water jet mining tool is designed. The nozzle structure is determined by simulation analysis method. The experimental study of water jet breaking hydrate is carried out by using this mining tool. It is determined that the critical velocity of hydrates breaking with water jet is 24 m/s. The parameters of the jet process under the different nozzle aperture are optimized. Engineering chart of jet crushing for the production test was eventually obtained. In May 2017, for non diagenetic nature gas hydrate reservoir, the solid fluidization Production test was success in Shenhu area of South China sea for the first time.For the new process of marine non-diagenetic ngh exploitation, the minimum requirements of ngh commercial exploitation is that gas production reach 1.2×10^5 m^3/d. The construction process parameters which meet the commercial exploitation of ngh are obtained, such as pore diameter is 0.8m, jet displacement is $2.39m^3$/min, drag-back velocity is 5m/min, coiled tubing sizes is 2-3/8 inch, nozzle hole diameter is 4mm, and number of nozzle holes is 31.

Keywords: Marine non-diagenetic NGH; New technology of jet flow breaking; Water jet flow crushing efficiency; Construction parameters of commercial production of NGH;



TEXAS A&M UNIVERSITY CORPUS CHRISTI

11th International Methane Hydrate R&D Workshop

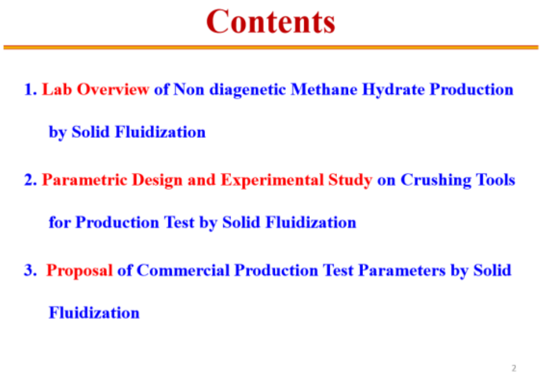
Non Diagenetic Nature Gas Hydrate Production by Solid Fluidization

——Experimental System and Jet Crushing Experimental Research

Reporter: Guorong Wang
Qingyou Liu

Email: swpi2002@163.com
Southwest Petroleum University

December 6, 2017



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Chengdu, China

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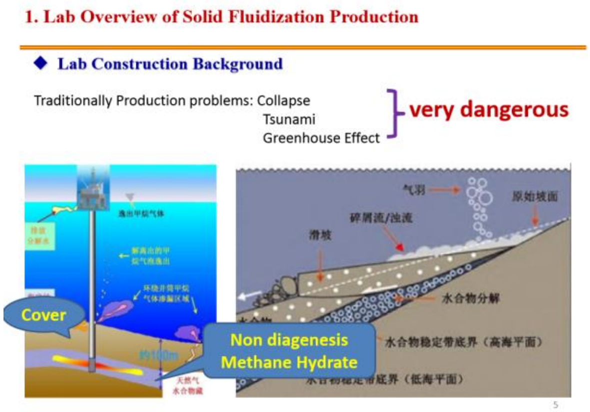
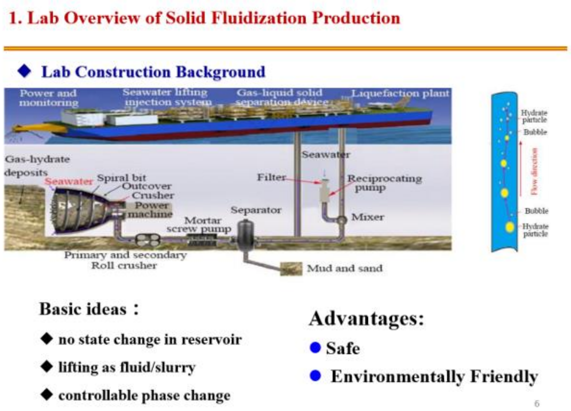


1. Lab Overview of Solid Fluidization Production

◆ Lab Construction Background

Traditionally Production problems: Collapse
Tsunami
Greenhouse Effect
very dangerous



1. Lab Overview of Solid Fluidization Production

◆ Lab Construction Background

Basic ideas：

- ◆ no state change in reservoir
- ◆ lifting as fluid/slurry
- ◆ controllable phase change

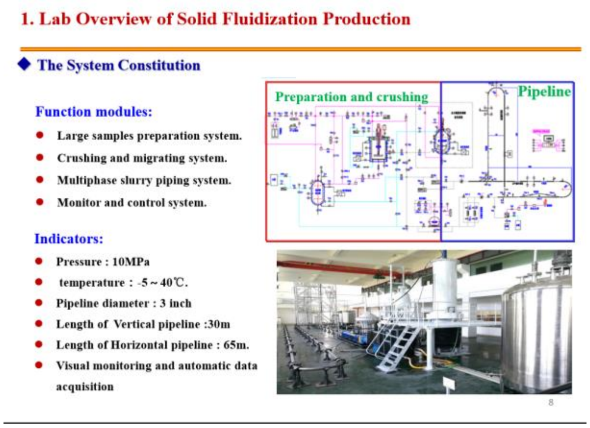
Advantages:

- ● Safe
- ● Environmentally Friendly

1. Lab Overview of Solid Fluidization Production

◆ Lab Establishment

- ➤ December, 2014, the Sichuan Hydrate Production Collaborative Innovation Center
- ➤ April, 2015, the world's first Solid Fluidization exploitation Lab of Non Diagenetic Nature Gas Hydrate has been built.



1. Lab Overview of Solid Fluidization Production

◆ The System Constitution

Function modules:

- ● Large samples preparation system.
- ● Crushing and migrating system.
- ● Multiphase slurry piping system.
- ● Monitor and control system.

Indicators:

- ● Pressure : 10MPa
- ● temperature : -5 ~ 40℃.
- ● Pipeline diameter : 3 inch
- ● Length of Vertical pipeline :30m
- ● Length of Horizontal pipeline : 65m.
- ● Visual monitoring and automatic data acquisition

1. Lab Overview of Solid-state Fluidization Production

◆ **The Function of Simulation Experimental System**

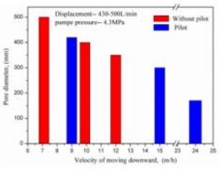
- Rapid preparation of large sample
- Evaluation the crushing efficient
- Safety transportation of methane hydrate
- Evaluation of the decomposition of methane hydrate
- Dynamic state change rule of slurry
- Simulation of safety law of well control.

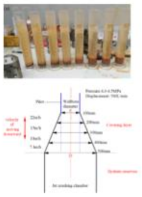
Water depth of 1200 m : preparation+ crushing+ pipeline transportation+ phase state+ separation+ test

2. Parametric Design and Experimental Study of Crushing Tools

◆ **Particles Flow-back Effect, Borehole Regularity and Diameter of Nozzle Jet Crushing**

- **The optimization of nozzles structure**
- **Conical transition section between pilot hole and borehole**
- **Parameter optimization of velocity and times of upward and downward for coiled tubing , pump pressure and displacement**

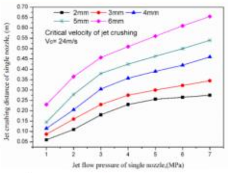


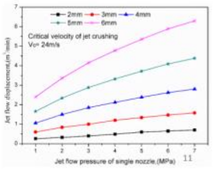


2. Parametric Design and Experimental Study of Crushing Tools

◆ **Novel Tools of Jet Crushing**

- **The critical velocity of jet: 24m/s**
- **The diameter of the pore: 0.5m, jet pressure 4.3MPa, nozzle diameter 2mm.**
- **Parameters, such as pressure, displacement, move speed, times of jet crushing are optimized for different nozzle hole diameter.**

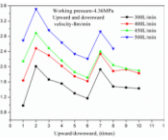


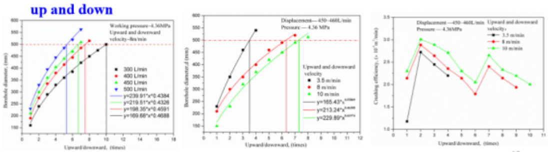


2. Parametric Design and Experimental Study of Crushing Tools

◆ **Engineering Chart of Jet Crushing for the Production test**

- **The different crushing diameters and crushing efficiency required special range of construction process parameters**
- **Nozzle running velocity, 8 m/min, displacement, 500L/min, borehole diameter, 500mm, need 5 times up and down**





Jet crushing borehole diameter and crushing efficiency

2. Parametric Design and Experimental Study of Crushing Tools

◆ **The First Successful of Solid Fluidization Production for Marine non diagenetic Nature Gas Hydrate**

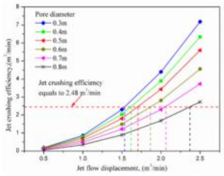
- **In May 2017, for non diagenetic nature gas hydrate reservoir, the solid fluidization Production test was success in Shenhu area of South China sea for the first time.**
- **The newly designed crushing tools and its parameters is well contributed significantly in the whole process.**

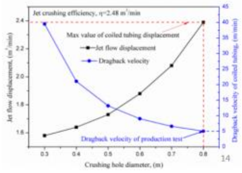
3. Proposal of Parameters for Commercial Production test by Solid Fluidization

◆ **Predication of Jet Crushing Tool Parameters for Solid Fluidization**

■ **Commercial Jet Mining Efficiency**

Parameters	gas production （V）	Saturation （Sr ）	Porosity （ϕ）	MH reserves （φ）	Mining efficiency （η）
Unit	10^4 m³/d	—	—	m³/m³	m³/min
Value	**12**	**50%**	**0.4**	**168**	**2.48**





Thank you!

Guorong Wang

Email: swpi2002@163.com

Southwest Petroleum University

Recent Status of Methane Hydrate R&D Program in Japan

Dr. Norio Tenma – AIST, Tokyo, Japan

Methane Hydrate (MH) exists as a solid in permafrost or marine sediment in the condition of high pressure and low temperatures. As MH dissociates a gas and water by depressurization or heating, new natural gas resources are expected. As MH exists around offshore Japan, "Research Consortium for Methane Hydrate Resources in Japan" (also known as MH21) was established in FY2001, "Japan's Methane Hydrate R&D Program" have been conducted from FY2001(1).

The 2nd off-shore production test (Gas production test) was conducted in Daini-Atsumi Knoll, the eastern Nankai Trough from April to July, 2017 (2).
The purpose of this test were 1) aiming to solve a problem caused by sand production and gas/water separation at the first off-shore production test, and 2) to confirm the increase in gas production rates during the production test. In the test, two production wells were used to apply two type of sand management device. And, total amount of gas production from first well was about 40,850 m^3 in 12 days, and second production well was 222,587 m^3 in 24 days (3). Data analysis and evaluation are in progress by MH21 Research Consortium.

Also, MH21 started an assessment of the Shallow type MH in 2010. Especially for 3 years during 2013 through 2015, we conducted an intensive exploration of Shallow type MH in Japan Sea. Based on the data from these surveys, amount of shallow methane hydrate resources at one specific mound in Joetsu was estimated (4).

Acknowledgement
This study is a part of the program of the Research Consortium for Methane Hydrate Resources in Japan (MH21 Research Consortium).

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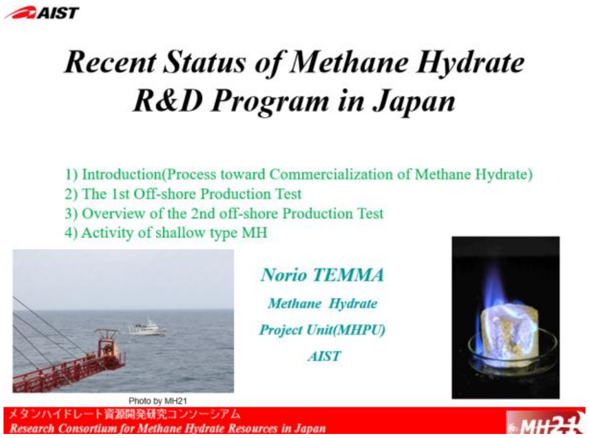


AIST

Recent Status of Methane Hydrate R&D Program in Japan

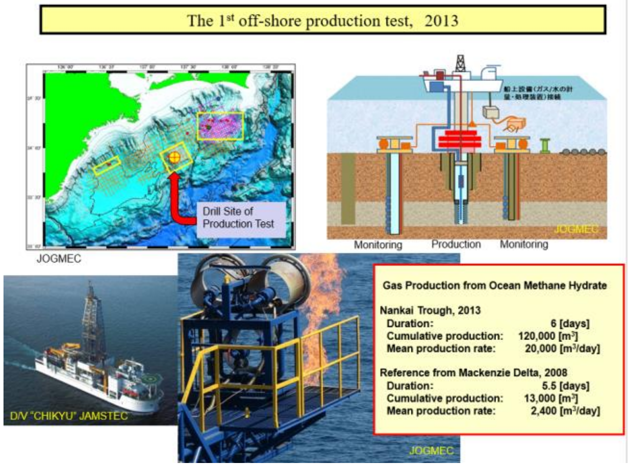
1) Introduction(Process toward Commercialization of Methane Hydrate)
2) The 1st Off-shore Production Test
3) Overview of the 2nd off-shore Production Test
4) Activity of shallow type MH

Norio TEMMA
Methane Hydrate Project Unit(MHPU)
AIST

Photo by MH21

メタンハイドレート資源開発研究コンソーシアム
Research Consortium for Methane Hydrate Resources in Japan

MH21



The 1st off-shore production test, 2013

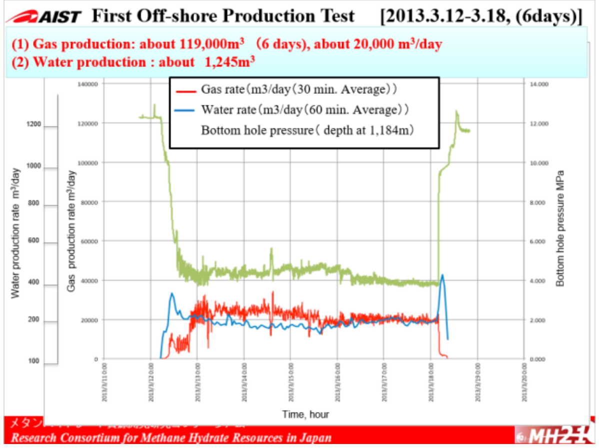
Gas Production from Ocean Methane Hydrate

Nankai Trough, 2013

Duration:	6 [days]
Cumulative production:	120,000 [m^3]
Mean production rate:	20,000 [m^3/day]

Reference from Mackenzie Delta, 2008

Duration:	5.5 [days]
Cumulative production:	13,000 [m^3]
Mean production rate:	2,400 [m^3/day]



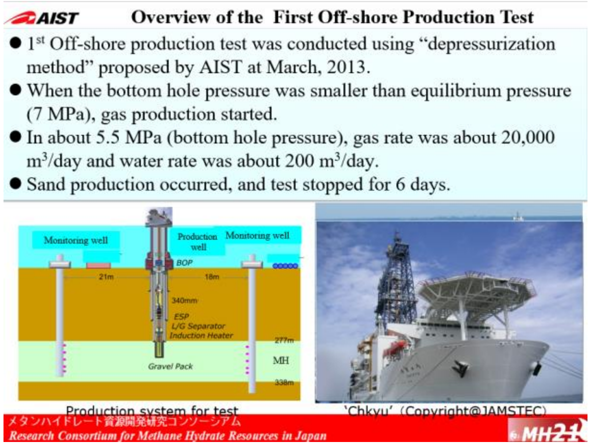
AIST

First Off-shore Production Test [2013.3.12-3.18, (6days)]

(1) Gas production: about 119,000m^3 (6 days), about 20,000 m^3/day
(2) Water production : about 1,245m^3

メタンハイドレート資源開発研究コンソーシアム
Research Consortium for Methane Hydrate Resources in Japan

MH21



AIST

Overview of the First Off-shore Production Test

- 1st Off-shore production test was conducted using "depressurization method" proposed by AIST at March, 2013.
- When the bottom hole pressure was smaller than equilibrium pressure (7 MPa), gas production started.
- In about 5.5 MPa (bottom hole pressure), gas rate was about 20,000 m^3/day and water rate was about 200 m^3/day.
- Sand production occurred, and test stopped for 6 days.

Production system for test

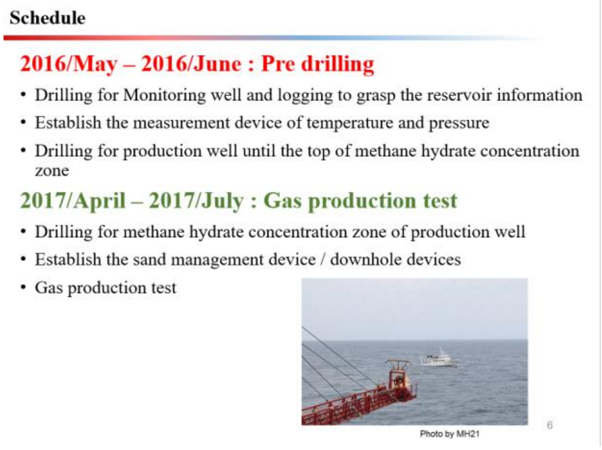
'Chkyu' (Copyright@JAMSTEC)

メタンハイドレート資源開発研究コンソーシアム
Research Consortium for Methane Hydrate Resources in Japan

MH21

The 2nd Offshore Production Test was conducted in Nankai Trough
(April-July, 2017)

Photo by MH21



Schedule

2016/May – 2016/June : Pre drilling

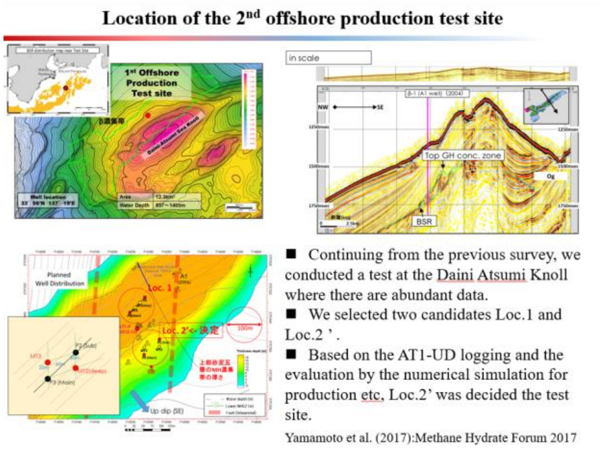
- Drilling for Monitoring well and logging to grasp the reservoir information
- Establish the measurement device of temperature and pressure
- Drilling for production well until the top of methane hydrate concentration zone

2017/April – 2017/July : Gas production test

- Drilling for methane hydrate concentration zone of production well
- Establish the sand management device / downhole devices
- Gas production test

Photo by MH21

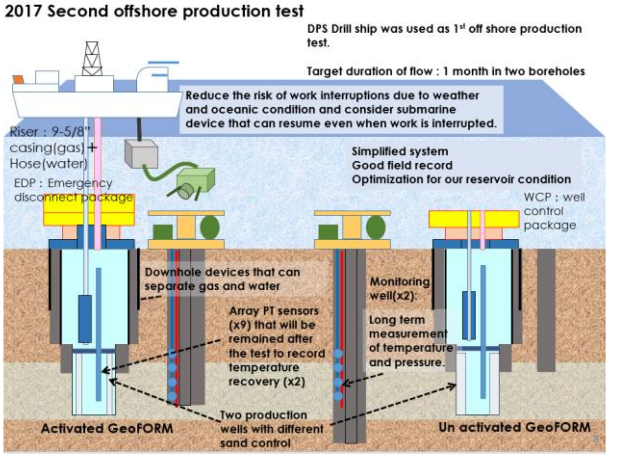
6



Location of the 2nd offshore production test site

- Continuing from the previous survey, we conducted a test at the Daini Atsumi Knoll where there are abundant data.
- We selected two candidates Loc.1 and Loc.2 ' .
- Based on the AT1-UD logging and the evaluation by the numerical simulation for production etc, Loc.2' was decided the test site.

Yamamoto et al. (2017):Methane Hydrate Forum 2017



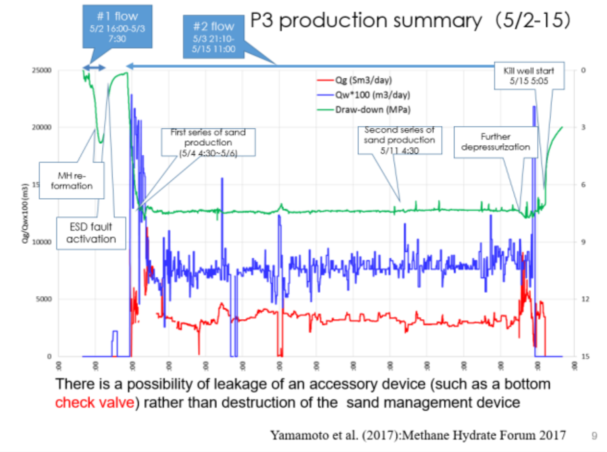
2017 Second offshore production test

DPS Drill ship was used as 1st off shore production test.

Target duration of flow : 1 month in two boreholes

Reduce the risk of work interruptions due to weather and oceanic condition and consider submarine device that can resume even when work is interrupted.

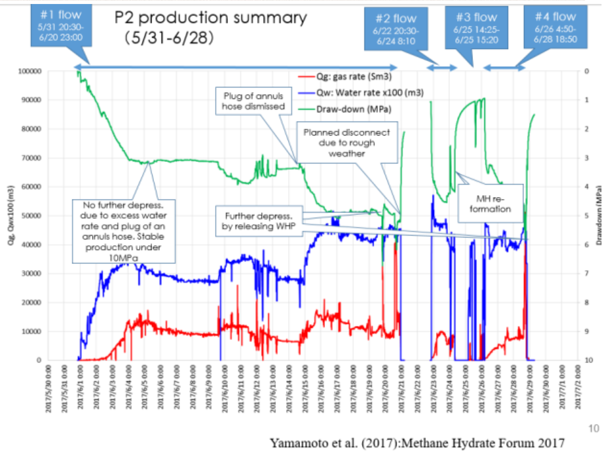
Simplified system
Good field record
Optimization for our reservoir condition



P3 production summary（5/2-15)

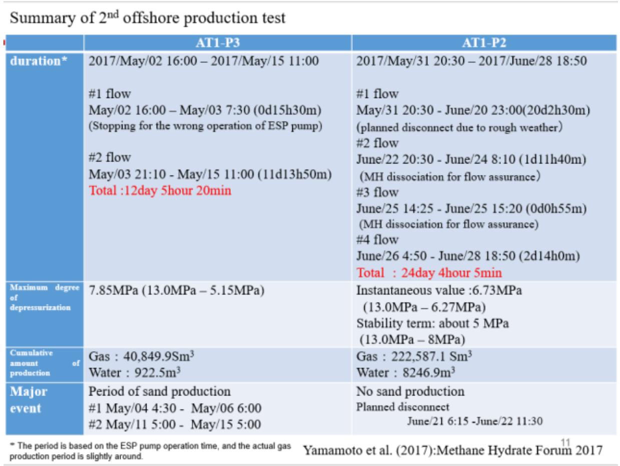
There is a possibility of leakage of an accessory device (such as a bottom check valve) rather than destruction of the sand management device

Yamamoto et al. (2017):Methane Hydrate Forum 2017



P2 production summary（5/31-6/28)

Yamamoto et al. (2017):Methane Hydrate Forum 2017



Summary of 2nd offshore production test

	AT1-P3	AT1-P2
duration*	2017/May/02 16:00 – 2017/May/15 11:00 #1 flow May/02 16:00 – May/03 7:30 (0d15h30m) (Stopping for the wrong operation of ESP pump) #2 flow May/03 21:10 - May/15 11:00 (11d13h50m) Total :12day 5hour 20min	2017/May/31 20:30 – 2017/June/28 18:50 #1 flow May/31 20:30 - June/20 23:00(20d2h30m) (planned disconnect due to rough weather) #2 flow June/22 20:30 - June/24 8:10 (1d11h40m) (MH dissociation for flow assurance) #3 flow June/25 14:25 - June/25 15:20 (0d0h55m) (MH dissociation for flow assurance) #4 flow June/26 4:50 - June/28 18:50 (2d14h0m) Total ： 24day 4hour 5min
Maximum degree of depressurization	7.85MPa (13.0MPa – 5.15MPa)	Instantaneous value :6.73MPa (13.0MPa – 6.27MPa) Stability term: about 5 MPa (13.0MPa – 8MPa)
Cumulative amount of production	Gas：40,849.9Sm³ Water：922.5m³	Gas：222,587.1 Sm³ Water：8246.9m³
Major event	Period of sand production #1 May/04 4:30 - May/06 6:00 #2 May/11 5:00 - May/15 5:00	No sand production Planned disconnect June/21 6:15 -June/22 11:30

* The period is based on the ESP pump operation time, and the actual gas production period is slightly around.

Yamamoto et al. (2017):Methane Hydrate Forum 2017

Second Offshore Methane Hydrate Production Test Finishes

In April 2017, the Agency for Natural Resources and Energy (ANRE) launched an offshore production test, commissioned to the Japan Oil, Gas and Metals National Corporation (JOGMEC), to dissolve methane hydrate and extract natural gas in the offshore sea area between Atsumi Peninsula to Shima Peninsula (Daini Atsumi Knoll) using the Deep Sea Drilling Vessel Chikyu. On June 28, 2017, it finished the test in a timely manner.

ANRE will collect equipment in the sea areas around the testing point.

1. Background

Methane hydrate is a compound that consists of methane and water that is crystallized in a low-temperature, high-pressure state. A considerable amount of methane hydrate is estimated to be present in the undersea areas surrounding Japan, and is expected to be a source of domestic natural gas in the future.

2. Test results

The second offshore methane hydrate production test was conducted, aiming to solve a problem caused by sand intrusion into a well during the first test and to confirm the increase in gas production rates during a three- to four-week production test.

As a result of this test, while one of the two production wells suffered the sand-intrusion problem, ANRE achieved a certain level of success from the second well, in which no problems occurred. However, ANRE could not clearly confirm an increase in the production rates at either of the wells, leaving challenges in establishing gas production technologies unsolved.

Reference: Amount of gas produced during the second test (provisional value)
First production well: Approximately 35,000 m3 in total in 12 days
Second production well: Approximately 200,000 m3 in total in 24 days

3. Future actions

ANRE will conduct a thorough investigation with external experts to determine the test results and causal factors, as well as prepare the final draft paper of a development roadmap for the future commercialization of methane hydrate, and then include the roadmap in the next version of the Basic Plan on Ocean Policy.

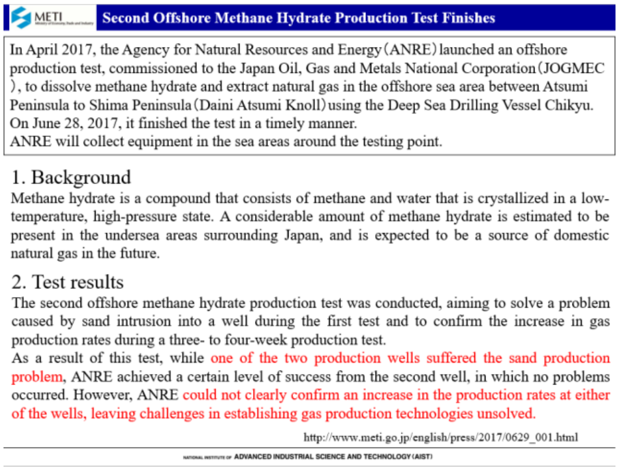
Release date

June 29, 2017

Division in Charge

Petroleum and Natural Gas Division, Natural Resources and Fuel Department, Agency for Natural Resources and Energy

http://www.meti.go.jp/english/press/2017/0629_001.html



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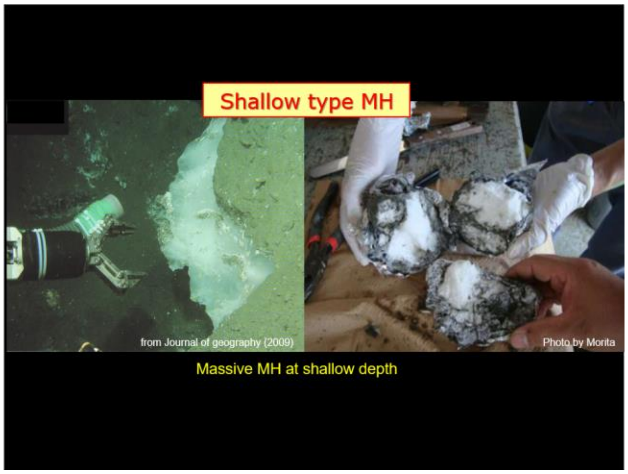
http://www.meti.go.jp/english/press/2017/0629_001.html

NATIONAL INSTITUTE OF ADVANCED INDUSTRIAL SCIENCE AND TECHNOLOGY (AIST)

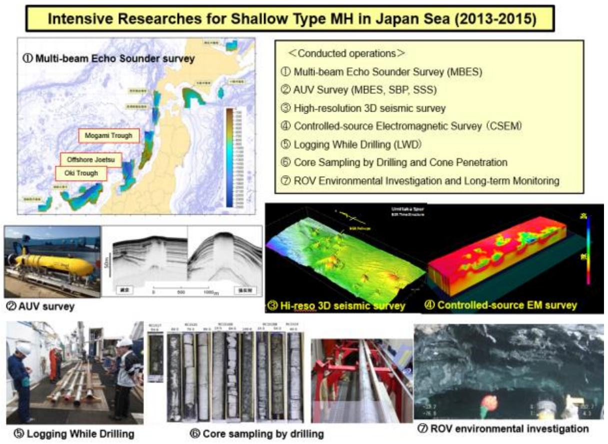


Shallow type MH

from Journal of geography (2009)

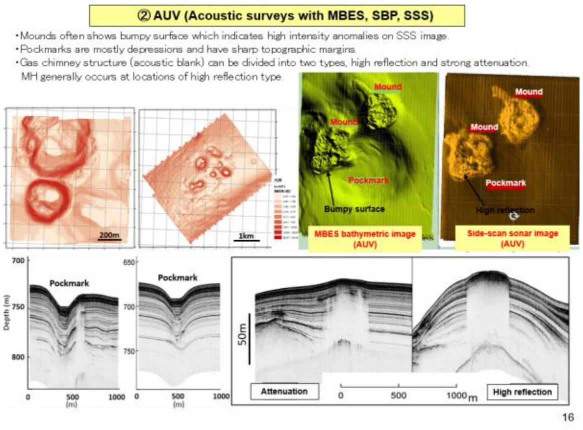
Photo by Morita

Massive MH at shallow depth



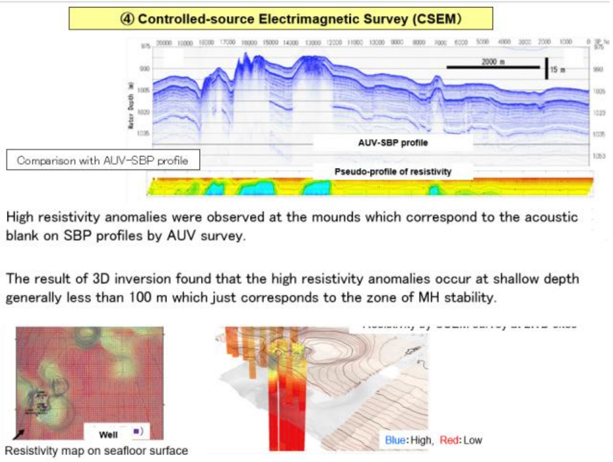
Intensive Researches for Shallow Type MH in Japan Sea (2013-2015)

<Conducted operations>
① Multi-beam Echo Sounder Survey (MBES)
② AUV Survey (MBES, SBP, SSS)
③ High-resolution 3D seismic survey
④ Controlled-source Electromagnetic Survey (CSEM)
⑤ Logging While Drilling (LWD)
⑥ Core Sampling by Drilling and Cone Penetration
⑦ ROV Environmental Investigation and Long-term Monitoring



② AUV (Acoustic surveys with MBES, SBP, SSS)

- Mounds often shows bumpy surface which indicates high intensity anomalies on SSS image.
- Pockmarks are mostly depressions and have sharp topographic margins.
- Gas chimney structure (acoustic blank) can be divided into two types, high reflection and strong attenuation. MH generally occurs at locations of high reflection type.



④ Controlled-source Electrimagnetic Survey (CSEM)

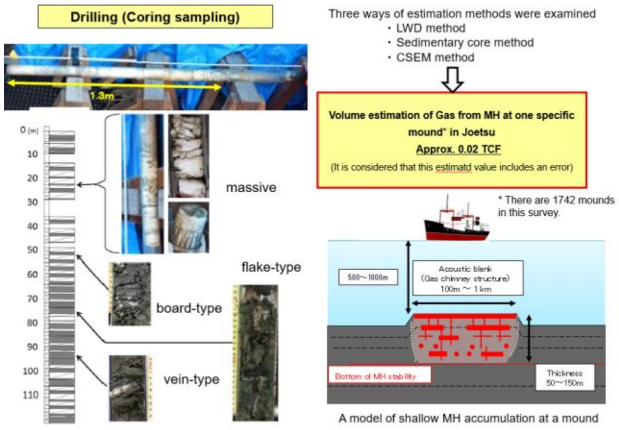
Comparison with AUV-SBP profile

High resistivity anomalies were observed at the mounds which correspond to the acoustic blank on SBP profiles by AUV survey.

The result of 3D inversion found that the high resistivity anomalies occur at shallow depth generally less than 100 m which just corresponds to the zone of MH stability.

Resistivity map on seafloor surface

Blue: High, Red: Low



Drilling (Coring sampling)

Three ways of estimation methods were examined
- LWD method
- Sedimentary core method
- CSEM method

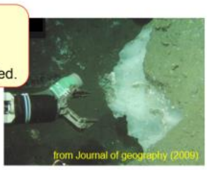
Volume estimation of Gas from MH at one specific mound* in Joetsu
Approx. 0.02 TCF
(It is considered that this estimatd value includes an error)

* There are 1742 mounds in this survey.

A model of shallow MH accumulation at a mound

Current status of the Methane Hydrate Exploration Project in Japan

Shallow type (Japan Sea)
- Scattered distribution occurring at topographical anomalies (mounds and pockmarks)
- Conventional production methods unable to be applied.



Feasibility study on the technological concepts for recovery of shallow type MH was started from November, 2016.

Thanks for your attention

ACKNOWLEDGEMENTS:
This study was financially supported by the Research Consortium for Methane Hydrate Resources in Japan (MH21 Research Consortium) in the Japan's Methane Hydrate R&D Program by the Ministry of Economy, Trade and Industry (METI).

The National Report on Gas Hydrate R&D Program in Korea

Joo Yong Lee[1]

[1]Korea Institute of Geoscience and Mineral Resources, Korea
e-mail: jyl@kigam.re.kr

Abstract

The research on gas hydrates in Korea mainly focuses the hydrates as new energy resources. The Korean government has launched Gas Hydrate Development program in 2005, and studies on gas hydrates in various research areas have been performed ever since. The Korean National Gas Hydrate R&D Program is managed by the Korea Gas Hydrate R&D Organization and funded by the Ministry of Trade, Industry, and Energy. The program is conducted by a consortium of Korea Institute of Geoscience and Mineral Resources, the Korea National Oil Corporation, and the Korea Gas Corporation.

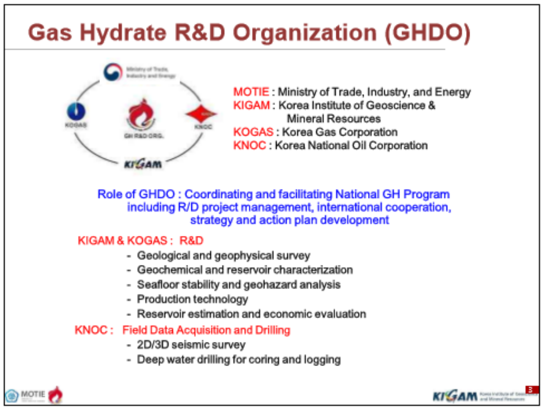
The research includes assessing the distribution of hydrates in the Ulleung Basin, developing resource assessment technique for both pore-filling hydrate-bearing sand deposits and grain-displacing hydrate-bearing mud deposits, establishing geologic models for hydrate reservoirs, characterizing physical properties of hydrate-bearing sediments, developing production technology, and designing production system. During the phase 1 (2005~2007), detailed 2D and 3D seismic survey are continued and identified specific target area for comprehensive explorations including drilling expeditions, focusing on BSR, seismic chimney structures, acoustic blanking zones, enhanced reflection, and gas seepage area. The first deep drilling expedition, UBGH01 was performed in 2007. During the phase 2(2008~2011), The second deep drilling expedition was performed in 2010, aiming locating potential field test sites in the Ulleung Basin. In the phase 3 (2012~2019), the main goal is establishing optimal design of test production by expanding filed applicability of gas hydrate production technique. Also, studies on grain-displacing hydrate-bearing deposits have been initiated, including classification and mapping of chimney structures in the Ulleung Basin.

Gas Hydrate R&D Program in Korea

Gas Hydrate R&D Organization

National GH Program (2007-2019)

- **Technical Road Map**
- G&G R&D
- Production Technology R&D
- Environmental Impact R&D



Gas Hydrate R&D Organization (GHDO)

MOTIE : Ministry of Trade, Industry, and Energy
KIGAM : Korea Institute of Geoscience & Mineral Resources
KOGAS : Korea Gas Corporation
KNOC : Korea National Oil Corporation

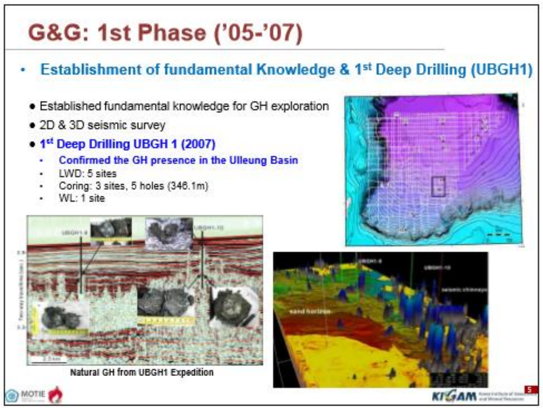
Role of GHDO : Coordinating and facilitating National GH Program including R/D project management, international cooperation, strategy and action plan development

KIGAM & KOGAS : R&D
- Geological and geophysical survey
- Geochemical and reservoir characterization
- Seafloor stability and geohazard analysis
- Production technology
- Reservoir estimation and economic evaluation

KNOC : Field Data Acquisition and Drilling
- 2D/3D seismic survey
- Deep water drilling for coring and logging

National GH Program (2007-2019)

- Technical Road Map
- **G&G R&D**
- Production Technology R&D
- Environmental Impact R&D

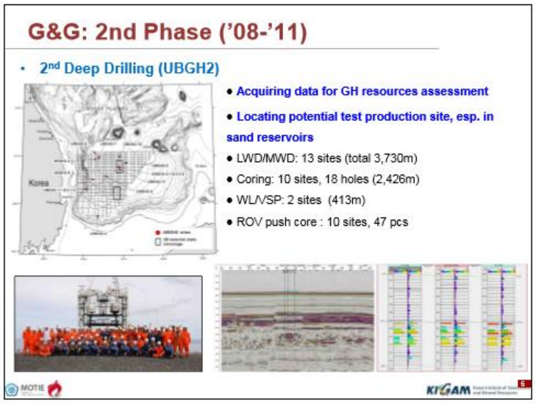


G&G: 1st Phase ('05-'07)

- Establishment of fundamental Knowledge & 1st Deep Drilling (UBGH1)

- Established fundamental knowledge for GH exploration
- 2D & 3D seismic survey
- **1st Deep Drilling UBGH 1 (2007)**
  - **Confirmed the GH presence in the Ulleung Basin**
  - LWD: 5 sites
  - Coring: 3 sites, 5 holes (346.1m)
  - WL: 1 site

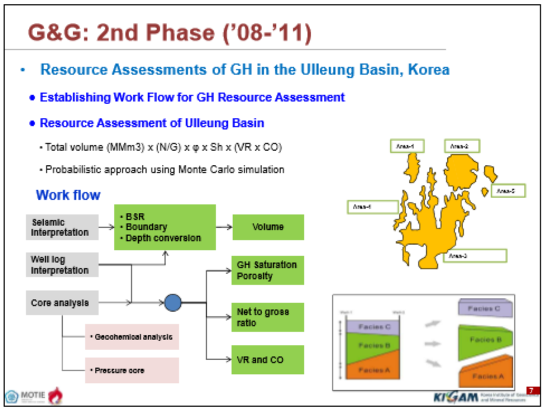
Natural GH from UBGH1 Expedition



G&G: 2nd Phase ('08-'11)

- 2nd Deep Drilling (UBGH2)

- **Acquiring data for GH resources assessment**
- **Locating potential test production site, esp. in sand reservoirs**
- LWD/MWD: 13 sites (total 3,730m)
- Coring: 10 sites, 18 holes (2,426m)
- WL/VSP: 2 sites (413m)
- ROV push core : 10 sites, 47 pcs

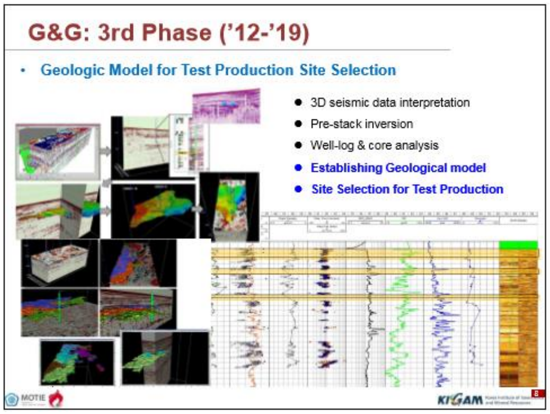


G&G: 2nd Phase ('08-'11)

- Resource Assessments of GH in the Ulleung Basin, Korea

- **Establishing Work Flow for GH Resource Assessment**
- **Resource Assessment of Ulleung Basin**
  - Total volume (MMm3) x (N/G) x φ x Sh x (VR x CO)
  - Probabilistic approach using Monte Carlo simulation

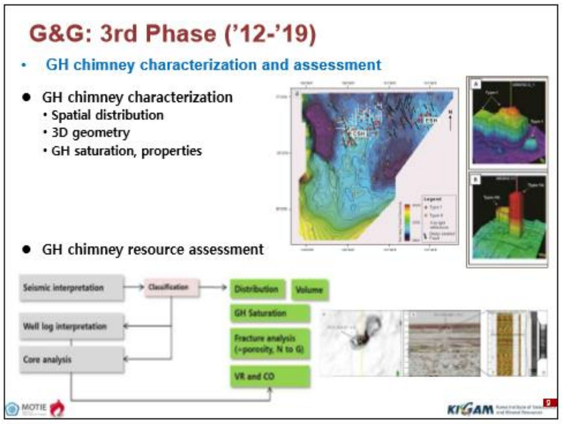
Work flow



G&G: 3rd Phase ('12-'19)

- Geologic Model for Test Production Site Selection

- 3D seismic data interpretation
- Pre-stack inversion
- Well-log & core analysis
- **Establishing Geological model**
- **Site Selection for Test Production**



G&G: 3rd Phase ('12-'19)

- GH chimney characterization and assessment

- GH chimney characterization
  - Spatial distribution
  - 3D geometry
  - GH saturation, properties
- GH chimney resource assessment

Seismic interpretation → Classification → Distribution, Volume

Well log interpretation

Core analysis

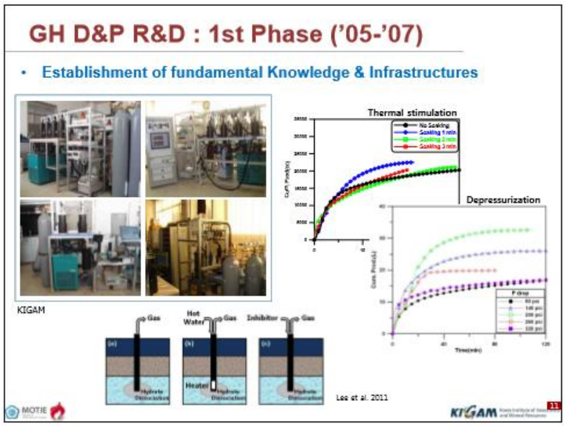
GH Saturation

Fracture analysis (+porosity, N to G)

VR and CO

National GH Program (2007-2019)

- Technical Road Map
- G&G R&D
- **Production Technology R&D**
- Environmental Impact R&D

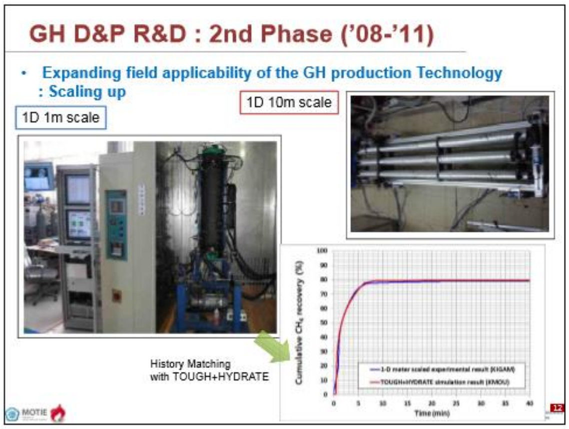


GH D&P R&D : 1st Phase ('05-'07)

- Establishment of fundamental Knowledge & Infrastructures

KIGAM

Lee et al. 2011



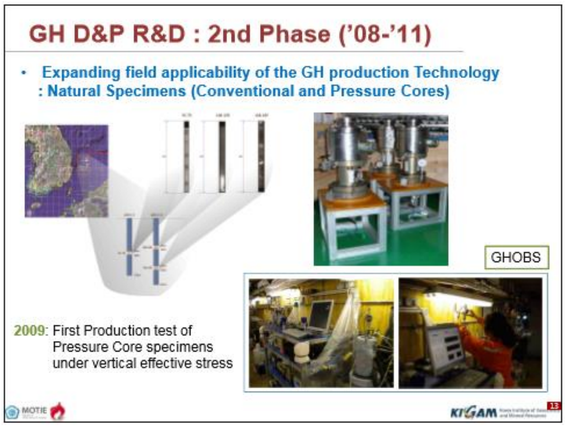
GH D&P R&D : 2nd Phase ('08-'11)

- Expanding field applicability of the GH production Technology : Scaling up

1D 1m scale

1D 10m scale

History Matching with TOUGH+HYDRATE

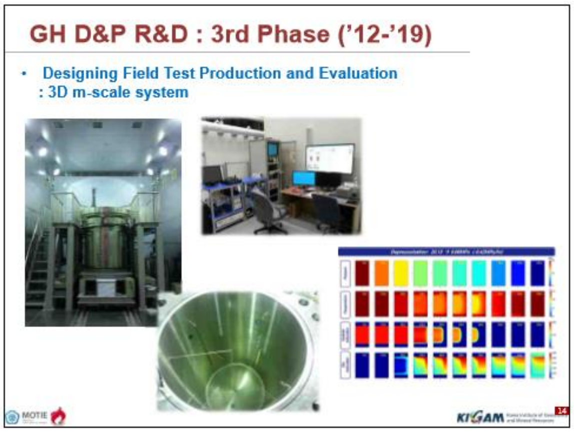


GH D&P R&D : 2nd Phase ('08-'11)

- Expanding field applicability of the GH production Technology : Natural Specimens (Conventional and Pressure Cores)

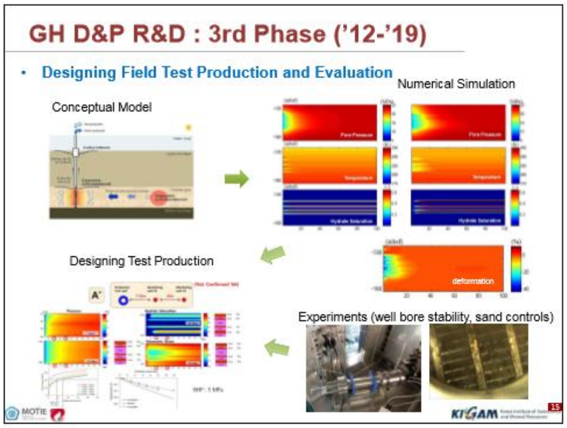
GHOBS

2009: First Production test of Pressure Core specimens under vertical effective stress



GH D&P R&D : 3rd Phase ('12-'19)

- Designing Field Test Production and Evaluation : 3D m-scale system



GH D&P R&D : 3rd Phase ('12-'19)

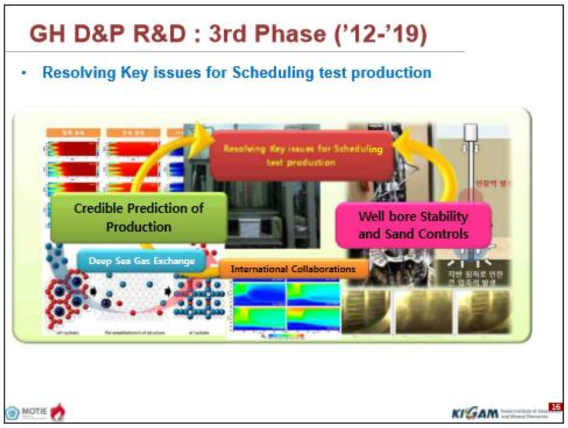
- Designing Field Test Production and Evaluation

Numerical Simulation

Conceptual Model

Designing Test Production

Experiments (well bore stability, sand controls)



GH D&P R&D : 3rd Phase ('12-'19)

- Resolving Key issues for Scheduling test production

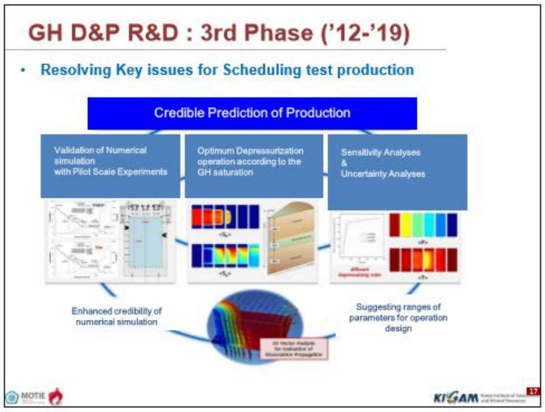
Resolving Key issues for Scheduling test production

Credible Prediction of Production

Well bore Stability and Sand Controls

Deep Sea Gas Exchange

International Collaborations



GH D&P R&D : 3rd Phase ('12-'19)

- Resolving Key issues for Scheduling test production

Credible Prediction of Production

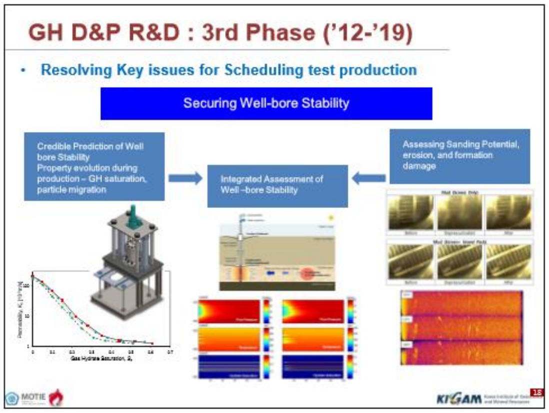
Validation of Numerical simulation
with Pilot Scale Experiments

Optimum Depressurization operation according to the GH saturation

Sensitivity Analyses
&
Uncertainty Analyses

Enhanced credibility of numerical simulation

Suggesting ranges of parameters for operation design



GH D&P R&D : 3rd Phase ('12-'19)

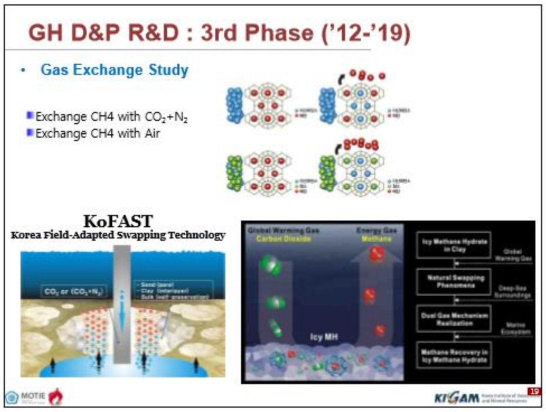
- Resolving Key issues for Scheduling test production

Securing Well-bore Stability

Credible Prediction of Well bore Stability
Property evolution during production – GH saturation, particle migration

Integrated Assessment of Well –bore Stability

Assessing Sanding Potential, erosion, and formation damage



GH D&P R&D : 3rd Phase ('12-'19)

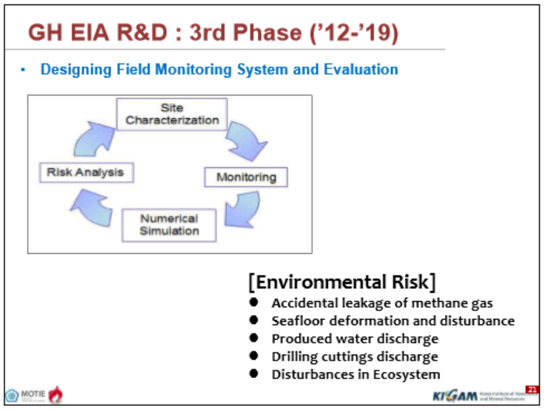
- Gas Exchange Study

- Exchange CH4 with CO_2+N_2
- Exchange CH4 with Air

KoFAST
Korea Field-Adapted Swapping Technology

National GH Program (2007-2019)

- Technical Road Map
- G&G R&D
- Production Technology R&D
- Environmental Impact R&D



GH EIA R&D : 3rd Phase ('12-'19)

- Designing Field Monitoring System and Evaluation

Site Characterization

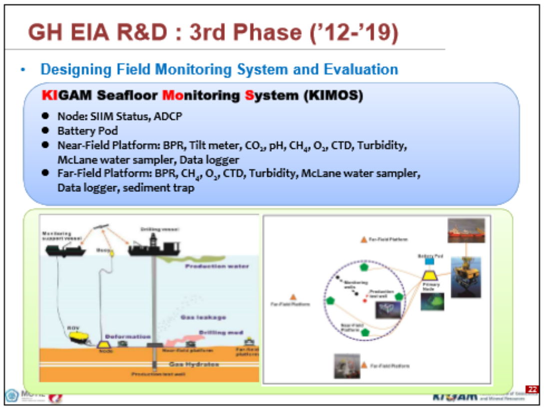
Monitoring

Numerical Simulation

Risk Analysis

[Environmental Risk]

- Accidental leakage of methane gas
- Seafloor deformation and disturbance
- Produced water discharge
- Drilling cuttings discharge
- Disturbances in Ecosystem



GH EIA R&D : 3rd Phase ('12-'19)

- Designing Field Monitoring System and Evaluation

KIGAM Seafloor Monitoring System (KIMOS)

- Node: SIIM Status, ADCP
- Battery Pod
- Near-Field Platform: BPR, Tilt meter, CO_2, pH, CH_4, O_2, CTD, Turbidity, McLane water sampler, Data logger
- Far-Field Platform: BPR, CH_4, O_2, CTD, Turbidity, McLane water sampler, Data logger, sediment trap

Thank for your attention!

Comments and Questions?

Courtesy of UBGH2 Science Party(KIGAM GH Dept.) :)

RESEARCH PRESENTATIONS

TEXAS A&M UNIVERSITY CORPUS CHRISTI

HOKKAIDO UNIVERSITY

UNIVERSITAS BERGENSIS

HNEI

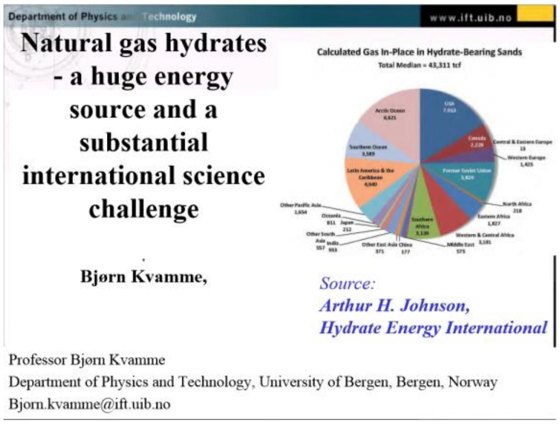
AIST
NATIONAL INSTITUTE OF
ADVANCED INDUSTRIAL SCIENCE
AND TECHNOLOGY (AIST)

Natural gas hydrates - a substantial non-equilibrium challenge

Dr. Bjørn Kvamme Department of Physics and Technology, University of Bergen, Norway
Bjorn.kvamme@uib.no

ABSTRACT

The amount of natural gas trapped in the form of hydrate is huge and might exceed all known conventional sources of fossil fuels by a factor of two. Most of these hydrate structure were formed from biogenic hydrocarbon sources and as such almost pure methane hydrate. There are several possible ways to produce these hydrates. Pressure reduction and various ways of thermal stimulation has dominated the research focus. A fundamental challenge related to any strategy for hydrate utilization is that these hydrates in porous media can never reach thermodynamic equilibrium. This is a consequence of the number of active phases compared to the number of active components that contribute to hydrate phase transitions. Even in the simplest case of only methane and water it is well known that only one independent thermodynamic property can be defined for the system to reach equilibrium. Adding more hydrocarbons, or other hydrate formers, to the system does not make it easier to reach equilibrium since a variation of hydrates can be formed. The combined first and second laws of thermodynamics will control the system so that the most stable hydrate will form first, under constraints of mass and heat transport. Subsequently a theoretically infinite number of hydrate phases of varying composition will form. Since both temperature and pressure always is locally defined in a sediment structure containing hydrate the system is over determined in mathematical language. Practically this implies that various phase transitions that leads to hydrate dissociation will compete with other phase transitions that leads to hydrate formation. This is a multi-scale problem that ranges from quantum mechanics related to mineral/fluid interactions, and corresponding structures and associate thermodynamic properties, all the way up to reservoir scale. Average atom partial charges on mineral surface are complex Quantum mechanics problem which depends on the surrounding fluids. There are two reasons that these mineral/fluid interactions are important for hydrate. Water structure towards most mineral surfaces shows extreme density features. As example there is theoretical and experimental evidence that density of the first water layer may be as much as three times liquid water density. The corresponding low water chemical potential makes it impossible for hydrate to directly attach to the mineral surfaces. But the water structures might trap molecules like methane and such lead to favorable hydrate nucleation. Hydrate phase transitions are nano-scale phenomena happening across a thin interface of roughly 1 – 1.5 nm. The mass transport process is diffusion. As such these phase transitions are within the volumetric scale that can be reached by molecular dynamics (MD) simulations although time scales are challenging. Speeding up the simulations by doing Monte Carlo (MC) potentially steps overrides the natural entropy development of the system. Another challenge is that the mass transport of the phase transition is related to a large reservoir outside which is controlled by hydrodynamics. And finally the whole fluid flow in sediment is described by Darcy’s law. Similar applies to associate heat transport on all levels. A multi-scale modeling strategy is described and various examples on different are used to illustrate various aspects of the non-equilibrium nature of hydrates in porous medium. Hydrate in porous media is a truly multi-disciplinary challenge that needs international collaboration across scientific disciplines.



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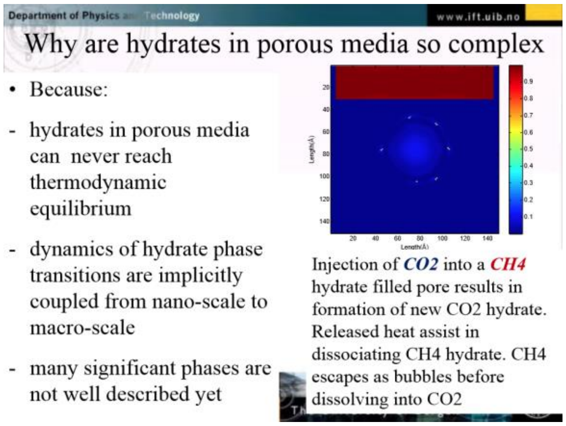
Natural gas hydrates - a huge energy source and a substantial international science challenge

Calculated Gas In-Place in Hydrate-Bearing Sands
Total Median = 43,311 tcf

Bjørn Kvamme,

Source:
Arthur H. Johnson,
Hydrate Energy International

Professor Bjørn Kvamme
Department of Physics and Technology, University of Bergen, Bergen, Norway
Bjorn.kvamme@ift.uib.no



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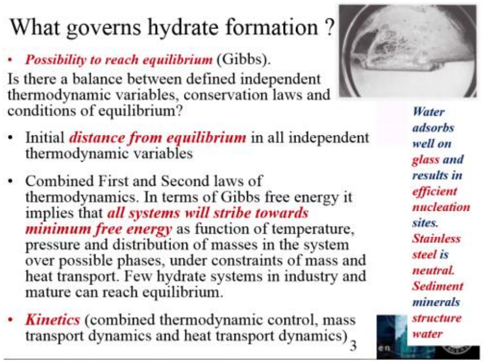
Why are hydrates in porous media so complex

- Because:
- hydrates in porous media can never reach thermodynamic equilibrium
- dynamics of hydrate phase transitions are implicitly coupled from nano-scale to macro-scale
- many significant phases are not well described yet

Injection of ***CO2*** into a ***CH4*** hydrate filled pore results in formation of new CO2 hydrate. Released heat assist in dissociating CH4 hydrate. CH4 escapes as bubbles before dissolving into CO2



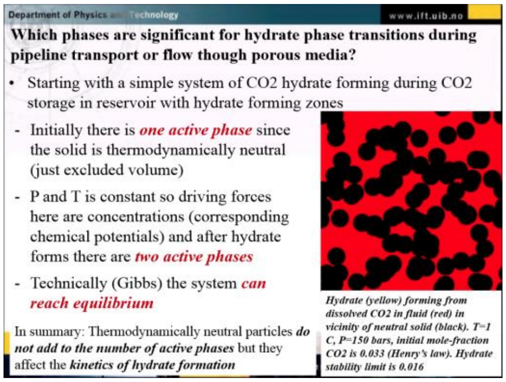
What governs hydrate formation ?

- ***Possibility to reach equilibrium*** (Gibbs).

Is there a balance between defined independent thermodynamic variables, conservation laws and conditions of equilibrium?

- Initial ***distance from equilibrium*** in all independent thermodynamic variables
- Combined First and Second laws of thermodynamics. In terms of Gibbs free energy it implies that ***all systems will stribe towards minimum free energy*** as function of temperature, pressure and distribution of masses in the system over possible phases, under constraints of mass and heat transport. Few hydrate systems in industry and mature can reach equilibrium.
- ***Kinetics*** (combined thermodynamic control, mass transport dynamics and heat transport dynamics) 3

Water adsorbs well on glass and results in efficient nucleation sites. Stainless steel is neutral. Sediment minerals structure water



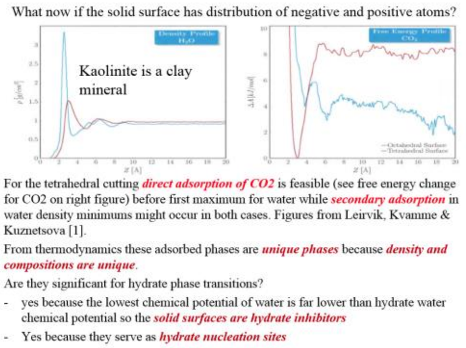
Department of Physics and Technology www.ift.uib.no

Which phases are significant for hydrate phase transitions during pipeline transport or flow though porous media?

- Starting with a simple system of CO2 hydrate forming during CO2 storage in reservoir with hydrate forming zones
- Initially there is ***one active phase*** since the solid is thermodynamically neutral (just excluded volume)
- P and T is constant so driving forces here are concentrations (corresponding chemical potentials) and after hydrate forms there are ***two active phases***
- Technically (Gibbs) the system ***can reach equilibrium***

Hydrate (yellow) forming from dissolved CO2 in fluid (red) in vicinity of neutral solid (black). T=1 C, P=150 bars, initial mole-fraction CO2 is 0.033 (Henry's law). Hydrate stability limit is 0.016

In summary: Thermodynamically neutral particles ***do not add to the number of active phases*** but they affect the ***kinetics of hydrate formation***



What now if the solid surface has distribution of negative and positive atoms?

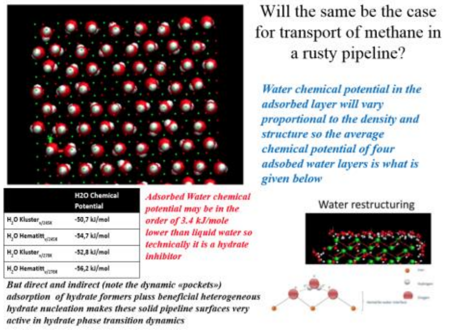
Kaolinite is a clay mineral

For the tetrahedral cutting ***direct adsorption of CO2*** is feasible (see free energy change for CO2 on right figure) before first maximum for water while ***secondary adsorption*** in water density minimums might occur in both cases. Figures from Leirvik, Kvamme & Kuznetsova [1].

From thermodynamics these adsorbed phases are ***unique phases*** because ***density and compositions are unique***.

Are they significant for hydrate phase transitions?

- yes because the lowest chemical potential of water is far lower than hydrate water chemical potential so the ***solid surfaces are hydrate inhibitors***
- Yes because they serve as ***hydrate nucleation sites***



Will the same be the case for transport of methane in a rusty pipeline?

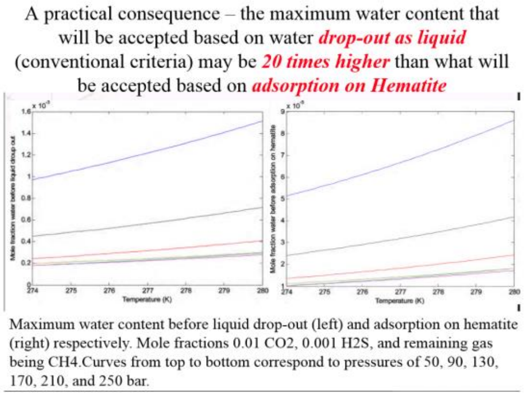
Water chemical potential in the adsorbed layer will vary proportional to the density and structure so the average chemical potential of four adsobed water layers is what is given below

	H2O Chemical Potential
H_2O Kluster [illegible]	-50,7 kJ/mol
H_2O Hematitt [illegible]	-54,7 kJ/mol
H_2O Kluster [illegible]	-52,8 kJ/mol
H_2O Hematitt [illegible]	-56,2 kJ/mol

Adsorbed Water chemical potential may be in the order of 3.4 kJ/mole lower than liquid water so technically it is a hydrate inhibitor

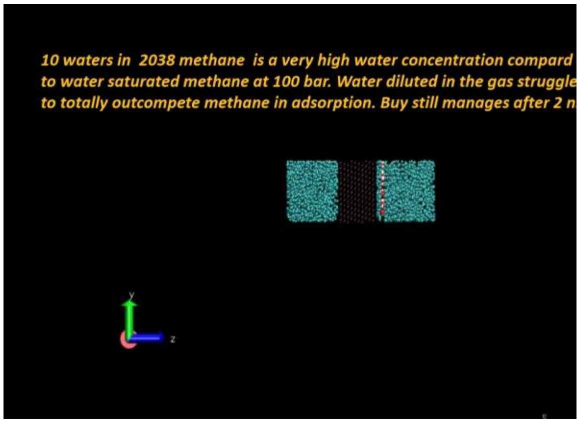
Water restructuring

But direct and indirect (note the dynamic «pockets») adsorption of hydrate formers pluss beneficial heterogeneous hydrate nucleation makes these solid pipeline surfaces very active in hydrate phase transition dynamics



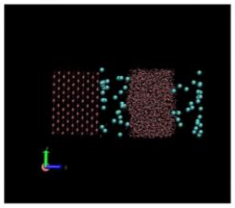
A practical consequence – the maximum water content that will be accepted based on water ***drop-out as liquid*** (conventional criteria) may be ***20 times higher*** than what will be accepted based on ***adsorption on Hematite***

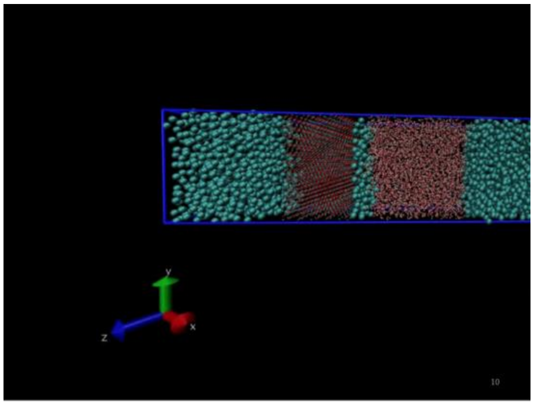
Maximum water content before liquid drop-out (left) and adsorption on hematite (right) respectively. Mole fractions 0.01 CO2, 0.001 H2S, and remaining gas being CH4.Curves from top to bottom correspond to pressures of 50, 90, 130, 170, 210, and 250 bar.



10 waters in 2038 methane is a very high water concentration compard to water saturated methane at 100 bar. Water diluted in the gas struggle to totally outcompete methane in adsorption. Buy still manages after 2 n

Secondary adsorption of methane (trapped in adsorbed H2O)

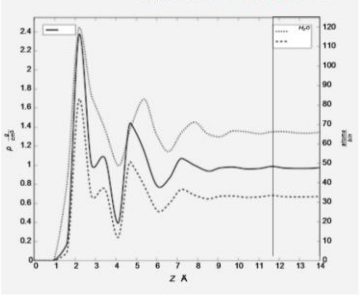




Experimental results on adsorbed water gives details on each atom

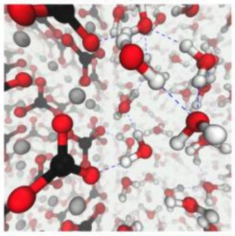
P. Geissbühler, P. Fenter, E. DiMasi, G. Srajer, L.B. Sorensen, and N.C. Sturchio. Three-dimensional structure of the calcite–water interface by surface X-ray scattering. Surface Science, 573(2):191–203, 2004

The cusp in the oxygen density between first and second maximum is due to indirect correlations which involves hydrogen. Locations of main peaks and minima is in striking agreement. Also integrals over density profiles are in striking agreements.

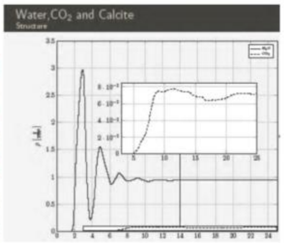


Secondary and primary adsorption of guest molecules

Primary adsorption is adsorption directly on solid surface. Secondary adsorption is trapping of hydrate formers in strctured adsobed water



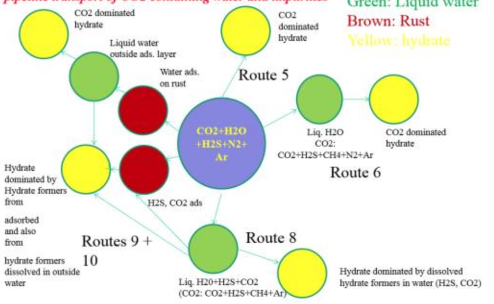
Simple water models like SPC, TIP4P and many other have no short range interaction on H atoms so density profile based on ozygen locations



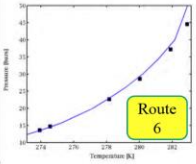
Note the extreme density of the first adsobed water layer but also the subsequent water density minimum which gives space for trapping CO2. Simulated structure is in accordance with experimental data (IR)

Some of the routes that can lead to CO2 hydrate during pipeline transport of CO2 containing water and impurities

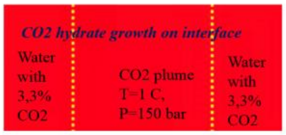
Blue: CO2-phase
Green: Liquid water
Brown: Rust
Yellow: hydrate



Most hydrate evaluation software only focus on route 5



Hydrate from CO2 and liquid water given only T fixed and P dependent variable. (Kvamme & Tanaka,1995)

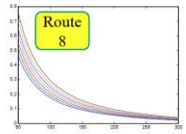


CO2 hydrate growth on interface

Water with 3,3% CO2

CO2 plume T=1 C, P=150 bar

Water with 3,3% CO2



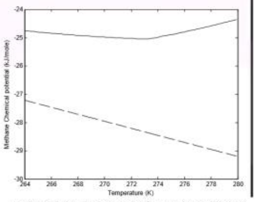
Left: Relative saturation of CO2 in water versus neccesary pressure (horisontal axis) to produce hydrate (upper curve for 6 C and lower for 0 C)

Kvamme, Bjørn. *Initiation and growth of hydrate from nucleation theory.* International Journal of Offshore and Polar Engineering 2002; 12:256-262

Kvamme, Bjørn. *Droplets of dry ice and cold liquid CO2 for self transport to large depths.* International Journal of Offshore and Polar Engineering 2003; 13(1):1-8

But CH_4 hydrate will still dissociate towards N_2 which is undersaturated on CH_4

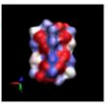
- But the kinetic rates are low !
- Hydrate will also dissociate towards water undersaturated with methane so during flow and fluid exchange in the pores many different scenarios are possible



Estimated chemical potential for CH_4 in equilibrium hydrate (-) versus chemical potential for 10 mole % CH_4 mixed into a gas phase originally containing 1mole % CO_2 and rest N_2 (--) at 80 bars pressure. Pressures on the solid curve are the estimated equilibrium pressures for pure CH_4 hydrate

Investigating competing phase transitions in porous media (read: solid material surfaces) requires multiscale modeling approach

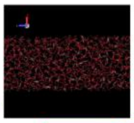
Charge distribution for hematite by Gaussian03



from

quantum (characterisation of charge distribution in model molecules, from below nano in scale)

MD for Studies of mechanisms, thermodyn, interface properties and parametrisation



to

nano (Molecular Dynamics simulations, MD)

and

micro (Phase Field Theory)

Simulation of hydrate growth dynamics on interface of a CO2 plume using PFT

Conclusions

- Number of ***active phases*** involved in hydrate phase transitions in porous media are ***too many*** to secure thermodynamic equilibrium
- It does not help if the number of components increase – rather the opposite since the ***most stable hydrates*** (minimum free energy) will form ***first***, and ***selective adsorption*** followed by liquid side water interface concentrations will ***dictate*** dynamically ***available masses*** for hydrate formation

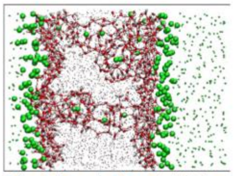
$$\begin{aligned}\mu_i^{gas} &= \frac{1}{\beta}\ln(\beta\Lambda_i^3) + \frac{1}{\beta}\ln(x_iN) - \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial N_i}\right)_{T,V,N_{j\neq i}} \\ &= \frac{1}{\beta}\ln(\beta\Lambda_i^3) + \frac{1}{\beta}\ln(x_iN) - \frac{1}{\beta}\left(\frac{\partial \ln Q^{2D}}{\partial N_i}\right)_{T,V,N_{j\neq i}} \\ &\quad - \frac{1}{\beta}\ln Q_i^{1D} \\ &= \frac{1}{\beta}\ln(\beta\Lambda_i^3) + \frac{1}{\beta}\ln(x_iN) - \frac{1}{\beta}(\beta\mu_i^{2D}) - \frac{1}{\beta}\ln Q_i^{1D}\end{aligned}$$

A simple illustration using a 2D adsorption model (Kvamme, *Thermodynamic limitations of the CO2/N2 mixture injected into CH4 hydrate in the Ignik Sikumi field trial*, J. Chem. Eng. Data, 2016, 61 (3), pp 1280–1295).
If we consider ***10 mole % CO2*** in a CO2/N2 gas mixture this result in estimated ***32% CO2 adsorbed*** on liquid water surface at 30 bar and 273 K.

Conclusions cont.

- And ***no natural gas*** mixture have a perfect ***relative ratio*** of gas molecules, as compared ***to available cavities*** in structures I and II. So when the most stable hydrates have consumed the «best» hydrate formers a variety of structure I and II hydrates will form.

- These hydrates will have ***varying composition*** and ***unique free energies***, depending on what molecules that are available to extract from the hydrate former phase.
- Often it ends up with methane as the final excess gas molecule, which will the typically form a structure I hydrate.



Methane hydrate growing from a gas/water interface

In the ultimate limit an infinite number of hydrate phases can form – with infinitely small changes in free energies. from lowest free energy and up to (typically) free energy of methane hydrate structure I.

In a non-equilibrium situation *it is very rare to find unconditional* phase transitions in *one direction*. Competition between formation and dissociation phase transitions under constraints of mass- and heat transport is the more typical situation

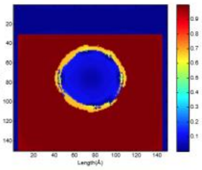
For any of these phase Transitions ***k*** to proceed unconditionally in one direction:

$$\Delta G_k \le 0$$

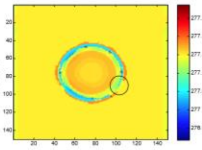
and the impact of changes in all independent thermodynamic variables (M=T, P, concentrations) n also result in negative free energy change

$$\left[\frac{\partial \Delta G_k}{\partial M_n}\right] dM_n \le 0$$

Initial CH4 hydrate core (blue) surrounded by CO2 (brown). New CO2 hydrate forms around core while leaving some regions heated and dissociated CH4 from hydrate escape

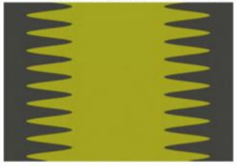


Note the temperature distribution due to formation of new CO2 hydrate and dissociation of CH4 hydrate

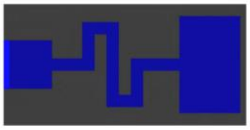


Conclusions cont.

- Solid surfaces are significant phases for hydrate phase transitions because:
  - they give rice to ***confinements*** (non-thermodynamic effect) for ***efficient nucleation***
  - they serve as regions of ***hydrate former enrichment*** through primary or secondary adsorption.
  - they serve as ***efficient*** (2D mass-transport) ***nucleation sites***.
  - the first layers of water adsorbed are efficient hydrate inhibitors so ***no real "hydrate cementing"*** of grains.



Excluded regions (minerals) have kinetic effects and physical interaction characteristics have thermodynamic effects

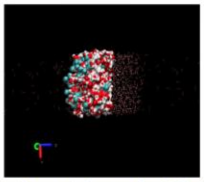


- The use of N2/CO2 mixtures for producing hydrate while at the same time storing CO2 is tempting bacause even flue gas might be stored directly in hydrate.
- But:
  - Hydrate CH4/CO2 swap is possible through ***direct solid state*** conversion (***extremely slow***)

and

  - a second mechanism in which ***CO2 hydrate forms*** from injection gas and water. Associated ***heat release dissociate*** in situ CH4 hydrate. Too ***much N2 deactivates*** the fast mechanism

Conclusions cont.



Liquid water slab exposed to CO2 at 83 bars and 276 K. CO2 phase to the right (but hard to see).
Fairly thick (roughly 1.2 nm) and dynamic interface

- ***Hydrates in real sediments*** are in a situation of ***stationary flow*** ranging from diffusion (very close reservoir) to various levels of hydrodynamics depending on fracture systems that brings in ground water from above and/or hydrocarbons from below.
- There is a need for a ***multi-stage modeling strategy*** to build up realistic non-equilibrium description of hydrates in sediments
- And in the macro-end there is a need for a ***reservoir simulator*** that can adopt this new physical description (read: ***dynamic non-equilibrium*** with competing phase transitions)
- ***Implicit geomechanics*** is a must since hydrate phase transitions can be very fast

Conclusions cont.

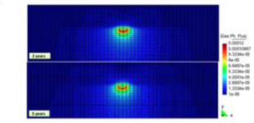


Figure 4. CH_4 gas flux inside the reservoir after two and five years of production.

Simulated production of gas from Bjørnøya hydrate using pressure reduction. Results not readable here but papers available !

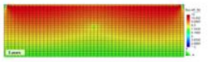


Figure 7. Effective stress in the y-direction after five years of production.

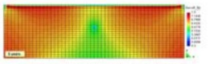
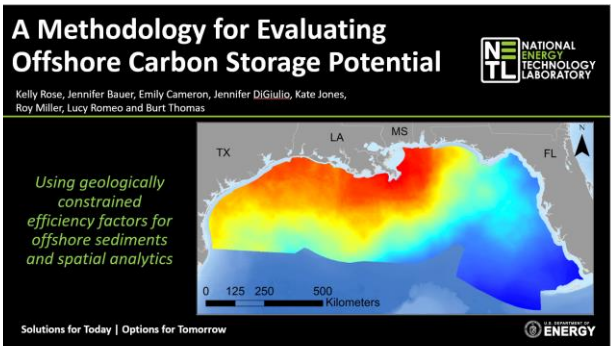


Figure 8. Effective stress in the x-direction after five years of production.

A Methodology for Evaluation Offshore Carbon Storage Potential

Dr. Kelly Rose, NETL Albany, DOE, Kelly.Rose@NETL.DOE.GOV

Offshore carbon storage in geological reservoirs is one important option for storing carbon dioxide that would otherwise be emitted to the atmosphere as a result of anthropogenic activities. Effective carbon storage requires both safety and permanence. One attractive National storage option includes subsurface geologic storage in offshore formations, similar to those that hold oil, gas, or brine. The major advantage of offshore storage is that it decreases the risk of leakage into fresh groundwater resources and minimizes the effects on human population centers. However, as with onshore storage options, there are many uncertainties surrounding offshore storage. These include issues related to both safety and permanence. In this paper, we conduct a literature review of the current storage methodologies for onshore carbon storage in saline formations, and contrast the offshore and onshore characteristics of reservoirs that allow us to make recommendations about future work to support offshore storage estimates and research. We conclude with the suggestion that despite important differences between onshore and offshore systems, carbon can be stored safely and permanently in offshore saline geologic formations. Furthermore, we propose development of a similar storage resource calculation for onshore and offshore systems. For our efforts we focus on the US-DOE-NETL advised methodology for calculating carbon storage resource estimates in saline formations.

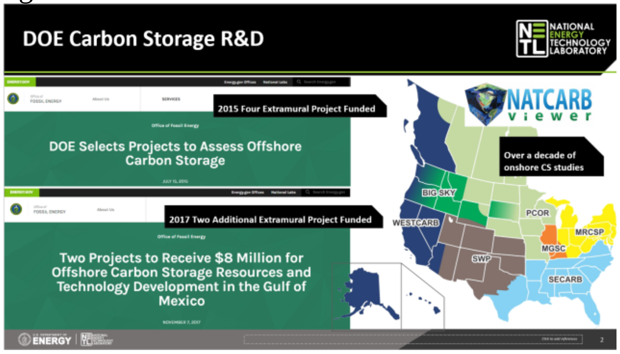


A Methodology for Evaluating Offshore Carbon Storage Potential

Kelly Rose, Jennifer Bauer, Emily Cameron, Jennifer DiGiulio, Kate Jones,
Roy Miller, Lucy Romeo and Burt Thomas

Using geologically constrained efficiency factors for offshore sediments and spatial analytics

Solutions for Today | Options for Tomorrow



DOE Carbon Storage R&D

2015 Four Extramural Project Funded

Office of Fossil Energy

DOE Selects Projects to Assess Offshore Carbon Storage

JULY 15, 2015

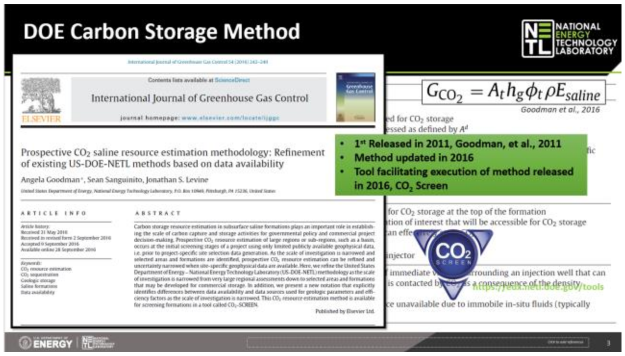
2017 Two Additional Extramural Project Funded

Office of Fossil Energy

Two Projects to Receive $8 Million for Offshore Carbon Storage Resources and Technology Development in the Gulf of Mexico

NOVEMBER 7, 2017

Over a decade of onshore CS studies



DOE Carbon Storage Method

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Prospective CO_2 saline resource estimation methodology: Refinement of existing US-DOE-NETL methods based on data availability

Angela Goodman*, Sean Sanguinito, Jonathan S. Levine

United States Department of Energy, National Energy Technology Laboratory, P.O. Box 10940, Pittsburgh, PA 15236, United States

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ABSTRACT

Carbon storage resource estimation in subsurface saline formations plays an important role in establishing the scale of carbon capture and storage activities for governmental policy and commercial project decision-making. Prospective CO_2 resource estimation of large regions or sub-regions, such as a basin, occurs at the initial screening stages of a project using only limited publicly available geophysical data, i.e. prior to project-specific site selection data generation. As the scale of investigation is narrowed and selected areas and formations are identified, prospective CO_2 resource estimation can be refined and uncertainty narrowed when site-specific geophysical data are available. Here, we refine the United States Department of Energy – National Energy Technology Laboratory (US-DOE-NETL) methodology as the scale of investigation is narrowed from very large regional assessments down to selected areas and formations that may be developed for commercial storage. In addition, we present a new notation that explicitly identifies differences between data availability and data sources used for geologic parameters and efficiency factors as the scale of investigation is narrowed. This CO_2 resource estimation method is available for screening formations in a tool called CO_2-SCREEN.

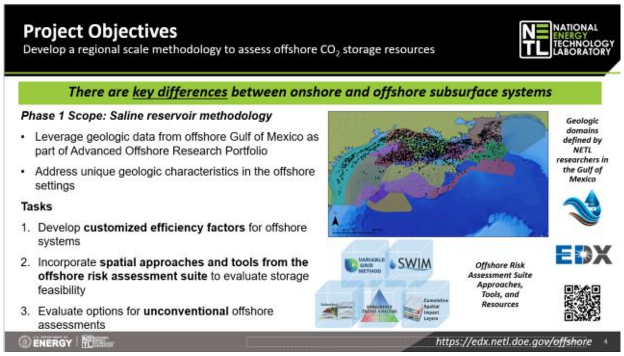
Published by Elsevier Ltd.

$$G_{CO_2} = A_t h_g \phi_t \rho E_{saline}$$

Goodman et al., 2016

- 1st Released in 2011, Goodman, et al., 2011
- Method updated in 2016
- Tool facilitating execution of method released in 2016, CO_2 Screen

https://edx.netl.doe.gov/tools



Project Objectives

Develop a regional scale methodology to assess offshore CO_2 storage resources

There are <u>key differences</u> between onshore and offshore subsurface systems

Phase 1 Scope: Saline reservoir methodology

- Leverage geologic data from offshore Gulf of Mexico as part of Advanced Offshore Research Portfolio
- Address unique geologic characteristics in the offshore settings

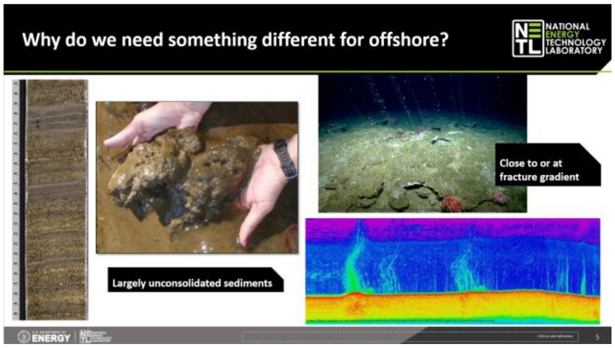
Tasks

1. Develop **customized efficiency factors** for offshore systems
2. Incorporate **spatial approaches and tools from the offshore risk assessment suite** to evaluate storage feasibility
3. Evaluate options for **unconventional** offshore assessments

Geologic domains defined by NETL researchers in the Gulf of Mexico

Offshore Risk Assessment Suite Approaches, Tools, and Resources

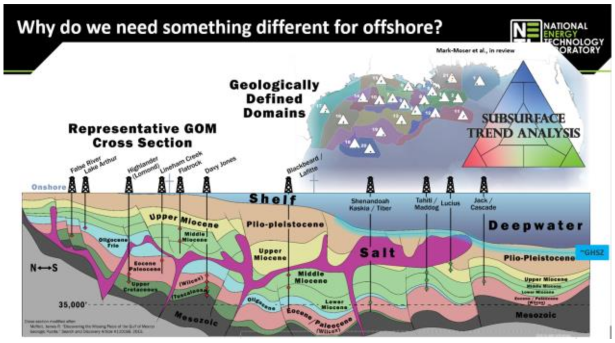
https://edx.netl.doe.gov/offshore



Why do we need something different for offshore?

Close to or at fracture gradient

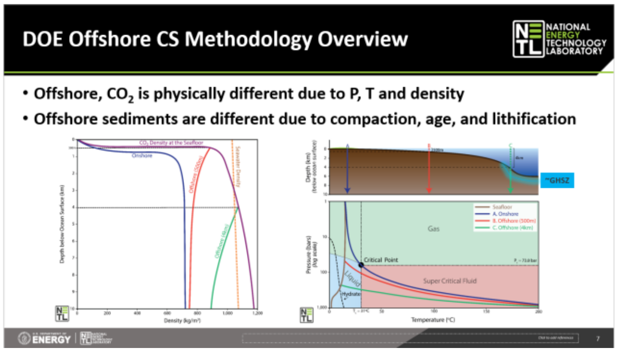
Largely unconsolidated sediments



Why do we need something different for offshore?

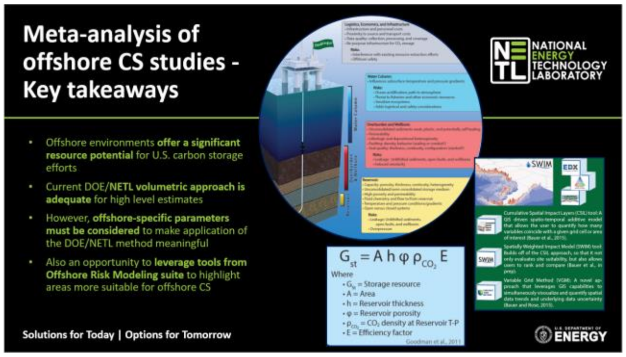
Mark-Moser et al., in review

Cross section modified after: Moffett, James R. "Discovering the Missing Piece of the Gulf of Mexico Geologic Puzzle." Search and Discovery Article #10XXX, 2012.



DOE Offshore CS Methodology Overview

- **Offshore, CO_2 is physically different due to P, T and density**
- **Offshore sediments are different due to compaction, age, and lithification**



Meta-analysis of offshore CS studies - Key takeaways

- Offshore environments **offer a significant resource potential** for U.S. carbon storage efforts
- Current DOE/**NETL volumetric approach is adequate** for high level estimates
- However, **offshore-specific parameters must be considered** to make application of the DOE/NETL method meaningful
- Also an opportunity to **leverage tools from Offshore Risk Modeling suite** to highlight areas more suitable for offshore CS

$$G_{st} = A\,h\,\varphi\,\rho_{CO_2}\,E$$

Where
- G_{st} = Storage resource
- A = Area
- h = Reservoir thickness
- φ = Reservoir porosity
- ρ_{CO_2} = CO_2 density at Reservoir T-P
- E = Efficiency factor

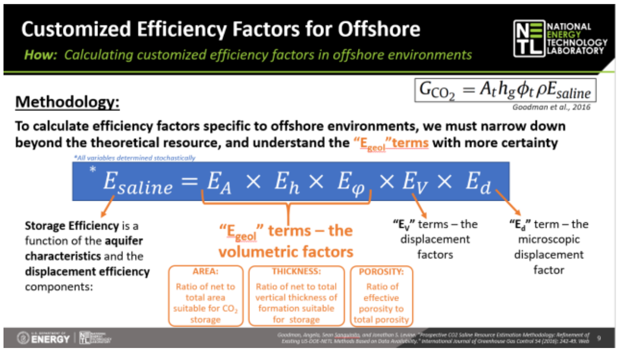
Goodman et al., 2011

Cumulative Spatial Impact Layers (CSIL) tool: A GIS driven spatio-temporal additive model that allows the user to quantify how many variables coincide with a given grid cell or area of interest (Bauer et al., 2015).

Spatially Weighted Impact Model (SWIM) tool: Builds off of the CSIL approach, so that it not only evaluates site suitability, but also allows users to rank and compare (Bauer et al., in prep).

Variable Grid Method (VGM): A novel approach that leverages GIS capabilities to simultaneously visualize and quantify spatial data trends and underlying data uncertainty (Bauer and Rose, 2015).

Solutions for Today | Options for Tomorrow



Customized Efficiency Factors for Offshore

***How:** Calculating customized efficiency factors in offshore environments*

$$G_{CO_2} = A_t h_g \phi_t \rho E_{saline}$$

Goodman et al., 2016

Methodology:

To calculate efficiency factors specific to offshore environments, we must narrow down beyond the theoretical resource, and understand the "E_{geol}" terms with more certainty

*All variables determined stochastically

$$^{*}E_{saline} = E_A \times E_h \times E_\varphi \times E_V \times E_d$$

Storage Efficiency is a function of the **aquifer characteristics** and the **displacement efficiency** components:

"E_{geol}" terms – the volumetric factors

AREA: Ratio of net to total area suitable for CO_2 storage

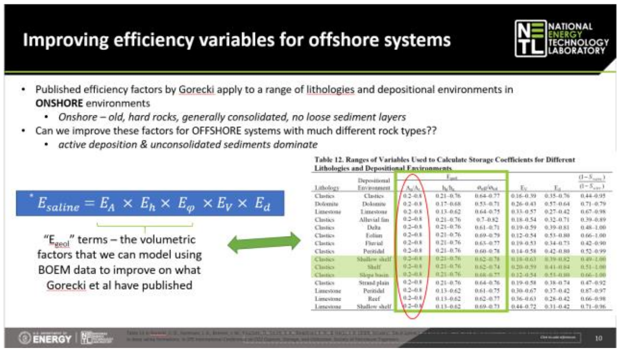
THICKNESS: Ratio of net to total vertical thickness of formation suitable for storage

POROSITY: Ratio of effective porosity to total porosity

"E_V" terms – the displacement factors

"E_d" term – the microscopic displacement factor

Goodman, Angela, Sean Sanguinito, and Jonathan S. Levine. "Prospective CO2 Saline Resource Estimation Methodology: Refinement of Existing US-DOE-NETL Methods Based on Data Availability." International Journal of Greenhouse Gas Control 54 (2016): 242-49. Web



Improving efficiency variables for offshore systems

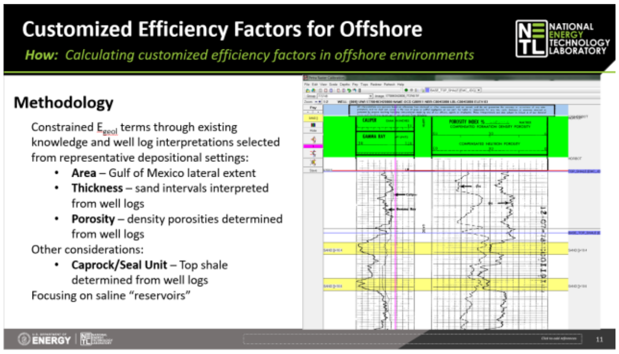
- Published efficiency factors by Gorecki apply to a range of lithologies and depositional environments in **ONSHORE** environments
  - *Onshore – old, hard rocks, generally consolidated, no loose sediment layers*
- Can we improve these factors for OFFSHORE systems with much different rock types??
  - *active deposition & unconsolidated sediments dominate*

$$^{*}E_{saline} = E_A \times E_h \times E_\varphi \times E_V \times E_d$$

"E_{geol}" terms – the volumetric factors that we can model using BOEM data to improve on what Gorecki et al have published

Table 12. Ranges of Variables Used to Calculate Storage Coefficients for Different Lithologies and Depositional Environments

Lithology	Depositional Environment	E_{geol}			E_V	E_d	$\frac{(1-S_{wirr})}{(1-S_{wirr})}$
		A_n/A_t	h_n/h_g	φ_e/φ_{tot}			
Clastics	Clastics	0.2–0.8	0.21–0.76	0.64–0.77	0.16–0.39	0.35–0.76	0.44–0.95
Dolomite	Dolomite	0.2–0.8	0.17–0.68	0.53–0.71	0.26–0.43	0.57–0.64	0.71–0.79
Limestone	Limestone	0.2–0.8	0.13–0.62	0.64–0.75	0.33–0.57	0.27–0.42	0.67–0.98
Clastics	Alluvial fan	0.2–0.8	0.21–0.76	0.7–0.82	0.18–0.54	0.32–0.71	0.39–0.89
Clastics	Delta	0.2–0.8	0.21–0.76	0.61–0.71	0.19–0.59	0.39–0.81	0.48–1.00
Clastics	Eolian	0.2–0.8	0.21–0.76	0.69–0.79	0.12–0.54	0.53–0.80	0.66–1.00
Clastics	Fluvial	0.2–0.8	0.21–0.76	0.63–0.77	0.19–0.53	0.34–0.73	0.42–0.90
Clastics	Peritidal	0.2–0.8	0.21–0.76	0.60–0.78	0.14–0.58	0.42–0.80	0.52–0.99
Clastics	Shallow shelf	0.2–0.8	0.21–0.76	0.62–0.78	0.18–0.63	0.39–0.82	0.49–1.00
Clastics	Shelf	0.2–0.8	0.21–0.76	0.62–0.74	0.20–0.59	0.41–0.84	0.51–1.00
Clastics	Slope basin	0.2–0.8	0.21–0.76	0.68–0.77	0.12–0.54	0.53–0.80	0.66–1.00
Clastics	Strand plain	0.2–0.8	0.21–0.76	0.64–0.76	0.19–0.58	0.38–0.74	0.47–0.92
Limestone	Peritidal	0.2–0.8	0.13–0.62	0.61–0.75	0.30–0.67	0.37–0.42	0.87–0.97
Limestone	Reef	0.2–0.8	0.13–0.62	0.62–0.77	0.36–0.63	0.28–0.42	0.66–0.98
Limestone	Shallow shelf	0.2–0.8	0.13–0.62	0.69–0.73	0.44–0.72	0.31–0.42	0.71–0.96



Customized Efficiency Factors for Offshore

***How:** Calculating customized efficiency factors in offshore environments*

Methodology

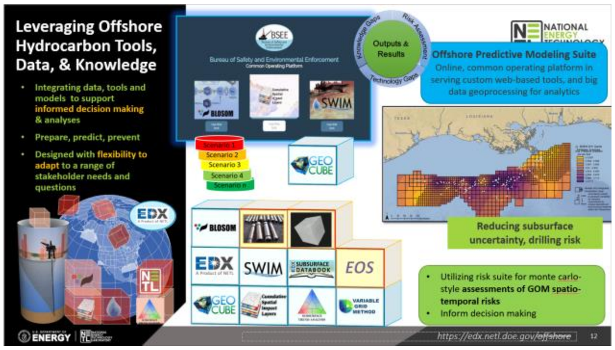
Constrained E_{geol} terms through existing knowledge and well log interpretations selected from representative depositional settings:

- **Area** – Gulf of Mexico lateral extent
- **Thickness** – sand intervals interpreted from well logs
- **Porosity** – density porosities determined from well logs

Other considerations:

- **Caprock/Seal Unit** – Top shale determined from well logs

Focusing on saline "reservoirs"



Leveraging Offshore Hydrocarbon Tools, Data, & Knowledge

- Integrating data, tools and models to support informed decision making & analyses
- Prepare, predict, prevent
- Designed with flexibility to adapt to a range of stakeholder needs and questions

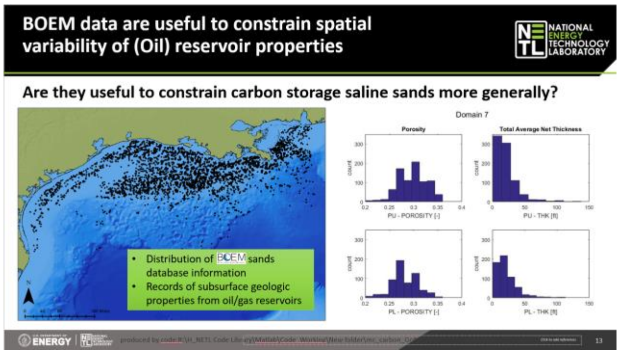
Offshore Predictive Modeling Suite

Online, common operating platform in serving custom web-based tools, and big data geoprocessing for analytics

Reducing subsurface uncertainty, drilling risk

- Utilizing risk suite for monte carlo-style **assessments of GOM spatio-temporal risks**
- Inform decision making

https://edx.netl.doe.gov/offshore

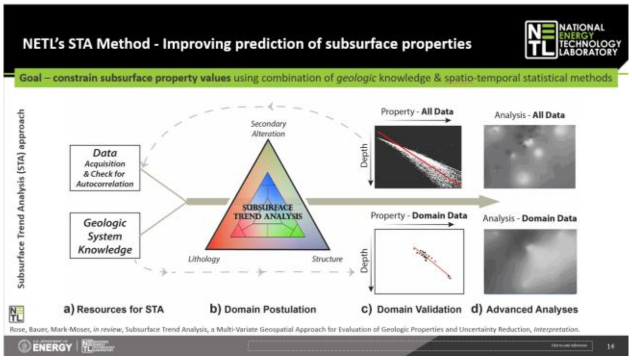


BOEM data are useful to constrain spatial variability of (Oil) reservoir properties

Are they useful to constrain carbon storage saline sands more generally?

- Distribution of BOEM sands database information
- Records of subsurface geologic properties from oil/gas reservoirs

produced by code R:\H_NETL Code Library\Matlab\Code_Working\New folder\mc_carbon_

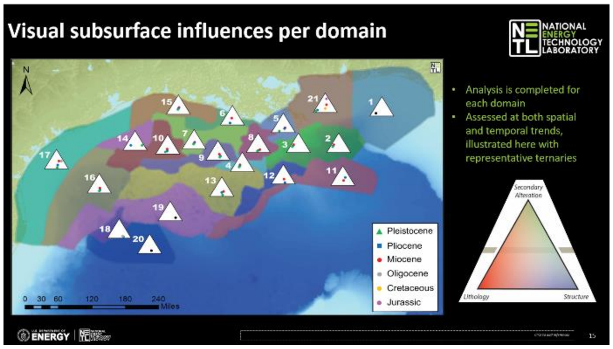


NETL's STA Method - Improving prediction of subsurface properties

Goal – constrain subsurface property values using combination of *geologic* knowledge & spatio-temporal statistical methods

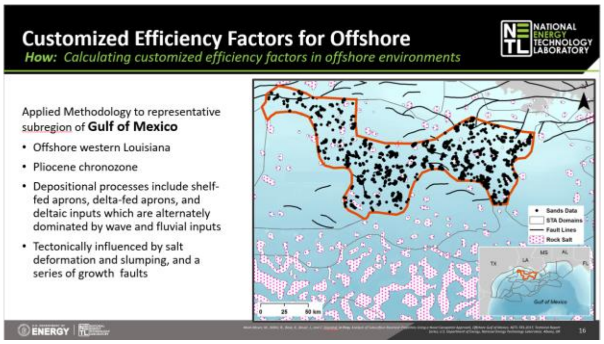
a) Resources for STA b) Domain Postulation c) Domain Validation d) Advanced Analyses

Rose, Bauer, Mark-Moser, *in review*, Subsurface Trend Analysis, a Multi-Variate Geospatial Approach for Evaluation of Geologic Properties and Uncertainty Reduction, *Interpretation.*



Visual subsurface influences per domain

- Analysis is completed for each domain
- Assessed at both spatial and temporal trends, illustrated here with representative ternaries

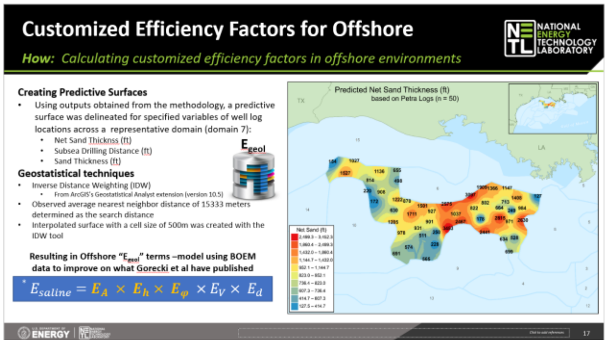


Customized Efficiency Factors for Offshore

***How:** Calculating customized efficiency factors in offshore environments*

Applied Methodology to representative subregion of **Gulf of Mexico**

- Offshore western Louisiana
- Pliocene chronozone
- Depositional processes include shelf-fed aprons, delta-fed aprons, and deltaic inputs which are alternately dominated by wave and fluvial inputs
- Tectonically influenced by salt deformation and slumping, and a series of growth faults



Customized Efficiency Factors for Offshore

***How:** Calculating customized efficiency factors in offshore environments*

Creating Predictive Surfaces

- Using outputs obtained from the methodology, a predictive surface was delineated for specified variables of well log locations across a representative domain (domain 7):
  - Net Sand Thicknss (ft)
  - Subsea Drilling Distance (ft)
  - Sand Thickness (ft)

E_{geol}

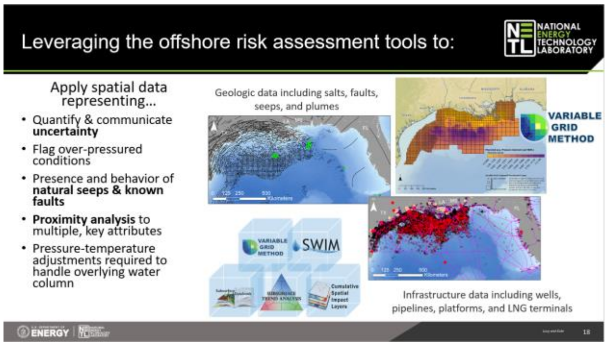
Geostatistical techniques

- Inverse Distance Weighting (IDW)
  - From ArcGIS's Geostatistical Analyst extension (version 10.5)
- Observed average nearest neighbor distance of 15333 meters determined as the search distance
- Interpolated surface with a cell size of 500m was created with the IDW tool

Resulting in Offshore "E_{geol}" terms –model using BOEM data to improve on what Gorecki et al have published

$$^{*}E_{saline} = E_A \times E_h \times E_\varphi \times E_V \times E_d$$

Predicted Net Sand Thickness (ft) based on Petra Logs (n = 50)



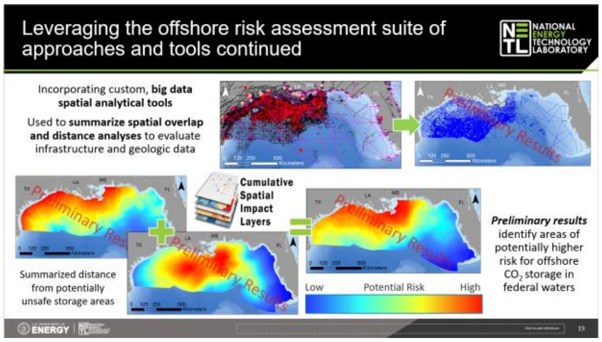
Leveraging the offshore risk assessment tools to:

Apply spatial data representing…

- Quantify & communicate **uncertainty**
- Flag over-pressured conditions
- Presence and behavior of **natural seeps & known faults**
- **Proximity analysis** to multiple, key attributes
- Pressure-temperature adjustments required to handle overlying water column

Geologic data including salts, faults, seeps, and plumes

Infrastructure data including wells, pipelines, platforms, and LNG terminals



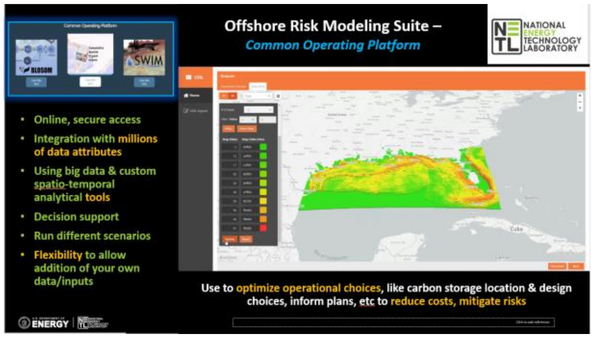
Leveraging the offshore risk assessment suite of approaches and tools continued

Incorporating custom, **big data spatial analytical tools**

Used to **summarize spatial overlap and distance analyses** to evaluate infrastructure and geologic data

Summarized distance from potentially unsafe storage areas

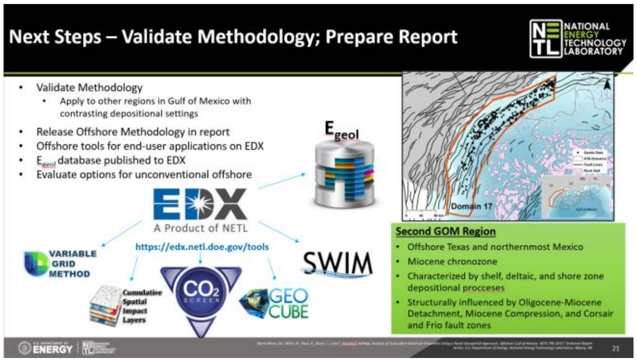
Preliminary results identify areas of potentially higher risk for offshore CO_2 storage in federal waters



Offshore Risk Modeling Suite – *Common Operating Platform*

- Online, secure access
- Integration with millions of data attributes
- Using big data & custom spatio-temporal analytical tools
- Decision support
- Run different scenarios
- Flexibility to allow addition of your own data/inputs

Use to optimize operational choices, like carbon storage location & design choices, inform plans, etc to reduce costs, mitigate risks

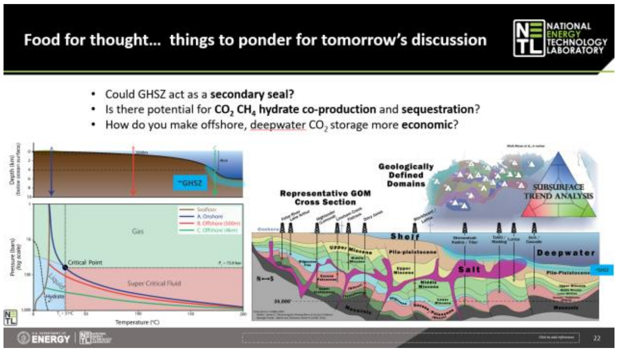


Next Steps – Validate Methodology; Prepare Report

- Validate Methodology
  - Apply to other regions in Gulf of Mexico with contrasting depositional settings
- Release Offshore Methodology in report
- Offshore tools for end-user applications on EDX
- E_{geol} database published to EDX
- Evaluate options for unconventional offshore

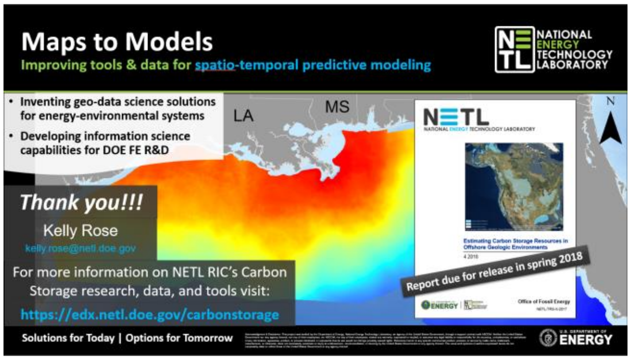
Second GOM Region

- Offshore Texas and northernmost Mexico
- Miocene chronozone
- Characterized by shelf, deltaic, and shore zone depositional procceses
- Structurally influenced by Oligocene-Miocene Detachment, Miocene Compression, and Corsair and Frio fault zones



Food for thought… things to ponder for tomorrow's discussion

- Could GHSZ act as a **secondary seal?**
- Is there potential for **CO_2 CH_4 hydrate co-production** and **sequestration**?
- How do you make offshore, deepwater CO_2 storage more **economic**?



Maps to Models

Improving tools & data for spatio-temporal predictive modeling

- Inventing geo-data science solutions for energy-environmental systems
- Developing information science capabilities for DOE FE R&D

Thank you!!!

Kelly Rose

kelly.rose@netl.doe.gov

For more information on NETL RIC's Carbon Storage research, data, and tools visit:

https://edx.netl.doe.gov/carbonstorage

Report due for release in spring 2018

Solutions for Today | Options for Tomorrow

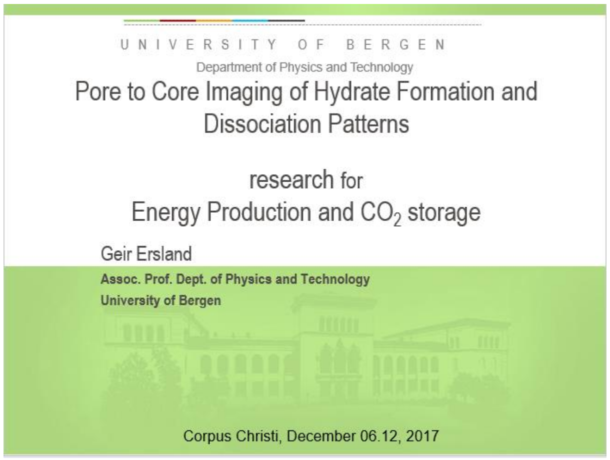
Pore-to-Core Imaging of Hydrate formation and dissociation patterns

Geir Ersland*, Stian Almenningen, Martin Fernø and Arne Graue

Department of Physics and Technology, University of Bergen, Bergen, Norway

*e-mail: Geir.Ersland@uib.no<mailto:Geir.Ersland@uib.no>

We report on visualization of CO2 and CH4 gas hydrate formation and dissociation patterns within porous sandstone using MRI and micromodels with sandstone pore shapes and sizes. The effect of salinity and saturation is identified on both scales. Direct observations of hydrate phase transition patterns in pores using micromodels at reservoir conditions provides an improved understanding of sedimentary gas hydrate and how such system respond to pressure depletion and thermal stimulation.



UNIVERSITY OF BERGEN

Department of Physics and Technology

Pore to Core Imaging of Hydrate Formation and Dissociation Patterns

research for

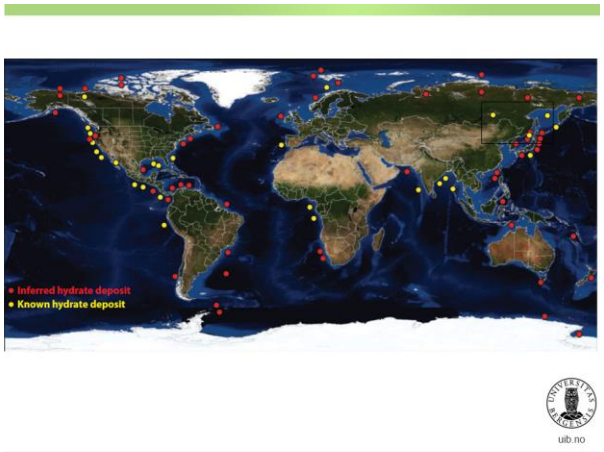
Energy Production and CO_2 storage

Geir Ersland

Assoc. Prof. Dept. of Physics and Technology

University of Bergen

Corpus Christi, December 06.12, 2017



• Inferred hydrate deposit

• Known hydrate deposit

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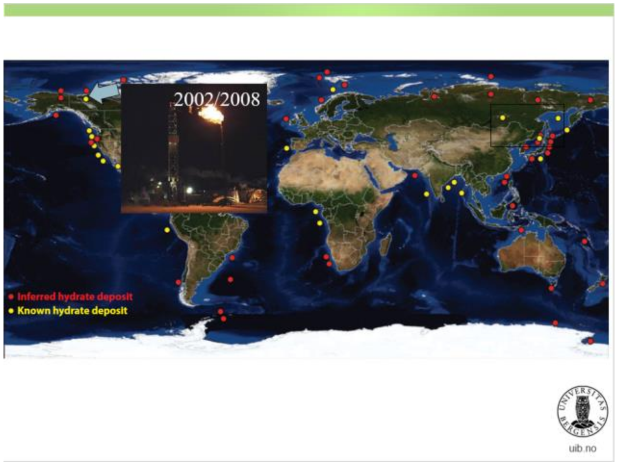

2002/2008

• Inferred hydrate deposit

• Known hydrate deposit

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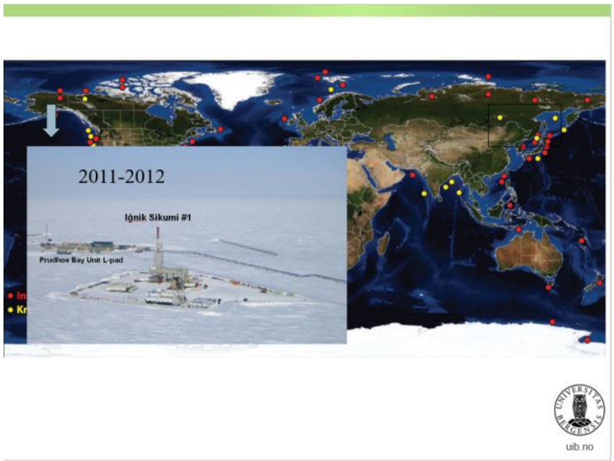

2011-2012

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2013 offshore Japan

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2017

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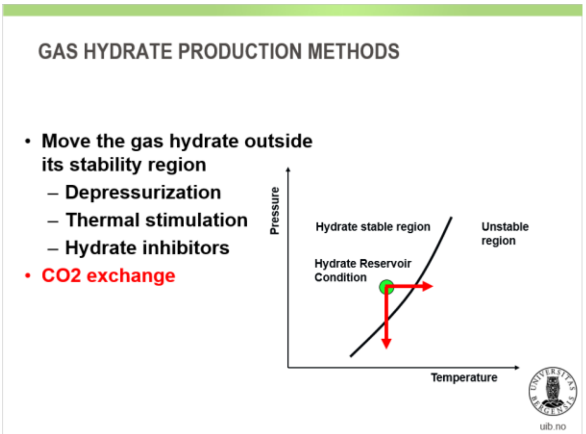

GAS HYDRATE PRODUCTION METHODS

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

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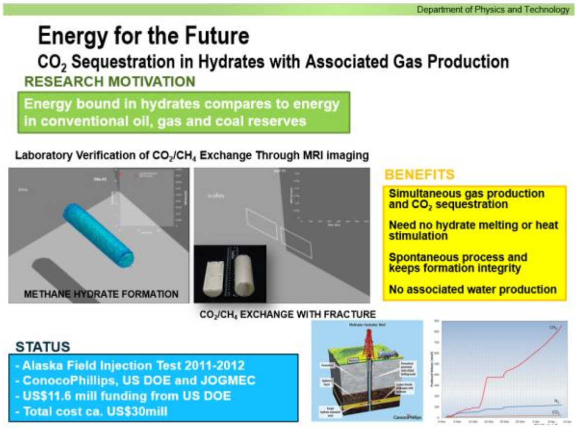


Department of Physics and Technology

Energy for the Future

CO_2 Sequestration in Hydrates with Associated Gas Production

RESEARCH MOTIVATION

Energy bound in hydrates compares to energy in conventional oil, gas and coal reserves

Laboratory Verification of CO_2/CH_4 Exchange Through MRI imaging

BENEFITS

Simultaneous gas production and CO_2 sequestration

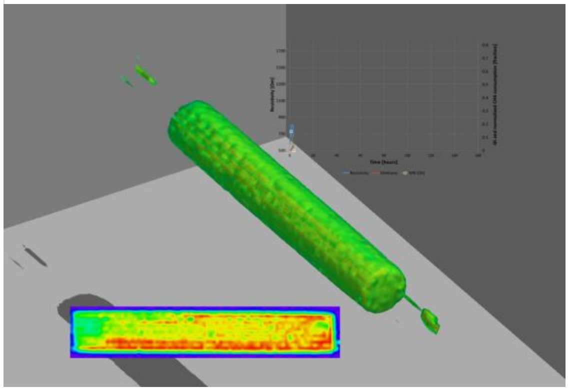
Need no hydrate melting or heat stimulation

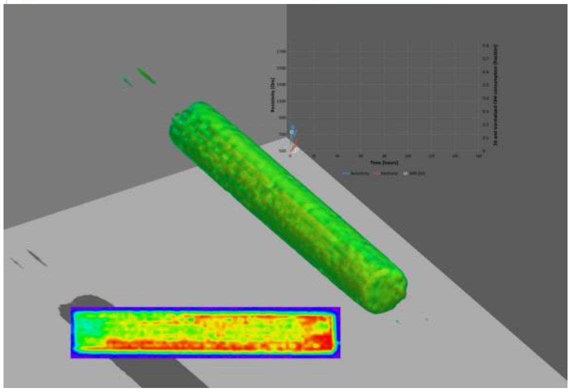
Spontaneous process and keeps formation integrity

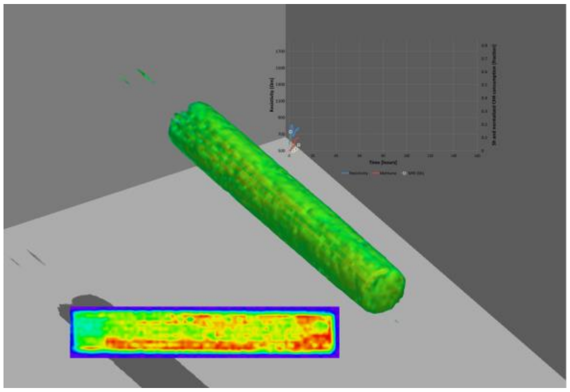
No associated water production

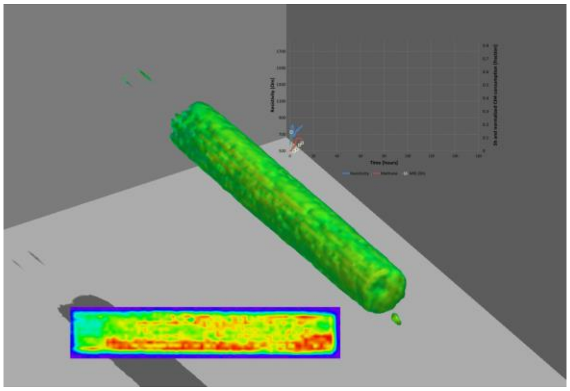
STATUS

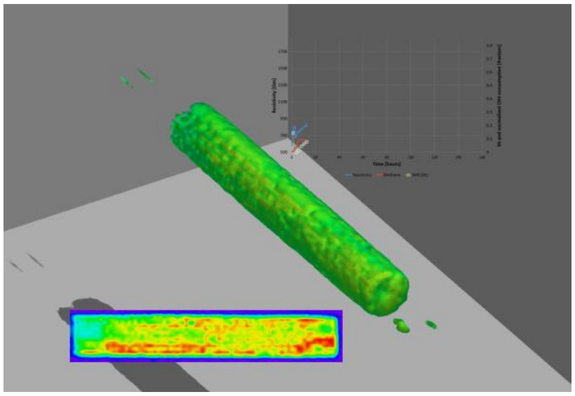
- Alaska Field Injection Test 2011-2012
- ConocoPhillips, US DOE and JOGMEC
- US$11.6 mill funding from US DOE
- Total cost ca. US$30mill

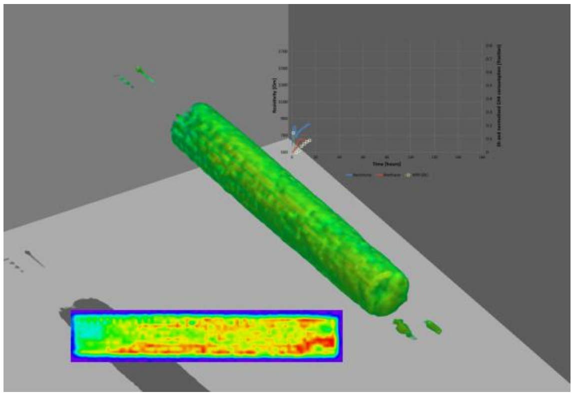


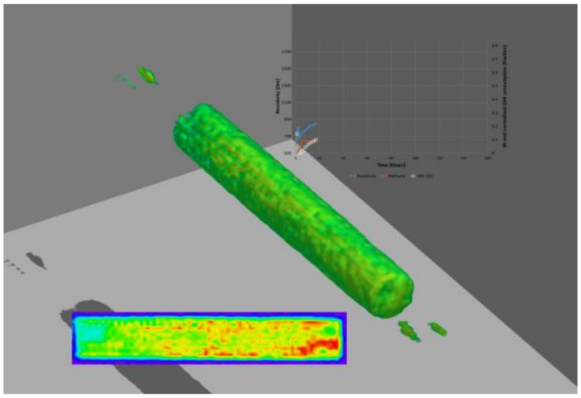


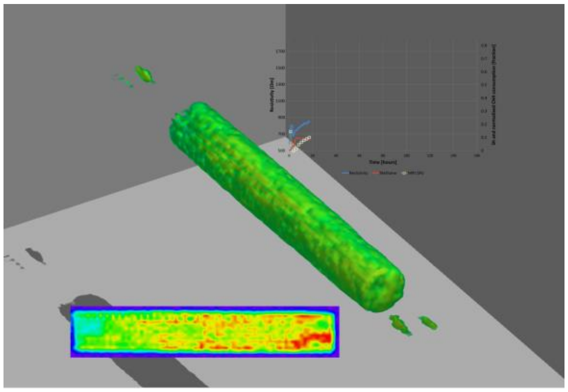


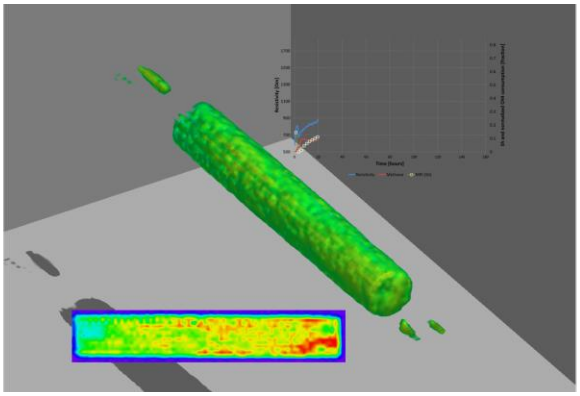


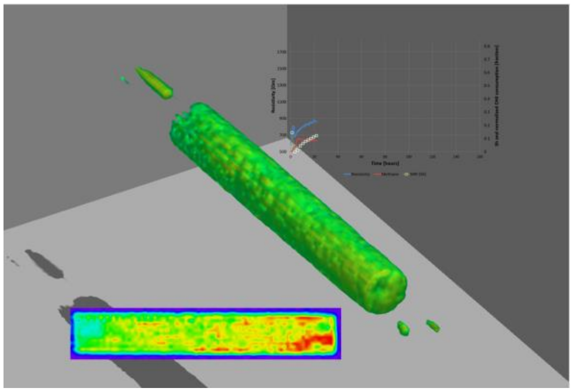


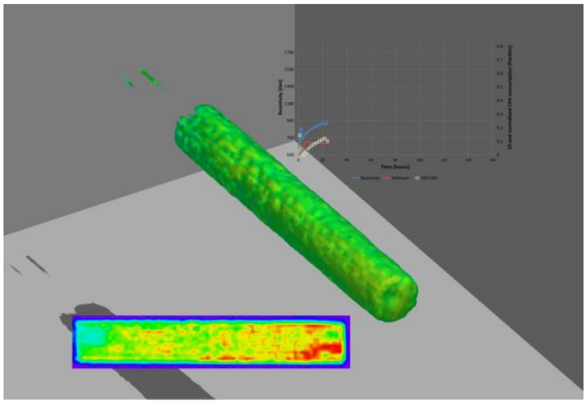


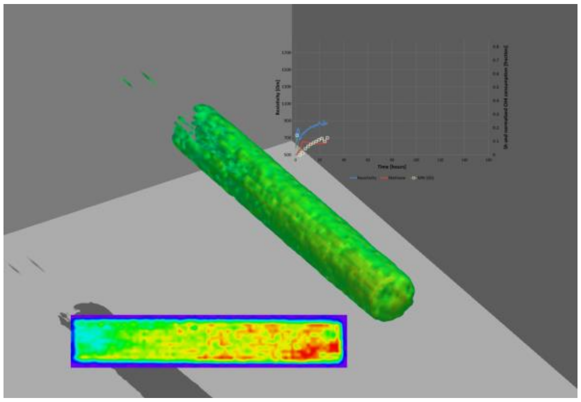


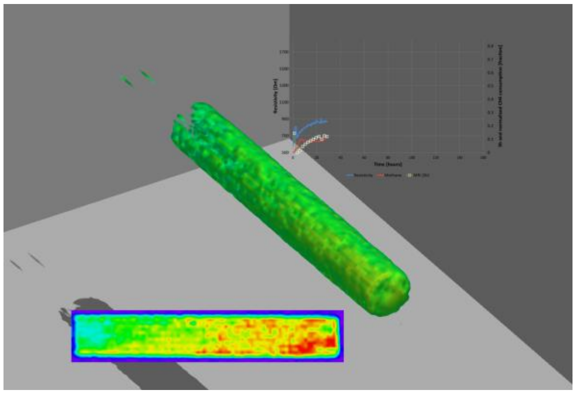
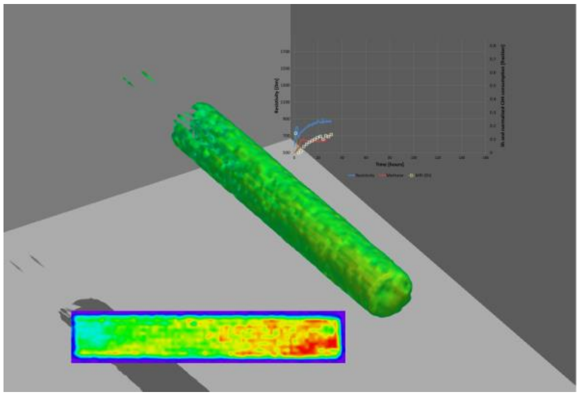
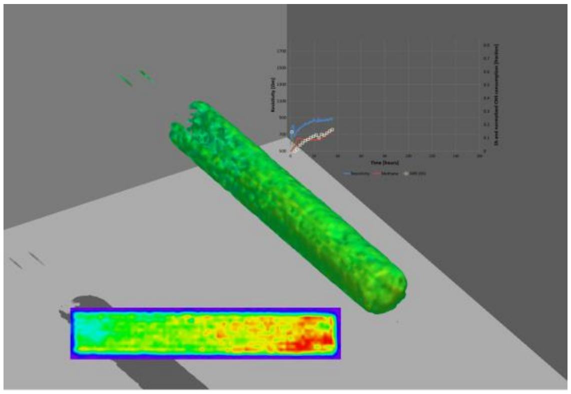
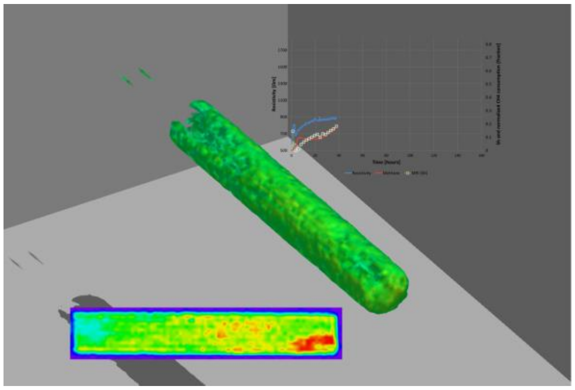
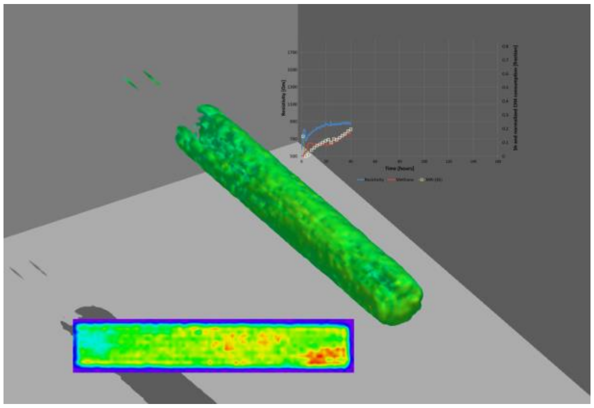
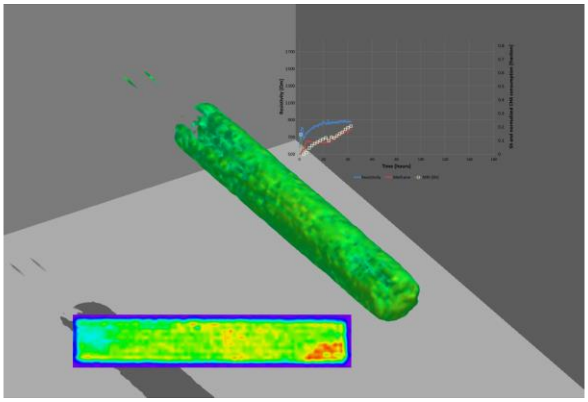
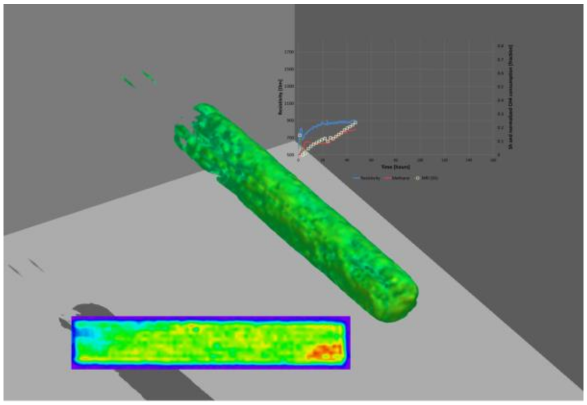
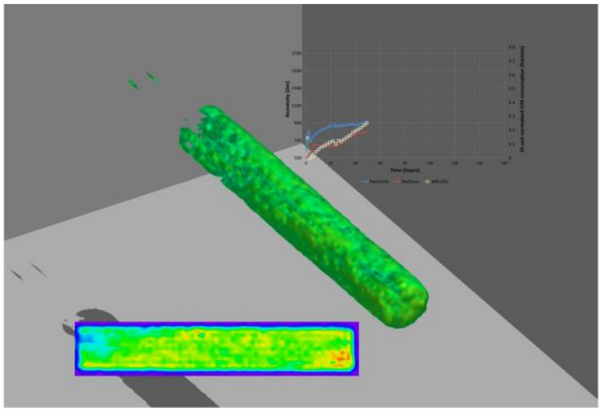


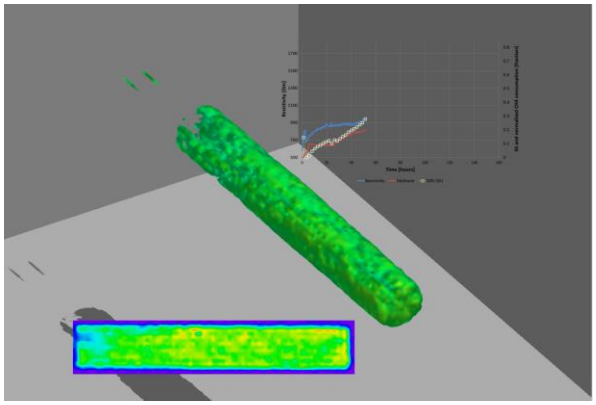


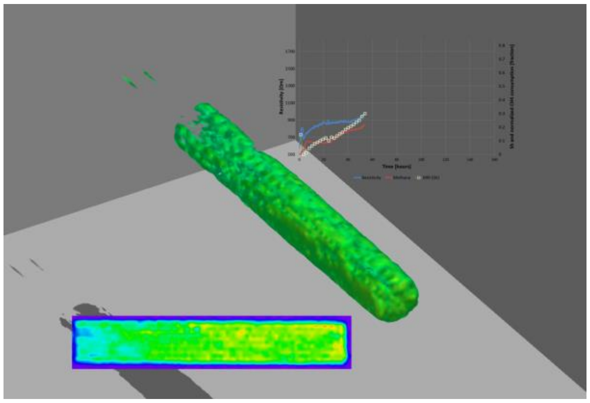


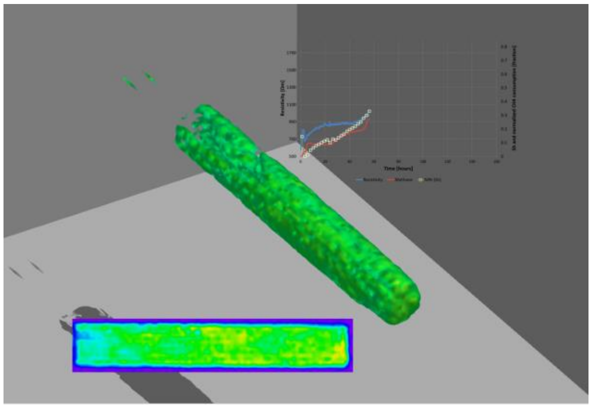


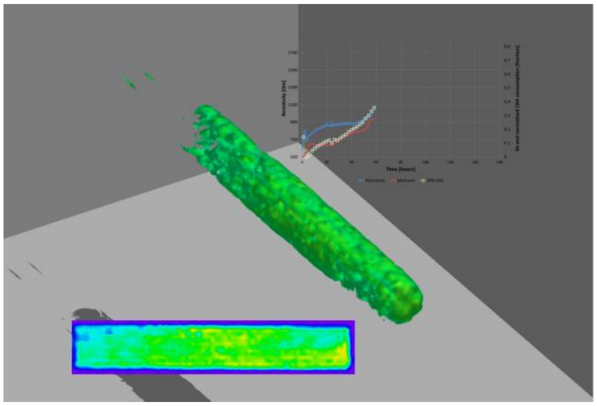


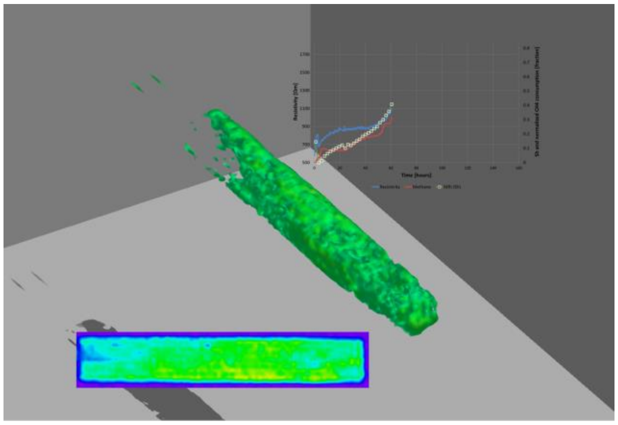










Time [hours]
Resistivity
Methane


Time [hours]
Resistivity
Methane


Time [hours]
Resistivity
Methane


Time [hours]
Resistivity
Methane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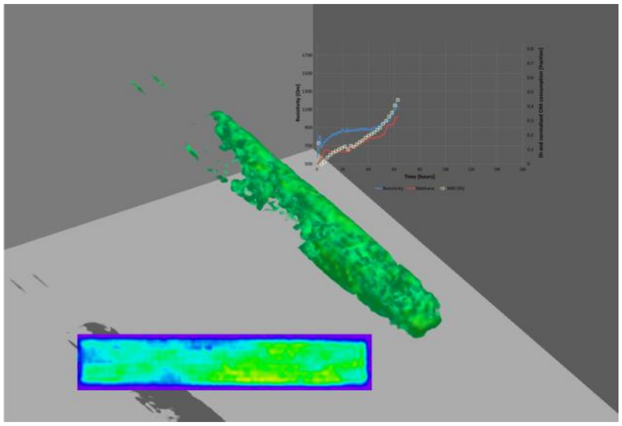
Resistivity
Methane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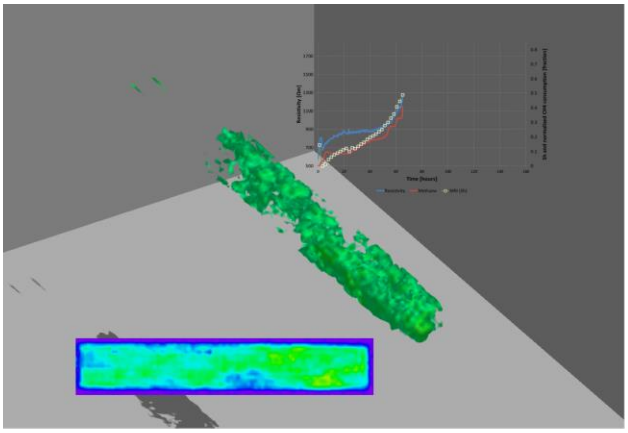
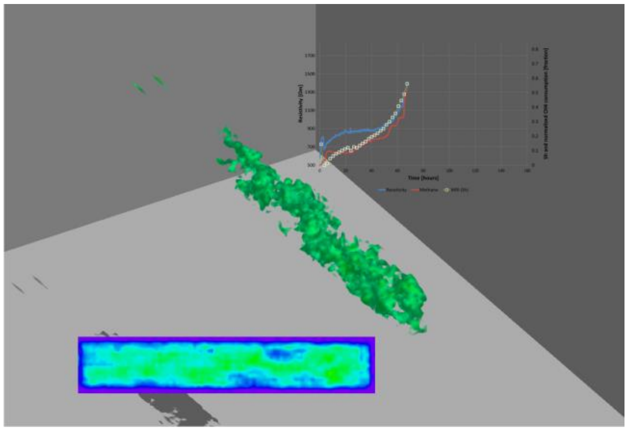
Methane


Time [hours]
Resistivity
Methane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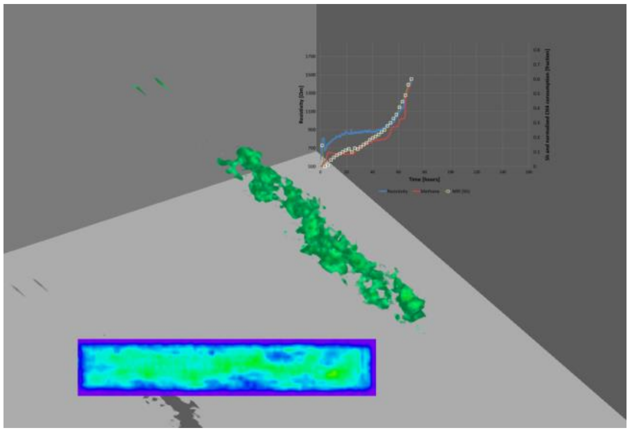
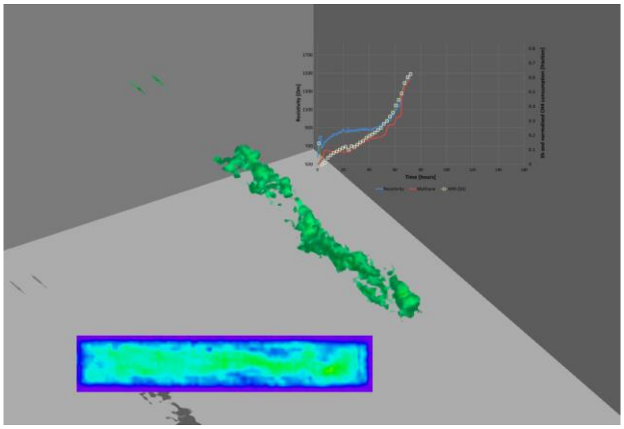
Resistivity
Methane


Resistivity [Ωm]
Time [hours]
Sh and normalized CH4 consumption [fraction]
Resistivity
Methane
MRI (Sh)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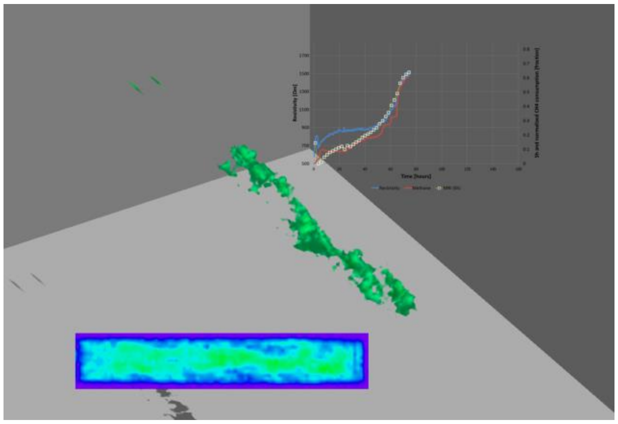
Time [hours]
Sh and normalized CH4 consumption [fraction]
Resistivity
Methane
MRI (Sh)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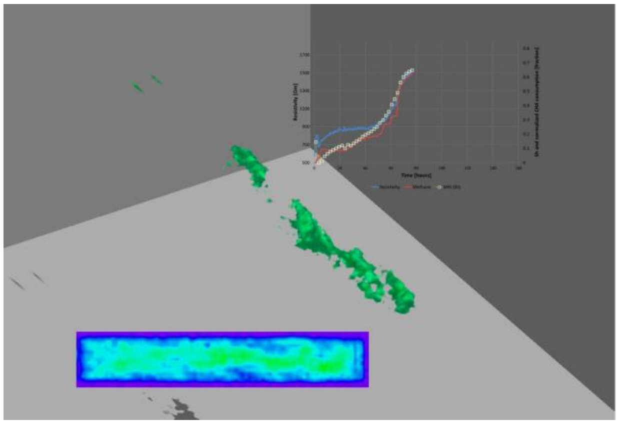
Time [hours]
Sh and normalized CH4 consumption [fraction]
Resistivity
Methane
MRI (Sh)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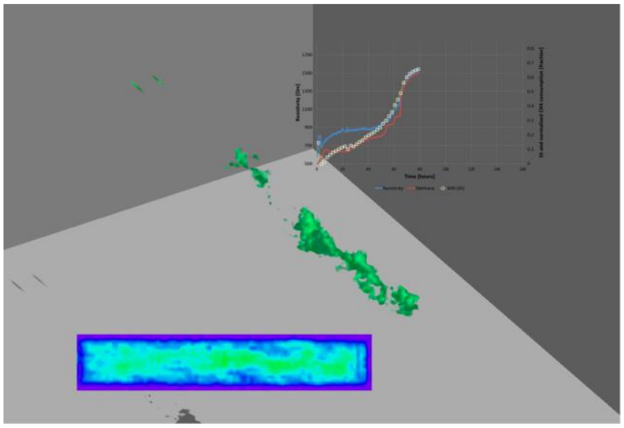
Time [hours]
Sh and normalized CH4 consumption [fraction]
Resistivity
Methane
MRI (Sh)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Time [hours]
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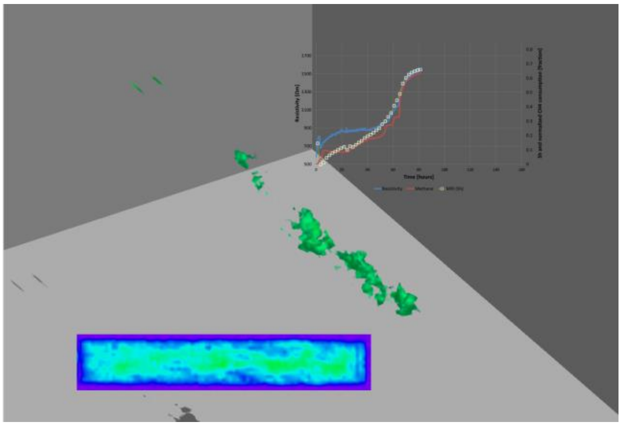
Resistivity
Methane
MRI (Sh)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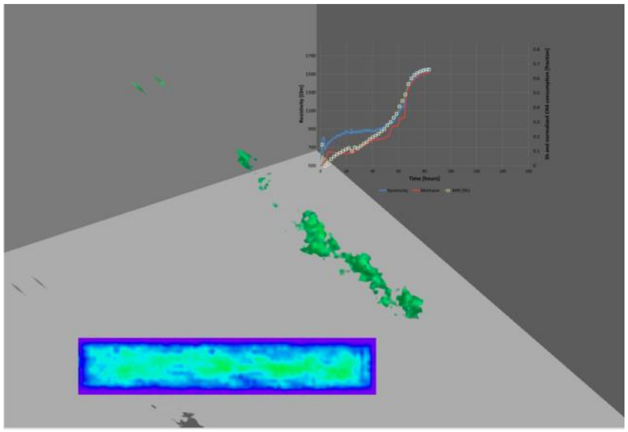
Time [hours]
Sh and normalized CH4 consumption [fraction]
Resistivity
Methane
MRI (Sh)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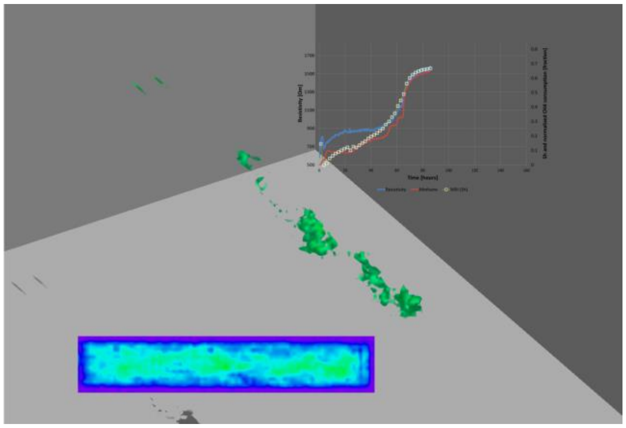
Time [hours]
Sh and normalized CH4 consumption [fraction]
Resistivity
Methane
MRI (Sh)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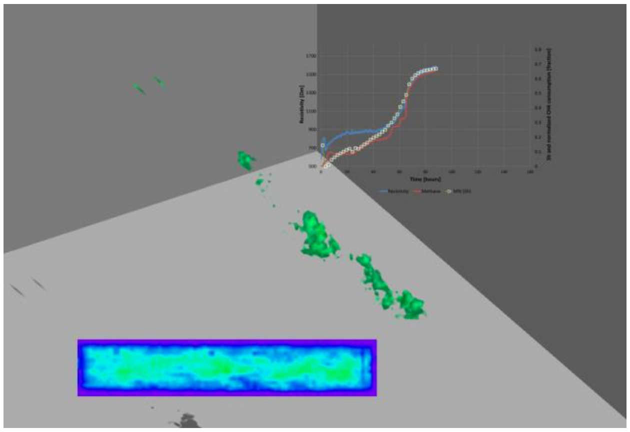
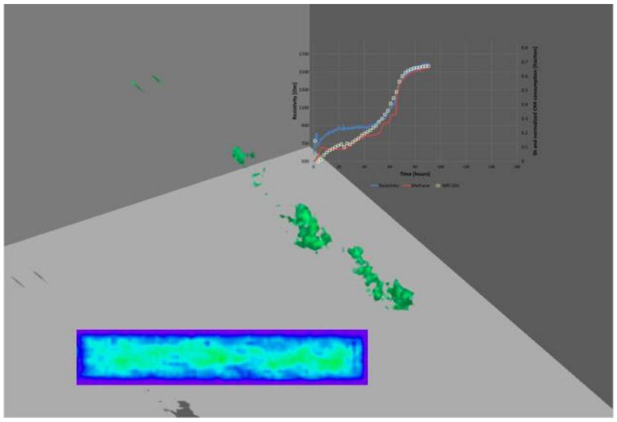
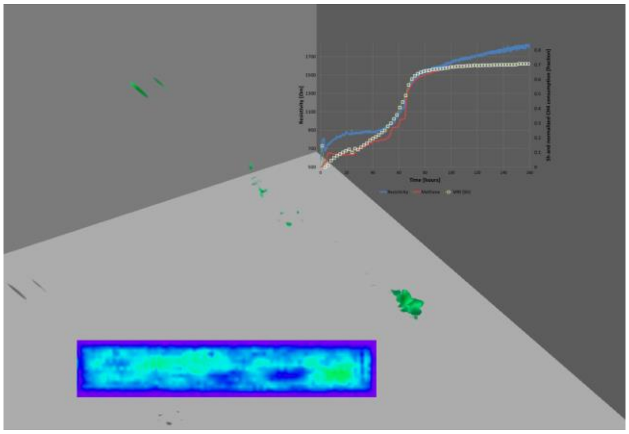
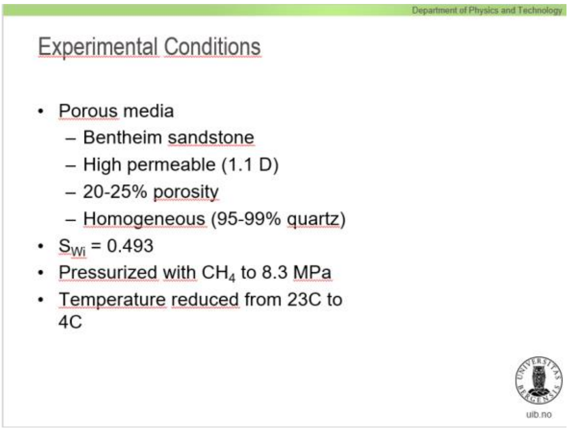
Time [hours]
Sh and normalized CH4 consumption [fraction]
Resistivity
Methane
MRI (Sh)



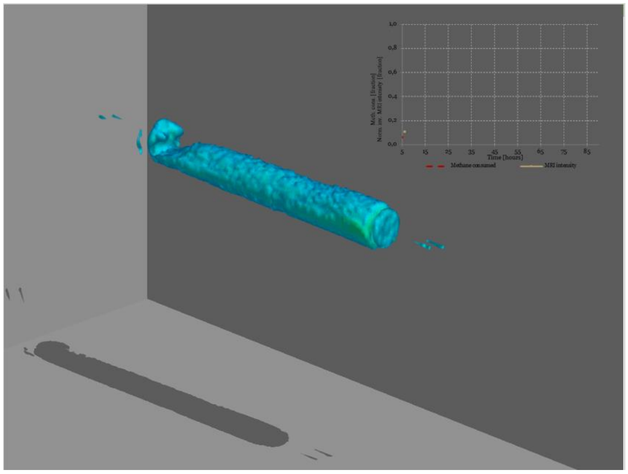


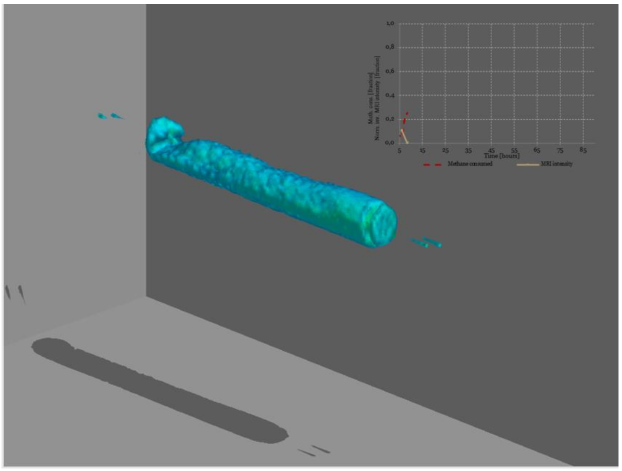


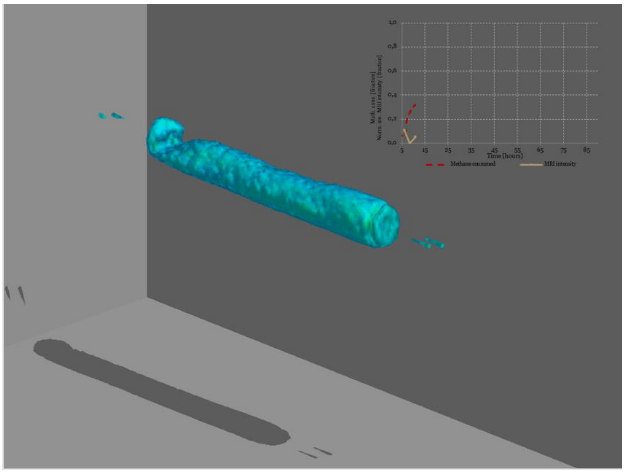


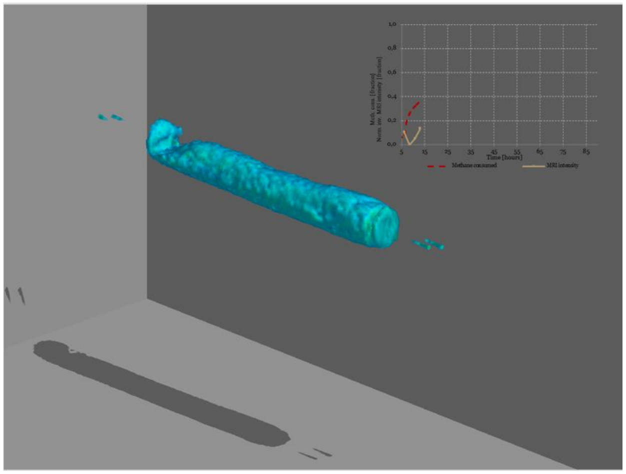
Experimental Conditions

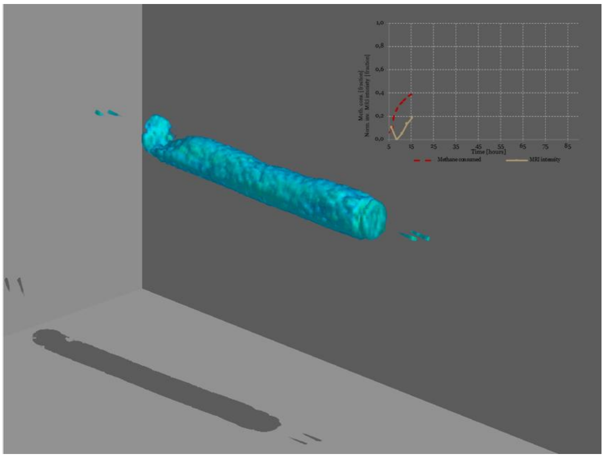
- Porous media
  - Bentheim sandstone
  - High permeable (1.1 D)
  - 20-25% porosity
  - Homogeneous (95-99% quartz)
- S_{wi} = 0.493
- Pressurized with CH_4 to 8.3 MPa
- Temperature reduced from 23C to 4C







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Meth. cons. [fraction]
Norm. inv. MRI intensity [fraction]
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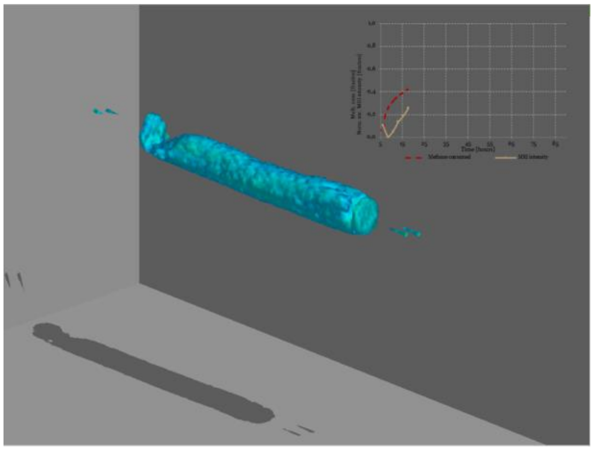
Time [hours]
Methane consumed
MRI intensity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Methane consumed
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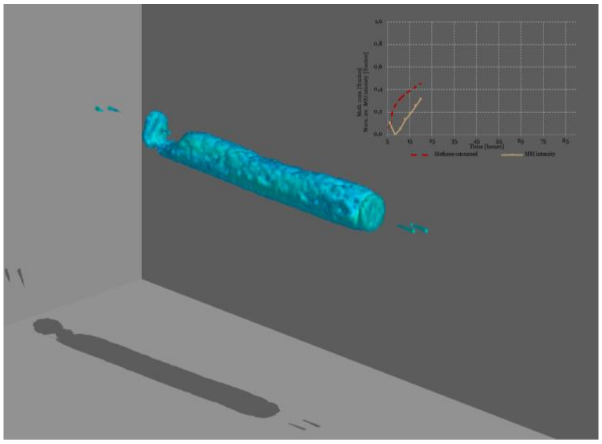
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Methane consumed
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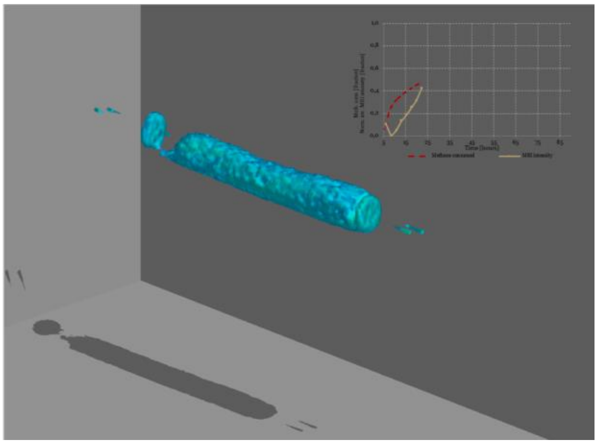
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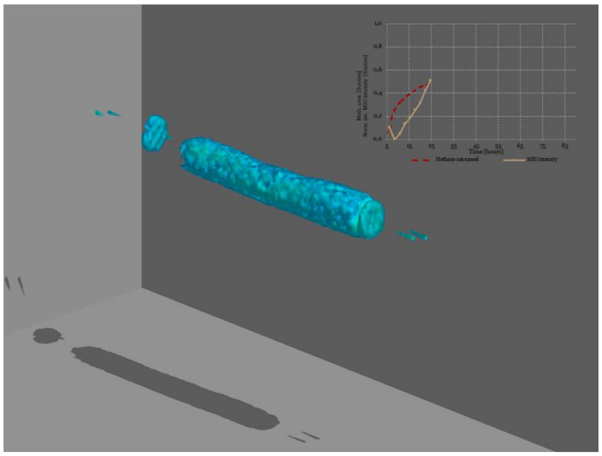
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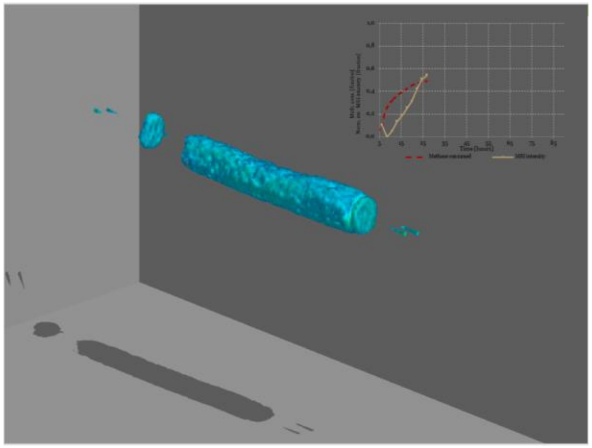
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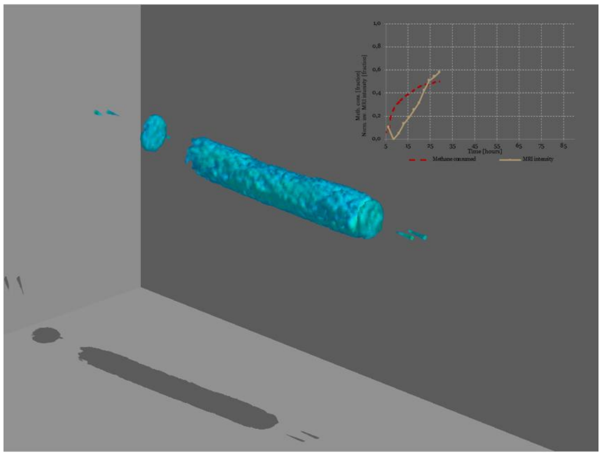
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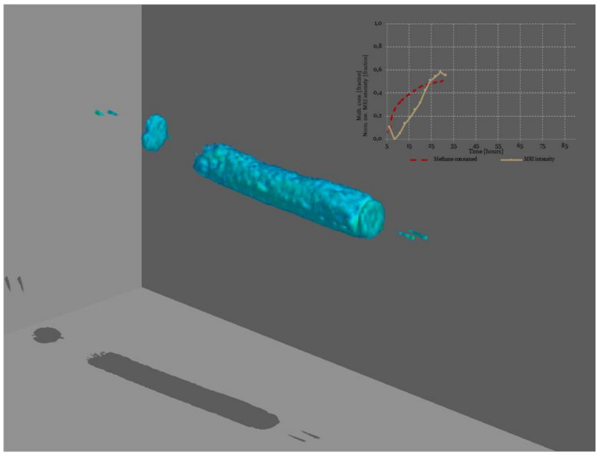
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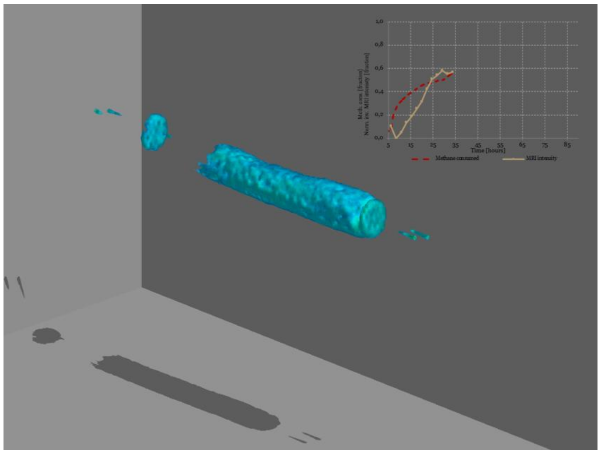
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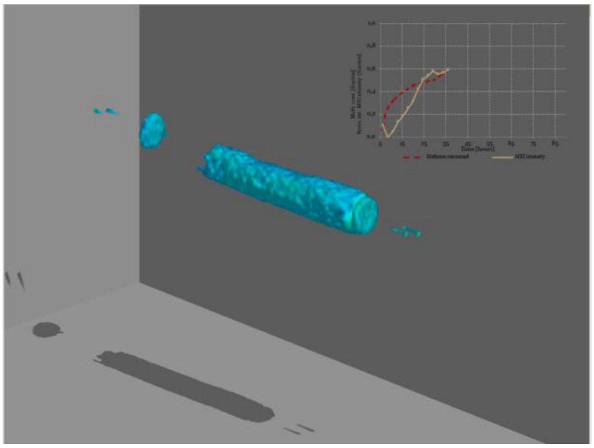
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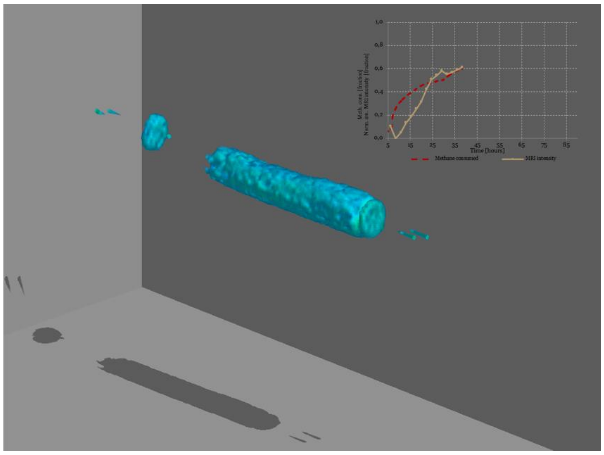
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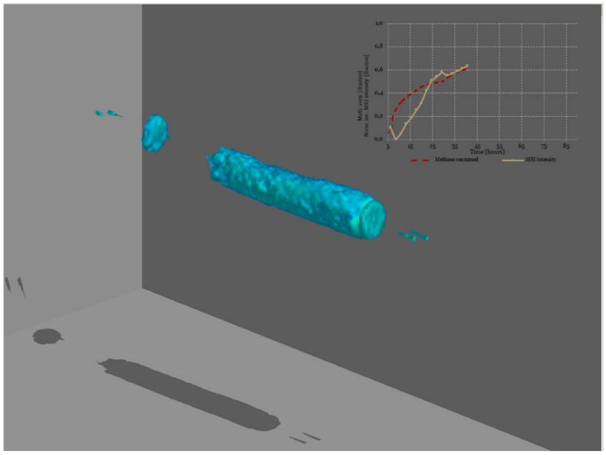
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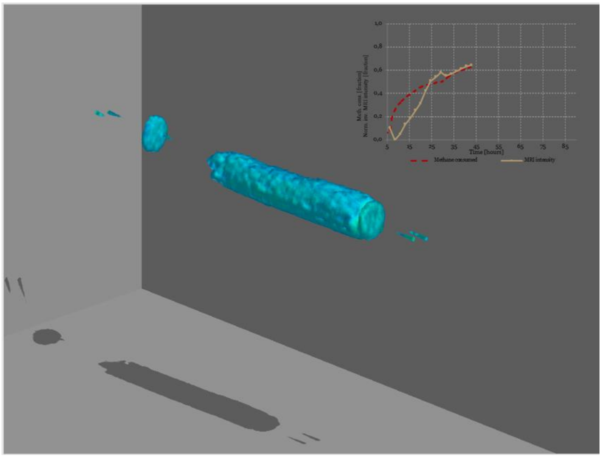
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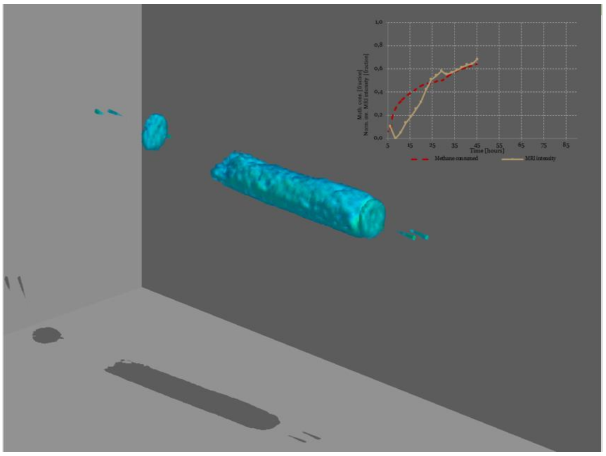
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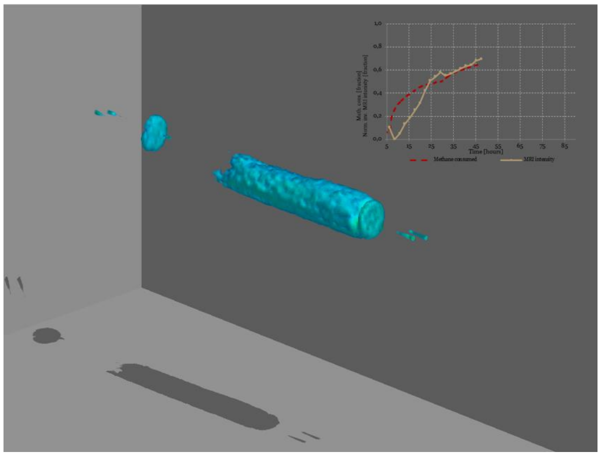
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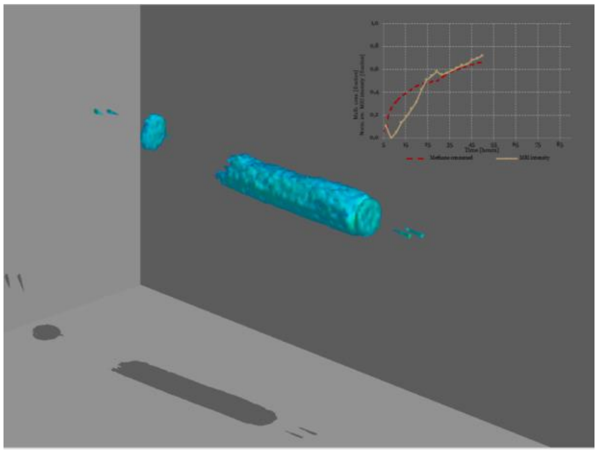
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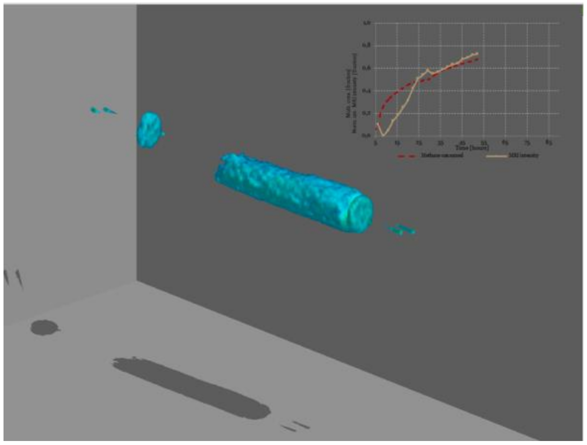
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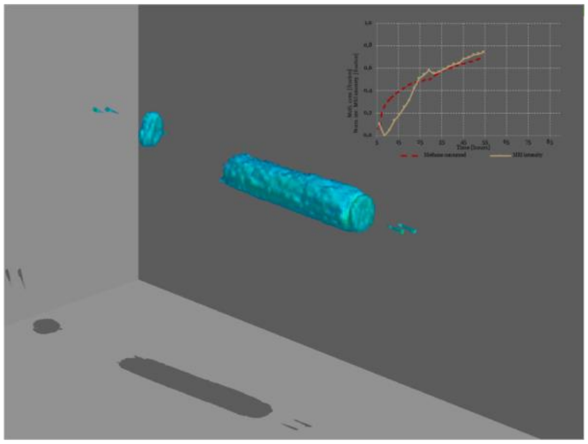
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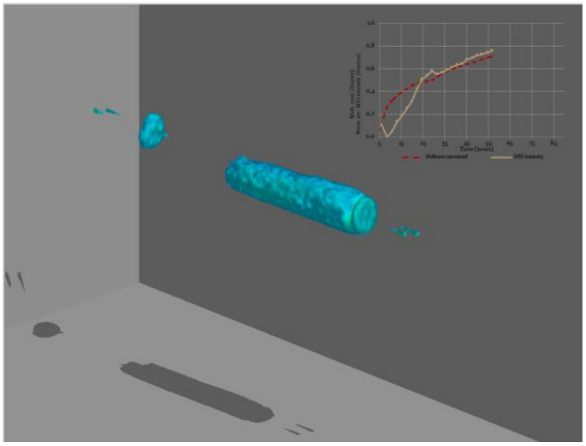
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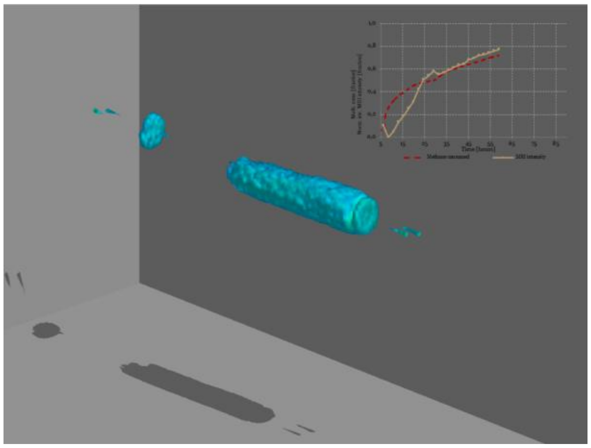
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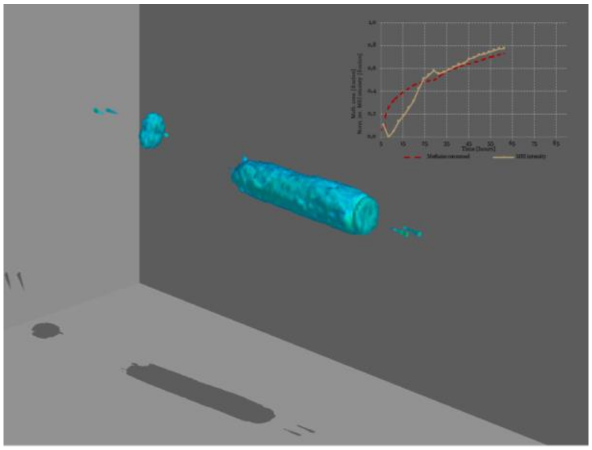
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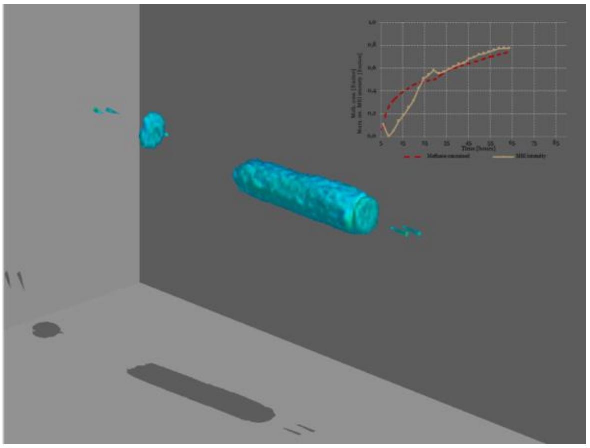

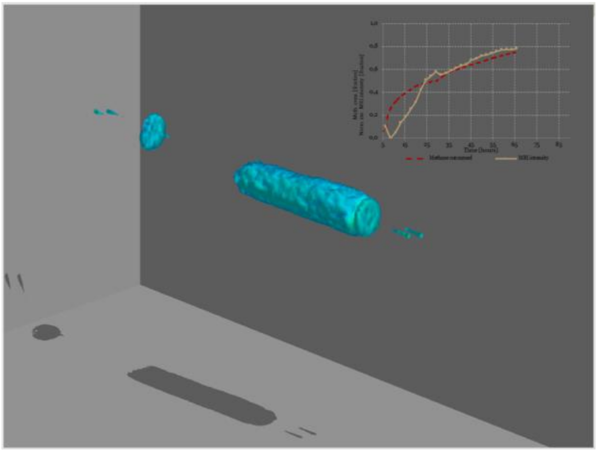

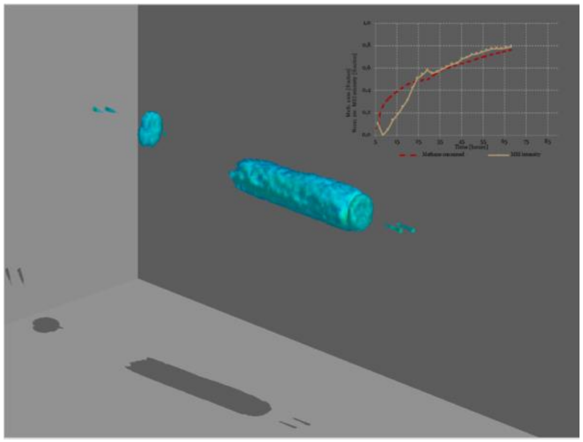

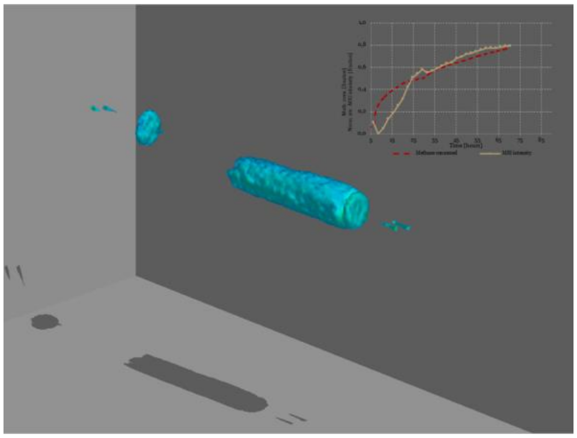

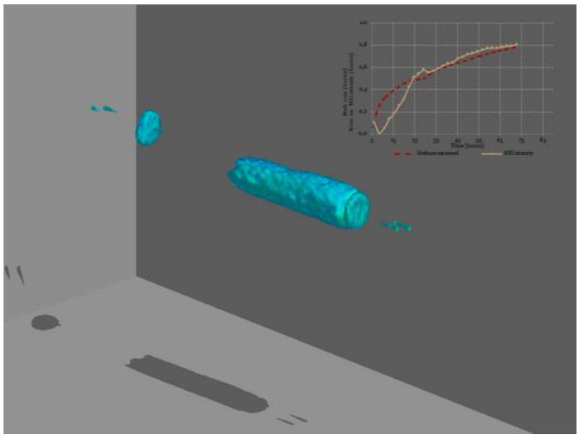

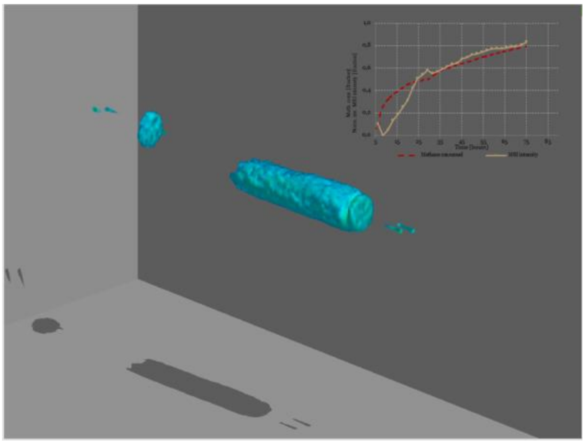

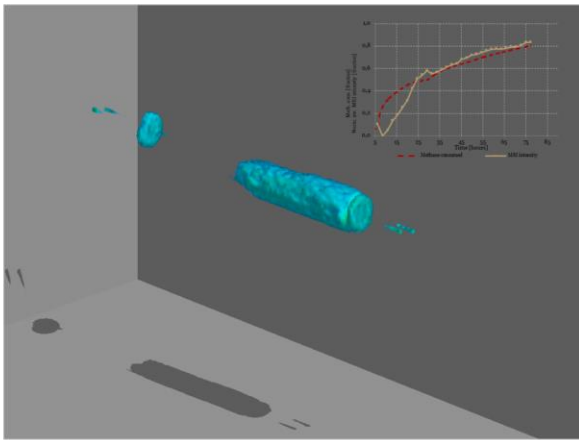

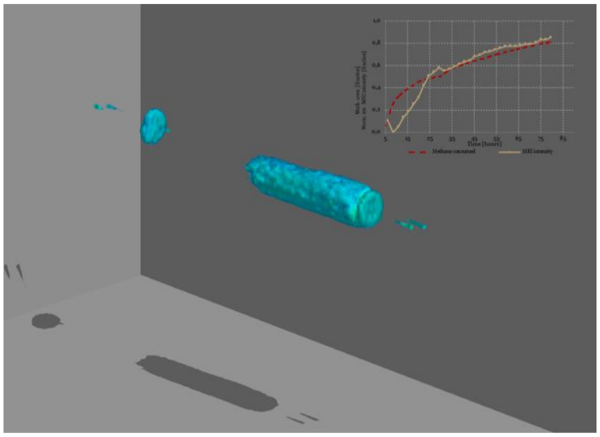

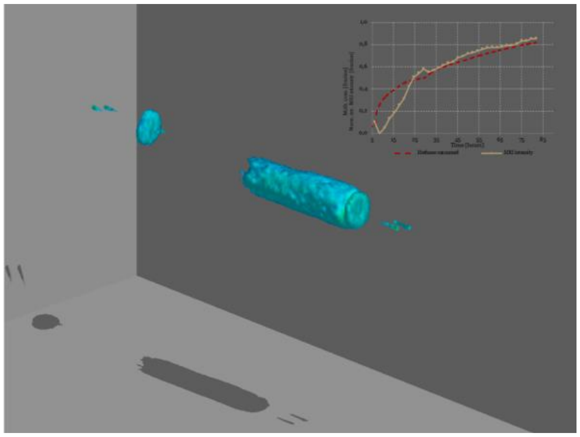

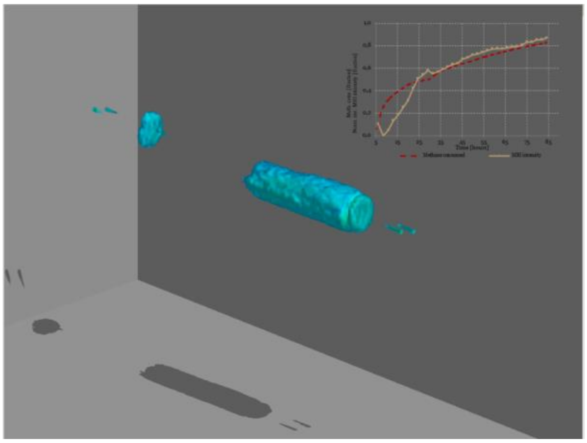

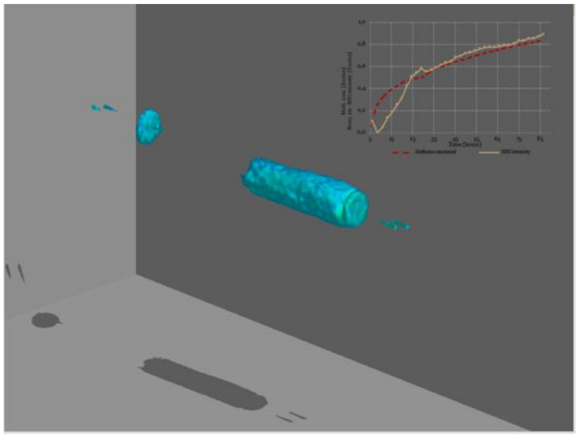

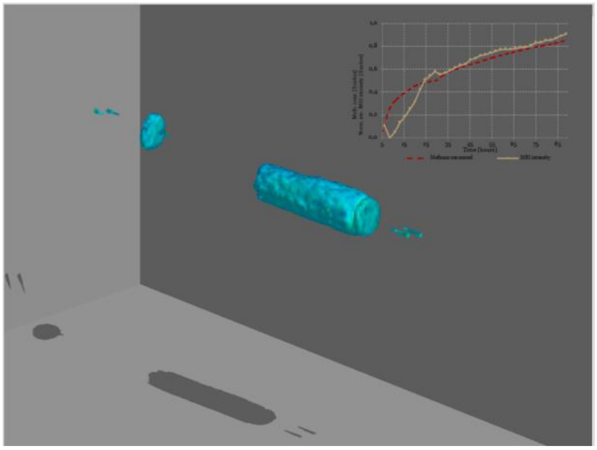

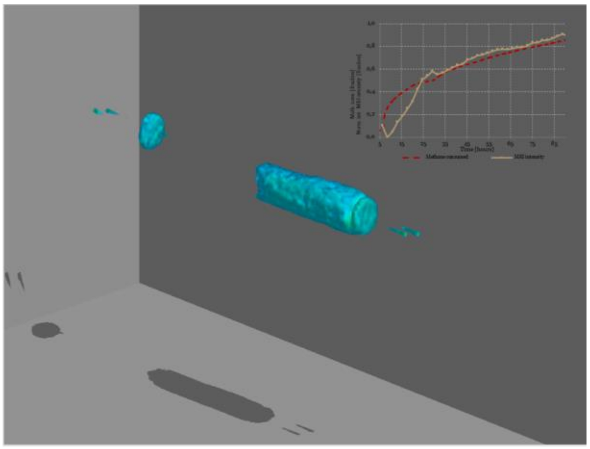

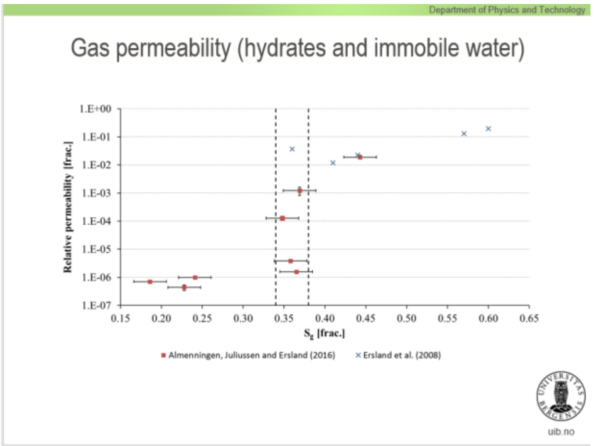

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Gas permeability (hydrates and immobile water)

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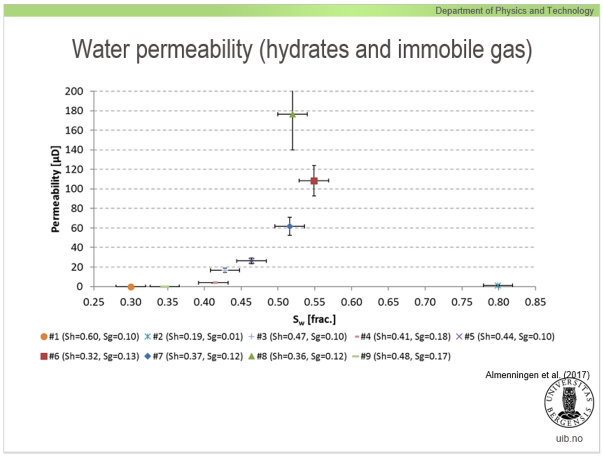

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Water permeability (hydrates and immobile gas)

Almenningen et al. (2017)

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Depressurization – Experimental procedure

- Pressure reduced and maintained above the three-phase equilibrium line
- Pressure reduced below the hydration pressure
  - Sequential pressure steps (3.96, 3.89 and 3.82 MPa)
- Dissociation quantified based on PVT and/or MRI

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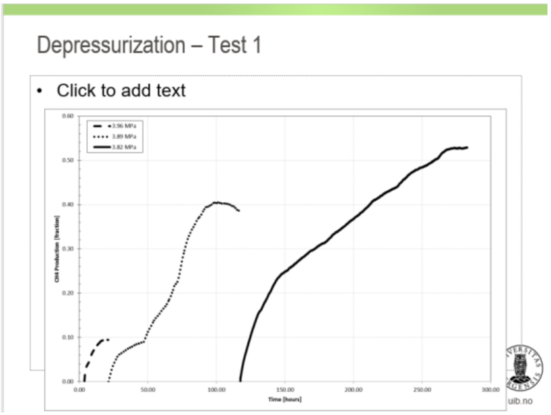
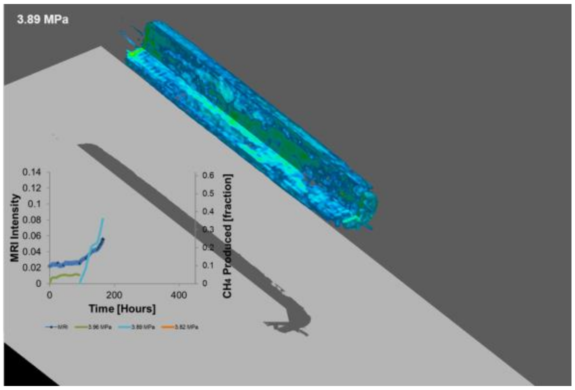
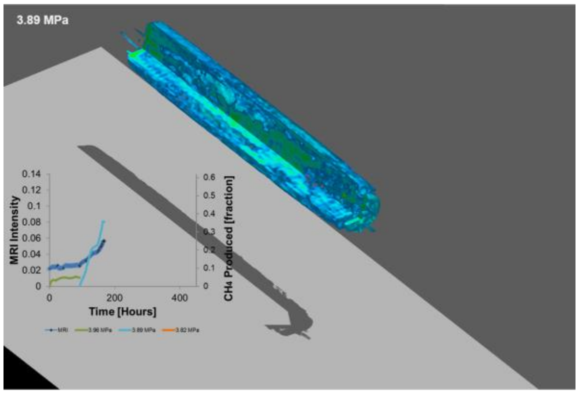


Depressurization – Test 1

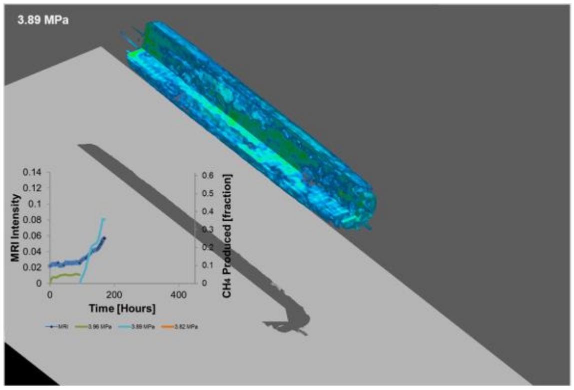
- Click to add text



3.89 MPa



3.89 MPa



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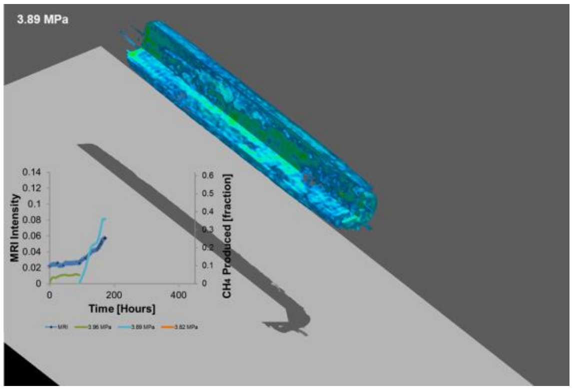

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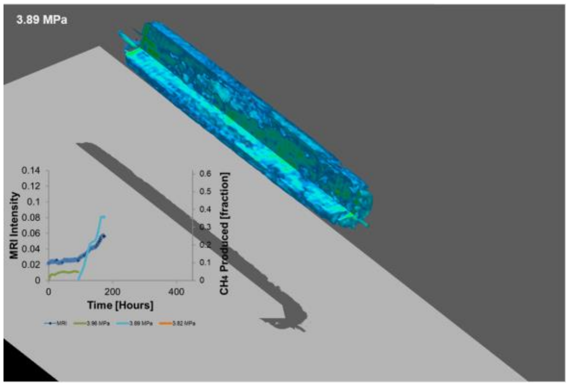

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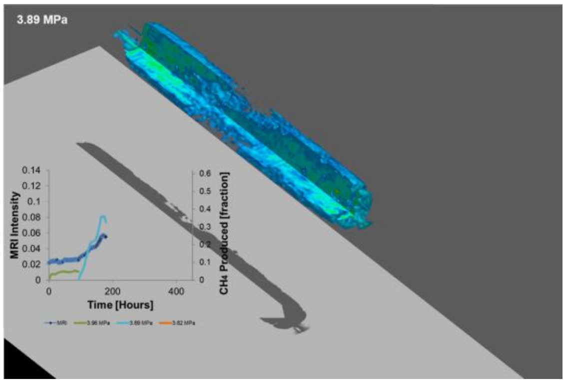

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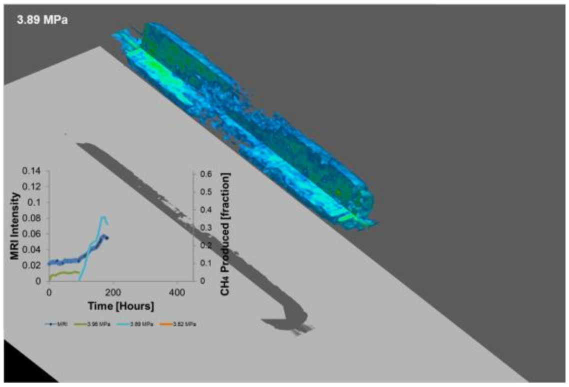
3.89 MPa
MRI Intensity
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
Time [Hours]
0
200
400
CH₄ Produced [fraction]
0.6
0.5
0.4
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0.2
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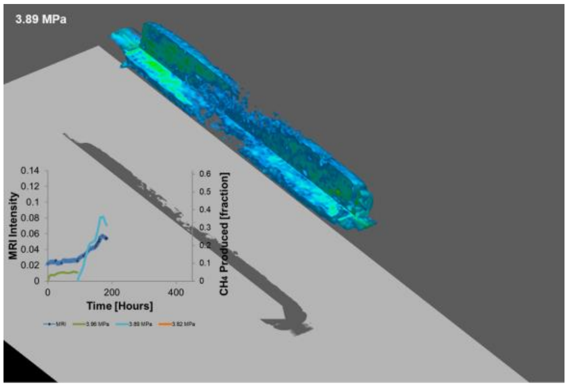
MRI
3.96 MPa
3.89 MPa
3.82 MPa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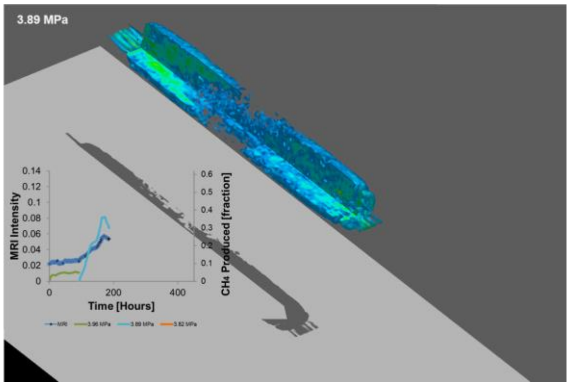
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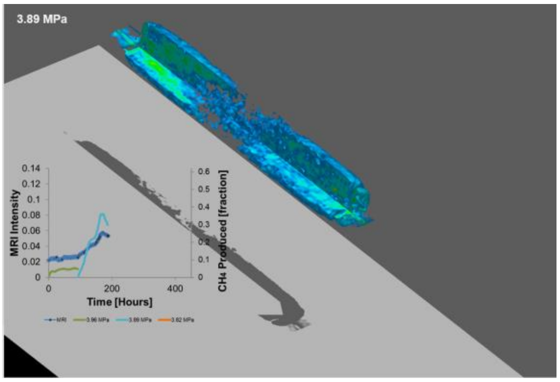
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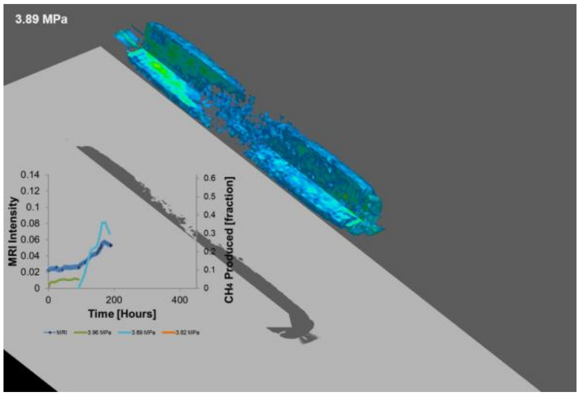
3.82 MPa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MRI
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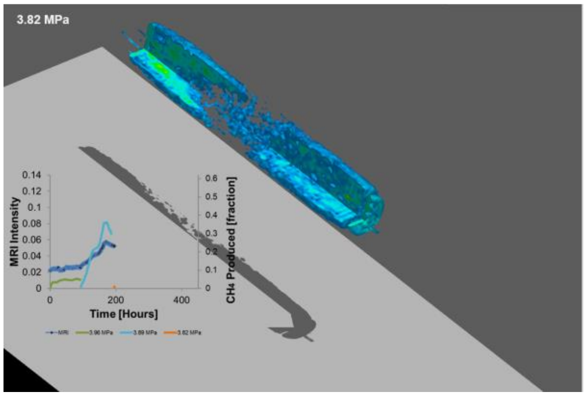
3.82 MPa
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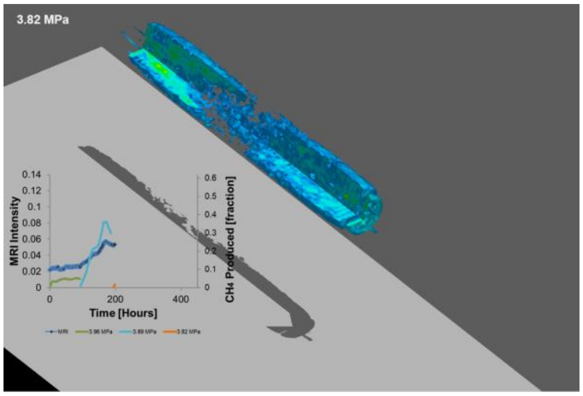
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MRI Intensity
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Time [Hours]
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CH₄ Produced [fraction]
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MRI
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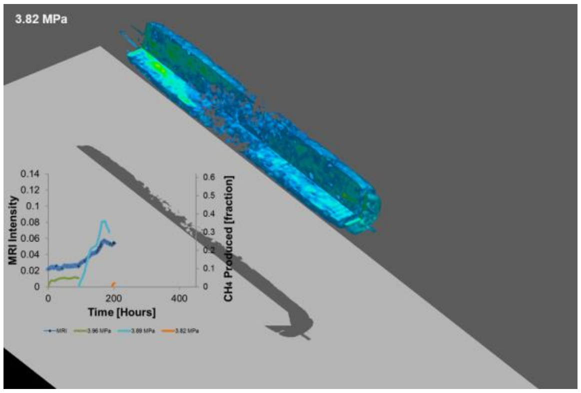
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MRI Intensity
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Time [Hours]
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CH₄ Produced [fraction]
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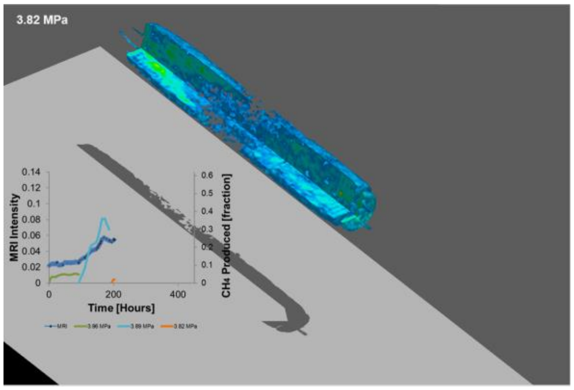

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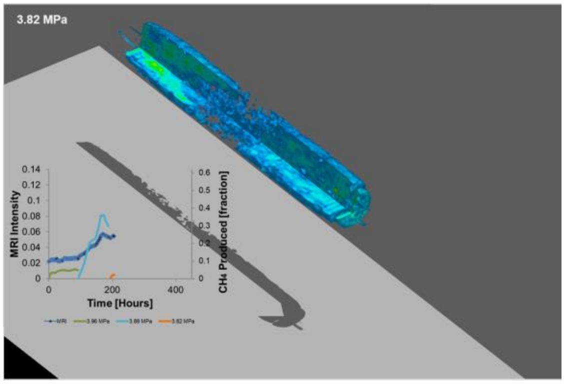

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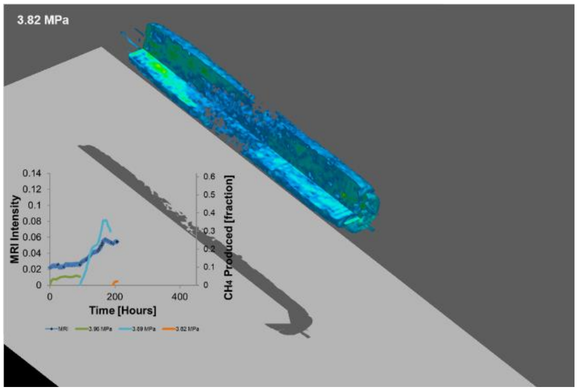

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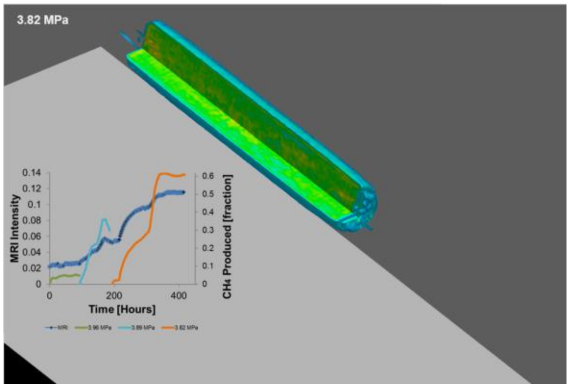
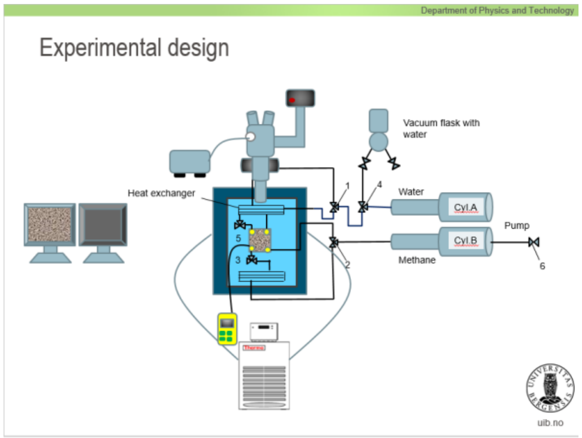


3.82 MPa



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Experimental design

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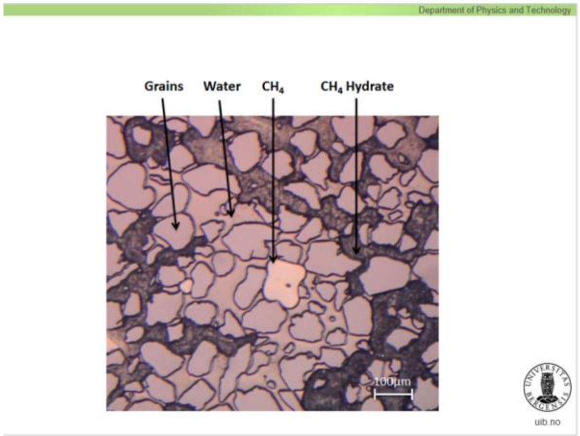

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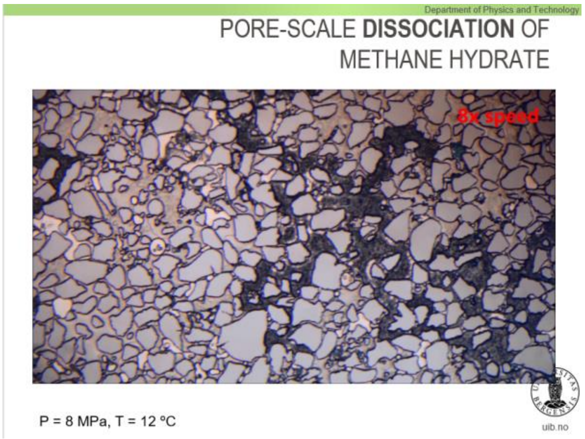

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PORE-SCALE **DISSOCIATION** OF METHANE HYDRATE

P = 8 MPa, T = 12 °C

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Hydrate formation

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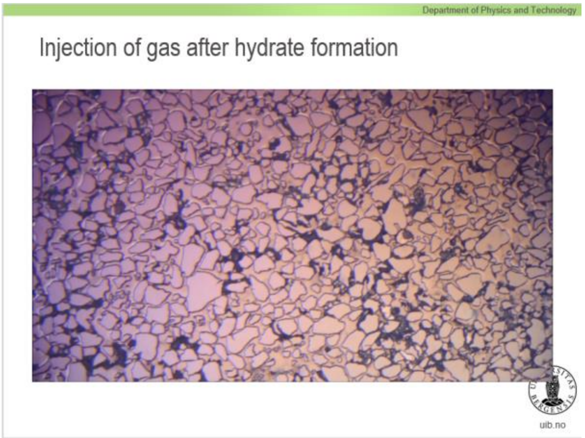

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Injection of gas after hydrate formation

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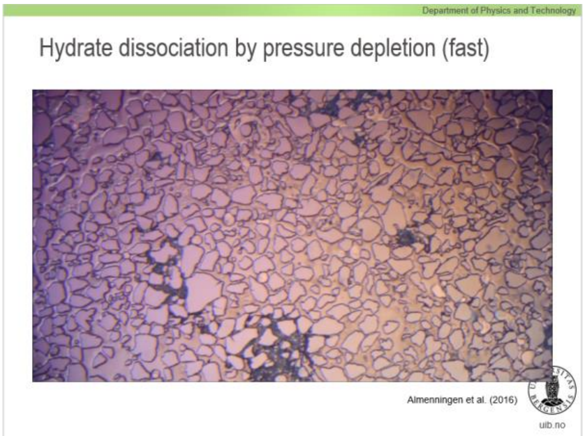

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Hydrate dissociation by pressure depletion (fast)

Almenningen et al. (2016)

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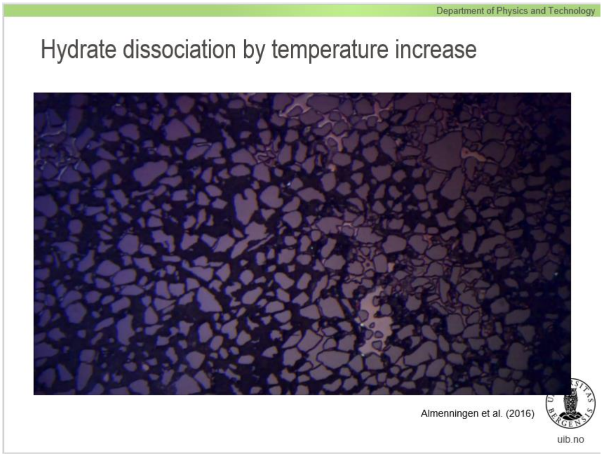

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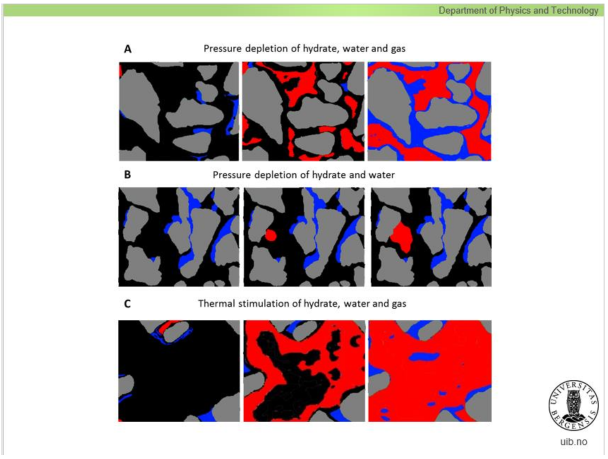
Hydrate dissociation by temperature increase

Almenningen et al. (2016)

uib.no



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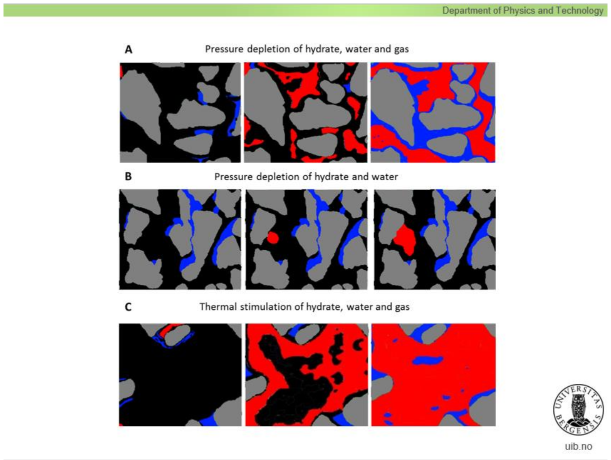

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A Pressure depletion of hydrate, water and gas

B Pressure depletion of hydrate and water

C Thermal stimulation of hydrate, water and gas

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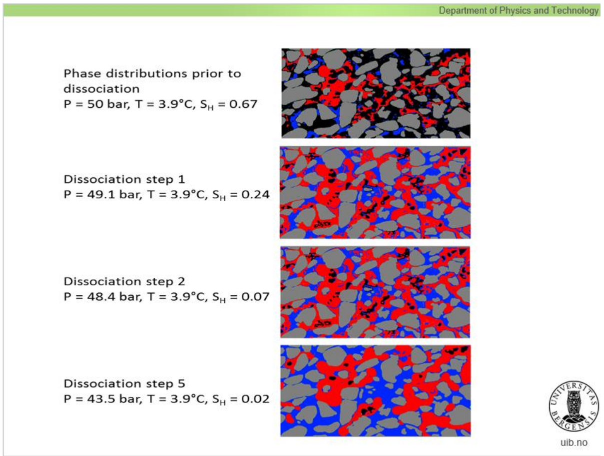

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Phase distributions prior to dissociation
P = 50 bar, T = 3.9°C, S_H = 0.67

Dissociation step 1
P = 49.1 bar, T = 3.9°C, S_H = 0.24

Dissociation step 2
P = 48.4 bar, T = 3.9°C, S_H = 0.07

Dissociation step 5
P = 43.5 bar, T = 3.9°C, S_H = 0.02

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References

- Almenningen, S. and G. Ersland. 2017. *Water permeability measurements on hydrate-saturated sandstone cores with immobile gas*. The 31th International Symposium of the Society of Core Analysts, Vienna, Austria, 27/8-1/9.
- Almenningen, S., J. Flatlandsmo, M. Fernø and G. Ersland. 2017. Multiscale Laboratory Verification of Depressurization for Production of Sedimentary Methane Hydrates. *SPE Journal* **22** (1).
- Almenningen, S., H. Juliussen and G. Ersland. 2016. *Permeability measurements on hydrate-bearing sandstone cores with excess water*. The 30th International Symposium of the Society of Core Analysts, Snowmass, Colorado, 21-26 August.
- Ersland, G., J. Husebø, A. Graue, B. Kvamme, B. Baldwin, J.J. Howard and J. Stevens. 2008. *Measurements of Gas Permeability and Non-Darcy Flow in Gas-Water Hydrate Systems*. Proceedings of the 6th International Conference on Gas Hydrates, Vancouver, Canada, 6-20 July.

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Enhancement of Gas Hydrate Reservoir Performance by Deep Depressurization below the Quadruple Point

Yoshihiro Konno[1], Yusuke Jin[2], Koya Akamine[3], Motoyoshi Naiki[3], and Norio Tenma[2]

[1]The University of Tokyo

[2]National Institute of Advanced Industrial Science and Technology (AIST)

[3]Japan Oil Engineering Co., Ltd.

Depressurization is a promising gas production method for sandy gas hydrate reservoirs; however, recovery factor is considered to be plateaued after the sensible heat of reservoir is exhausted. Heat supply is the only way to continue gas production from such low-temperature reservoirs. Although injection of heat carrier such as steam and hot water is effective, the energy profit ratio generally decreases due to the process of heat production. To overcome these problems, we propose a new heat supply concept using the latent heat of ice formation. In this method, the bottom hole pressure is deeply depressurized below the quadruple point to form ice intentionally during hydrate dissociation. The latent heat of ice is expected to be used for hydrate dissociation and enhance gas recovery. As a part of a Japanese national hydrate research program (MH21, funded by the Ministry of Economy, Trade, and Industry), we conducted laboratory experiments and numerical simulations to evaluate the effect of ice formation on gas productivity. It was found that depressurization-induced gas production can be accelerated by ice formation during hydrate dissociation at a pressure below the quadruple point.1 Laboratory experiments using a large scale vessel revealed that the recovery factor when applying this method was 65% which is a comparable level of conventional natural gas production.2 Based on these results, we conducted numerical simulations for hypothetical low-temperature reservoirs commonly observed in the arctic region to evaluate the applicability of this method in real fields. The simulation predicted that the acceleration of gas production can be achieved during 1 year production. It indicates that this method is a promising enhanced recovery for sandy gas hydrate reservoirs.

References:

1. Konno, Y., Uchiumi, T., Oyama, H., Jin, Y., Nagao, J., Masuda, Y., and Ouchi, H. (2012). Dissociation behavior of methane hydrate in sandy porous media below the quadruple point. Energy & Fuels, 26(7), 4310-4320.

2. Konno, Y., Jin, Y., Shinjou, K., and Nagao, J. (2014). Experimental evaluation of the gas recovery factor of methane hydrate in sandy sediment. RSC Advances, 4(93), 51666 51675.

DATA NOT PUBLISHED TO DATE, PRESENTATION NOT AVAILABLE

Calibration and validation of a numerical model against experimental data of methane hydrate formation and dissociation in a sandy porous medium

Yin Zhenyuan[a,b], George Moridis[c,d,a], Chong Zheng Rong[a], Praveen Linga[a*]

[a]Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117585, Singapore

[b]Lloyd's Register Global Technology Centre Pte Ltd, Singapore 138522

[c]Petroleum Engineering Dept., Texas A&M University, TX 77840, USA

[d]Earth Sciences Division, Lawrence Berkeley National Laboratory, CA 94720, USA

* Corresponding author.

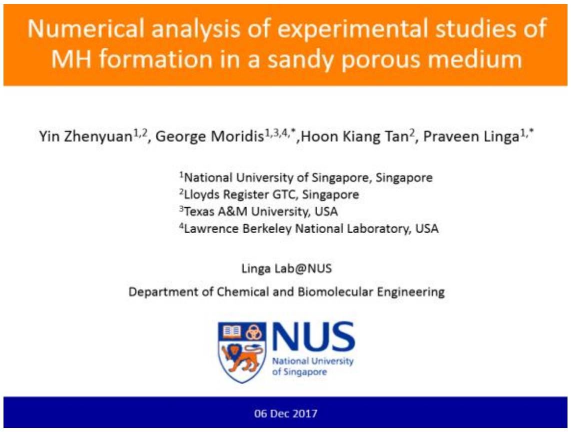
E-mail address: gjmoridis@lbl.gov (G Moridis); Praveen.linga@nus.edu.sg. (P Linga)

Abstract

Methane hydrates (MH) are known to trap enormous amounts of CH_4 in oceanic and permafrost-associated deposits, and are being considered as a potential future energy source.
Several powerful numerical simulators were developed to describe the behavior of natural hydrate-bearing sediments (HBS). The complexity and strong nonlinearities in HBS do not allow analytical solutions for code validation. The only reliable method to develop confidence in these models is through comparisons to laboratory and/or field experiments.

The objective of this study is to reproduce numerically the results from earlier experiments of MH formation and depressurization (and the corresponding fluid production) in 1.0L reactor involving unconsolidated sand, thus validating and calibrating the TOUGH+Hydrate v1.5 simulator. We faithfully describe the reactor geometry and the experimental process that involves both hydrate formation and dissociation. We demonstrate that the laboratory experiments can only be captured by a kinetic hydration model. There is an excellent agreement between observations and predictions (a) of the cumulative gas depletion (during formation) and production (during dissociation) and (b) of pressure over time. The temperature agreement is less satisfactory, and the deviations are attributed to the fixed locations of the limited number of sensors that cannot fully capture the hydrate heterogeneity. We also predict the spatial distributions over time of the various phase (gas, aqueous and hydrate) saturations. Thus, hydrates form preferentially along the outer boundary of the sand core, and the hydrate front moves inward leaving a significant portion of the sand at the center hydrate-free. During depressurization, dissociation advances again inward from the reactor boundary to the center of the reactor. As expected, methane gas accumulates initially at the locations of most intense dissociation, and then gradually migrates to the upper section of the reactor because of buoyancy and of the pressure gradient caused by the pressure outlet. Sensitivity analysis indicates that the composite thermal conductivity of the HBS and the kinetic parameters of the

hydration reaction are the dominant factors. The absolute permeability of the sand does not play a significant role in this small reactor.



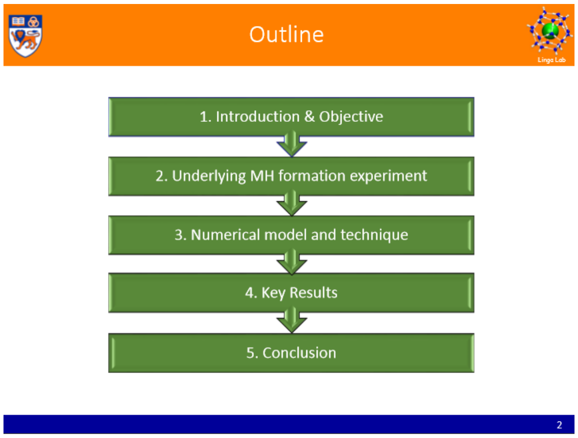
Numerical analysis of experimental studies of MH formation in a sandy porous medium

Yin Zhenyuan[1,2], George Moridis[1,3,4,*], Hoon Kiang Tan[2], Praveen Linga[1,*]

[1]National University of Singapore, Singapore
[2]Lloyds Register GTC, Singapore
[3]Texas A&M University, USA
[4]Lawrence Berkeley National Laboratory, USA

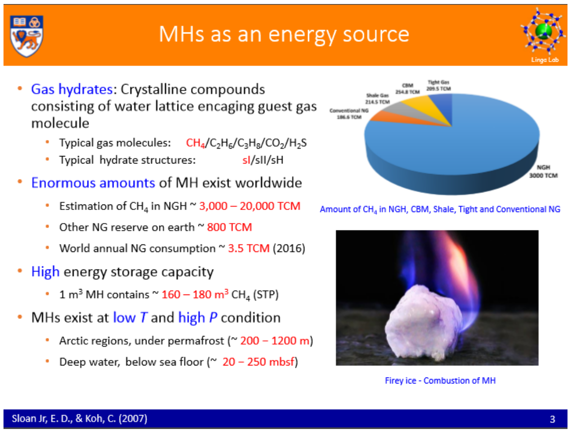
Linga Lab@NUS
Department of Chemical and Biomolecular Engineering

06 Dec 2017



Outline

1. Introduction & Objective
2. Underlying MH formation experiment
3. Numerical model and technique
4. Key Results
5. Conclusion



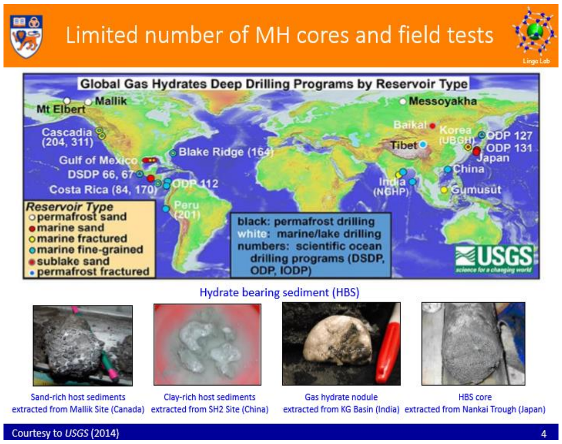
MHs as an energy source

- Gas hydrates: Crystalline compounds consisting of water lattice encaging guest gas molecule
  - Typical gas molecules: $CH_4/C_2H_6/C_3H_8/CO_2/H_2S$
  - Typical hydrate structures: sI/sII/sH
- Enormous amounts of MH exist worldwide
  - Estimation of CH_4 in NGH ~ 3,000 – 20,000 TCM
  - Other NG reserve on earth ~ 800 TCM
  - World annual NG consumption ~ 3.5 TCM (2016)
- High energy storage capacity
  - 1 m^3 MH contains ~ 160 – 180 m^3 CH_4 (STP)
- MHs exist at low *T* and high *P* condition
  - Arctic regions, under permafrost (~ 200 – 1200 m)
  - Deep water, below sea floor (~ 20 – 250 mbsf)

Amount of CH_4 in NGH, CBM, Shale, Tight and Conventional NG

Firey ice - Combustion of MH

Sloan Jr, E. D., & Koh, C. (2007)



Limited number of MH cores and field tests

Hydrate bearing sediment (HBS)

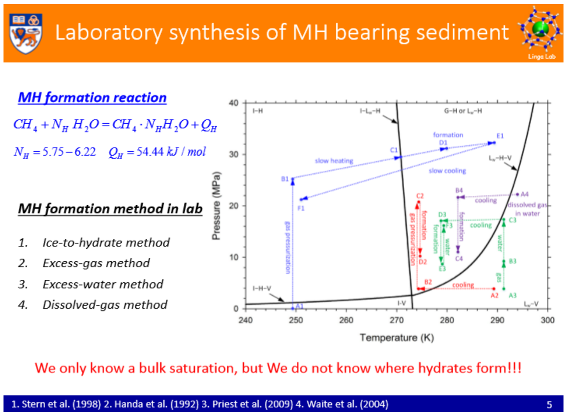
Sand-rich host sediments extracted from Mallik Site (Canada)

Clay-rich host sediments extracted from SH2 Site (China)

Gas hydrate nodule extracted from KG Basin (India)

HBS core extracted from Nankai Trough (Japan)

Courtesy to *USGS* (2014)



Laboratory synthesis of MH bearing sediment

MH formation reaction

$$CH_4 + N_H\, H_2O = CH_4 \cdot N_H H_2O + Q_H$$

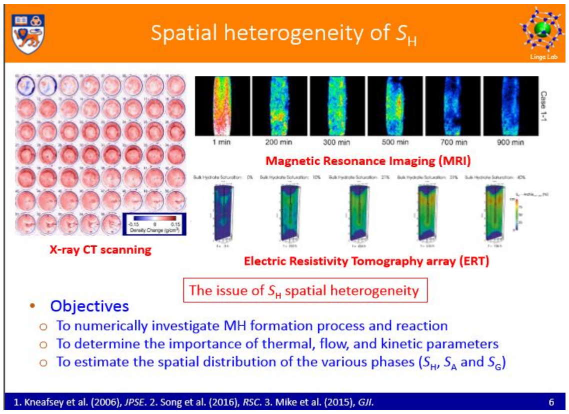
$$N_H = 5.75 - 6.22 \quad Q_H = 54.44\ kJ/mol$$

MH formation method in lab

1. *Ice-to-hydrate method*
2. *Excess-gas method*
3. *Excess-water method*
4. *Dissolved-gas method*

We only know a bulk saturation, but We do not know where hydrates form!!!

1. Stern et al. (1998) 2. Handa et al. (1992) 3. Priest et al. (2009) 4. Waite et al. (2004)



Spatial heterogeneity of S_H

X-ray CT scanning

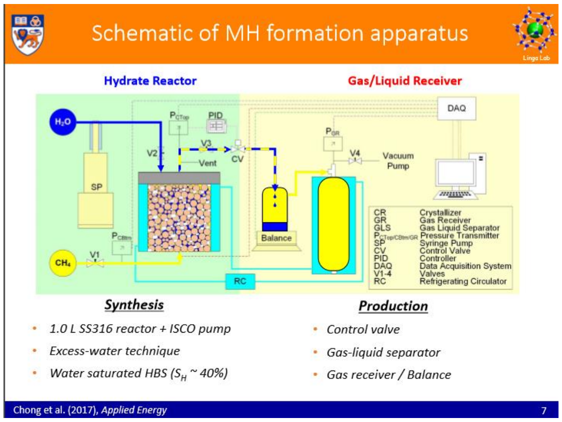
Magnetic Resonance Imaging (MRI)

Electric Resistivity Tomography array (ERT)

The issue of S_H spatial heterogeneity

- Objectives
  - To numerically investigate MH formation process and reaction
  - To determine the importance of thermal, flow, and kinetic parameters
  - To estimate the spatial distribution of the various phases (S_H, S_A and S_G)

1. Kneafsey et al. (2006), *JPSE*. 2. Song et al. (2016), *RSC*. 3. Mike et al. (2015), *GJI*.



Schematic of MH formation apparatus

Hydrate Reactor

Gas/Liquid Receiver

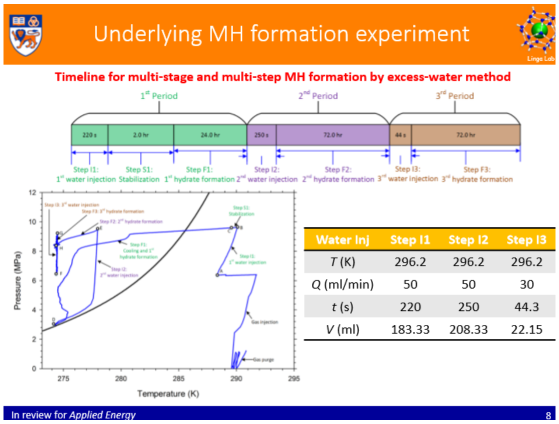
Synthesis

- *1.0 L SS316 reactor + ISCO pump*
- *Excess-water technique*
- *Water saturated HBS (S_H ~ 40%)*

Production

- *Control valve*
- *Gas-liquid separator*
- *Gas receiver / Balance*

Chong et al. (2017), *Applied Energy* 7



Underlying MH formation experiment

Timeline for multi-stage and multi-step MH formation by excess-water method

Water Inj	Step I1	Step I2	Step I3
T (K)	296.2	296.2	296.2
Q (ml/min)	50	50	30
t (s)	220	250	44.3
V (ml)	183.33	208.33	22.15

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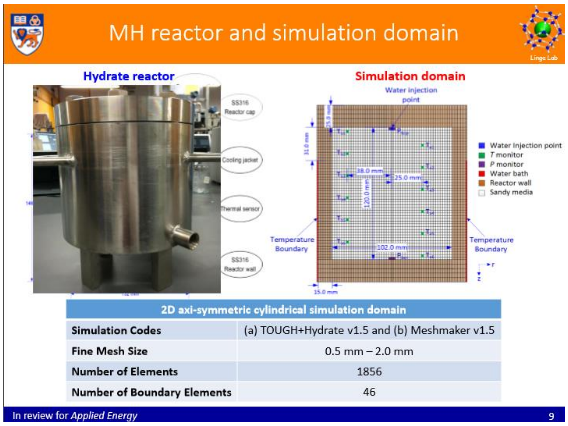

MH reactor and simulation domain

Hydrate reactor

Simulation domain

2D axi-symmetric cylindrical simulation domain	
Simulation Codes	(a) TOUGH+Hydrate v1.5 and (b) Meshmaker v1.5
Fine Mesh Size	0.5 mm – 2.0 mm
Number of Elements	1856
Number of Boundary Elements	46

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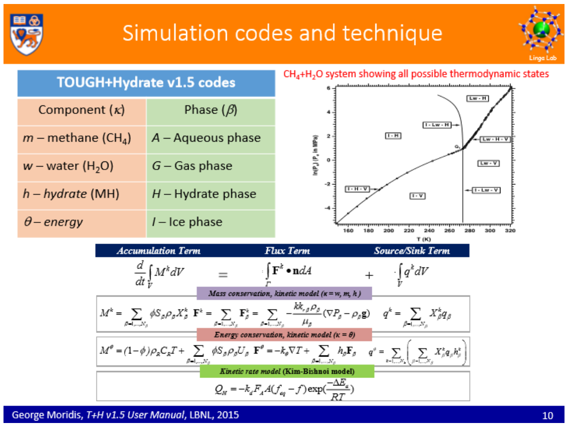


Simulation codes and technique

TOUGH+Hydrate v1.5 codes	
Component (κ)	Phase (β)
m – methane (CH_4)	A – Aqueous phase
w – water (H_2O)	G – Gas phase
h – *hydrate* (MH)	H – Hydrate phase
θ – *energy*	I – Ice phase

CH_4+H_2O system showing all possible thermodynamic states

Accumulation Term *Flux Term* *Source/Sink Term*

$$\frac{d}{dt}\int_V M^k dV = \int_\Gamma \mathbf{F}^k \bullet \mathbf{n} dA + \int_V q^k dV$$

Mass conservation, kinetic model ($\kappa = w, m, h$)

$$M^k = \sum_{\beta=1,\dots,N_\beta} \phi S_\beta \rho_\beta X_\beta^k \quad \mathbf{F}^k = \sum_{\beta=1,\dots,N_\beta} \mathbf{F}_\beta^k = \sum_{\beta=1,\dots,N_\beta} -\frac{k k_{r\beta}\rho_\beta}{\mu_\beta}(\nabla P_\beta - \rho_\beta \mathbf{g}) \quad q^k = \sum_{\beta=1,\dots,N_\beta} X_\beta^k q_\beta$$

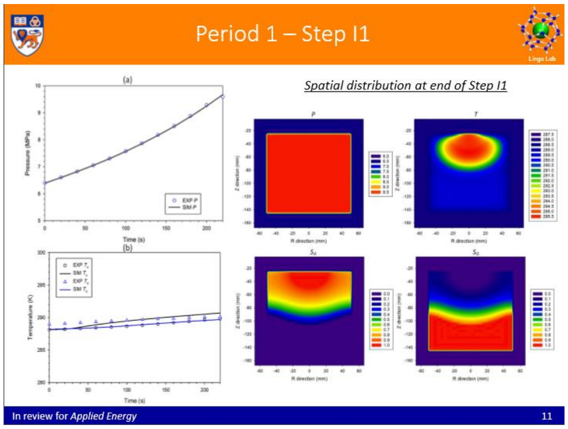
Energy conservation, kinetic model ($\kappa = \theta$)

$$M^\theta = (1-\phi)\rho_R C_R T + \sum_{\beta=1,\dots,N_\beta} \phi S_\beta \rho_\beta U_\beta \quad \mathbf{F}^\theta = -k_\theta \nabla T + \sum_{\beta=1,\dots,N_\beta} h_\beta \mathbf{F}_\beta \quad q^\theta = \sum_{k=1,\dots,N_k}\left(\sum_{\beta=1,\dots,N_\beta} X_\beta^k q_\beta h_\beta^k\right)$$

Kinetic rate model (Kim-Bishnoi model)

$$Q_H = -k_d F_A A(f_{eq} - f)\exp\left(\frac{-\Delta E_a}{RT}\right)$$

George Moridis, *T+H v1.5 User Manual*, LBNL, 2015 10



Period 1 – Step I1

Spatial distribution at end of Step I1

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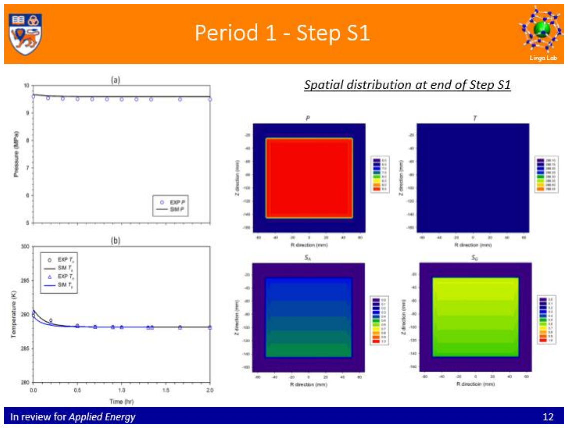

Period 1 - Step S1

Spatial distribution at end of Step S1

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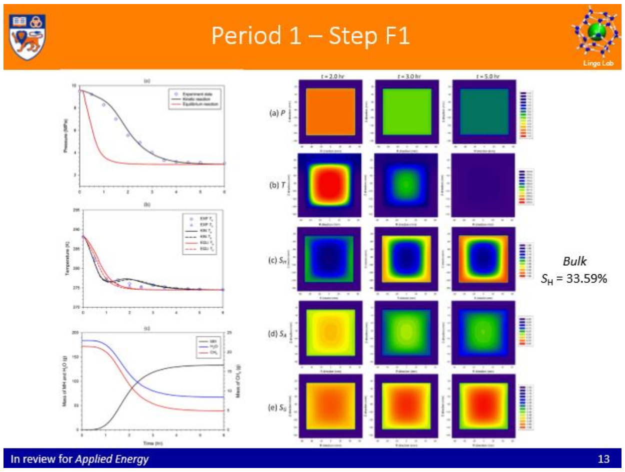

Period 1 – Step F1

Bulk
S_H = 33.59%

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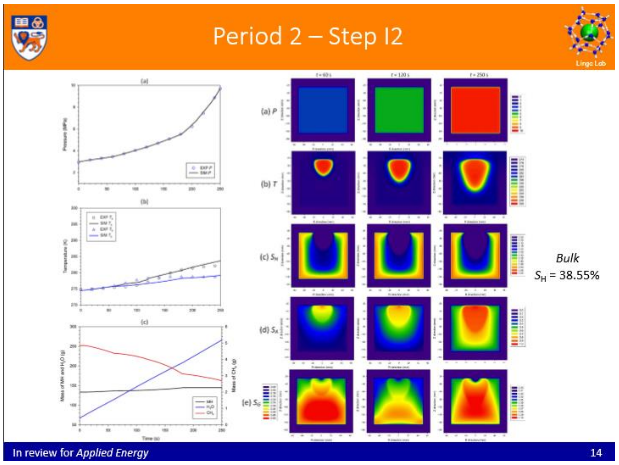

Period 2 – Step I2

Bulk
S_H = 38.55%

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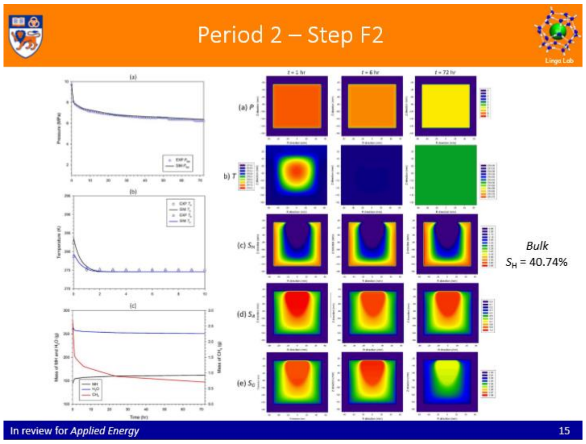
Period 2 – Step F2



Bulk
S_H = 40.74%

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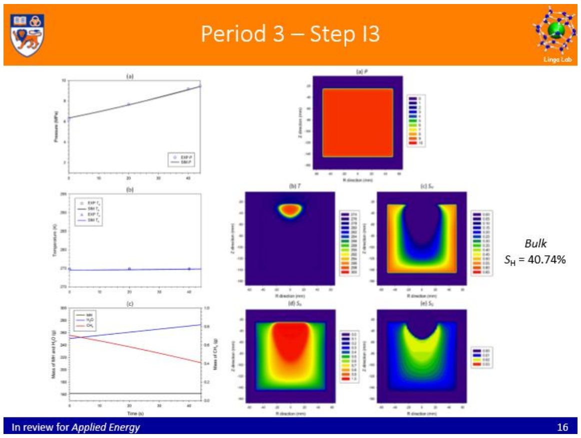
Period 3 – Step I3



Bulk
S_H = 40.74%

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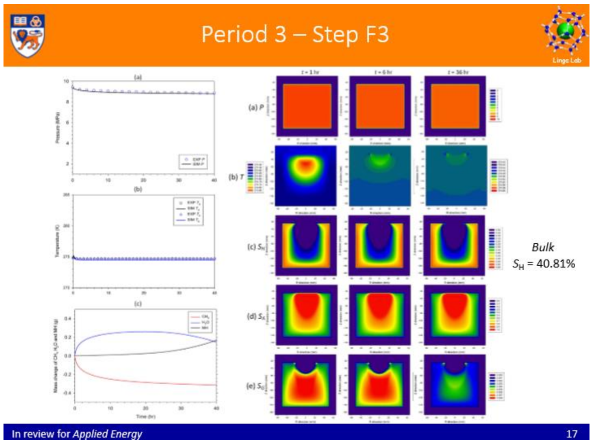
Period 3 – Step F3



Bulk
S_H = 40.81%

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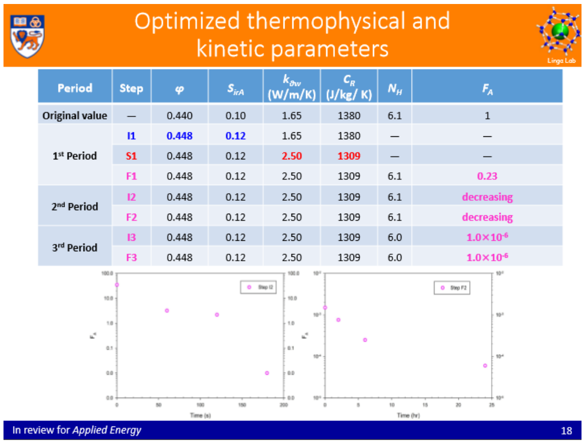
Optimized thermophysical and kinetic parameters



Period	Step	φ	S_{irA}	$k_{\vartheta w}$ (W/m/K)	C_R (J/kg/ K)	N_H	F_A
Original value	—	0.440	0.10	1.65	1380	6.1	1
1st Period	I1	**0.448**	**0.12**	1.65	1380	—	—
	S1	0.448	0.12	**2.50**	**1309**	—	—
	F1	0.448	0.12	2.50	1309	6.1	**0.23**
2nd Period	I2	0.448	0.12	2.50	1309	6.1	**decreasing**
	F2	0.448	0.12	2.50	1309	6.1	**decreasing**
3rd Period	I3	0.448	0.12	2.50	1309	6.0	**1.0×10^{-6}**
	F3	0.448	0.12	2.50	1309	6.0	**1.0×10^{-6}**

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Conclusions

- MH formation in sandy media is a kinetic reaction, excluding the possibility of an equilibrium reaction
- The dominant processes during MH formation in the 1.0 L reactor are thermal processes
  - Cooling
  - Warm water injection
- Uniformity of S_H distributions appears to be nearly impossible
  - Water/Gas injector location
  - Gravity drainage effects/Capillary-driven redistribution of phases
  - The geometry of the reactor/ non-uniformity of the cooling process
  - Cooling rate and heat flux from surrounding environment
- To quantify the S_A, S_G and S_H using numerical techniqe besides expensive experimental measurement (MRI, X-ray CT, ERT)

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Acknowledgement

- A/Prof Praveen Linga (NUS) praveen.linga@nus.edu.sg
- Prof George Moridis (LBNL) gjmoridis@lbl.gov

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ICGH10 Singapore (2020)

Praveen LINGA and Iftekhar KARIMI

Supported by

Dr. Jurgen Mienert – University of Tromsø

4D Seismics and Ocean Observatories in Arctic Gas Hydrate Research Jurgen Mienert

Centre for Arctic Gas Hydrate, Environment and Climate (CAGE) University of Tromso - The Arctic University of Norway
We do apply high-resolution time lapse seismic studies that are integrated with seafloor observations to image and detect major changes in subseabed fluid migration and seabed-fluid release. Our 3D P-cable seismic system enables us to achieve high-resolution imaging of the sub seafloor while K-lander observatories detect and image gas releases from the seafloor. The big questions for such a study are: What monitoring is important to evaluate the development of pathways for fluids that may lead to gas blowouts from gas hydrate reservoirs? What monitoring is important to understand the evolution of benthic life in newly created cold seep environments of the Arctic? Seismic time-lapse monitoring has demonstrated already its great potential and societal relevance in the hydrocarbon industry. Here it is used to determine for example where the injected greenhouse gas CO2 is moving to within a CO2 storage site. We study the vast amounts of the natural methane gas (CH4) stored under the Arctic Ocean floor often occurring as ice-like, crystalline compounds called hydrates. These hydrates can consist of both hydrocarbon gases originating from thermogenic sources of hydrocarbon reservoirs deep below the ocean floor and/or from biogenic shallow sources. The Arctic holds vast undiscovered reserves of hydrates with mixtures of thermogenic and biogenic methane.

Our comprehensive time-lapse (4D) seismic studies have the aim: to track fracture network developments and gas plume migration with the gas hydrate stability zone, and to demonstrate instabilities within the gas hydrate reservoir.

Such a study can provide quantitative information to better understand detailed gas migration pathways, which may control the development of gas chimneys and/or plumes in the reservoir and episodic gas release from the seabed into the ocean.

UIT
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Environment and Climate

4D seismics and Ocean Observatories in Arctic Gas Hydrate Research

Jurgen Mienert

Malin Bénédicte Stefan Andreia

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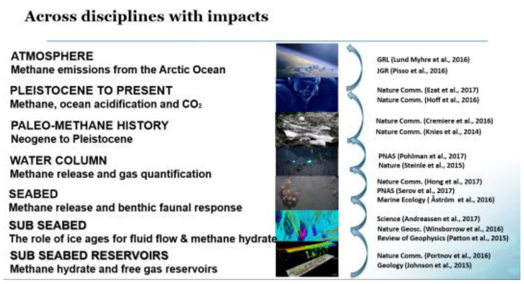
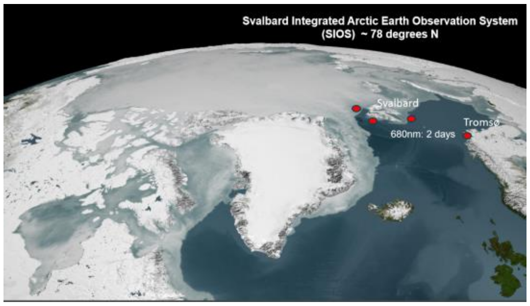


Across disciplines with impacts

ATMOSPHERE Methane emissions from the Arctic Ocean	GRL (Lund Myhre et al., 2016) JGR (Pisso et al., 2016)
PLEISTOCENE TO PRESENT Methane, ocean acidification and CO_2	Nature Comm. (Ezat et al., 2017) Nature Comm. (Hoff et al., 2016)
PALEO-METHANE HISTORY Neogene to Pleistocene	Nature Comm. (Cremiere et al., 2016) Nature Comm. (Knies et al., 2014)
WATER COLUMN Methane release and gas quantification	PNAS (Pohlman et al., 2017) Nature (Steinle et al., 2015)
SEABED Methane release and benthic faunal response	Nature Comm. (Hong et al., 2017) PNAS (Serov et al., 2017) Marine Ecology (Åström et al., 2016)
SUB SEABED The role of ice ages for fluid flow & methane hydrate	Science (Andreassen et al., 2017) Nature Geosc. (Winsborrow et al., 2016) Review of Geophysics (Patton et al., 2015)
SUB SEABED RESERVOIRS Methane hydrate and free gas reservoirs	Nature Comm. (Portnov et al., 2016) Geology (Johnson et al., 2015)

Our location: Gateway to the Arctic (~ 70 degrees N)

CAGE – Centre for Arctic Gas Hydrate, Environment and Climate



Svalbard Integrated Arctic Earth Observation System (SIOS) ~ 78 degrees N

Our boat - RV Helmer Hanssen

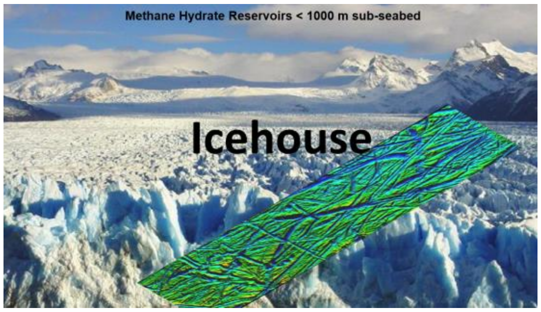
Our new ice-breaking vessel

Gross tonnage	10900T
4 diesel gensets (A/C)	15MW
Two (Z-drives) aft	11MW
Two tunnel thrusters fwd	2,2MW

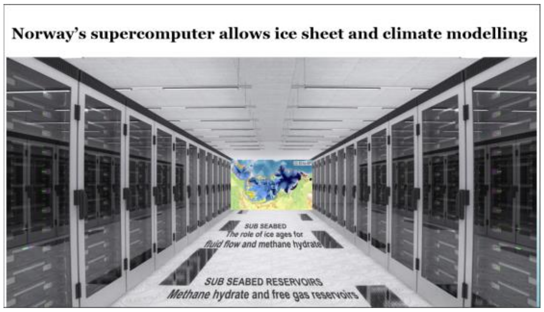
- Dynamic Positioning (DP 1)
- PC-3 *Year-round operation in second-year ice which may include multi-year ice inclusions.*

Photos: Ø. Mikelb

Length over all (LOA):	100,0m
Breadth:	21,0m
Draft:	8,5m



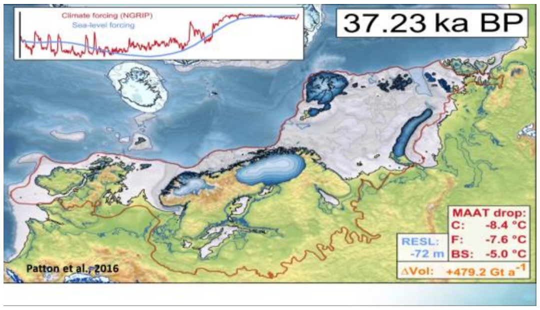
Methane Hydrate Reservoirs < 1000 m sub-seabed



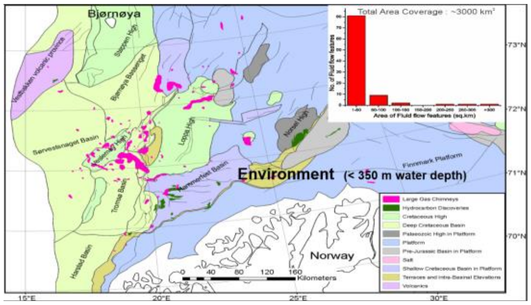
Norway's supercomputer allows ice sheet and climate modelling

SUB SEABED
The role of ice ages for fluid flow and methane hydrate

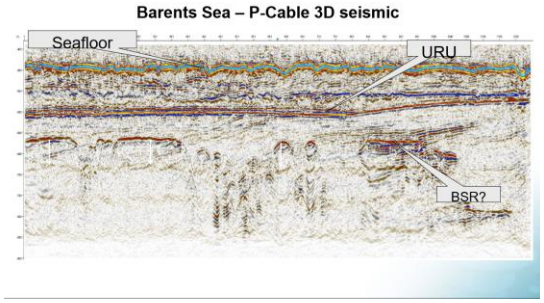
SUB SEABED RESERVOIRS
Methane hydrate and free gas reservoirs



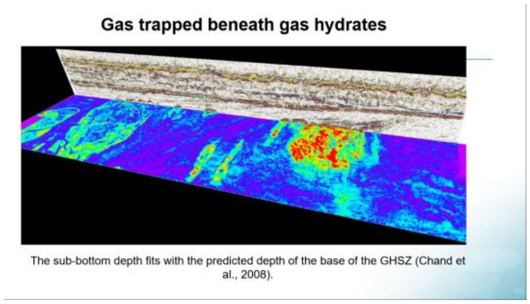
Patton et al., 2016



Environment (< 350 m water depth)

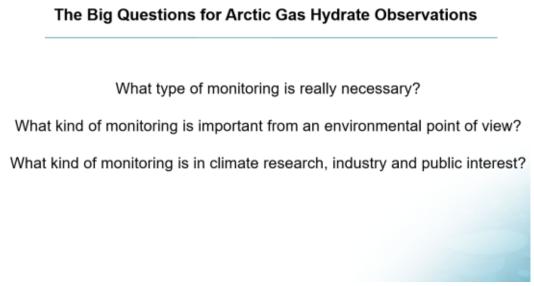


Barents Sea – P-Cable 3D seismic



Gas trapped beneath gas hydrates

The sub-bottom depth fits with the predicted depth of the base of the GHSZ (Chand et al., 2008).

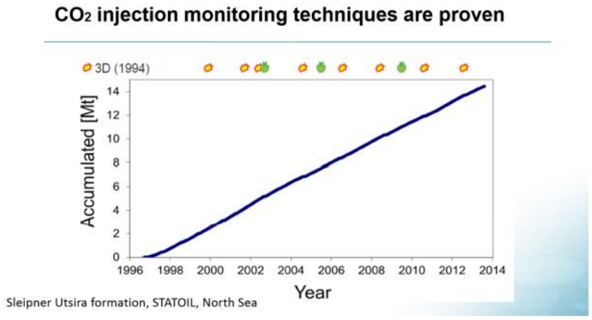


The Big Questions for Arctic Gas Hydrate Observations

What type of monitoring is really necessary?

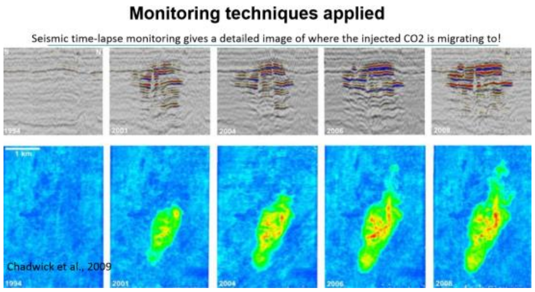
What kind of monitoring is important from an environmental point of view?

What kind of monitoring is in climate research, industry and public interest?



CO_2 injection monitoring techniques are proven

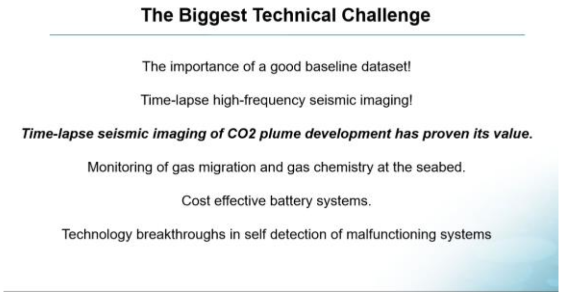
Sleipner Utsira formation, STATOIL, North Sea



Monitoring techniques applied

Seismic time-lapse monitoring gives a detailed image of where the injected CO2 is migrating to!

Chadwick et al., 2009



The Biggest Technical Challenge

The importance of a good baseline dataset!

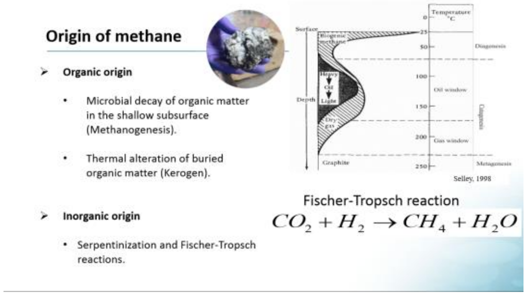
Time-lapse high-frequency seismic imaging!

Time-lapse seismic imaging of CO2 plume development has proven its value.

Monitoring of gas migration and gas chemistry at the seabed.

Cost effective battery systems.

Technology breakthroughs in self detection of malfunctioning systems



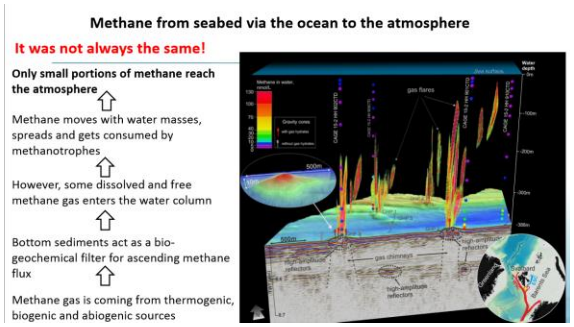
Origin of methane

- **Organic origin**
  - Microbial decay of organic matter in the shallow subsurface (Methanogenesis).
  - Thermal alteration of buried organic matter (Kerogen).
- **Inorganic origin**
  - Serpentinization and Fischer-Tropsch reactions.

Selley, 1998

Fischer-Tropsch reaction

$$CO_2 + H_2 \rightarrow CH_4 + H_2O$$



Methane from seabed via the ocean to the atmosphere

It was not always the same!

Only small portions of methane reach the atmosphere

⇧

Methane moves with water masses, spreads and gets consumed by methanotrophes

⇧

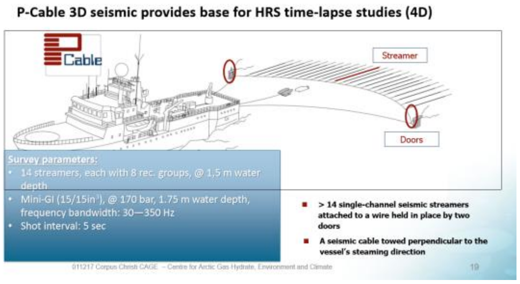
However, some dissolved and free methane gas enters the water column

⇧

Bottom sediments act as a bio-geochemical filter for ascending methane flux

⇧

Methane gas is coming from thermogenic, biogenic and abiogenic sources

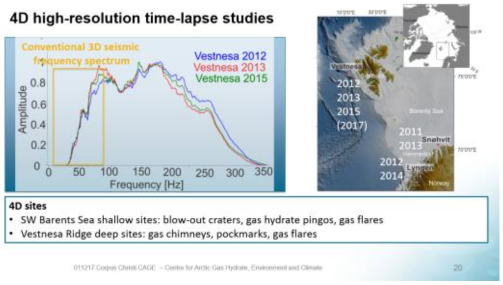


P-Cable 3D seismic provides base for HRS time-lapse studies (4D)

Survey parameters:

- 14 streamers, each with 8 rec. groups, @ 1,5 m water depth
- Mini-GI (15/15in³), @ 170 bar, 1.75 m water depth, frequency bandwidth: 30—350 Hz
- Shot interval: 5 sec

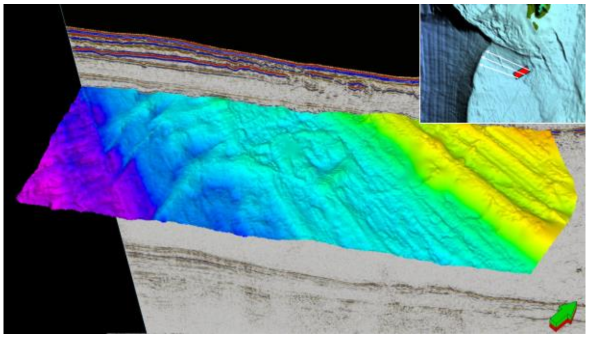
- **> 14 single-channel seismic streamers attached to a wire held in place by two doors**
- **A seismic cable towed perpendicular to the vessel's steaming direction**

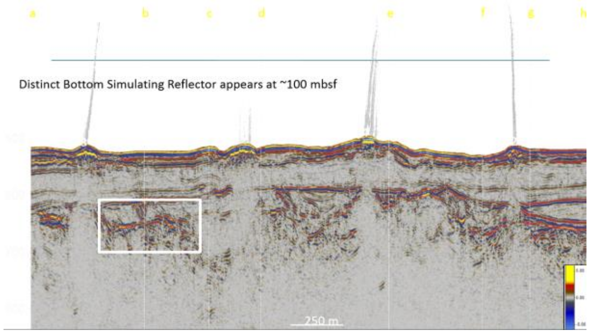


4D high-resolution time-lapse studies

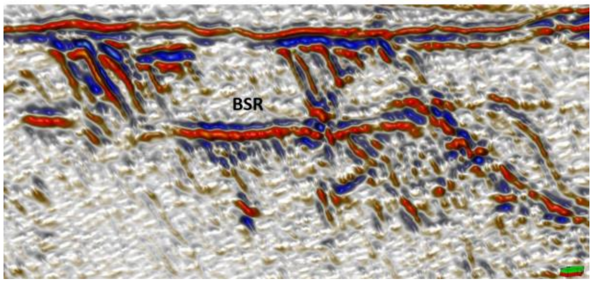
4D sites

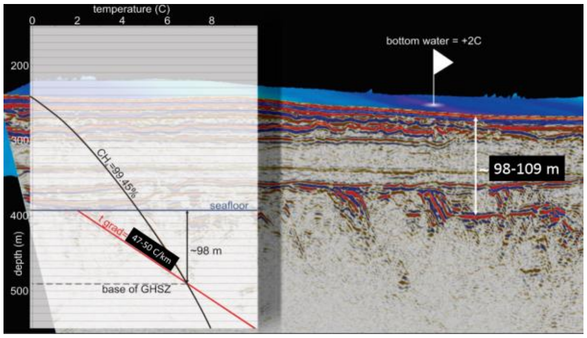
- SW Barents Sea shallow sites: blow-out craters, gas hydrate pingos, gas flares
- Vestnesa Ridge deep sites: gas chimneys, pockmarks, gas flares

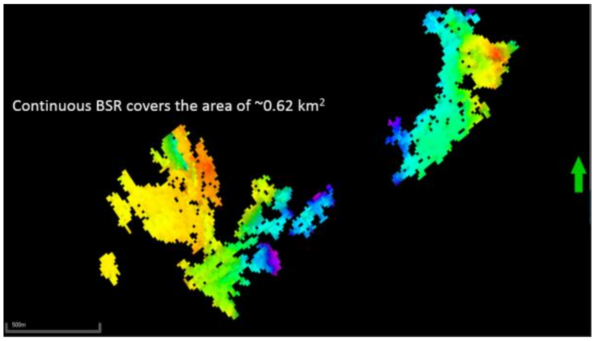




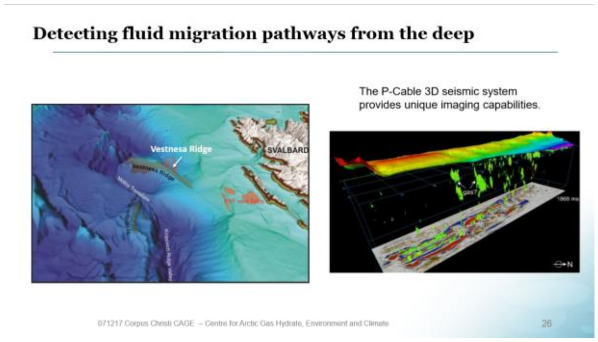
Distinct Bottom Simulating Reflector appears at ~100 mbsf







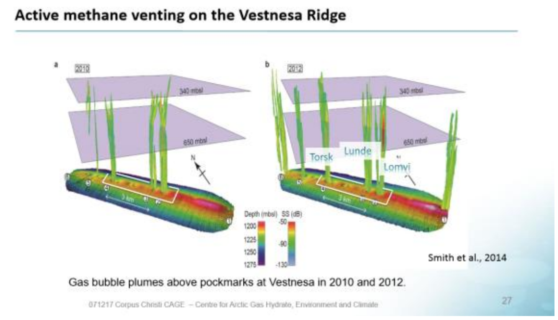
Continuous BSR covers the area of ~0.62 km^2



Detecting fluid migration pathways from the deep

The P-Cable 3D seismic system provides unique imaging capabilities.

071217 Corpus Christi CAGE – Centre for Arctic Gas Hydrate, Environment and Climate 26

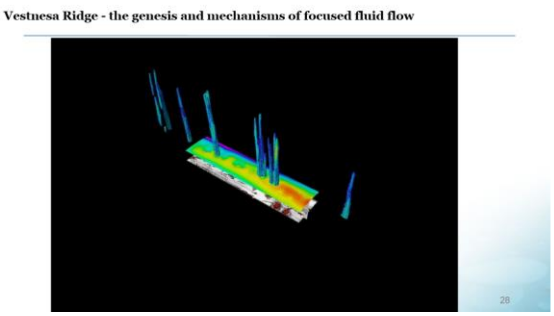


Active methane venting on the Vestnesa Ridge

Smith et al., 2014

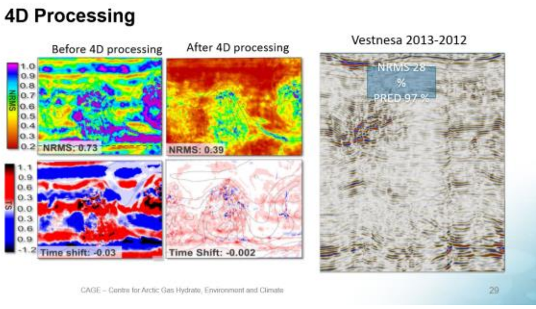
Gas bubble plumes above pockmarks at Vestnesa in 2010 and 2012.

071217 Corpus Christi CAGE – Centre for Arctic Gas Hydrate, Environment and Climate 27



Vestnesa Ridge - the genesis and mechanisms of focused fluid flow

28



4D Processing

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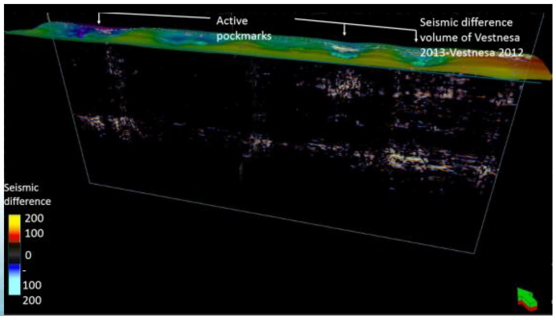
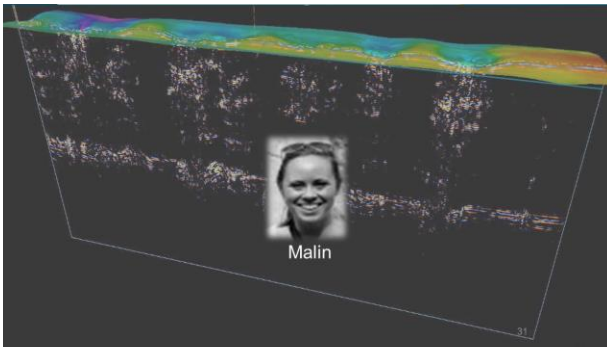
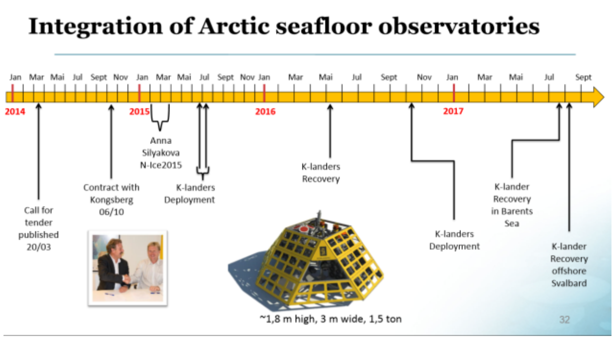






Integration of Arctic seafloor observatories

Call for tender published 20/03

Contract with Kongsberg 06/10

Anna Silyakova N-Ice2015

K-landers Deployment

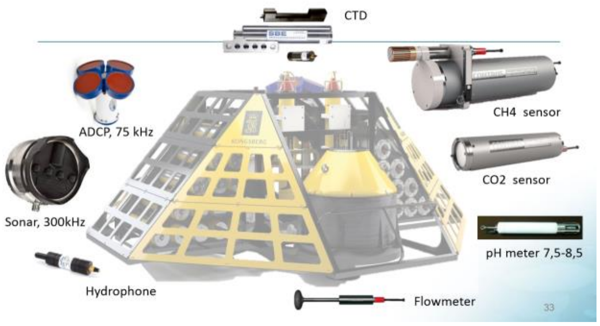
K-landers Recovery

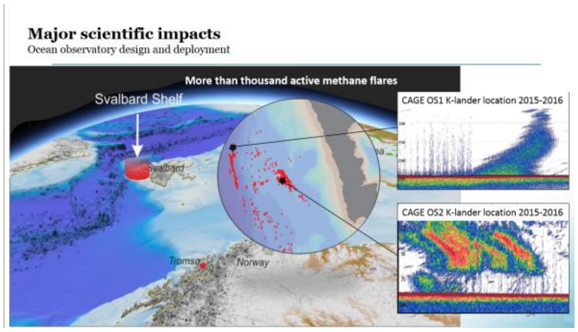
K-landers Deployment

K-lander Recovery in Barents Sea

K-lander Recovery offshore Svalbard

~1,8 m high, 3 m wide, 1,5 ton

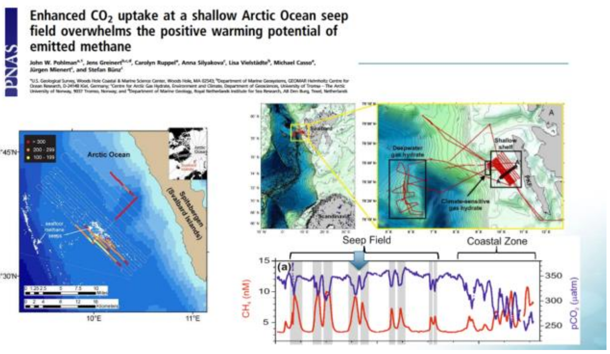




Major scientific impacts

Ocean observatory design and deployment

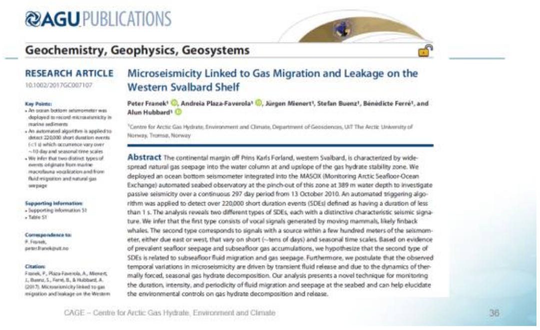
More than thousand active methane flares



PNAS

Enhanced CO_2 uptake at a shallow Arctic Ocean seep field overwhelms the positive warming potential of emitted methane

John W. Pohlman[a,1], Jens Greinert[b,c,d], Carolyn Ruppel[a], Anna Silyakova[c], Lisa Vielstädte[b], Michael Casso[a], Jürgen Mienert[c], and Stefan Bünz[c]



AGU PUBLICATIONS

Geochemistry, Geophysics, Geosystems

RESEARCH ARTICLE

10.1002/2017GC007107

Microseismicity Linked to Gas Migration and Leakage on the Western Svalbard Shelf

Peter Franek[1], Andreia Plaza-Faverola[1], Jürgen Mienert[1], Stefan Buenz[1], Bénédicte Ferré[1], and Alun Hubbard[1]

[1]Centre for Arctic Gas Hydrate, Environment and Climate, Department of Geosciences, UiT The Arctic University of Norway, Tromsø, Norway

Key Points:
- An ocean bottom seismometer was deployed to record microseismicity in marine sediments
- An automated algorithm is applied to detect 220,000 short duration events (<1 s) which occurrence vary over ~10 day and seasonal time scales
- We infer that two distinct types of events originate from marine macrofauna vocalization and from fluid migration and natural gas seepage

Supporting Information:
- Supporting Information S1
- Table S1

Correspondence to:
P. Franek,
peter.franek@uit.no

Citation:
Franek, P., Plaza-Faverola, A., Mienert, J., Buenz, S., Ferré, B., & Hubbard, A. (2017). Microseismicity linked to gas migration and leakage on the Western

Abstract The continental margin off Prins Karls Forland, western Svalbard, is characterized by widespread natural gas seepage into the water column at and upslope of the gas hydrate stability zone. We deployed an ocean bottom seismometer integrated into the MASOX (Monitoring Arctic Seafloor-Ocean Exchange) automated seabed observatory at the pinch-out of this zone at 389 m water depth to investigate passive seismicity over a continuous 297 day period from 13 October 2010. An automated triggering algorithm was applied to detect over 220,000 short duration events (SDEs) defined as having a duration of less than 1 s. The analysis reveals two different types of SDEs, each with a distinctive characteristic seismic signature. We infer that the first type consists of vocal signals generated by moving mammals, likely finback whales. The second type corresponds to signals with a source within a few hundred meters of the seismometer, either due east or west, that vary on short (~tens of days) and seasonal time scales. Based on evidence of prevalent seafloor seepage and subseafloor gas accumulations, we hypothesize that the second type of SDEs is related to subseafloor fluid migration and gas seepage. Furthermore, we postulate that the observed temporal variations in microseismicity are driven by transient fluid release and due to the dynamics of thermally forced, seasonal gas hydrate decomposition. Our analysis presents a novel technique for monitoring the duration, intensity, and periodicity of fluid migration and seepage at the seabed and can help elucidate the environmental controls on gas hydrate decomposition and release.

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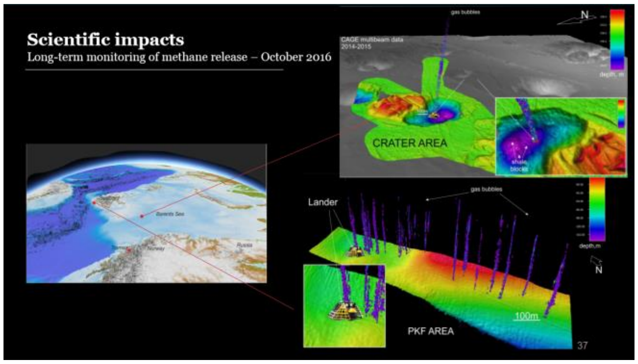
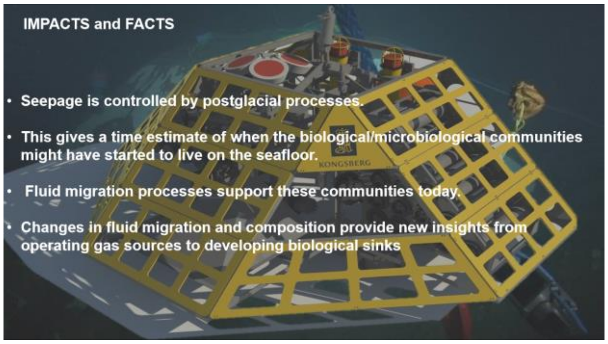


Scientific impacts

Long-term monitoring of methane release – October 2016



IMPACTS and FACTS

- Seepage is controlled by postglacial processes.
- This gives a time estimate of when the biological/microbiological communities might have started to live on the seafloor.
- Fluid migration processes support these communities today.
- Changes in fluid migration and composition provide new insights from operating gas sources to developing biological sinks

Enhance strategic international cooperation

Thank you for your attention!

Jurgen Mienert

cage.uit.no

Dr. Xin Lu – China National Offshore Oil Corporation

Experimental study on the effective thermal conductivity of pressure-tight sampling corer Natural gas hydrate samples of South China Sea

Prof. Xin Lu
CNOOC

Gas hydrates are considered as a potential strategic energy source for sustainable development. Thermal properties of gas hydrate-bearing sediments directly govern the heat transfer process during hydrate decomposition which couples with phase transitions and multiphase flows. The effective thermal conductivity of a multiphase system represents the composite capacity to conduct heat. In May 2017, CNOOC relied on the Deepwater Engineering Survey vessel "HYSY 708" at the station of Liwan in the northern part of the South China Sea. Using fully self-developed technology, process and equipment, at the depth of 1310m and the depth of hydrate ore body was 117~196m, the world's first successful implementation of shallow non diagenetic hydrate solid fluidization well testing and production in ocean water, marking China's has made a historic breakthrough in the key technology of natural gas hydrate exploration and development with independent intellectual property rights. Basing on the above condition and the sample of core by operation， here we report on point heat source measurements of the effective thermal conductivity of methane hydrate-bearing sediments through a thermistor-based method combining with X-ray CT observations. Methane hydrates were formed at different saturations, with various initial water contents, and in porous matrices simulated by grains with differing thermal conductivities. It is indicated that the effective thermal conductivity of sediments negatively correlated with the hydrate saturation, while an increase of initial water contents and thermal conductivity of grains has a positive impact on the elevation of the effective thermal conductivity. Moreover, the effective thermal conductivity was found to slightly increase with the proceeding of hydrate decomposition. Typical effective medium models were evaluated with the mea-surements of this study, and a hybrid fitting model combining three forms of self-consistent models was proposed, with the optimal weighting parameters determined via the genetic algorithm. The effective prediction of the measurements in this work and results in literatures corroborates the feasibility of the model. This study could help in understanding the evolutions of sediment thermal properties during gas production and their effects on large-scale hydrate decomposition when expanded to field scale tests.

PRESENTATION WITHDRAWN

Dr. Na Wei, Southwest Petroleum University, weina8081@163.com

The first solid fluidization exploitation experimental system of marine natural gas hydrate in the world

Abstract: The reserves of marine natural gas hydrate, one of the most potential unconventional energy sources after shale gas, coal seam gas and tight gas, are about 100 times as much as that of terrestrial frozen soil. In marine environment, most of the veins, bulk hydrates and hydrates in fine-grained sediments belong to non-diagenetic natural gas hydrate, and there is no stable entrapment structure like conventional oil and gas fields and sandstone hydrate reservoirs. According to the physical characteristics and reservoir characteristics of marine non-diagenetic hydrate, Southwest Petroleum University innovatively proposes solid fluidization exploitation method, and establishes the first solid fluidization exploitation laboratory of marine natural gas hydrate in the world. The lab's position is "fully automated white-collar laboratory". The experimental system consists of rapid preparation and fragmentation of large samples, efficient pipe transportation, efficient separation and rapid detection modules and so on. The main functions of laboratory are rating of efficient rock breaking capacity, evaluation of rock carrying capacity in fluidization pilot exploitation of marine natural gas hydrate, evaluation of hydrate non-equilibrium decomposition and dynamic change laws of flow patterns, safe transportation of under different mining rates, and simulation of well control safety. The key technical indicators of laboratory are 12 MPa pressure, 65 m horizontal pipe, 30 m vertical pipe, and 1 decimeter pipe diameter. The laboratory can simulate the whole process of solid fluidization exploitation with 1200 m water depth, which is a landmark laboratory of Southwest Petroleum University with original innovation, independent design, independent research and development. The establishment of this laboratory is of great significance to the development of global gas hydrate research.

IN PLACE OF THE ORAL PRESENTATION A THOROUGH DESCRIPTION HAS BEEN INCLUDED

The first solid fluidization exploitation experimental system of marine natural gas hydrate in the world

Wei Na[1*] Zhou Shouwei[1] Zhao Jinzhou[1] Wu Kaisong[1] Guo Ping[1] Li Qingping[3] Fu Qiang[2] Gao Hang[4]
1 State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation of Southwest Petroleum University, Sichuan, China;
2 China National Offshore Oil Corporation, Beijing, China;
3 CNOOC Research Institute, Beijing, China;
4 Honghua Group, Sichuan, China.

Abstract: The reserves of marine natural gas hydrate, one of the most potential unconventional energy sources after shale gas, coal seam gas and tight gas, are about 100 times as much as that of terrestrial frozen soil. In marine environment, most of the veins, bulk hydrates and hydrates in fine-grained sediments belong to non-diagenetic natural gas hydrate, and there is no stable entrapment structure like conventional oil and gas fields and sandstone hydrate reservoirs. According to the physical characteristics and reservoir characteristics of marine non-diagenetic hydrate, Southwest Petroleum University innovatively proposes solid fluidization exploitation method, and establishes the first solid fluidization exploitation laboratory of marine natural gas hydrate in the world. The lab's position is "fully automated white-collar laboratory". The experimental system consists of rapid preparation and fragmentation of large samples, efficient pipe transportation, efficient separation and rapid detection modules and so on. The main functions of laboratory are rating of efficient rock breaking capacity, evaluation of rock carrying capacity in fluidization pilot exploitation of marine natural gas hydrate, evaluation of hydrate non-equilibrium decomposition and dynamic change laws of flow patterns, safe transportation of under different mining rates, and simulation of well control safety. The key technical indicators of laboratory are 12 MPa pressure, 65 m horizontal pipe, 30 m vertical pipe, and 1 decimeter pipe diameter. The laboratory can simulate the whole process of solid fluidization exploitation with 1200 m water depth, which is a landmark laboratory of Southwest Petroleum University with original innovation, independent design, independent research and development. The establishment of this laboratory is of great significance to the development of global gas hydrate research.

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[*] Corresponding author.

E-mail address: weina8081@163.com (Na Wei).

Keywords: Natural gas hydrate; Solid fluidization; Laboratory; The whole process simulation; Physical simulation; Preparation system; Breaking system; Pipe transportation system

Introduction

Natural gas hydrate, commonly known as "combustible ice", is a kind of crystalloid "clathrate compound" formed by the interaction of methane and other hydrocarbon gases or volatile liquids with water, and it's one of the most potential unconventional energy sources after shale gas, coal seam gas and tight gas [1,2]. Generally, we can obtain 164 m^3 methane and 0.8 m^3 water from the decomposition of natural gas hydrate per volume unit [3]. Natural gas hydrate is mainly distributed in terrestrial permafrost area and deep sea environment (referred to the definition of United States Geological Survey which is in short of USGS as water depth more than 1000 m in 2008), the total amount of which reached 7.6×10^{18} m^3, and the carbon content is 2 times as much as that of the proved fossil fuels [4] (including coal, oil and conventional natural gas etc.), of which the marine natural gas hydrate reserves are about 100 times as much as that of the land frozen soil [5], as shown in Figure 1 [6]. Therefore, the safe and efficient exploitation of natural gas hydrate, especially of natural gas hydrate in deep sea, is the frontier field of innovational technology in the world [7-10]. The United States, Canada, Germany and our neighbors such as Japan, India, South Korea and other countries have made long-term research program of natural gas hydrate [11]. Japan, Canada and the United States etc. conducted a short-term test of natural gas hydrate in the permafrost region of MARLIK, Canada in 2002 and 2008 and in the permafrost region of Alaska, USA in 2012. In March 2013, Japan successfully carried out the pilot exploitation of natural gas hydrate in its offshore waters. And China successfully tested the pilot exploitation of natural gas hydrate in Shenhu sea area, South China Sea in 2017 [12-17].

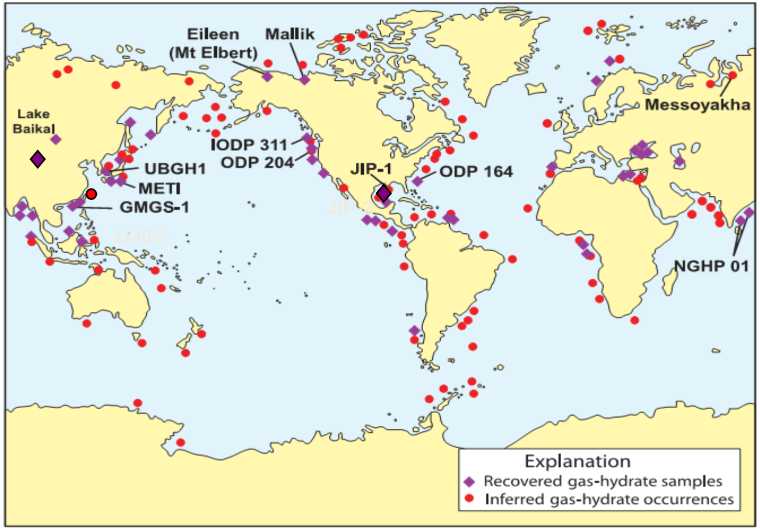

Figure 1. Distribution of natural gas hydrate resources in the world

Existing forms of natural gas hydrate are mainly as follows [18-21]: ①sandstone reservoir, distributed in the rock intergranular pores of polar permafrost; ②sandstone reservoir, distributed in rock intergranular pores of seabed formation; ③Non sandstone reservoirs, filled with fractures in rock formations; ④Vein and bulk hydrate, accompanied by a small amount of sediment; ⑤hydrate, dispersed in a fine-grained sediment with pellets. According to the existing drilling core data and exploration geological data, different forms of hydrate are shown in Figure 2.


Hydrate in clastic rock

Hydrate in sandstone of turbidity current

Hydrate filling in fractures

Hillock shaped hydrate in the seabed of Mexico Gulf

Figure 2. Different forms of natural gas hydrate

In marine environment, most of the veins, bulk hydrates and hydrates in fine-grained sediments belong to non-diagenetic natural gas hydrate, and there is no stable entrapment structure like conventional oil and gas fields and sandstone hydrate reservoirs. Moreover, there is no rock structure as a reservoir skeleton, the hydrate itself is the skeleton instead. Reservoir is unstable, the hydrate layer is easily decomposed by external influences, and the reservoir is easy to collapse and the decomposition of hydrate is hard to control. At the same time, the decomposition of natural gas hydrate in the shallow sea will lead to instability of the seabed structure foundation, will cause the submarine slip and other potential engineering geological disasters, and will result in greenhouse effect and other environmental safety issues, as shown in Figure 3. Therefore, catastrophic accidents, potential geological hazards, ecological damage, environmental greenhouse effect, production control, equipment risks and safety risks caused by insensible exploitation of non-diagenetic weak cemented natural gas hydrates of shallow strata of deep sea have always been the focus of hydrate exploitation, and we must adopt a safe and effective method of scientific and technological innovation to carry out green exploitation of such hydrate resources.

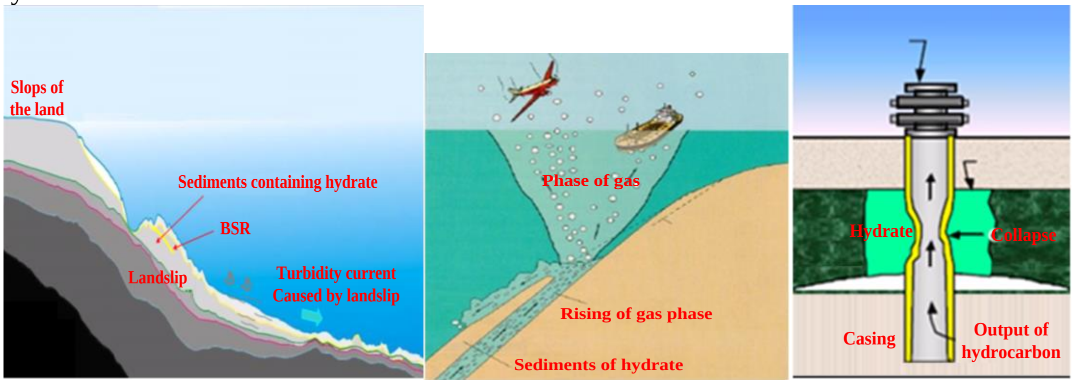

Figure 3. Environmental risks, equipment risks and production control risks

1 Technical ideas of solid fluidization exploitation of marine non-diagenetic gas hydrate

Nowadays, all the pilot exploitations in the world have been carried out in the ore body of diagenetic gas hydrate, and the exploitation techniques and methods of marine non-diagenetic gas hydrate are still blank, in which situation solid fluidization exploitation method is expected to be the frontier of science and technology innovation and one of the revolutionary technology to exploit non-diagenetic natural gas hydrates properly in the shallow layer of the world's ocean. The basic principle is as follows: use mining equipment to exploit natural gas hydrate orebody under relatively stable temperature and pressure at the bottom of the sea, crush the sediment containing the gas hydrate into fine particles and then mix with seawater, transport the mixer to offshore platform using closed pipes, and then develop post-processing in the offshore platform, the process flow is shown in Figure 4. The advantages are as follows: ①The entire mining process is carried out in the submarine natural gas hydrate zone, without changing the original temperature and pressure conditions of natural gas hydrates, it's similar to the construction of an artificial enclosed area consisting of submarine pipes and pumping systems, functioning as the sealing effect of the cap rock of conventional oil and gas reservoirs to transform the unenclosed natural gas hydrate orebody into a decomposing-controlled artificial closed orebody in a closed system. Thus, marine natural gas hydrates won't decompose in large quantities, which makes the situ development come true and can avoid engineering geological disasters and greenhouse effect resulting from the decomposition of natural gas hydrates; ②Meanwhile, this method takes advantage of natural changes in temperature and pressure of natural gas hydrate during transmission, realizing orderly-controlled decomposition in the scope of airtight transmission line.

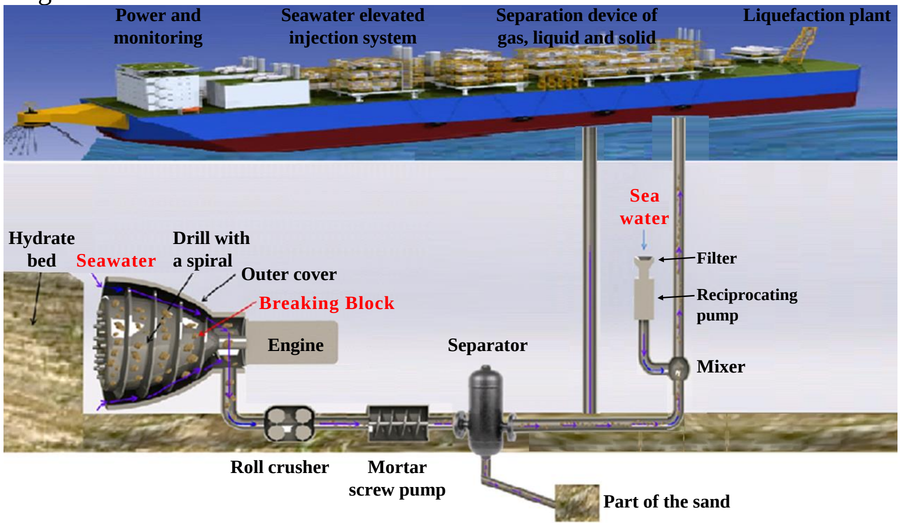

Figure 4. The solid fluidization exploitation process of marine non-diagenetic natural gas hydrate

2 Solid fluidization exploitation laboratory of marine non-diagenetic natural gas hydrate

Based on this industrial background, the world's first "marine non-diagenetic natural gas hydrate solid fluidization exploitation laboratory" was established at Southwest Petroleum University on April 28, 2015, in order to verify and carry out scientific research on the technology of solid fluidization, as shown in Figure 5. The lab is positioned as a "fully automated white-collar laboratory", the experimental system consists of rapid preparation and fragmentation of large samples, efficient pipe transportation, efficient separation and rapid detection modules and so on. The main functions of laboratory are rating of efficient rock breaking capacity, evaluation of rock carrying capacity in the pilot exploitation of marine natural gas hydrate fluidization, evaluation of hydrate non-equilibrium decomposition and dynamic change laws of flow patterns, safe transportation of under different mining rates, and simulation of well control safety. The key technical indicators of laboratory are 12 MPa pressure, 65 m horizontal pipe, 30 m vertical pipe, and 1 decimeter in-pipe diameter. The laboratory can simulate the whole process of solid fluidization exploitation with 1200 m water depth, which is a landmark laboratory of Southwest Petroleum University with original innovation, independent design, independent research and development.

Figure 5. The first solid fluidization exploitation laboratory of marine non-diagenetic natural gas hydrate in the world

2.1 Main functions of the laboratory

According to the technical idea of marine non-diagenetic natural gas hydrate solid fluidization exploitation, the laboratory has the following main functions:

①Rapid preparation of large samples of 1 m^3 and high performance of rock-breaking capacity;

②Safety transportation of hydrate under different mining rate;

③Evaluation of the non-equilibrium decomposition of hydrate and the law of dynamic change of fluid state;

④Simulation of the law of well control safety.

2.2 Process of marine non-diagenetic natural gas hydrate solid fluidization exploitation experimental system

In combination with the marine non-diagenetic natural gas hydrate solid fluidization exploitation and the main functions of the laboratory, the experimental design ideas and concepts are as follows:

①Similar prototype: hydrate reservoir depth of 1200 m, pipeline diameter of 0.380~0.508 m, pipeline length of 1,200~4,500 m. It can't be completed just through one similar experiment in the existing conditions due to the fact that length diameter ratio of the line is too large, therefore, we choose to complete pipe flow simulation in the whole process combining each experimental data through multiple cycles, multiple pressure (high pressure to low pressure), and multiple heat exchange and heating, and we magnify experimental flow parameters as much as possible to ensure safe and efficient transportation in condition that well control safety is meet.

②Simulate to prefabricate natural gas hydrate (sand included) sample according to the component of marine natural gas hydrate, and then add pre-prepared sea water to form hydrate slurry while breaking the sample,;

③Then the slurry is transferred to the circulation piping system, to simulate the multiphase pipeline transportation flow of gas hydrate slurry in the actual process of the exploitation;

④The horizontal and vertical wellbore can work independently in the experiment: horizontal section is focused on solving the problem of solid phase migration, and the vertical pipe section is focused on the prediction, measurement, pressure evolution and regulation of multi-phase flow characteristic parameters in the condition of hydrate phase change;

⑤The separation system is used to process and measure the decomposition of hydrate and decomposed products after the pipeline transportation is finished;

⑥Make it come true to control the operation and collet the testing data and image in the process of multiphase transportation, and have the capacity to monitor, process, analyze, display and store in real time;

⑦Through experimental research, the theoretical model of multiphase flow in solid fluidization exploitation is formed, perfected and enriched.

According to the experimental design ideas and concepts, the flow of solid fluidization exploitation experimental system of marine natural gas hydrate is divided into the following 5 functional modules (the specific experimental system flow is shown in Figure 6:

①Marine natural gas hydrate sample preparation module;
②Marine natural gas hydrate fragmentation and fidelity migration module;
③Experimental module of pipe transportation characteristics of marine natural gas hydrate slurry;
④Marine natural gas hydrate output separation module;
⑤Dynamic image capture, data acquisition and safety control module.

Figure 6. The process of marine natural gas hydrate solid fluidization exploitation experimental system

2.3 Key equipment of marine non-diagenetic natural gas hydrate solid fluidization exploitation experimental system

1) Preparing and breaking system of the hydrate

The device is mainly used to simulate hydrate deposits within 1200 m water depth at different temperatures and pressures. The system can rapidly generate natural gas hydrate of 1.062 m^3 within 24 hours through bubbling, spraying, mixing and other links, and break it into hydrate clastic in specified size and then output in accordance with the experimental requirements, in order to meet the needs of solid fluidization exploitation and pipeline transportation and experimental separation, as shown in Figure 7. The main performance indexes are as follows:

①Design pressure: 16 MPa;
②Design temperature: -10 ~ 60 ℃;
③Size of pot body: Phi 950 mm×1500 mm;
④Total volume of cavity: 1062 L;
⑤Medium: quartz sand, sea water, methane, chemical reagents and so on.

Figure 7. Preparing and breaking system of the hydrate

2）Slurry circulating pump

The power unit of complex medium fluid flow process of solid fluidization exploitation is the key equipment which is expected to adapt to the requirements of gas-liquid-solid (natural gas, sand, solid of the hydrate, and seawater) multiphase pipeline transportation. Southwest Petroleum University worked out a set of single-screw slurry circulating pump through its own design, research and development, and commission. The device is an essential power device for the purpose of ensuring the transmission and pipeline transportation characteristics of hydrates, as shown in Figure 8, and the main performance indexes are as follows:

①Displacement: 24 L/s;
②Design pressure: 16 MPa;
③Volume fraction of solid: less than 30%;
④Inlet and outlet pipe diameter: 3 inches;
⑤Lift: more than 100 m.

Figure 8. Slurry circulating pump

3）Dynamic pressure regulator

The method of solid fluidization exploitation is to transport the solid ore from water of 1200 m depth to the platform, and the pipeline pressure is from 12 MPa to atmospheric pressure. The pipeline loop of “marine natural gas hydrate solid fluidization exploitation experimental system” is a closed cycle system, but the fluid pressure of which can’t be reduced or be adjusted dynamically in a closed environment. Based on this objective and physical reality, Southwest Petroleum University has creatively designed and developed a dynamic pressure regulator. The device can dynamically adjust the pressure(from 12 MPa to 1 MPa) of the pipeline flow in the condition of material balance, according to the pressure reduction to cycle the gas-liquid-solid mixing phase of 30 m water depth, as shown in Figure 9. The main performance indexes are as follows:

①Working pressure: 12 MPa;
②Design pressure: 16 MPa;
③Working temperature: -10 ~ 60 ℃;
④Design temperature: 60 ℃;
⑤Size of working chamber: 1.15 m^3;
⑥The working medium: sea water, methane.

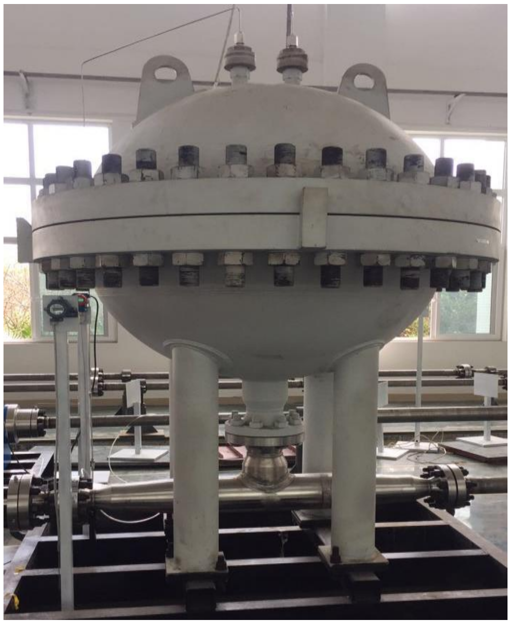

Figure 9. Dynamic pressure regulator

4）Efficient three-phase separator

The efficient three-phase separator consists of three-phase separator, storage tank, water storage tank, methane gas tank, gas flow meter and ball valve. Its main function is to separate and measure the quality of solid phase, gas and sea phase after the cycling experiment. The main performance indexes are as follows:

①Displacement: 0~24 L/s;
②Design pressure: 16 MPa;
③The design temperature is between -10 ℃ and 60 ℃;
④Inlet and outlet pipe diameter: 76.2 mm;
⑤The solid particle size: less than 10 mm.

Figure 10. Efficient three-phase separator

5）Real-time phase content monitoring sampler

The pipeline loop of “marine natural gas hydrates solid fluidization exploitation experimental system” is designed to realize the physical process in a closed circulatory system by constant depressurization and heating up. Therefore, the solid phase of natural gas hydrate in the pipeline is continuously gasified into free gas during the process of depressurization and heating, causing the dynamic change of the proportion of gas, liquid, and solid phase in the pipeline transportation system. Therefore, the sampler was used to analyze and measure the proportion of gas, liquid, and solid phase by using the method of physical settlement, taking advantage of the density difference among gas, liquid, and solid. The instantaneous component ratio of the slurry in each 30 m cycle was analyzed by the device to evaluate the decomposition efficiency of the hydrate solid phase and the migration efficiency of the sea sand. The “real-time phase content monitoring sampler” is mainly composed of sampling and measuring device, mass flowmeter and quick opening switch. The main performance indexes are as follows:

①Design pressure: 16 MPa;
②Working pressure: 12 MPa;
③Design temperature: -10 ~ 60 ℃;
④Length of kettle body: 200 mm;
⑤Diameter: Phi 25 mm;
⑥Width of the visual window: 14 mm;
⑦Length of the visual window: 100 mm.

Figure 11. Real-time phase content monitoring sampler

6）Pipeline temperature control system

The pipeline temperature control system is mainly used to simulate the temperature rise of the hydrate slurry in the rising flow of every 30 m pipeline in the sea. Therefore, thermal compensation to the vertical pipe is used to simulate the thermal exchange from the sea environment to the sea pipe by using the method of the electric heating and artificially forced heat transformation, as shown in Figure 12. The main performance indexes are as follows:

①Heating length: 30 m;
②Maximum heating power: 4 kW;
③Highest heating temperature: 60 ℃;
④Working temperature: 0~40 ℃;
⑤Heating mode: electric heating, temperature control.

Figure 12. Pipeline temperature control system

7）Automatic monitoring system

The automatic monitoring system can automatically collect and control the key parameters of the whole experimental system, as shown in Figure 13. The main performance indexes are as follows:

①Opening, closing and monitoring of automatic valve;
②Control and monitoring of temperature compensation;
③Control and monitoring of the dynamic regulation of pressure;
④Control and monitoring of the temperature and pressure of the kettle;
⑤Control and monitoring of the speed and stroke of crushing device;
⑥Monitoring of the temperature and pressure in pipeline;
⑦Monitoring of the image in high speed pipeline complex medium multiphase flow.

Figure 13. Automatic monitoring system

3 Conclusion

1）The “solid fluidization exploitation” adopts mechanical crushing to start pipeline transportation, and then develop in advantage of automatic decomposition, precipitation and lifting of the hydrate, to turn the uncontrollable into controllable and realize safe and green drilling. The pilot exploitation and development of non-diagenetic hydrate are still blank, and solid fluidization exploitation method is expected to be the frontier of science and technology innovation and one of the revolutionary technology to develop non-diagenetic natural gas hydrates properly in the shallow layer of the world’s ocean.

2）Solid fluidization exploitation laboratory of marine natural gas hydrate is positioned as a “fully automated white-collar laboratory". The main functions of laboratory are rating of efficient rock breaking capacity, evaluation of rock carrying capacity in marine natural gas hydrate fluidization pilot exploitation, evaluation of hydrate non-equilibrium decomposition and flow patterns dynamic change laws, safe transportation under different mining rates, and simulation of well control safety. The key technical indicators of laboratory are 12 MPa pressure, 65 m horizontal pipe, and 30 m vertical pipe. The laboratory can simulate the whole process of solid fluidization exploitation with 1200 m water depth.

3）The establishment of the first solid fluidization exploitation experimental system of marine natural gas hydrate in the world has a positive and far-reaching significance in promoting the development of natural gas hydrate research worldwide.

Acknowledgement

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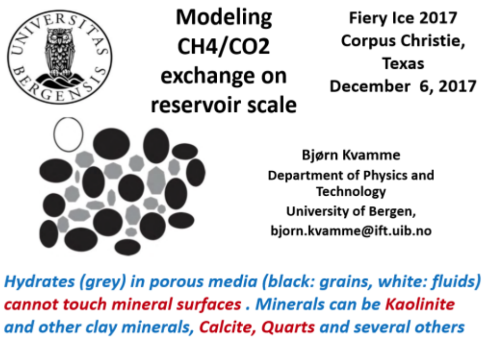
Modeling CH4/CO2 exchange on reservoir scale

Dr. Bjørn Kvamme Department of Physics and Technology, University of Bergen, Norway
Bjorn.kvamme@uib.no

ABSTRACT

Hydrates in sediments will never be able to reach equilibrium. The reason is that there are too many phases that are active in terms of significance for hydrate thermodynamics. Solid mineral surfaces are active because they structure water to densities far beyond liquid water densities. As example maximum density of first adsorbed layer of water on Calcite is by experiments found to be in the order of 2.4 times liquid water density. The corresponding chemical potential of water in this adsorbed layer is far lower that liquid water chemical potential and out of reach for any hydrate water chemical potential. While this characteristic property of mineral surfaces as being thermodynamic inhibitor and thus exclude any real "cementing" of hydrate in porous media there is also another side of these mineral surfaces. Some hydrate formers like CO_2 and H_2S can adsorb directly on some mineral surface while other hydrate formers like for instance CH_4 can be trapped in adsorbed water structures. In either case this primary or secondary adsorption leads to up-concentration of hydrate formers in structured water. This gives a beneficial situation for primary nucleation of hydrate. Hydrate crystal surfaces by itself serve as adsorption sites for water and hydrate formers from various phases (gas, liquid, mineral adsorbed). In summary this leads to many phases of significance for hydrate phase transitions which have to be accounted for in a balance between number of variables and conservation laws plus equilibrium conditions. It is easy to verify that even the simplest system of methane, liquid water and hydrate is highly thermodynamically over specified with pressure and temperature defined locally in a pore in a sediment. It does not change the situation of more hydrate formers are added to the system since the first and second laws of thermodynamics will dictate the hydrate formation towards the most stable hydrate first, under constraints of mass and heat transport. With respect to the latter it is important to keep in mind that hydrate formation on the gas/liquid interface is subject to mass availability which differ from average "bulk" gas since it is the adsorbed gas phase on the liquid water interface can be substantially different from the gas phase composition. In summary a number of different hydrates can form since the chemical potential of hydrate formers in various phase are not the same. As example hydrate formed from liquid water and gas will give a different hydrate composition that hydrate formed from adsorbed hydrate formers. And the associated free energies of each hydrate phase will be different, and by definition each of these hydrate phases are unique phases. Hydrates in sediments can therefore not even be considered as being in quasi equilibrium since many slow processes have substantial impact over long time scales and are parts of methane fluxes from natural gas hydrate reservoirs worldwide, as in some cases also development of geo mechanical instabilities. During hydrate production slow kinetic processes under stationary conditions developed during geological time scales can become highly significant when fluid flow in the sediments changes. Implementation of true non-equilibrium analysis, and corresponding thermodynamic and kinetic models is a necessity in development of future generations of hydrate reservoir simulators. In this work we discuss a specific approach of using a reactive transport simulator as basis for treating various hydrate phase transitions as pseudo mineral reactions. Parameterization of other reservoir simulator variables like permeability versus hydrate saturation is also discussed. All the topics is well suited for international collaboration which could benefit the whole hydrate community, ranging from dynamics of methane fluxes over to hydrate production.

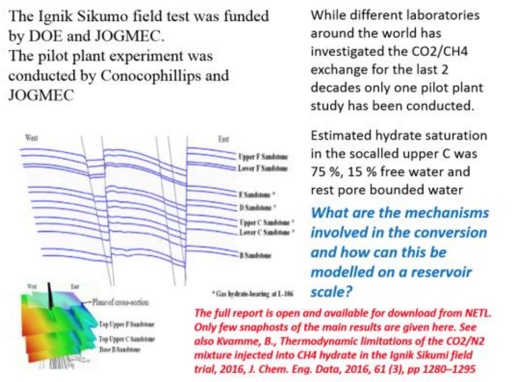


Modeling CH4/CO2 exchange on reservoir scale

Fiery Ice 2017
Corpus Christie, Texas
December 6, 2017

Bjørn Kvamme
Department of Physics and Technology
University of Bergen,
bjorn.kvamme@ift.uib.no

Hydrates (grey) in porous media (black: grains, white: fluids) cannot touch mineral surfaces . Minerals can be Kaolinite and other clay minerals, Calcite, Quarts and several others



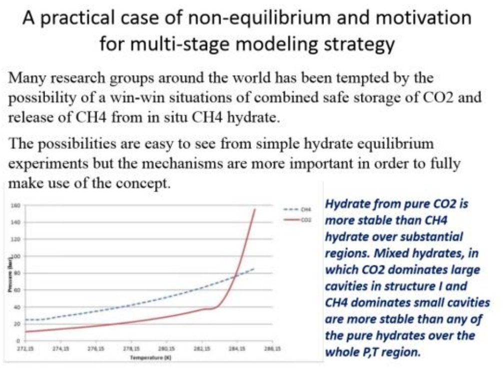
The Ignik Sikumo field test was funded by DOE and JOGMEC.
The pilot plant experiment was conducted by Conocophillips and JOGMEC

While different laboratories around the world has investigated the CO2/CH4 exchange for the last 2 decades only one pilot plant study has been conducted.

Estimated hydrate saturation in the socalled upper C was 75 %, 15 % free water and rest pore bounded water

What are the mechanisms involved in the conversion and how can this be modelled on a reservoir scale?

The full report is open and available for download from NETL. Only few snaphosts of the main results are given here. See also Kvamme, B., Thermodynamic limitations of the CO2/N2 mixture injected into CH4 hydrate in the Ignik Sikumi field trial, 2016, J. Chem. Eng. Data, 2016, 61 (3), pp 1280–1295

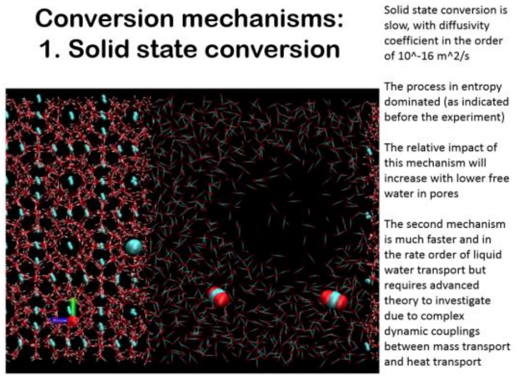


A practical case of non-equilibrium and motivation for multi-stage modeling strategy

Many research groups around the world has been tempted by the possibility of a win-win situations of combined safe storage of CO2 and release of CH4 from in situ CH4 hydrate.

The possibilities are easy to see from simple hydrate equilibrium experiments but the mechanisms are more important in order to fully make use of the concept.

Hydrate from pure CO2 is more stable than CH4 hydrate over substantial regions. Mixed hydrates, in which CO2 dominates large cavities in structure I and CH4 dominates small cavities are more stable than any of the pure hydrates over the whole P,T region.



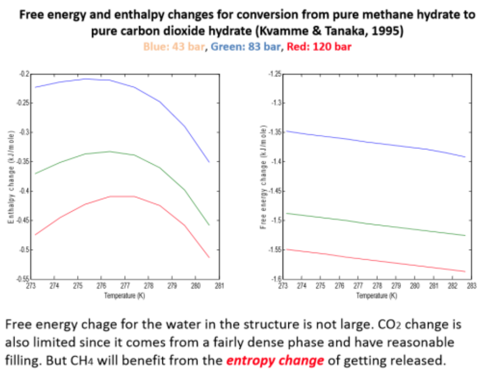
Conversion mechanisms: 1. Solid state conversion

Solid state conversion is slow, with diffusivity coefficient in the order of 10^-16 m^2/s

The process in entropy dominated (as indicated before the experiment)

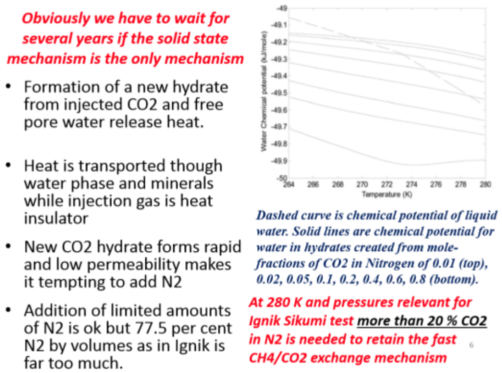
The relative impact of this mechanism will increase with lower free water in pores

The second mechanism is much faster and in the rate order of liquid water transport but requires advanced theory to investigate due to complex dynamic couplings between mass transport and heat transport



Free energy and enthalpy changes for conversion from pure methane hydrate to pure carbon dioxide hydrate (Kvamme & Tanaka, 1995)
Blue: 43 bar, Green: 83 bar, Red: 120 bar

Free energy chage for the water in the structure is not large. CO₂ change is also limited since it comes from a fairly dense phase and have reasonable filling. But CH₄ will benefit from the ***entropy change*** of getting released.

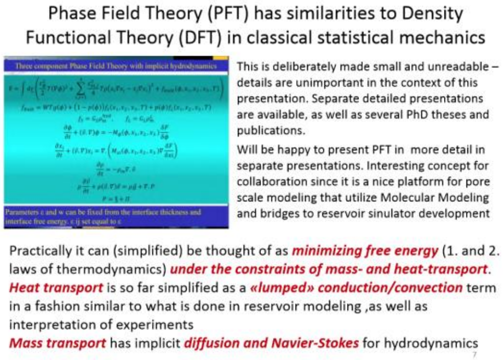


Obviously we have to wait for several years if the solid state mechanism is the only mechanism

- Formation of a new hydrate from injected CO2 and free pore water release heat.
- Heat is transported though water phase and minerals while injection gas is heat insulator
- New CO2 hydrate forms rapid and low permeability makes it tempting to add N2
- Addition of limited amounts of N2 is ok but 77.5 per cent N2 by volumes as in Ignik is far too much.

Dashed curve is chemical potential of liquid water. Solid lines are chemical potential for water in hydrates created from mole-fractions of CO2 in Nitrogen of 0.01 (top), 0.02, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8 (bottom).

At 280 K and pressures relevant for Ignik Sikumi test** **<u>more than 20 % CO2</u>** **in N2 is needed to retain the fast CH4/CO2 exchange mechanism



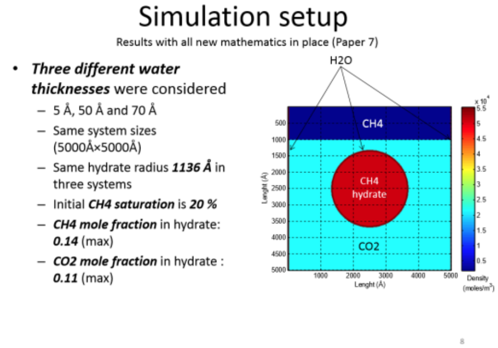
Phase Field Theory (PFT) has similarities to Density Functional Theory (DFT) in classical statistical mechanics

This is deliberately made small and unreadable – details are unimportant in the context of this presentation. Separate detailed presentations are available, as well as several PhD theses and publications.

Will be happy to present PFT in more detail in separate presentations. Interesting concept for collaboration since it is a nice platform for pore scale modeling that utilize Molecular Modeling and bridges to reservoir simulator development

Practically it can (simplified) be thought of as ***minimizing free energy*** (1. and 2. laws of thermodynamics) ***under the constraints of mass- and heat-transport***. ***Heat transport*** is so far simplified as a ***«lumped» conduction/convection*** term in a fashion similar to what is done in reservoir modeling ,as well as interpretation of experiments

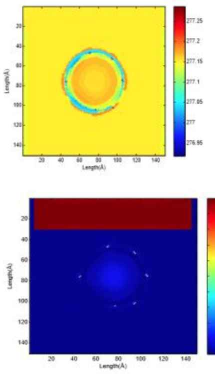
Mass transport has implicit ***diffusion and Navier-Stokes*** for hydrodynamics



Simulation setup

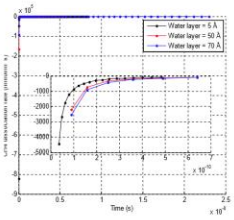
Results with all new mathematics in place (Paper 7)

- ***Three different water thicknesses*** were considered
  - 5 Å, 50 Å and 70 Å
  - Same system sizes (5000Å×5000Å)
  - Same hydrate radius ***1136 Å*** in three systems
  - Initial ***CH4 saturation*** is ***20 %***
  - ***CH4 mole fraction*** in hydrate: ***0.14*** (max)
  - ***CO2 mole fraction*** in hydrate : ***0.11*** (max)



It may not be easy to read from these figures but heat released from new CO2 hydrate formation mainly goes inwards through liquid water and hydrate while local cooling during in situ CH4 hydrate is smeared more out on interface towards CO2 due to low heat transport capacity of CO2.

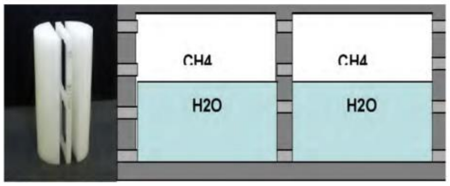
The thicker initial liquid water film around hydrate the longer period of fast exchange



What governs hydrate formation ?

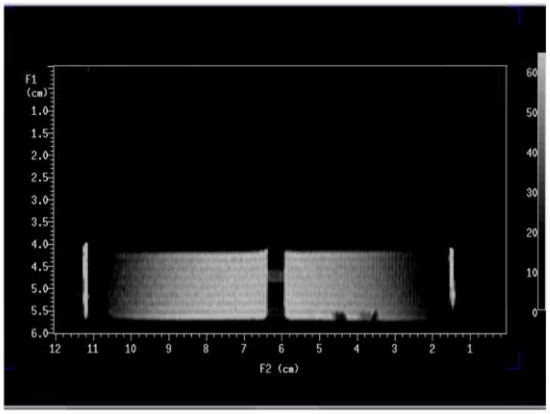
- ***Possibility to reach equilibrium*** (Gibbs). Is there balance between defined independent thermodynamic variables, conservation laws and conditions of equilibrium?
- Initial ***distance from equilibrium*** in all independent thermodynamic variables
- Combined First and Second laws of thermodynamics. In terms of Gibbs it implies that ***all systems will stribe towards minimum free energy*** as function of temperature, pressure and distribution of masses in the distem over possible phases, under constraints of mass and heat transport.
- ***Kinetics*** (combined thermodynamic control, mass transport dynamics and heat transport dynamics)

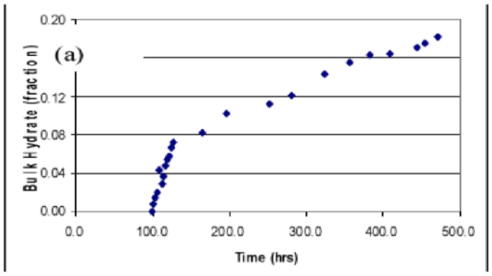
Experiments with methane and water at 83 bar and 3 C
Similar experiment with CO2 did not show any penetration of the hydrate film after 500 our (resolution ~ 100 micrometer)



Gibbs phase rule

- In this system there are two components and thus
- Two degrees of freedom when hydrate is formed ***homogeneously*** from dissolved methane. ***Hydrate equilibrium can be achieved***
- Only one degree of freedom whith hydrate forming ***heterogeneously*** on the gas/liquid interface. Overdetermined when both P and T is defined. ***Progress towards local and global minimum of free energy***





The most efficient hydrate nucleation is heterogeneous hydrate nucleation towards solid surfaces or liquid water surface

Guest molecules		Molar concentration	Molar concentration after CO_2 separation
Methane	(CH_4)	0.8448	0.8752
Ethane	(C_2H_6)	0.0876	0.0907
Propane	(C_3H_8)	0.0304	0.0314
Isobutane	(i-C_4H_{10})	0.0025	0.0026
Carbon dioxide	(CO_2)	0.0347	

Composition of the Sleipner gas (North Sea)

$$\begin{aligned}\mu_i^{gas} &= \frac{1}{\beta}\ln(\beta\Lambda_i^3) + \frac{1}{\beta}\ln(x_iN) - \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial N_i}\right)_{T,V,N_{j\neq i}}\\ &= \frac{1}{\beta}\ln(\beta\Lambda_i^3) + \frac{1}{\beta}\ln(x_iN) - \frac{1}{\beta}\left(\frac{\partial \ln Q^{2D}}{\partial N_i}\right)_{T,V,N_{j\neq i}}\\ &\quad - \frac{1}{\beta}\ln Q_i^{1D}\\ &= \frac{1}{\beta}\ln(\beta\Lambda_i^3) + \frac{1}{\beta}\ln(x_iN) - \frac{1}{\beta}(\beta\mu_i^{2D}) - \frac{1}{\beta}\ln Q_i^{1D}\end{aligned}$$

If ***liquid water is available*** then it is not actually the gas phase composition that determines which components that creates the hydrate – it is ***the adsorbed layer of hydrate formers***

Adsorption composition can be widely different than the «bulk» gas and is basically determined by the individual molecules attraction to water and thermodynamic state (simplified: how far from condensation)

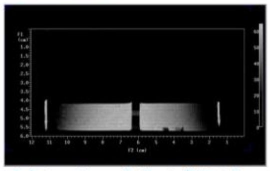
The symbols and details of this 2D adsoprtion theory is not interesting in this context. Will send the paper (Kvamme, B., *Thermodynamic limitations of the CO2/N2 mixture injected into CH4 hydrate in the Ignik Sikumi field trial*, J. Chem. Eng. Data, 2016, 61 (3), pp 1280–1295)

As a simple example of the estimated equilibrium between a gas phase consisting of 10 mole% CO2 in CO2/N2 mixture and a liquid water surface the adsorbed phase contains 32 mole% CO2 at 30 bar and 274 K

How many ***phases*** are actually then ***active and significant*** with respect to ***hydrate phase transitions*** in porous media?

- The minimum number of significant phases for one hydrate former in a pore is:

- Hydrate former phase
- Liquid water
- Adsorbed phase on mineral surfaces
- Initial hydrate forming
- Adsorbed on initial hydrate
- Additional hydrate phases (hydrate former from aquous solution, adsorbed, from gas, water from various phases)



Hydrate growing on a liquid water/CH4 interface. Initial hydrate formed from CH4 gas and liquid water. Then also growth from dissolved CH4 in water and third – some water from gas will adsorb on initial hydrate and create hydrate. These three events will give different hydrates. ***Black*** *is CH4 phase and hydrate. White is liquid*

So 5+ phases for two components gives a system over specified by minimum 3 independent thermodynamic variables when local T and P is defined by local flow

Gibbs Phase Rule

No. Of deg. Of freedom $\longrightarrow$ $$\tau = N - \pi + 2$$

No. Of components ↗ ↖ No. Of Phases

- Gibbs phase rule is actually very trivial and it is hard to see why it even has a name credited to the statement/equation. It is simply:
  - Number of independent thermodynamic variables (temperature, pressure and masses in all phases)

  minus conservation laws

  minus conditions of equilibrium

And the resulting number is the ***number of independent thermodynamic variables that must be fixed in order to make equilibrium possible.*** This is the degrees of freedom that appears in Gibbs phase rule.

Local temperature and pressure in a reservoir or in a pipeline is always given so any number of degrees of freedom different than two excludes possibility for full thermodynamic equilibrium

---

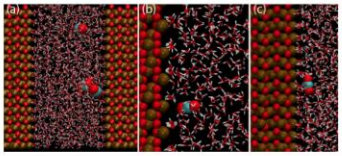
So – if the system ***cannot reach true thermodynamic equilibrium*** – then there is ***no rule that says chemical potential*** of hydrate formers ***is the same in all phases***

$$\mu_w^{H,i}(T,P,\vec{x}^H) = \mu_w^{H,0}(T,P) - \sum_j \nu_j \ln(1 + \sum_k h_{kj}^i)$$

$$h_{kj}^i = e^{-\beta(\mu_{kj}^i + \Delta g_{kj}^{inclusion})}$$

What is chemical potential for the guest in the «parent» phase ?
What is the resulting free energy of that specific hydrate phase ?

Right: CO2 (enhanced red and grey) adsorbing onto Hematite from water solution. Adsorbed CO2chemical potential: -39.21 kJ/mole at 274 K



The filling fraction of j in cavity type i is given by

$$\theta_{ij} = \frac{h_{ij}}{1 + \sum_j h_{ij}}$$

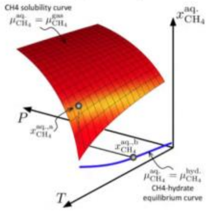
which then relates to the mole-fraction of j in the hydrate

$$x_j = \frac{\nu_{large}\theta_{large,j} + \nu_{small}\theta_{small,j}}{1 + \sum_j \nu_{large}\theta_{large,j} + \nu_{small}\theta_{small,j}}$$

$$x_{H2O}^{Hydrate} = 1 - \sum_j x_j$$

So any change in chemical potential of guest molecules due to changes in concentrations will lead to a new hydrate (composition and density will be different and by definition it is a new phase)

Any change in cavity partition function results in a new hydrate phase



In an non-equilibrium situation hydrate formed from dissolved methane in water (between **blue** curve and **red**) are different from other hydrates

---

$$\Delta G_i = \delta\left[x_w^{H,i}(\mu_w^{H,i} - \mu_w^p) + x_{CH4}^{H,i}(\mu_{CH4}^{H,i} - \mu_{CH4}^p)\right]$$

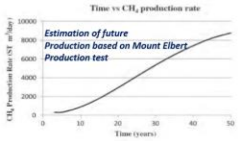
Free energy changes for *different* phase transitions involving hydrate from CH4

Table 1. Potential hydrate phase transition scenarios for a system of carbon dioxide with impurities as relevant for transportation pipeline. The change in the free energy for any of the processes mentioned in table 1 is calculated according to equation 1. Note that the different phase transitions may involve hydrate of different composition and as such the label hydrate for the phase does not distinguish between different free energy hydrates in this table.

i	δ	Initial phase(s)	Driving force	Final phase(s)
1	-1	Hydrate	Outside stability in terms of local P and/or T	Gas, Liquid water
2	-1	Hydrate	Sublimation (gas under saturated with water)	Gas
3	-1	Hydrate	Outside liquid water under saturated with respect to carbon dioxide and/or other enclathrated impurities originating from the carbon dioxide phase	Liquid water, (Gas)
4	-1	Hydrate	Hydrate gets in contact with solid walls at which adsorbed water have lower chemical potential than hydrate water	Liquid water, Gas
5	+1	Gas/fluid	Hydrate more stable than water and hydrate formers in the fluid phase	Hydrate
6	+1	Gas + Liquid water	Hydrate more stable than condensed water and hydrate formers from gas/fluid	Hydrate
7	+1	Surface reformation	Non-uniform hydrate rearranges due to mass limitations (lower free energy hydrate particles consumes mass from hydrates of higher free energy)	Hydrate
8	+1	Aqueous Phase	Liquid water super saturated with carbon dioxide and/or other hydrate formers, with reference to hydrate free energy	Hydrate
9	+1	Adsorbed	Adsorbed water on rust forms hydrate with adsorbed hydrate formers.	Hydrate
10	+1	Adsorbed +fluid	Water and hydrate formers from gas/fluid forms hydrate	Hydrate

Possible competing phase transitions involving hydrate with a basis from a system of CH4 containing water. More components in the CH4 phase will not change the picture as even more hydrate phases will occur (most stable hydrate form first)

Multi-scale modeling of hydrates in porous media and international collaboration



- There are many ***options*** for the various steps in multi-scale modeling
- On nano scale the are ***complementary*** hydrid methods (Molecular Dynamics with periodic Monte Carlo steps) to speed progress up and
- On nano to pore scale modeling there are also interesting ***complementary*** concepts – see next overhead for one example
- There is substantial value of ***symbiosis through international collaboration*** on theory, modeling, experiments and pilot experiments

On the reservoir level there are already a number of hydrate simulators so why do we need another one?

- Most existing hydrate simulators are either built up as extensions of ***oil/gas simulators*** or extensions of ***hydrogeological simulators***
- The various TOUGH HYDRATE versions started from the same framework as the TOUGH REACT versions.
- As such there is likely the possibility of making a new TOUGH HYDRATE based on TOUGH REACT in a similar fashion that we are extending our Reactive Transport code (RetrasoCodeBright)
- Considering each hydrate phase as a pseudo mineral opens up new possibilities
- Using free energy minimization tools which have been used for solving parallell gochemical reactions in flowing systems

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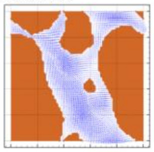
Permeability versus hydrate saturation

- Hydrate is unable to attach to mineral surfacs and will be pore filling like a special grain
- Evaluation of different possible pore structures from CT scan images of real porous material gives more than one structure with same porosity
- But there are significant differences in geomechanical stability of different possible structutures
- Illustration to the right are fromToru Sato (Tokyo University), which used Boltzmann flow to intep permability in Darcy flow
- This is a very interesting an conplementary concept to PFT. Since it starts from the hydrodynamic end it will easier handle large volumes, although with more simplified phase transition dynamics

Optimized pore structure based on CT scan and; below: estimated velocity profiles from lattice Boltzmann flow



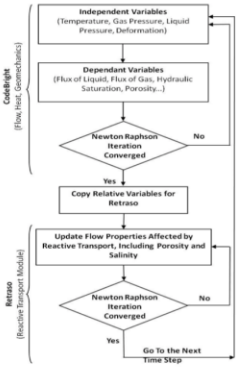
Numerical tool

Spatial discretization:
Finite elements (1D, 2D and 3D)

Temporal discretization:
Finite differences

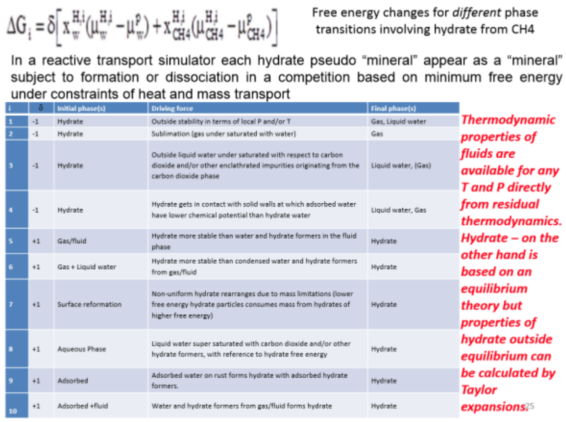
Non linear solver:
Newton-Raphson/Direct substitution
Approach / Global Implicit

We started out with the RetrasoCodeBight (RCB), which was an ideal gas hydrogeological simulator with implicit geomechanics, in 2006 and reworked it into a reactive transport simulator for aquifer storage for CO2 thorugh my programming and a PhD student (Shunping Liu), and funded by an USA cintrolled JIP. After 4 PhD's of reworking it further into a hydrate simulator there are still a number of very significant hydrate phase transition to include but we have a steady goal and we want to collaborate !



Thermodynamic data

- Thermodynamic data for fluid phases and water is available outside of equilibrium, with variable accuracy depending on equation of state. Molecular Dynamics (MD) simulations are alternatives for liquid CO2 containing impurities. (Kvamme et.al., *Phys.Chem.Chem.Phys.,* 2014, 16, 8623)
- Liquid water based on MD (Above reference or Kvamme & Tanaka, *J. Phys. Chem.* 1995, *99,* 7114-7119, also for outside equilibrium
- Hydrate thermodynamics (Kvamme & Tanaka, 1995) is also based on absolute thermodynamics but linked to an equilibrium theory. Hydrate properties outside equilibrium from Taylor expansions in all independent variable (temperature, pressure and concentrations). (Kvamme et.al., *Phys.Chem. Chem. Phys.,* 2013, 15, 2063.
- Ncessary properties for extensions to pressures and temperatures outside of equilibrium using MonteCarlo simulations of model hydrate systems
- See slide 39 for some examples of hydrate «reactions». Ovehead also repeated here for convenience



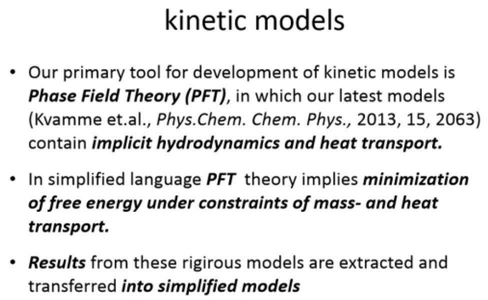
$$\Delta G_i = \delta\left[x_w^{H,i}(\mu_w^{H,i} - \mu_w^{P}) + x_{CH4}^{H,i}(\mu_{CH4}^{H,i} - \mu_{CH4}^{P})\right]$$

Free energy changes for *different* phase transitions involving hydrate from CH4

In a reactive transport simulator each hydrate pseudo “mineral” appear as a “mineral” subject to formation or dissociation in a competition based on minimum free energy under constraints of heat and mass transport

i	δ	Initial phase(s)	Driving force	Final phase(s)
1	-1	Hydrate	Outside stability in terms of local P and/or T	Gas, Liquid water
2	-1	Hydrate	Sublimation (gas under saturated with water)	Gas
3	-1	Hydrate	Outside liquid water under saturated with respect to carbon dioxide and/or other enclathrated impurities originating from the carbon dioxide phase	Liquid water, (Gas)
4	-1	Hydrate	Hydrate gets in contact with solid walls at which adsorbed water have lower chemical potential than hydrate water	Liquid water, Gas
5	+1	Gas/fluid	Hydrate more stable than water and hydrate formers in the fluid phase	Hydrate
6	+1	Gas + Liquid water	Hydrate more stable than condensed water and hydrate formers from gas/fluid	Hydrate
7	+1	Surface reformation	Non-uniform hydrate rearranges due to mass limitations (lower free energy hydrate particles consumes mass from hydrates of higher free energy)	Hydrate
8	+1	Aqueous Phase	Liquid water super saturated with carbon dioxide and/or other hydrate formers, with reference to hydrate free energy	Hydrate
9	+1	Adsorbed	Adsorbed water on rust forms hydrate with adsorbed hydrate formers.	Hydrate
10	+1	Adsorbed +fluid	Water and hydrate formers from gas/fluid forms hydrate	Hydrate

Thermodynamic properties of fluids are available for any T and P directly from residual thermodynamics. Hydrate – on the other hand is based on an equilibrium theory but properties of hydrate outside equilibrium can be calculated by Taylor expansions.



kinetic models

- Our primary tool for development of kinetic models is ***Phase Field Theory (PFT)***, in which our latest models (Kvamme et.al., *Phys.Chem. Chem. Phys.*, 2013, 15, 2063) contain ***implicit hydrodynamics and heat transport.***
- In simplified language ***PFT*** theory implies ***minimization of free energy under constraints of mass- and heat transport.***
- ***Results*** from these rigirous models are extracted and transferred ***into simplified models***

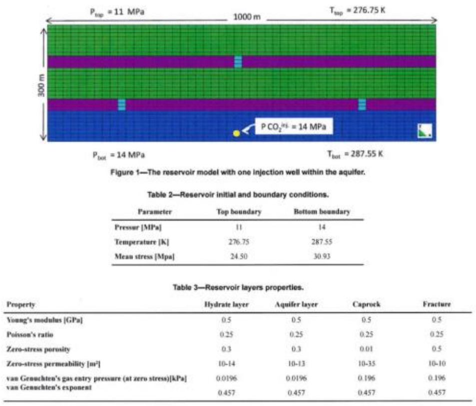


Figure 1—The reservoir model with one injection well within the aquifer.

Table 2—Reservoir initial and boundary conditions.

Parameter	Top boundary	Bottom boundary
Pressur [MPa]	11	14
Temperature [K]	276.75	287.55
Mean stress [Mpa]	24.50	30.93

Table 3—Reservoir layers properties.

Property	Hydrate layer	Aquifer layer	Caprock	Fracture
Young's modulus [GPa]	0.5	0.5	0.5	0.5
Poisson's ratio	0.25	0.25	0.25	0.25
Zero-stress porosity	0.3	0.3	0.01	0.5
Zero-stress permeability [m²]	10-14	10-13	10-35	10-10
van Genuchten's gas entry pressure (at zero stress)[kPa]	0.0196	0.0196	0.196	0.196
van Genuchten's exponent	0.457	0.457	0.457	0.457

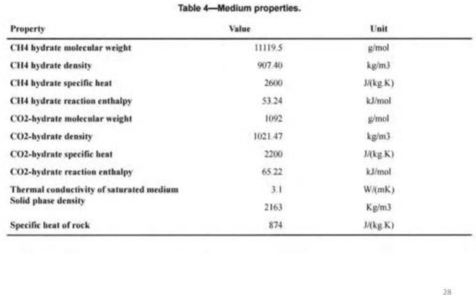


Table 4—Medium properties.

Property	Value	Unit
CH4 hydrate molecular weight	11119.5	g/mol
CH4 hydrate density	907.40	kg/m3
CH4 hydrate specific heat	2600	J/(kg.K)
CH4 hydrate reaction enthalpy	53.24	kJ/mol
CO2-hydrate molecular weight	1092	g/mol
CO2-hydrate density	1021.47	kg/m3
CO2-hydrate specific heat	2200	J/(kg.K)
CO2-hydrate reaction enthalpy	65.22	kJ/mol
Thermal conductivity of saturated medium	3.1	W/(mK)
Solid phase density	2163	Kg/m3
Specific heat of rock	874	J/(kg.K)

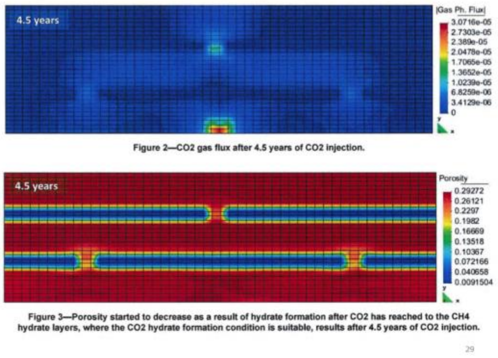


Figure 2—CO2 gas flux after 4.5 years of CO2 injection.

Figure 3—Porosity started to decrease as a result of hydrate formation after CO2 has reached to the CH4 hydrate layers, where the CO2 hydrate formation condition is suitable, results after 4.5 years of CO2 injection.

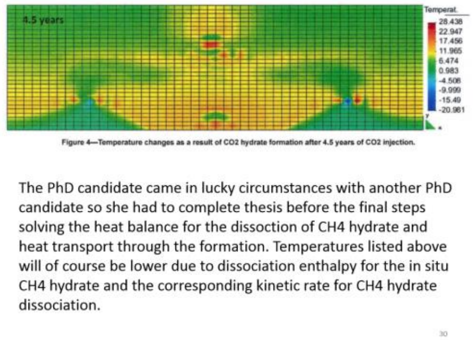
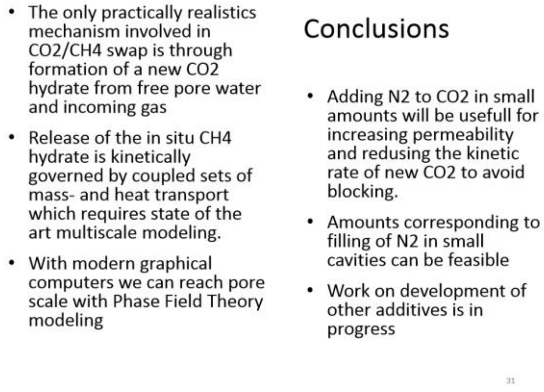


Figure 4—Temperature changes as a result of CO2 hydrate formation after 4.5 years of CO2 injection.

The PhD candidate came in lucky circumstances with another PhD candidate so she had to complete thesis before the final steps solving the heat balance for the dissoction of CH4 hydrate and heat transport through the formation. Temperatures listed above will of course be lower due to dissociation enthalpy for the in situ CH4 hydrate and the corresponding kinetic rate for CH4 hydrate dissociation.



Conclusions

- The only practically realistics mechanism involved in CO2/CH4 swap is through formation of a new CO2 hydrate from free pore water and incoming gas
- Release of the in situ CH4 hydrate is kinetically governed by coupled sets of mass- and heat transport which requires state of the art multiscale modeling.
- With modern graphical computers we can reach pore scale with Phase Field Theory modeling

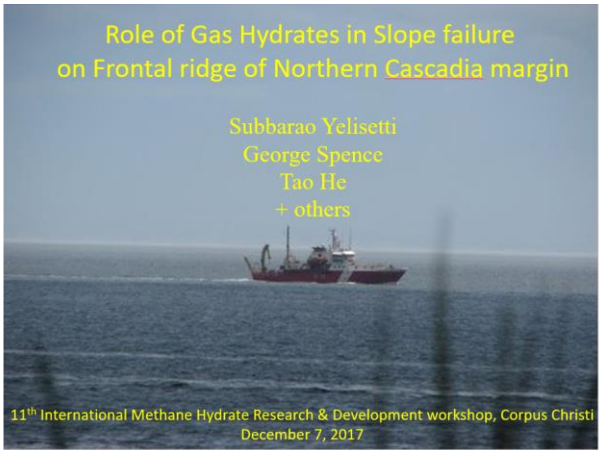
- Adding N2 to CO2 in small amounts will be usefull for increasing permeability and redusing the kinetic rate of new CO2 to avoid blocking.
- Amounts corresponding to filling of N2 in small cavities can be feasible
- Work on development of other additives is in progress

Dr. Subbarao Yelisetti – Texas A&M University – Kingsville

Role of gas hydrates in slope failure of northern Cascadia margin Subbarao Yelisettia*, Tao Heb and George Spencec aDepartment of Physics and Geosciences, Texas A&M University-Kingsville, Kingsville, Texas 78363, USA. bKey Laboratory of Orogenic Belts and Crustal Evolution, MOE (School of Earth and Space Sciences, Peking University), Beijing 100871, China. cSchool of Earth and Ocean Sciences, University of Victoria, Victoria, BC V8W 2Y2, Canada.

Abstract

Recent multibeam bathymetric and ocean bottom seismic studies from the northern Cascadia margin indicated several slope failure features associated with frontal accreted ridges near the foot of the continental slope. The combined volume estimate based on multibeam data of these slides (>1 km3) is approaching the mass failure volume for other slides that have generated large tsunamis-for example 1–3 km3 for a 1998 Papua New Guinea slide. The reason for these slope failure features is not clear although several lines of evidence indicate that there is some connection between the presence of hydrates and slope failure features on this margin. Vertical incidence and ocean bottom seismic data collected over the Slipstream slide indicate the presence of a bottom simulating reflector (BSR) at a depth of ~265-275 meters below the seafloor (mbsf). Tomographic velocity analyses of P- and S-waves indicate shallow high velocities at a depth of ~100 mbsf. The top of this high velocity layer coincides with the depth of the glide plane for this slide. On an adjacent frontal ridge, the depth of the glide plane associated with the Orca slide, matches with the depth of the BSR. In both these cases, the contrast in sediment strength between the hydrate saturated sediments and non-hydrated sediments could be providing the glide plane for failure. Shear stress distribution models for Slipstream slide indicate that the glide plane is more likely associated with the shallow high-velocity gas hydrate layer. These models further indicate that the sliding process starts from the top of the slope and then progressively retreats to the place of current headwall in a series of triangular blocks or wedges.



Role of Gas Hydrates in Slope failure on Frontal ridge of Northern Cascadia margin

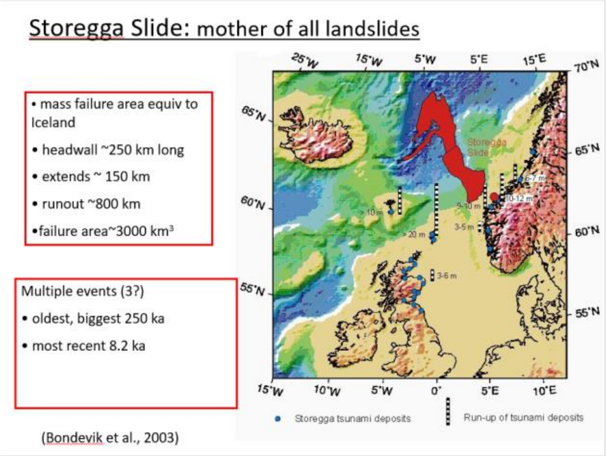
Subbarao Yelisetti
George Spence
Tao He
+ others

11th International Methane Hydrate Research & Development workshop, Corpus Christi
December 7, 2017

SeaJade Objectives

(Seafloor Earthquake Array – Japan CAnada CascaDia Experiment)

- To monitor earthquake activity on Canada's west coast
- To understand subsea-landslide and tsunami hazards



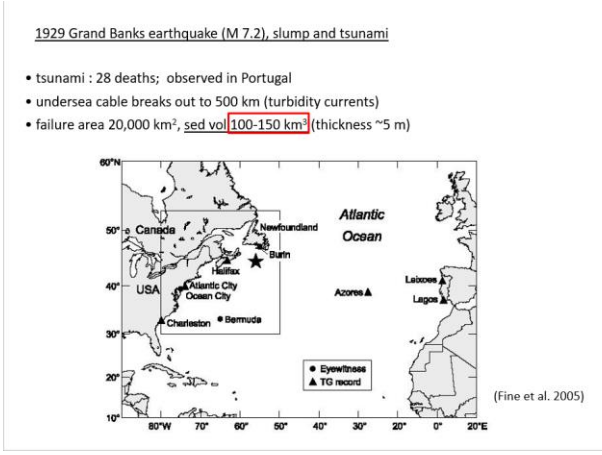
Storegga Slide: mother of all landslides

- mass failure area equiv to Iceland
- headwall ~250 km long
- extends ~ 150 km
- runout ~800 km
- failure area~3000 km^3

Multiple events (3?)

- oldest, biggest 250 ka
- most recent 8.2 ka

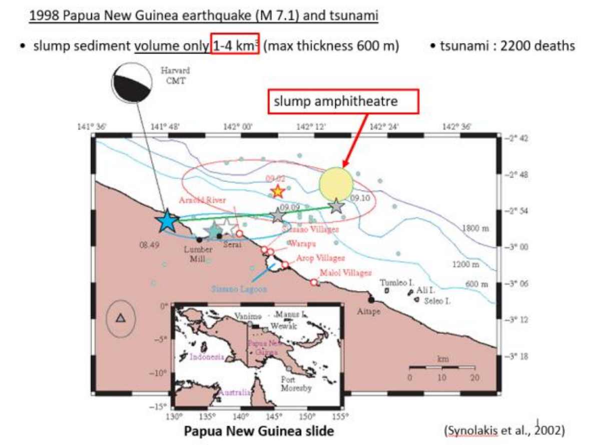
(Bondevik et al., 2003)



1929 Grand Banks earthquake (M 7.2), slump and tsunami

- tsunami : 28 deaths; observed in Portugal
- undersea cable breaks out to 500 km (turbidity currents)
- failure area 20,000 km^2, sed vol 100-150 km^3 (thickness ~5 m)

(Fine et al. 2005)



1998 Papua New Guinea earthquake (M 7.1) and tsunami

- slump sediment volume only 1-4 km^3 (max thickness 600 m)
- tsunami : 2200 deaths

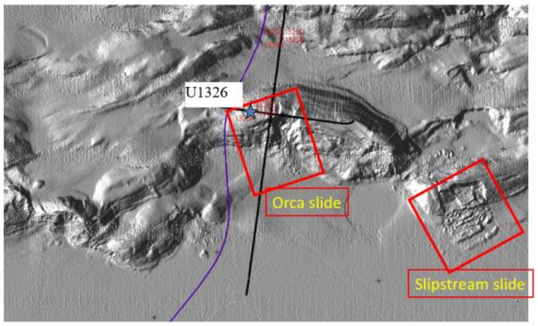
slump amphitheatre

Papua New Guinea slide

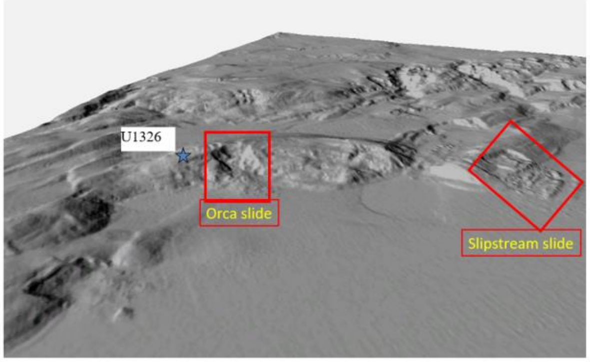
(Synolakis et al., 2002)

Cascadia margin, Vancouver Island

Swath bathymetry, U Washington, 2004

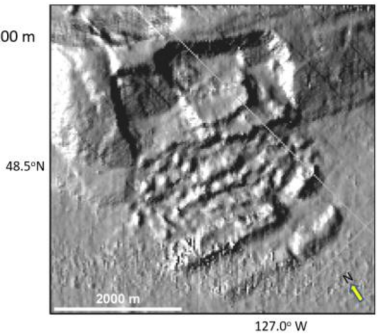


U1326 : IODP drilling, 2005



Slipstream slide

- headwall height ~ 100 m
- length ~ 3.3 km
- width ~ 2.5 km
- runout ~ 7 km
- volume ~ 0.33 km^3
- age ~ 14 ka



Slipstream slide

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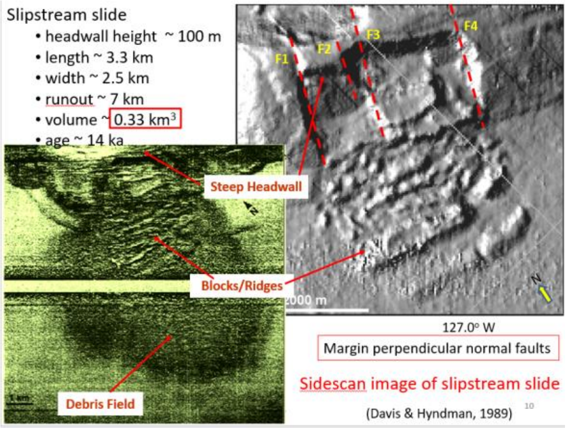


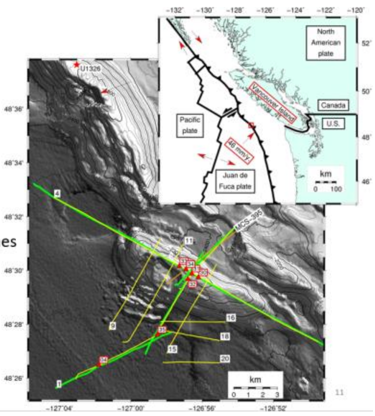
Margin perpendicular normal faults

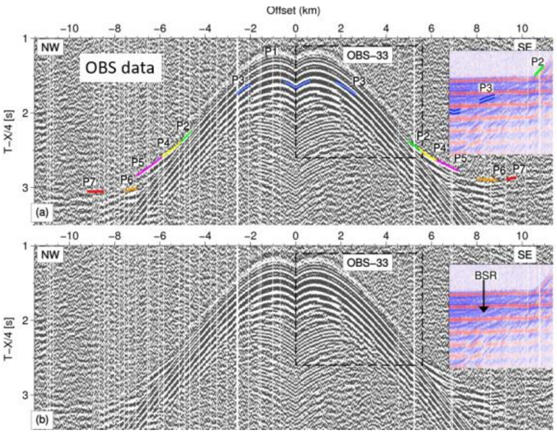
Sidescan image of slipstream slide

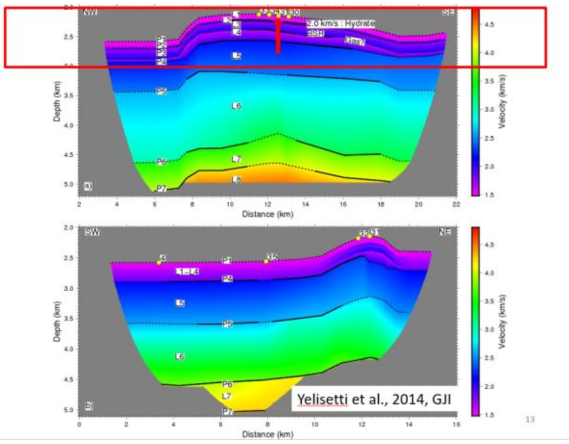
(Davis & Hyndman, 1989)

Study area

- 7 seismometers
- airgun~120 cu in.
- 2 refraction lines
- several reflection lines
- MCS line

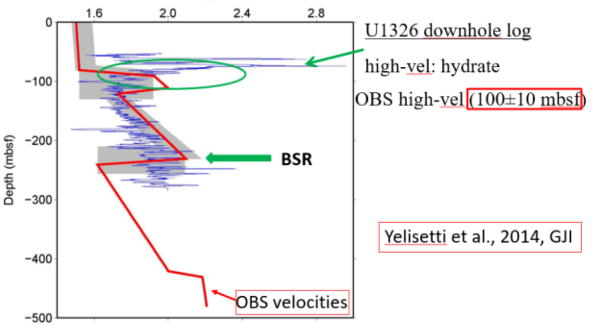






Yelisetti et al., 2014, GJI

Comparision with sonic log velocities



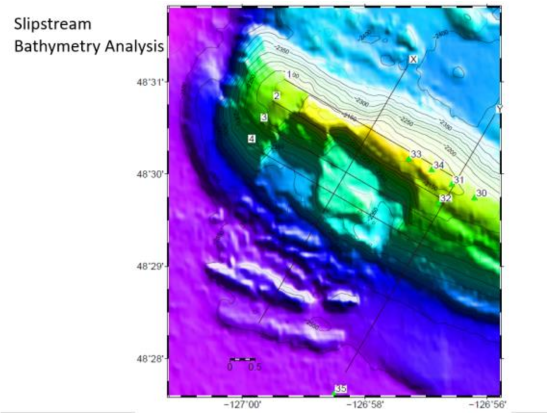
U1326 downhole log

high-vel: hydrate

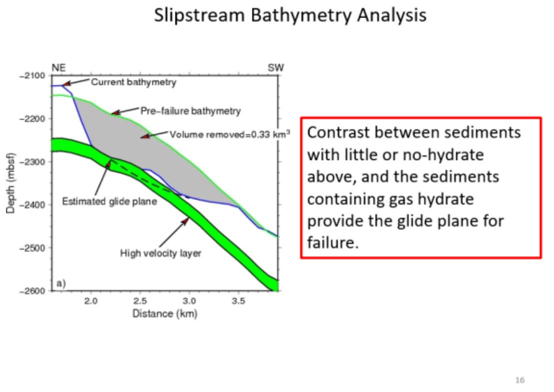
OBS high-vel (100±10 mbsf)

Yelisetti et al., 2014, GJI

OBS velocities

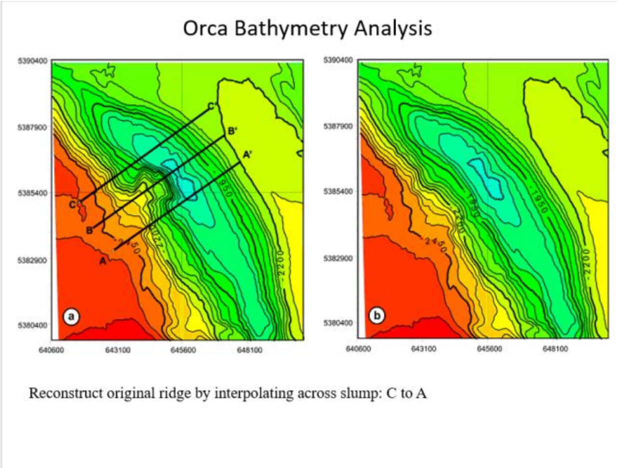


Slipstream Bathymetry Analysis



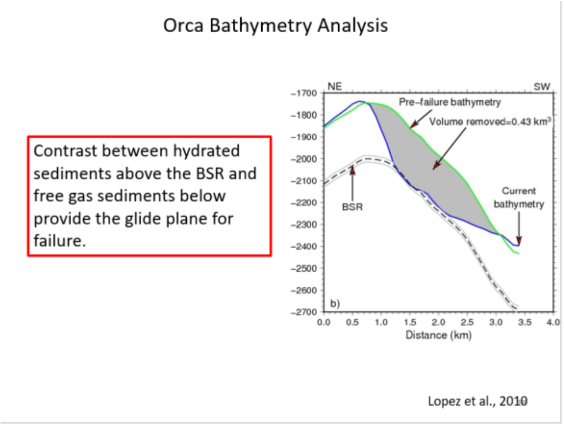
Slipstream Bathymetry Analysis

Contrast between sediments with little or no-hydrate above, and the sediments containing gas hydrate provide the glide plane for failure.



Orca Bathymetry Analysis

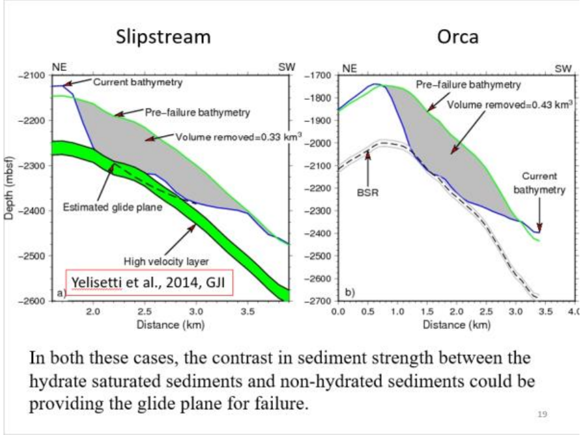
Reconstruct original ridge by interpolating across slump: C to A



Orca Bathymetry Analysis

Contrast between hydrated sediments above the BSR and free gas sediments below provide the glide plane for failure.

Lopez et al., 2010

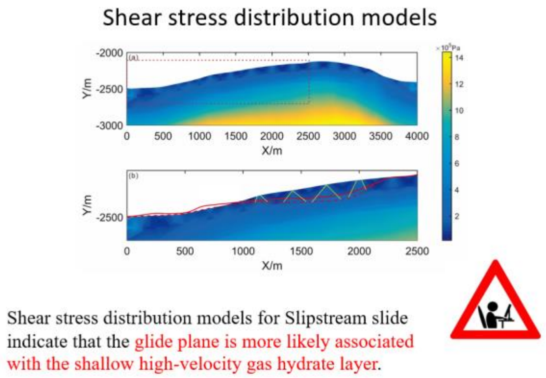


Slipstream

Orca

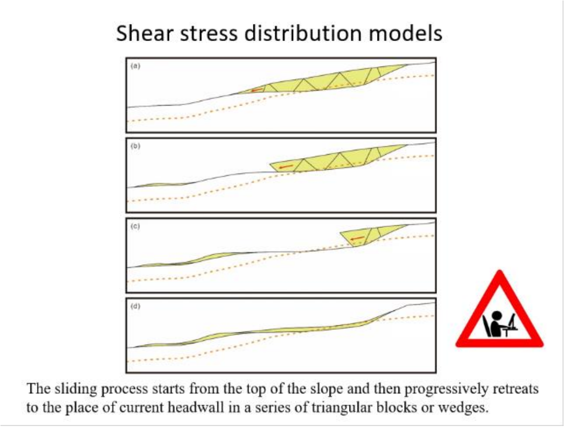
Yelisetti et al., 2014, GJI

In both these cases, the contrast in sediment strength between the hydrate saturated sediments and non-hydrated sediments could be providing the glide plane for failure.



Shear stress distribution models

Shear stress distribution models for Slipstream slide indicate that the glide plane is more likely associated with the shallow high-velocity gas hydrate layer.



Shear stress distribution models

The sliding process starts from the top of the slope and then progressively retreats to the place of current headwall in a series of triangular blocks or wedges.

3D Finite Element Modeling for Possible Creeping Behavior of Gas Hydrate-related Slipstream Submarine Slide, offshore Vancouver Island, Canada

Songbo Long, Tao He, Kun Lan, George D. Spence, and Subbarao Yelisetti

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THANK YOU

Subbarao Yelisetti subbarao.yelisetti@tamuk.edu www.web.uvic.ca/~subbarao/

Technology Status of Mining Guide Device of Natural Gas Hydrate in Seabed Shallow Layer

He Xia[1] Li Xuefeng[1] Zhong Lin[1] Wang Guorong[1] Liu Qingyou[2,5] Zhou Shouwei[3,5], Li Qingping[4] Fu Qiang[4] Wang Leizhen[1]

1College of Mechanical and Electrical Engineering, Southwest Petroleum University; 2. Key Laboratory for Fluid Machinery and Power Machinery of the Education Ministry of China, Xi Hua University, 610039; 3. China National Offshore Oil Corporation (CNOOC),Beijing,100010; 4.CNOOC Research Institute, Beijing,100027； 5. State Key Laboratory of Oil and Gas Reservoir Geology and Development Engineering, Southwest Petroleum University, Chengdu, 610500

Corresponding Email: zhonglin858296@163.com

Abstract The new method with solid fluidization exploitation of natural gas hydrate (NGH) and the new technology with jet flow mining crushing provide new ideas for the potential commercial exploitation of non-diagenetic NGH in seabed shallow layer, and the key point in commercial exploitation is to increase the mining efficiency, and furthermore the mining device guide is the essential technology, which determine the NGH commercial exploitation efficiency. For rotary steering, soft-bodied robots and continuous mechanical arm technology, the relevant guide technology applied to applicability evaluation of NGH mining are carried out, which demonstrates the feasibility of the guide tool of continuous tube with ultra-short radius and the technology of near-bit guidance robots with hydraulic jet mining. Based on this, the scientific problems of existing guidance technology applied to the mining guidance of seabed shallow NGH are proposed, which contain the stability of formation and borehole wall, equipment dimensions restricted by well diameter, the diversion of high curvature, in-situ real-time detection, the map construction of mining regional NGH reservoir and path planning of the unexploited area. Furthermore, the future potential development directions of research on the light weight, small size, high flexibility , high strength of mining guide devices and the real-time monitoring and evaluation of NGH reservoir location are put forward.

Key word: NGH in seabed shallow layer; Mining guide device; Scientific problems; Future development; Applicability evaluation of guide device; Feasibility demonstration of mining guide technology

TEXAS A&M UNIVERSITY CORPUS CHRISTI

11th International Methane Hydrate R&D Workshop

Technological Status of Mining Guiding Devices of Submarine Shallow Nature Gas Hydrate

Reporter: Lin Zhong

Email: 201699010108@swpu.edu.cn

Southwest Petroleum University

December 7, 2017

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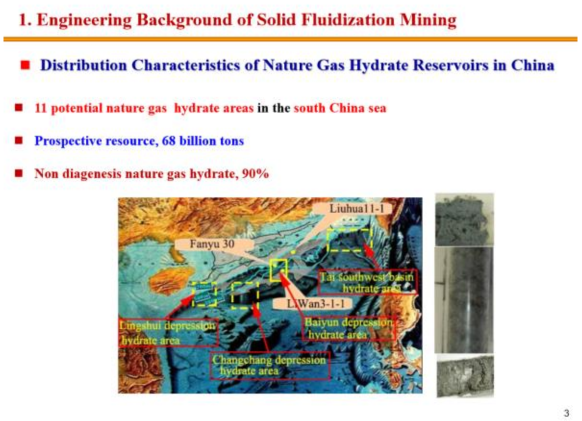
1. Engineering Background of Solid Fluidization Mining of Submarine Shallow Nature Gas Hydrate
2. Guiding Key Technologies of Solid Fluidization Mining
3. Applicability of Existing Guiding Technology
4. Development of Mining Guiding Devices



1. Engineering Background of Solid Fluidization Mining

Distribution Characteristics of Nature Gas Hydrate Reservoirs in China

- 11 potential nature gas hydrate areas in the south China sea
- Prospective resource, 68 billion tons
- Non diagenesis nature gas hydrate, 90%

1. Engineering Background of Solid Fluidization Mining

Types of Nature Gas Hydrate Reservoir in China

- Shallow reservoir and weak cementation
- Loose sediment for covering layer

1. Engineering Background of Solid-state Fluidization Mining

Classification of Nature Gas Hydrate Reservoir

Surficial layer 0～20m	Non diagenetic nature gas hydrates	Mining
Shallow layer 20～400m	Non diagenetic nature gas hydrates	Water jet crushing
Deep layer >400m	Diagenetic hydrates	Traditional mining methods such as pressure drop and heat injection

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1. Engineering Background of Solid Fluidization Mining

Urgent Problems of Nature Gas Hydrate Commercial Mining

- Traditionally Production problems---Collapse, Tsunami and Greenhouse Effect
- Urgent issue—Hydrate Phase change control, Mining formation Security
- A novel mining process need to be proposed for hydrate commercial mining

Collapse (Submarine landslide)

Phase change control Formation security

Tsunami and Greenhouse

1. Engineering Background of Solid Fluidization Mining

Solid Fluidization Mining Technology

Drill pipe into mud line and packer setting

Mechanical drilling pilot

Nozzle jet crushing fluidization

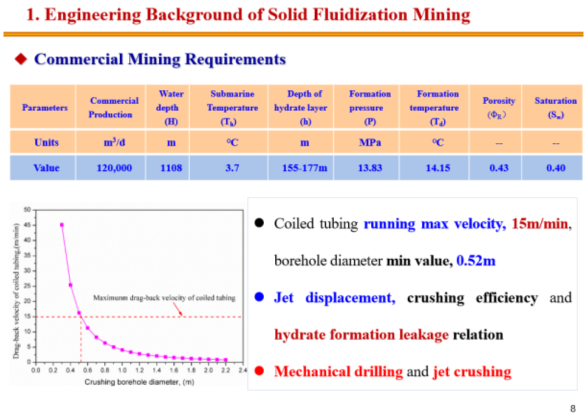
Recycle recovery hydrate slurry

In-situ sediment separation

Far-end sand backfill

Hydrate slurry pump lifting

Platform support system treatment



1. Engineering Background of Solid Fluidization Mining

Commercial Mining Requirements

Parameters	Commercial Production	Water depth (H)	Submarine Temperature (T_h)	Depth of hydrate layer (h)	Formation pressure (P)	Formation temperature (T_d)	Porosity (Φ_R)	Saturation (S_w)
Units	m^3/d	m	℃	m	MPa	℃	--	--
Value	120,000	1108	3.7	155-177m	13.83	14.15	0.43	0.40

- Coiled tubing running max velocity, 15m/min, borehole diameter min value, 0.52m
- Jet displacement, crushing efficiency and hydrate formation leakage relation
- Mechanical drilling and jet crushing

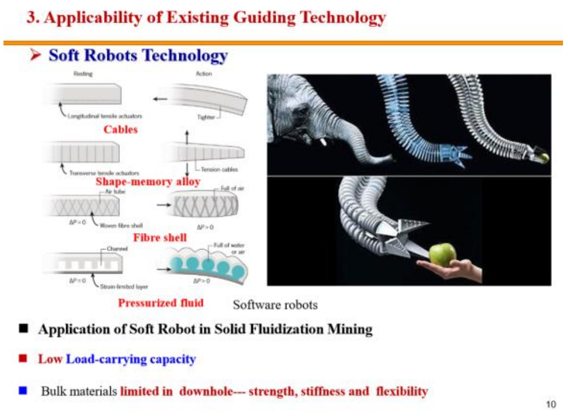
3. Applicability of Existing Guiding Technology

Rotary steerable Drilling Technology

(a) Push-back rotary steerable tool

(b) Directive rotary steerable tool

- **Push-the-bit rotary steerable tool**
  - **Drilling bit rotary angle---Lateral force (formation reacting force)**
  - **Not applicable non-diagenetic** hydrate formation
- **Point-the-bit rotary steerable tool**
  - Guiding offset mechanism including **cantilever bearing, eccentric ring and focal bearing.**
  - **Stable slope interval-- 0° to15°every 30m**
  - **Completing guide, minimum distance--180m**.
- **Flexible guidance, 20m- 400m**

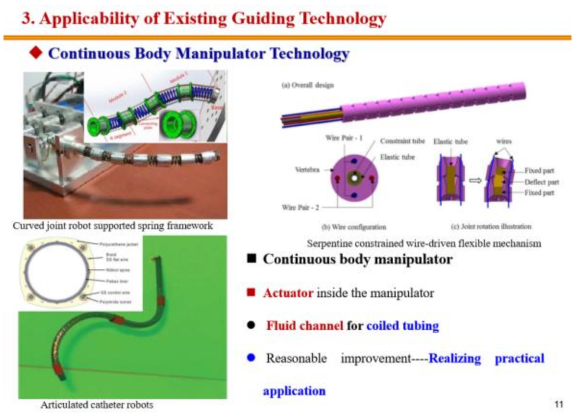


3. Applicability of Existing Guiding Technology

Soft Robots Technology

Software robots

- **Application of Soft Robot in Solid Fluidization Mining**
- **Low Load-carrying capacity**
- Bulk materials **limited in downhole--- strength, stiffness and flexibility**



3. Applicability of Existing Guiding Technology

Continuous Body Manipulator Technology

Curved joint robot supported spring framework

Serpentine constrained wire-driven flexible mechanism

Articulated catheter robots

- **Continuous body manipulator**
- **Actuator** inside the manipulator
- **Fluid channel for coiled tubing**
- Reasonable improvement----**Realizing practical application**

4. Development of Solid Fluidization Mining Guiding Devices

Development Direction of Mining Guiding Technology

4. Development of Solid Fluidization Mining Guiding Devices

Urgent Issue of Mining Guiding Devices for Commercial Mining

◆ **Stability** of hydrates formation and wellbore wall

◆ **Devices size** of borehole dimensions constraints

◆ **Distance and method** of in-situ real-time detection of efficient mining

◆ **Synchronous map construction** in hydrate mining and the **path planning of virgin areas**.

Thank you!

Lin Zhong

Email: 201699010108@swpu.edu.cn

Southwest Petroleum University

Feasibility Research on a Purification Technology of Natural Gas-hydrate Slurry by Sand Removal based on Hydrocyclone Separation

GuorongWang[1], Shunzuo Qiu[1],Yang Tang[1, 3], Qingyou Liu [2, 3]

[1]School of Mechatronic Engineering, Southwest Petroleum University,Chengdu,610500, China

[2]Key Laboratory for Fluid Machinery and Power Machinery of the Education Ministry of China, Xi Hua University, 610039, China

[3]State Key Laboratory of Oil and Gas Reservoir Geology and Development Engineering, Southwest Petroleum University, Chengdu, 610500, China

Corresponding Email:tangyanggreat@126.com

Abstract: Downhole real time separation technology is indispensable for solid fluidization and green exploitation of submarine shallow gas-hydrate. It is necessary to carry out research, because it can reduce energy consumption, increase mining efficiency and prevented gas-hydrate storage from collapse and leakage. Therefore, firstly anew exploitation and separation process was presented by our research group. And a hydrocyclone used for submarine gas-hydrate slurry was designed based on the properties of seabed gas-hydrate and the multiphase flow theory. Then separation efficiency of the hydrocyclone was analyzed, including particle sizes, inlet velocity, and sediment volume concentration, in gas-hydrate slurry by simulation method of Computational Fluid Dynamics (CFD). The simulation analysis results show that the separation efficiency of sand and gas-hydrate is more than 60%with the hydrocyclone in the conventional condition. For sand separation, when only the particle sizes was increased, the separation efficiency increased first and then decreased, and it reached the peak valuethatis98.63% at 30 um; when only the inlet velocity was increased, the separation efficiency first increased and then decreased, and reaches the peak value that is 98.63% at 12m/s; when only the sediment volume concentration was increased in gas-hydrate slurry, the separation efficiency always decreased, and it reached at 10%when thepeak value is 98.72%.Forgas-hydrate, increasingtheparticlesizes,the separation efficiency decreases, and reaches the peak at 10um, the peak value is 96.36%; Increasing inlet velocity, the separation efficiency first increases and then decrease, and reaches the peak at 12m/s, the peak value is 80.80%; Increasing sediment volume concentration in gas-hydrate slurry, the separation efficiency decreases, and reaches the peak at 10%, the peak value is 96.00%. According to this study, it is revealed that the hydrocyclone equipped with reasonable parameters has high separation efficiency and large amount of treatment for gas hydrate, and it will have a high feasibility and great application prospecting gas-hydrate exploitation. Keywords: Natural gas-hydrate; Hydrocyclone Separation; Sand-removal; CFD; Simulation analysis .

11th International Methane Hydrate Research and Development Workshop

Feasibility Research on a Purification Technology of Natural Gas-Hydrate Slurry by Sand Removal with Hydrocyclone Separation

——Study on Downhole Separation Device of Natural Gas Hydrate

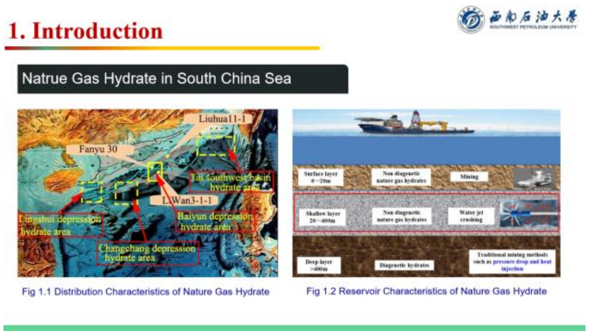
Reporter: Yang Tang
Email: tangyanggreat@swpu.edu.cn

Southwest Petroleum University
(西南石油大学)

December 7, 2017

Outline

- Introduction
- Methodology
- Results and Discussions
- Summary

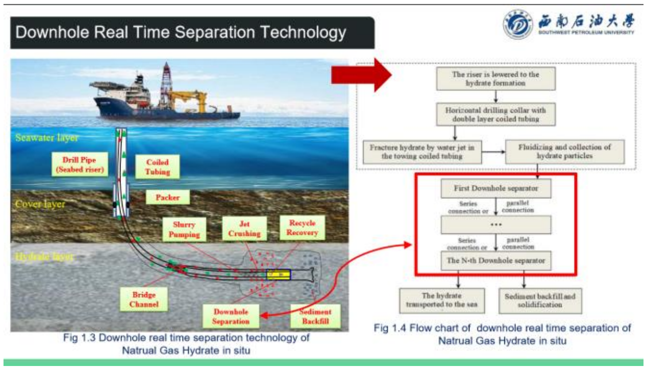


1. Introduction

Natrue Gas Hydrate in South China Sea

Fig 1.1 Distribution Characteristics of Nature Gas Hydrate

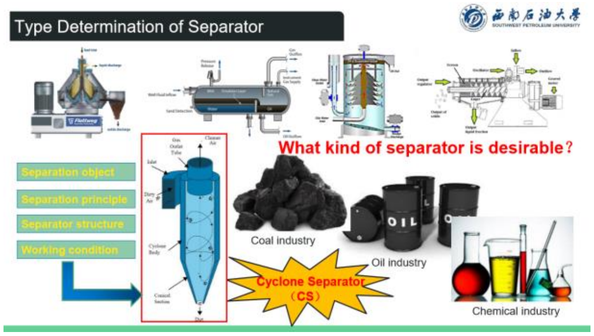
Fig 1.2 Reservoir Characteristics of Nature Gas Hydrate



Downhole Real Time Separation Technology

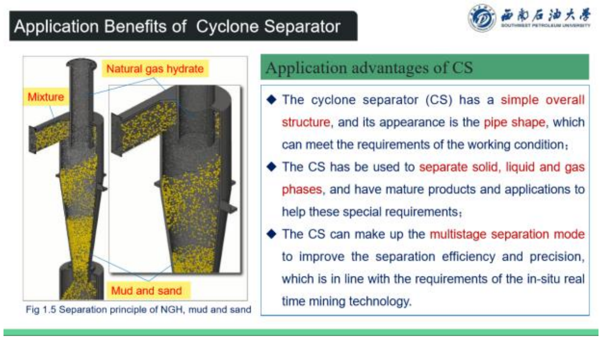
Fig 1.3 Downhole real time separation technology of Natrual Gas Hydrate in situ

Fig 1.4 Flow chart of downhole real time separation of Natrual Gas Hydrate in situ



Type Determination of Separator

What kind of separator is desirable?

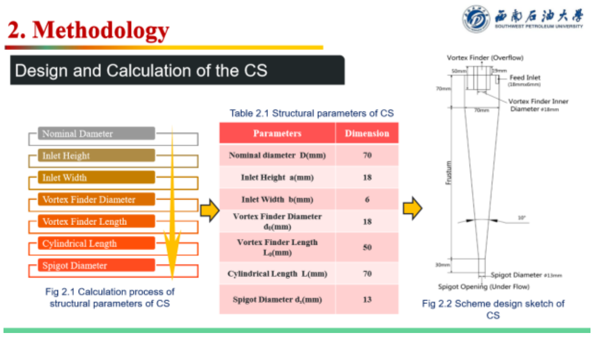


Application Benefits of Cyclone Separator

Fig 1.5 Separation principle of NGH, mud and sand

Application advantages of CS

- ◆ The cyclone separator (CS) has a simple overall structure, and its appearance is the pipe shape, which can meet the requirements of the working condition;
- ◆ The CS has be used to separate solid, liquid and gas phases, and have mature products and applications to help these special requirements;
- ◆ The CS can make up the multistage separation mode to improve the separation efficiency and precision, which is in line with the requirements of the in-situ real time mining technology.



2. Methodology

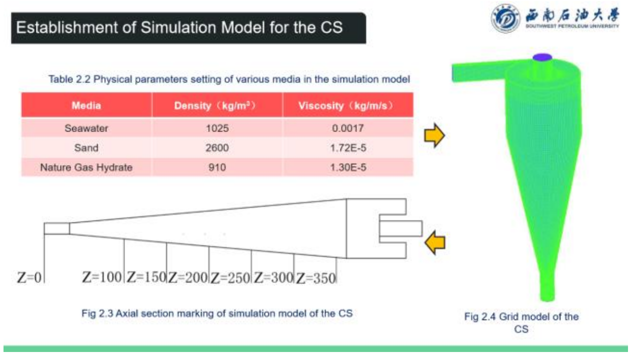
Design and Calculation of the CS

Fig 2.1 Calculation process of structural parameters of CS

Table 2.1 Structural parameters of CS

Parameters	Dimension
Nominal diameter D(mm)	70
Inlet Height a(mm)	18
Inlet Width b(mm)	6
Vortex Finder Diameter d_0(mm)	18
Vortex Finder Length L_0(mm)	50
Cylindrical Length L(mm)	70
Spigot Diameter d_s(mm)	13

Fig 2.2 Scheme design sketch of CS



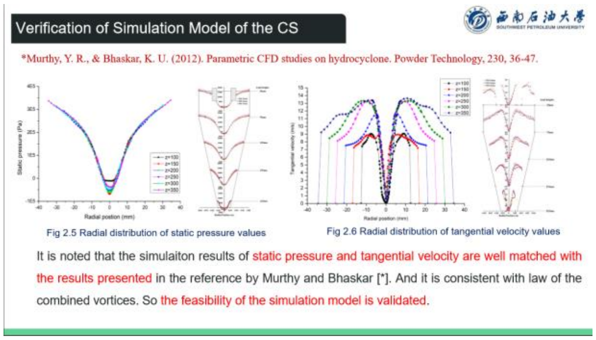
Establishment of Simulation Model for the CS

Table 2.2 Physical parameters setting of various media in the simulation model

Media	Density（kg/m^3）	Viscosity（kg/m/s）
Seawater	1025	0.0017
Sand	2600	1.72E-5
Nature Gas Hydrate	910	1.30E-5

Fig 2.3 Axial section marking of simulation model of the CS

Fig 2.4 Grid model of the CS



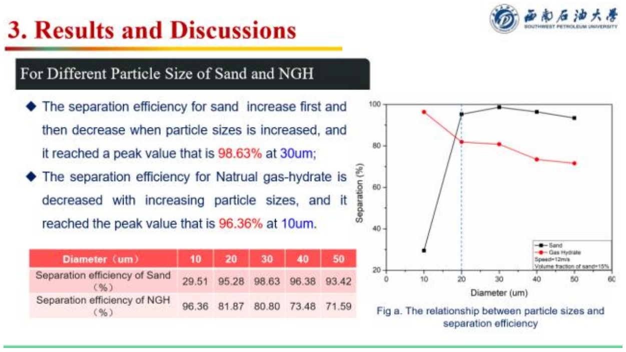
Verification of Simulation Model of the CS

*Murthy, Y. R., & Bhaskar, K. U. (2012). Parametric CFD studies on hydrocyclone. Powder Technology, 230, 36-47.

Fig 2.5 Radial distribution of static pressure values

Fig 2.6 Radial distribution of tangential velocity values

It is noted that the simulaiton results of static pressure and tangential velocity are well matched with the results presented in the reference by Murthy and Bhaskar [*]. And it is consistent with law of the combined vortices. So the feasibility of the simulation model is validated.



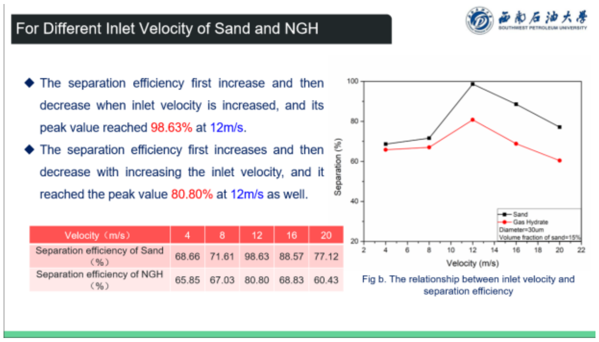
3. Results and Discussions

For Different Particle Size of Sand and NGH

- ◆ The separation efficiency for sand increase first and then decrease when particle sizes is increased, and it reached a peak value that is 98.63% at 30um;
- ◆ The separation efficiency for Natrual gas-hydrate is decreased with increasing particle sizes, and it reached the peak value that is 96.36% at 10um.

Diameter（um）	10	20	30	40	50
Separation efficiency of Sand（%）	29.51	95.28	98.63	96.38	93.42
Separation efficiency of NGH（%）	96.36	81.87	80.80	73.48	71.59

Fig a. The relationship between particle sizes and separation efficiency

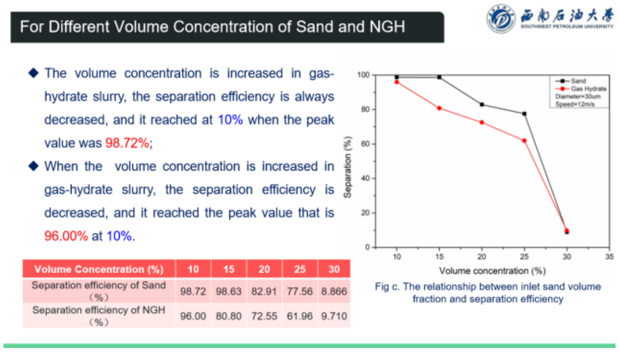


For Different Inlet Velocity of Sand and NGH

- ◆ The separation efficiency first increase and then decrease when inlet velocity is increased, and its peak value reached 98.63% at 12m/s.
- ◆ The separation efficiency first increases and then decrease with increasing the inlet velocity, and it reached the peak value 80.80% at 12m/s as well.

Velocity（m/s）	4	8	12	16	20
Separation efficiency of Sand（%）	68.66	71.61	98.63	88.57	77.12
Separation efficiency of NGH（%）	65.85	67.03	80.80	68.83	60.43

Fig b. The relationship between inlet velocity and separation efficiency

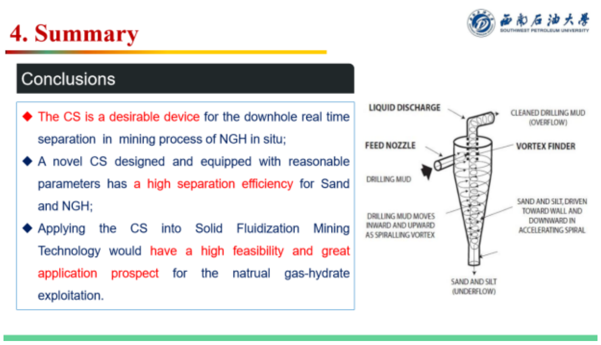


For Different Volume Concentration of Sand and NGH

- ◆ The volume concentration is increased in gas-hydrate slurry, the separation efficiency is always decreased, and it reached at 10% when the peak value was 98.72%;
- ◆ When the volume concentration is increased in gas-hydrate slurry, the separation efficiency is decreased, and it reached the peak value that is 96.00% at 10%.

Volume Concentration (%)	10	15	20	25	30
Separation efficiency of Sand（%）	98.72	98.63	82.91	77.56	8.866
Separation efficiency of NGH（%）	96.00	80.80	72.55	61.96	9.710

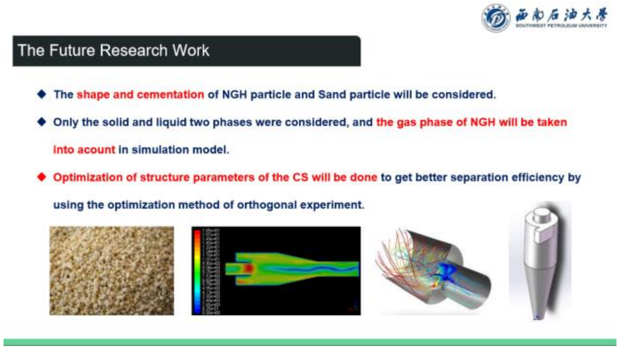
Fig c. The relationship between inlet sand volume fraction and separation efficiency



4. Summary

Conclusions

- ◆ The CS is a desirable device for the downhole real time separation in mining process of NGH in situ;
- ◆ A novel CS designed and equipped with reasonable parameters has a high separation efficiency for Sand and NGH;
- ◆ Applying the CS into Solid Fluidization Mining Technology would have a high feasibility and great application prospect for the natrual gas-hydrate exploitation.



The Future Research Work

- ◆ **The shape and cementation of NGH particle and Sand particle will be considered.**
- ◆ **Only the solid and liquid two phases were considered, and the gas phase of NGH will be taken into acount in simulation model.**
- ◆ **Optimization of structure parameters of the CS will be done to get better separation efficiency by using the optimization method of orthogonal experiment.**

Thank you !

Yang Tang

Email: tangyanggreat@swpu.edu.cn

Southwest Petroleum University

Geochemical Assessment of Coastal Gas Hydrate Loading off the Coast of New Zealand

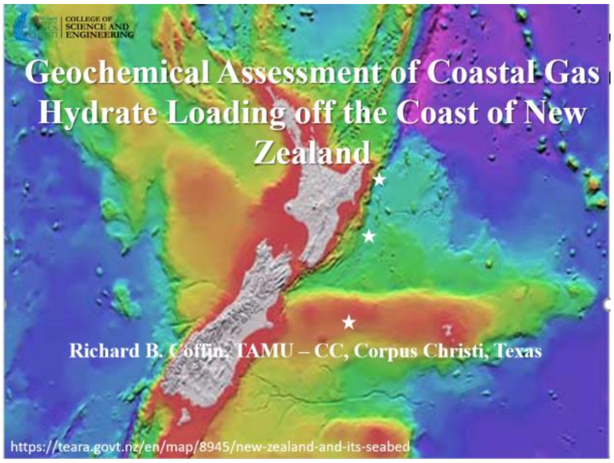
Dr. Richard Coffin – Texas A&M University – Corpus Christi, richard.coffin@tamucc.edu

Across world coastal oceans there have been extensive surveys with the application of seismic data to predict deep sediment gas hydrate loading. Over the past 10 years comparisons of seismic data and geochemistry show there is a need to combine these data for a more thorough understanding of the deep sediment gas hydrate loading. Initial observations in predicting hydrate presence with integration of seismic and geochemistry data off the mid Chilean margin suggested gas hydrate loading could be greater at a location where seismic data showed moderate gas blanking. On the Atwater Valley in the Gulf of Mexico geochemical assessment showed a region with a strong vertical rise in the BSR to be a site where gas hydrate are likely not stable as a result of salt diapir intrusions creating gas hydrate instability and higher vertical methane advection. Here we present a series of data along the eastern coast of New Zealand that include seismic profiles, geochemistry, controlled source electromagnetics, and heatflow to assess gas hydrate loading. This comparison of locations shows remarkable inconsistencies in the data sets applied to gas hydrate predictions. Through these locations comparisons include:

The Porangahau Ridge in the Hikurangi Margin where geochemical profiles focusing anaerobic methane oxidation display moderate vertical gas migration in a region that strong seismic, active heat flow, and controlled source electromagnetic data suggest deep gas hydrate loading and active fluid and gas advection. A carbon isotope mass balance shows the highest methane contribution to the location at a point where these instruments indicate strong advection. It is interesting these data do suggest moderate vertical methane migration relative to work done in the Gulf of Mexico and off the mid-Chilean margin.

Mahia Peninsula, located north from the Porangahau Ridge display strong similarity in geochemical and seismic data for assessment vertical methane fluxes in two different transects. However, porewater geochemical data from these transects compared to a “control” location where seismic data indicates no gas hydrate loading are similar. These data do confirm the realization that while gas hydrate loading assessment requires use of seismic data in the assessment there are likely extensive areas not identified. There is a need for future development of a better assessment of coastal gas hydrate loading.

Chatham Rise, a region where published seismic data was believed to contain gas hydrate loading was found to have a total absence of vertical methane migration. Thorough sediment porewater analysis at through this region showed no vertical methane fluxes to be present. In this location, radiocarbon data of shallow sediment carbonate and organic carbon suggest a potential for carbon dioxide migration. This observation has resulted in plans for a paleo-geochemical study to understand vertical carbon dioxide migration over climate cycles.



Geochemical Assessment of Coastal Gas Hydrate Loading off the Coast of New Zealand

Richard B. Coffin, TAMU – CC, Corpus Christi, Texas

https://teara.govt.nz/en/map/8945/new-zealand-and-its-seabed

Acknowledgements

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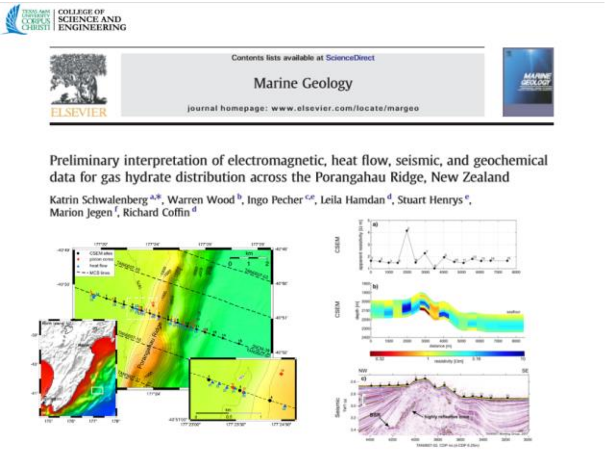
- Branden Yoza, University of Hawaii
- Jens Greinert, Geomar
- Joe Smith, US Naval Academy
- Paula Rose, TAMU-CC
- Kate Waghorn, University of Auckland
- Bryan Davy, GNS Wellington



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Marine Geology

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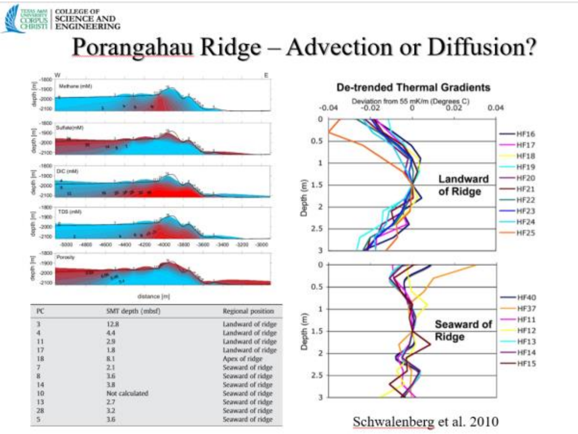
Preliminary interpretation of electromagnetic, heat flow, seismic, and geochemical data for gas hydrate distribution across the Porangahau Ridge, New Zealand

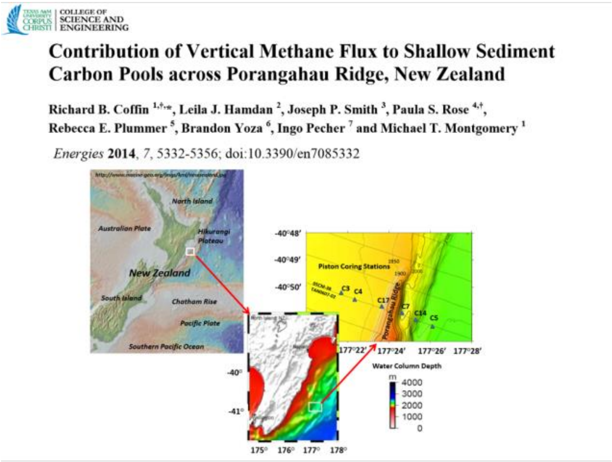
Katrin Schwalenberg[a,*], Warren Wood[b], Ingo Pecher[c,e], Leila Hamdan[d], Stuart Henrys[e], Marion Jegen[f], Richard Coffin[d]



Porangahau Ridge – Advection or Diffusion?

PC	SMT depth (mbsf)	Regional position
3	12.8	Landward of ridge
4	4.4	Landward of ridge
11	2.9	Landward of ridge
17	1.8	Landward of ridge
18	8.1	Apex of ridge
7	2.1	Seaward of ridge
8	3.6	Seaward of ridge
14	3.8	Seaward of ridge
10	Not calculated	Seaward of ridge
13	2.7	Seaward of ridge
28	3.2	Seaward of ridge
5	3.6	Seaward of ridge

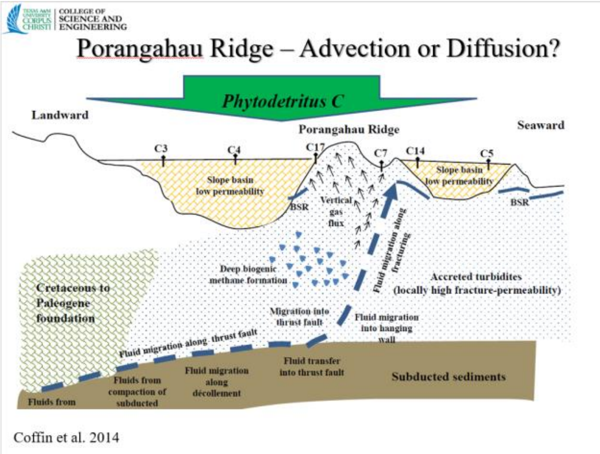
Schwalenberg et al. 2010



Contribution of Vertical Methane Flux to Shallow Sediment Carbon Pools across Porangahau Ridge, New Zealand

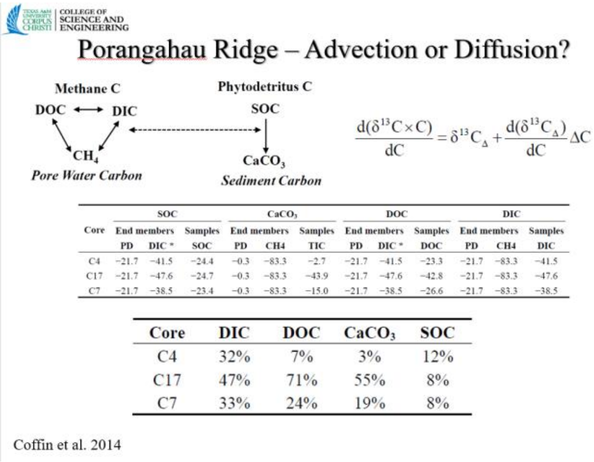
Richard B. Coffin[1,†,*], Leila J. Hamdan[2], Joseph P. Smith[3], Paula S. Rose[4,†], Rebecca E. Plummer[5], Brandon Yoza[6], Ingo Pecher[7] and Michael T. Montgomery[1]

Energies **2014**, *7*, 5332-5356; doi:10.3390/en7085332



Porangahau Ridge – Advection or Diffusion?

Coffin et al. 2014



Porangahau Ridge – Advection or Diffusion?

Methane C

DOC ⟷ DIC

CH$_4$

Pore Water Carbon

Phytodetritus C

SOC

CaCO$_3$

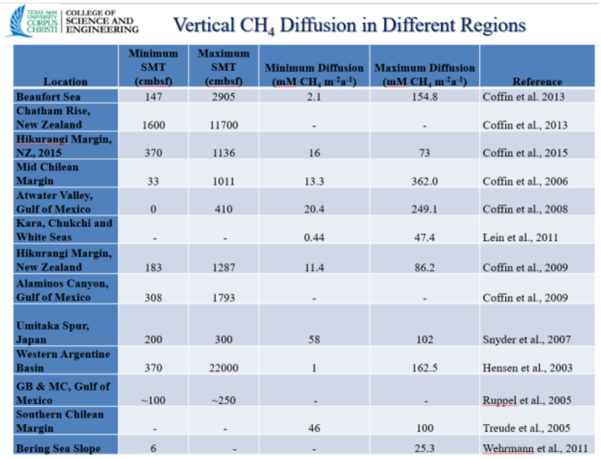
Sediment Carbon

$$\frac{d(\delta^{13}C\times C)}{dC}=\delta^{13}C_{\Delta}+\frac{d(\delta^{13}C_{\Delta})}{dC}\Delta C$$

Core	SOC			CaCO$_3$			DOC			DIC		
	End members		Samples	End members		Samples	End members		Samples	End members		Samples
	PD	DIC *	SOC	PD	CH4	TIC	PD	DIC *	DOC	PD	CH4	DIC
C4	−21.7	−41.5	−24.4	−0.3	−83.3	−2.7	−21.7	−41.5	−23.3	−21.7	−83.3	−41.5
C17	−21.7	−47.6	−24.7	−0.3	−83.3	−43.9	−21.7	−47.6	−42.8	−21.7	−83.3	−47.6
C7	−21.7	−38.5	−23.4	−0.3	−83.3	−15.0	−21.7	−38.5	−26.6	−21.7	−83.3	−38.5

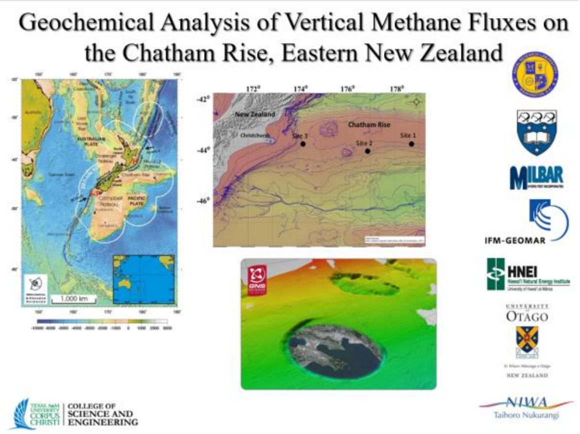
Core	DIC	DOC	CaCO$_3$	SOC
C4	32%	7%	3%	12%
C17	47%	71%	55%	8%
C7	33%	24%	19%	8%

Coffin et al. 2014

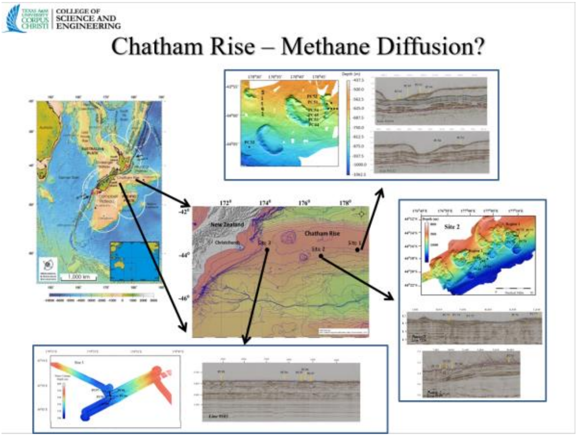


Vertical CH$_4$ Diffusion in Different Regions

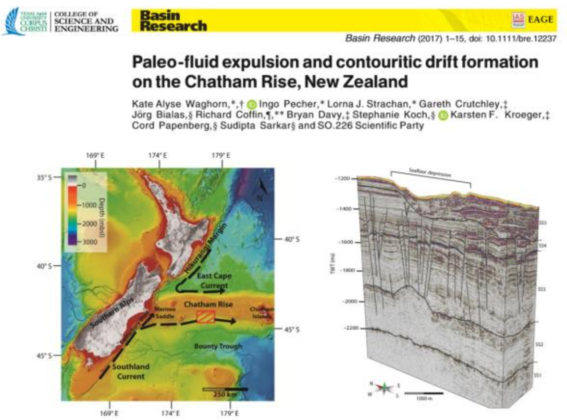
Location	Minimum SMT (cmbsf)	Maximum SMT (cmbsf)	Minimum Diffusion (mM CH$_4$ m^{-2}a^{-1})	Maximum Diffusion (mM CH$_4$ m^{-2}a^{-1})	Reference
Beaufort Sea	147	2905	2.1	154.8	Coffin et al. 2013
Chatham Rise, New Zealand	1600	11700	-	-	Coffin et al., 2013
Hikurangi Margin, NZ, 2015	370	1136	16	73	Coffin et al., 2015
Mid Chilean Margin	33	1011	13.3	362.0	Coffin et al., 2006
Atwater Valley, Gulf of Mexico	0	410	20.4	249.1	Coffin et al., 2008
Kara, Chukchi and White Seas	-	-	0.44	47.4	Lein et al., 2011
Hikurangi Margin, New Zealand	183	1287	11.4	86.2	Coffin et al., 2009
Alaminos Canyon, Gulf of Mexico	308	1793	-	-	Coffin et al., 2009
Umitaka Spur, Japan	200	300	58	102	Snyder et al., 2007
Western Argentine Basin	370	22000	1	162.5	Hensen et al., 2003
GB & MC, Gulf of Mexico	~100	~250	-	-	Ruppel et al., 2005
Southern Chilean Margin	-	-	46	100	Treude et al., 2005
Bering Sea Slope	6	-	-	25.3	Wehrmann et al., 2011



Geochemical Analysis of Vertical Methane Fluxes on the Chatham Rise, Eastern New Zealand



Chatham Rise – Methane Diffusion?



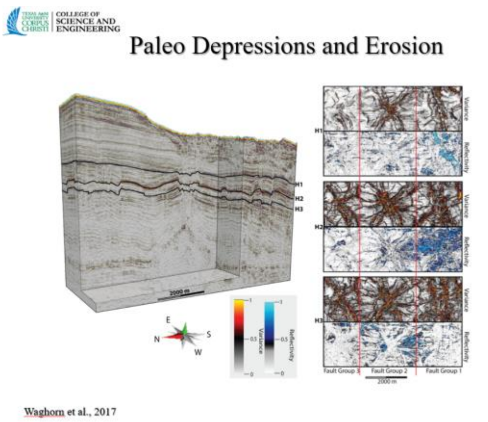
Basin Research

EAGE

Basin Research (2017) 1–15, doi: 10.1111/bre.12237

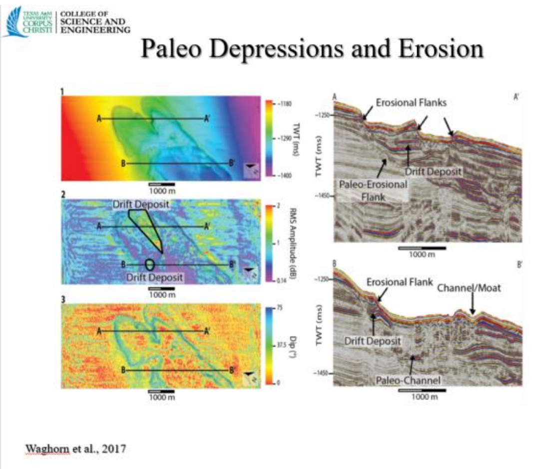
Paleo-fluid expulsion and contouritic drift formation on the Chatham Rise, New Zealand

Kate Alyse Waghorn,*,† Ingo Pecher,* Lorna J. Strachan,* Gareth Crutchley,‡ Jörg Bialas,§ Richard Coffin,¶,** Bryan Davy,‡ Stephanie Koch,§ Karsten F. Kroeger,‡ Cord Papenberg,§ Sudipta Sarkar§ and SO.226 Scientific Party



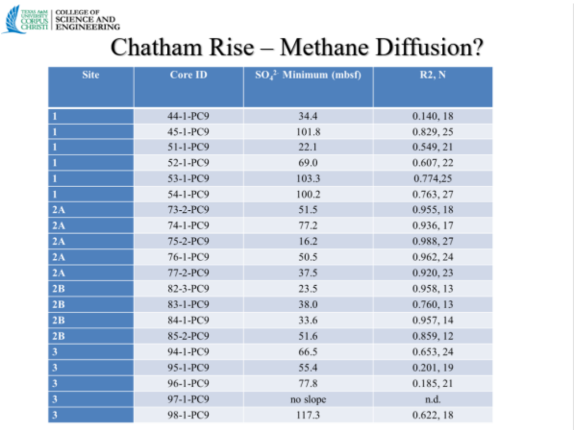
Paleo Depressions and Erosion

Waghorn et al., 2017



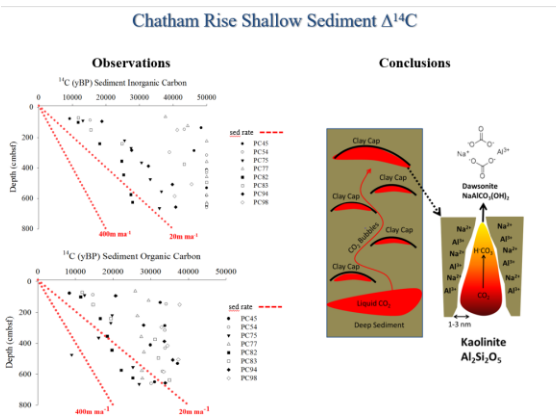
Paleo Depressions and Erosion

Waghorn et al., 2017



Chatham Rise – Methane Diffusion?

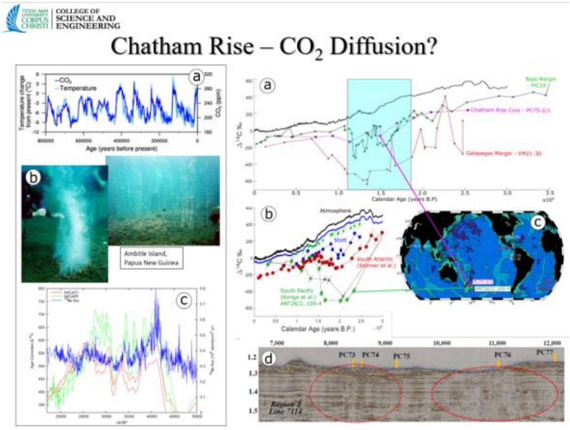
Site	Core ID	SO$_4^{2-}$ Minimum (mbsf)	R2, N
1	44-1-PC9	34.4	0.140, 18
1	45-1-PC9	101.8	0.829, 25
1	51-1-PC9	22.1	0.549, 21
1	52-1-PC9	69.0	0.607, 22
1	53-1-PC9	103.3	0.774,25
1	54-1-PC9	100.2	0.763, 27
2A	73-2-PC9	51.5	0.955, 18
2A	74-1-PC9	77.2	0.936, 17
2A	75-2-PC9	16.2	0.988, 27
2A	76-1-PC9	50.5	0.962, 24
2A	77-2-PC9	37.5	0.920, 23
2B	82-3-PC9	23.5	0.958, 13
2B	83-1-PC9	38.0	0.760, 13
2B	84-1-PC9	33.6	0.957, 14
2B	85-2-PC9	51.6	0.859, 12
3	94-1-PC9	66.5	0.653, 24
3	95-1-PC9	55.4	0.201, 19
3	96-1-PC9	77.8	0.185, 21
3	97-1-PC9	no slope	n.d.
3	98-1-PC9	117.3	0.622, 18



Chatham Rise Shallow Sediment Δ14C

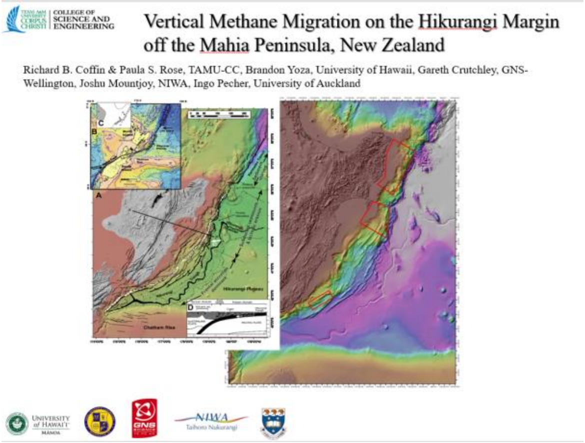
Observations

Conclusions



COLLEGE OF SCIENCE AND ENGINEERING

Chatham Rise – CO$_2$ Diffusion?



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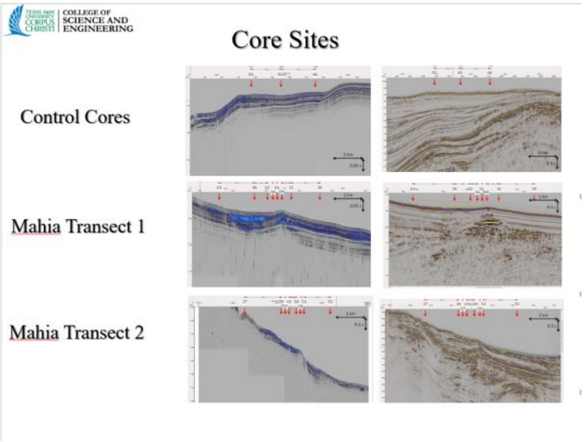
Vertical Methane Migration on the Hikurangi Margin off the Mahia Peninsula, New Zealand

Richard B. Coffin & Paula S. Rose, TAMU-CC, Brandon Yoza, University of Hawaii, Gareth Crutchley, GNS-Wellington, Joshu Mountjoy, NIWA, Ingo Pecher, University of Auckland



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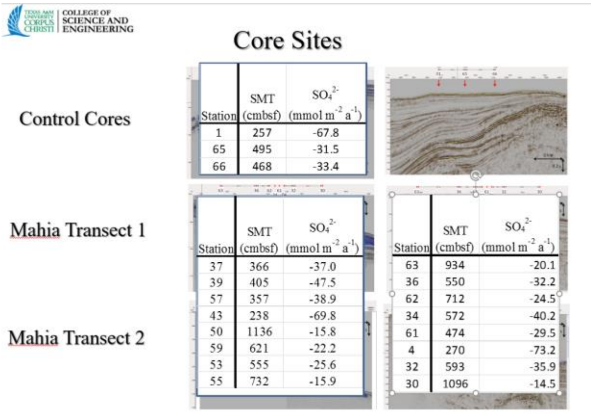
Core Sites

Control Cores

Mahia Transect 1

Mahia Transect 2



COLLEGE OF SCIENCE AND ENGINEERING

Core Sites

Control Cores

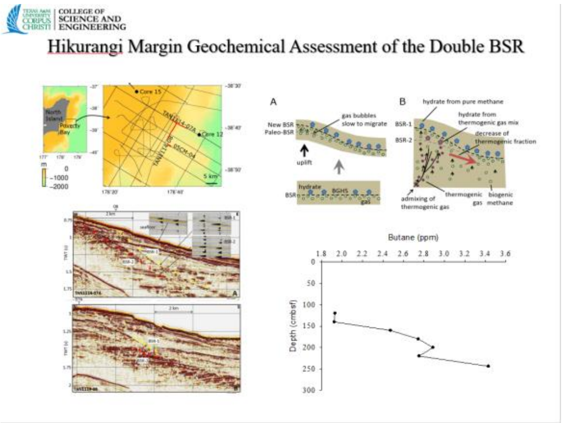
Station	SMT (cmbsf)	SO$_4^{2-}$ (mmol m^{-2} a^{-1})
1	257	-67.8
65	495	-31.5
66	468	-33.4

Mahia Transect 1

Station	SMT (cmbsf)	SO$_4^{2-}$ (mmol m^{-2} a^{-1})
37	366	-37.0
39	405	-47.5
57	357	-38.9
43	238	-69.8
50	1136	-15.8
59	621	-22.2
53	555	-25.6
55	732	-15.9

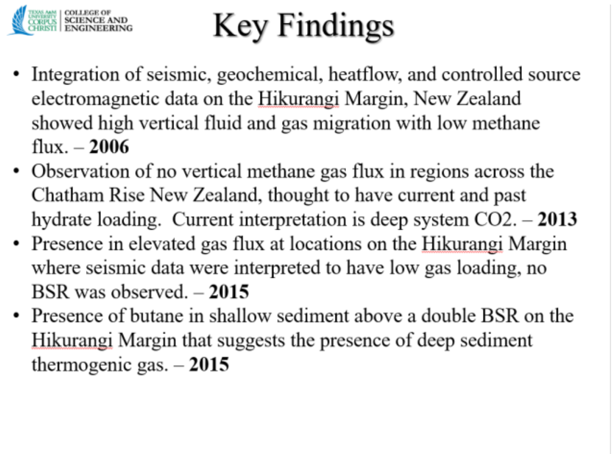
Mahia Transect 2

Station	SMT (cmbsf)	SO$_4^{2-}$ (mmol m^{-2} a^{-1})
63	934	-20.1
36	550	-32.2
62	712	-24.5
34	572	-40.2
61	474	-29.5
4	270	-73.2
32	593	-35.9
30	1096	-14.5



COLLEGE OF SCIENCE AND ENGINEERING

Hikurangi Margin Geochemical Assessment of the Double BSR



Key Findings

- Integration of seismic, geochemical, heatflow, and controlled source electromagnetic data on the Hikurangi Margin, New Zealand showed high vertical fluid and gas migration with low methane flux. – **2006**
- Observation of no vertical methane gas flux in regions across the Chatham Rise New Zealand, thought to have current and past hydrate loading. Current interpretation is deep system CO2. – **2013**
- Presence in elevated gas flux at locations on the Hikurangi Margin where seismic data were interpreted to have low gas loading, no BSR was observed. – **2015**
- Presence of butane in shallow sediment above a double BSR on the Hikurangi Margin that suggests the presence of deep sediment thermogenic gas. – **2015**

Organic matter remineralization pathways in Baltic Sea Basin sediments revealed through DNA and RNA sequencing

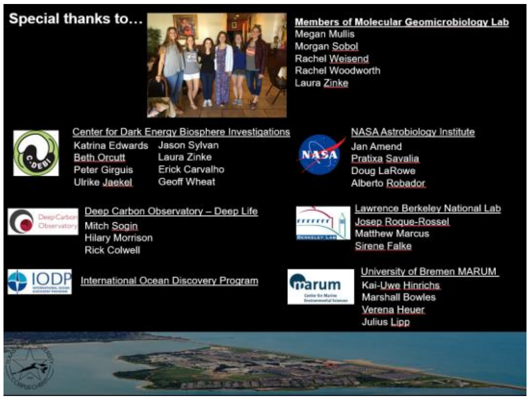
Brandi Kiel Reese, Laura A. Zinke, Ian PG Marshall, Jordan T. Bird, Hans Røy, Bo Barker Jørgensen, Karen G. Lloyd, Jan P. Amend

The Baltic Sea Basin has a dynamic climatic history. The Scandinavian ice sheet advanced and retreated numerous times throughout the Pleistocene and Holocene, affecting sediment deposition. Sediments deposited during warmer marine-brackish conditions tended to be rich in organic matter (over 5% of total sediment dry weight in some sediment) and methanogenic, indicating microbially-driven organic remineralization. Sediments deposited during glacial periods tended to be organic-poor and contained little to no methane. The microbial biomass and metabolic diversity in Baltic Sea sediments reflected these differences (Andren et al, 2015, Marshall *et al*., 2017), and it was hypothesized that microbial fermentation pathways differed between sediment types and depths. Here, we used metagenomics and metatranscriptomics to determine the types of organic matter catabolic pathways present in these sediments. We examined fermentation, carbohydrate active enzyme, and protease encoding genes in Baltic Sea sediments from four sites ranging between 20 cm to 80 meters below seafloor. Sediment microbial communities contained more carbohydrate active enzymes in the more organic rich, marine influenced sediments. Presence of fermentative pathways differed between sites and depths, with greater relative proportions of fermentation genes involved in pyruvate fermentation. Metatranscriptomics from three of these samples revealed that these pathways were not only present, but were transcribed. This is an important step in understanding the types of organic matter remineralization in marine sediments, and how microbial communities conserve energy through burial.

Methane (re)cycling in the deep subsurface

Brandi Kiel Reese
Texas A&M University-Corpus Christi

07 December 2017



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Rachel Woodworth
Laura Zinke

Center for Dark Energy Biosphere Investigations
Katrina Edwards
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Peter Girguis
Ulrike Jaekel
Jason Sylvan
Laura Zinke
Erick Carvalho
Geoff Wheat

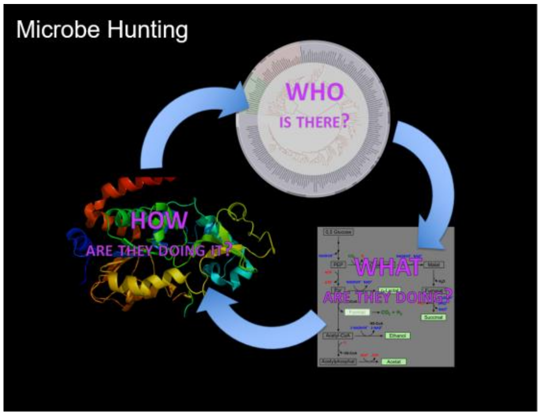
NASA Astrobiology Institute
Jan Amend
Pratixa Savalia
Doug LaRowe
Alberto Robador

Deep Carbon Observatory – Deep Life
Mitch Sogin
Hilary Morrison
Rick Colwell

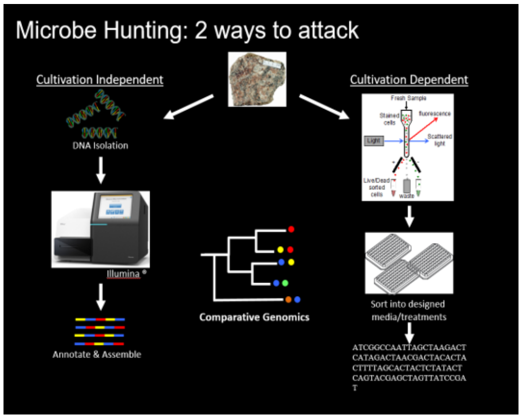
Lawrence Berkeley National Lab
Josep Roque-Rossel
Matthew Marcus
Sirene Falke

International Ocean Discovery Program

University of Bremen MARUM
Kai-Uwe Hinrichs
Marshall Bowles
Verena Heuer
Julius Lipp



Microbe Hunting



Microbe Hunting: 2 ways to attack

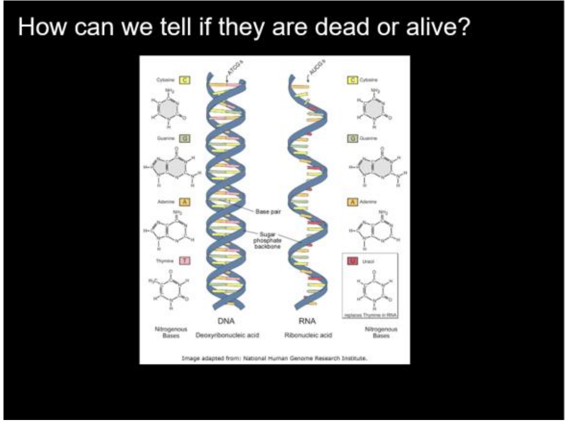
Cultivation Independent
DNA Isolation
Illumina ®
Annotate & Assemble

Comparative Genomics

Cultivation Dependent

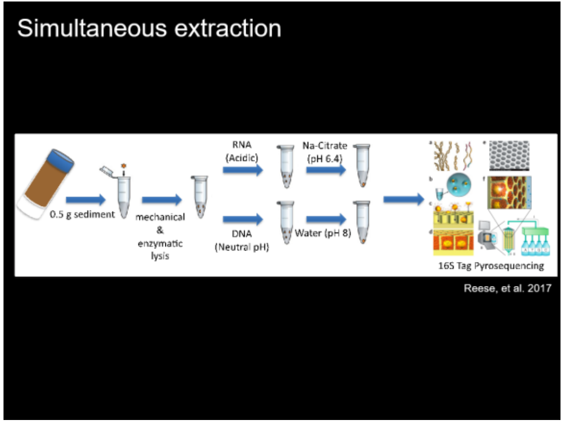
Sort into designed media/treatments

ATCGGCCAATTAGCTAAGACT
CATAGACTAACGACTACACTA
CTTTTAGCACTACTCTATACT
CAGTACGAGCTAGTTATCCGA
T



How can we tell if they are dead or alive?

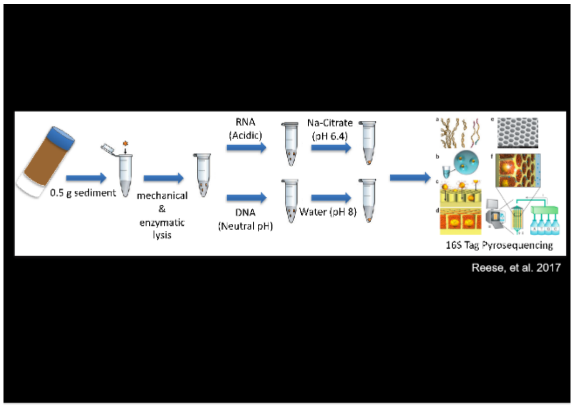
Image adapted from: National Human Genome Research Institute.



Simultaneous extraction

16S Tag Pyrosequencing

Reese, et al. 2017



16S Tag Pyrosequencing

Reese, et al. 2017

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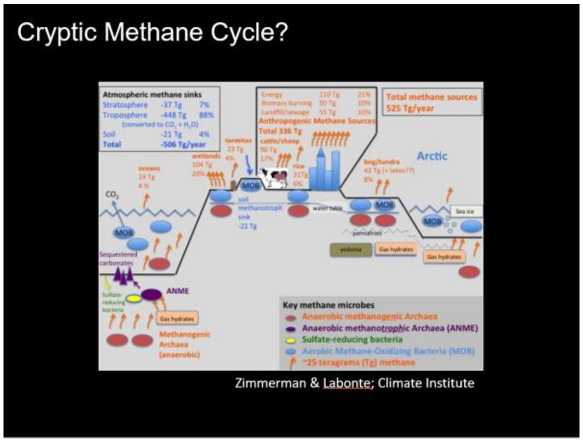
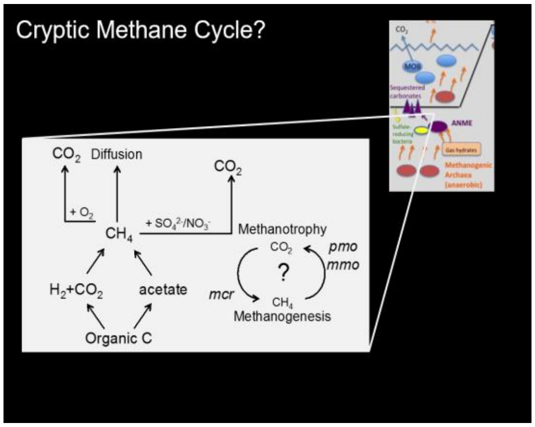
16S Tag Pyrosequencing

Reese, et al. 2017

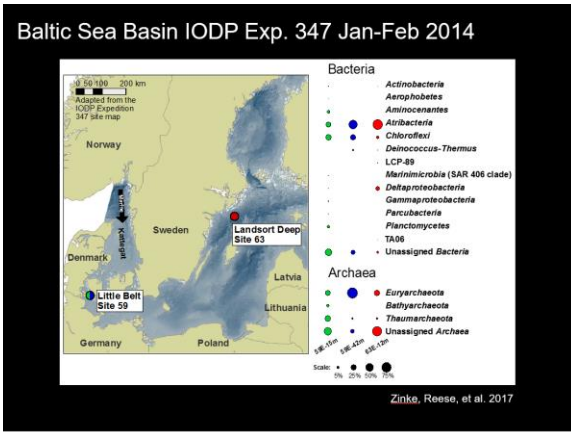


Cryptic Methane Cycle?

Zimmerman & Labonte; Climate Institute

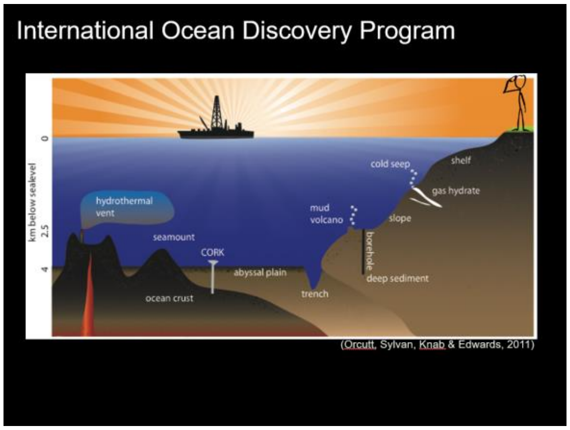


Cryptic Methane Cycle?



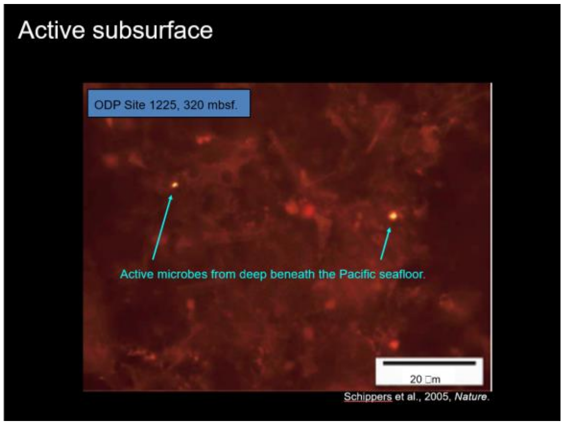
Baltic Sea Basin IODP Exp. 347 Jan-Feb 2014

Zinke, Reese, et al. 2017



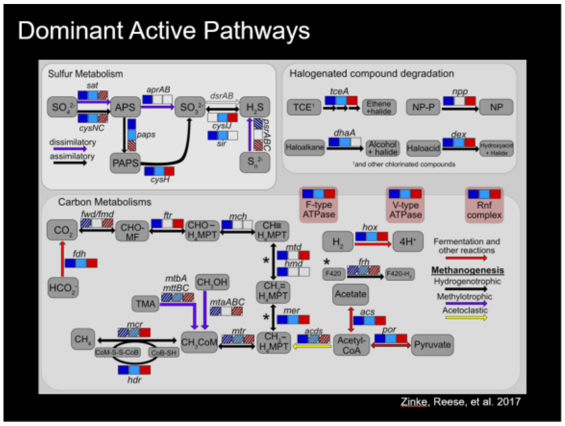
International Ocean Discovery Program

(Orcutt, Sylvan, Knab & Edwards, 2011)



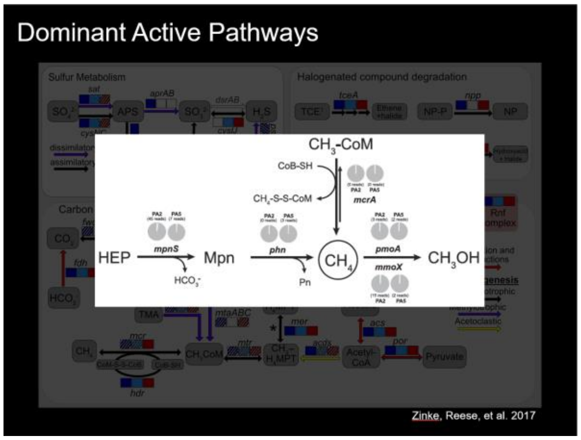
Active subsurface

Schippers et al., 2005, *Nature*.



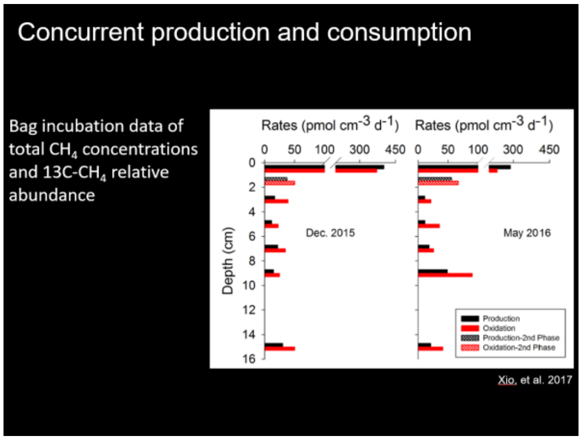
Dominant Active Pathways

Zinke, Reese, et al. 2017



Dominant Active Pathways

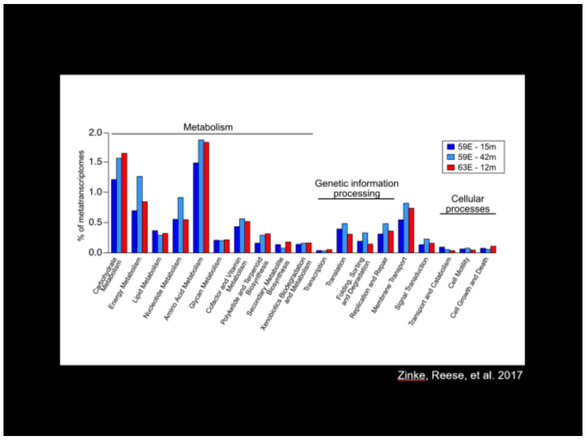
Zinke, Reese, et al. 2017



Concurrent production and consumption

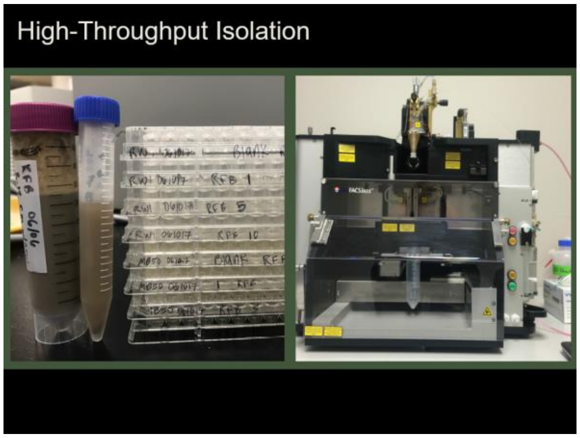
Bag incubation data of total CH_4 concentrations and 13C-CH_4 relative abundance

Xio, et al. 2017

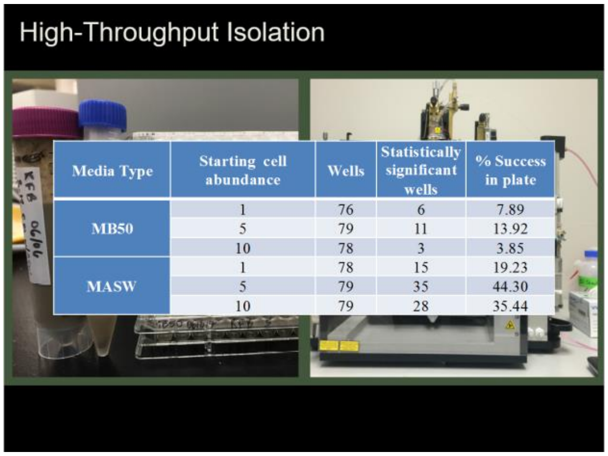


Zinke, Reese, et al. 2017

High-Throughput Isolation



High-Throughput Isolation



Media Type	Starting cell abundance	Wells	Statistically significant wells	% Success in plate
MB50	1	76	6	7.89
	5	79	11	13.92
	10	78	3	3.85
MASW	1	78	15	19.23
	5	79	35	44.30
	10	79	28	35.44

Thank you

brandi.reese@tamucc.edu

Factors Influencing Spatial Variability in Late Summer Methane Fluxes from the North Slope of Alaska

J. P. Smith[1*], R. B. Coffin[2,3], and P. S. Rose[2,3]

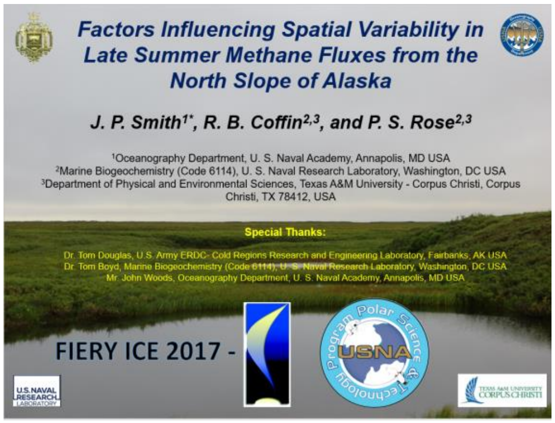
[1]Oceanography Department, U. S. Naval Academy, 572C Holloway Road, 9D, Annapolis, MD 21402-1363 USA.

[2]Marine Biogeochemistry (Code 6114), U. S. Naval Research Laboratory, Washington, DC 20375 USA.

[3]Department of Physical and Environmental Sciences, Texas A&M University - Corpus Christi, Corpus Christi, TX 78412, USA.

[4]U.S. Army ERDC- Cold Regions Research and Engineering Laboratory, Mail: P.O. Box 35170 Fort Wainwright, AK 99703-0170 USA.

Regional climate change in the Arctic can change the timing, duration, and intensity of the spring-summer thaw cycle leading to alteration of high-Arctic coastal landscapes, changes in sediment dynamics, changes in heat flux and the export of tundra-sourced organic matter (OM) to the coastal shelf, and changes in the flux of methane (CH_4) to the atmosphere. To better understand these potential changes, it is important to understand the scale of spatial variability in current OM accumulation and CH_4 flux and the geochemical and geophysical factors controlling this variability. In August 2013, soil cores were collected and gas traps were deployed at 9 locations spread across a study area of ~1800 km^2 on the North Slope of Alaska near Prudhoe Bay to measure soil parameters, CH_4 concentrations, and atmospheric CH_4 flux. Results showed significant differences in CH_4 concentrations with depth through the active layer (AL) of tundra wetland soils and variability in estimated daily CH_4 flux over a relatively small spatial area. Variations in biogeochemical, geophysical parameters such as soil composition, OM concentrations, water content, and AL depth from site-to-site play a large role in controlling the CH_4 flux regime as does the geological setting. Results of this study can be reviewed in the context of previous research and research conducted by others in order to try and better understand primary factors controlling spatial variability in CH_4 flux on the North Slope of Alaska. This enhanced understanding can be used to inform future research efforts to better constrain the scale at which future studies should be conducted to better quantify OM cycling on and CH_4 flux from the North Slope through the entire freeze-thaw cycle to enable better predictions of annual CH_4 flux under future Artic climate change scenarios.



Factors Influencing Spatial Variability in Late Summer Methane Fluxes from the North Slope of Alaska

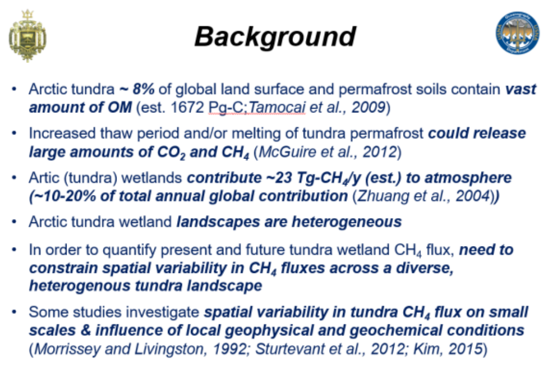
J. P. Smith[1*], R. B. Coffin[2,3], and P. S. Rose[2,3]

[1]Oceanography Department, U. S. Naval Academy, Annapolis, MD USA
[2]Marine Biogeochemistry (Code 6114), U. S. Naval Research Laboratory, Washington, DC USA
[3]Department of Physical and Environmental Sciences, Texas A&M University - Corpus Christi, Corpus Christi, TX 78412, USA

Special Thanks:

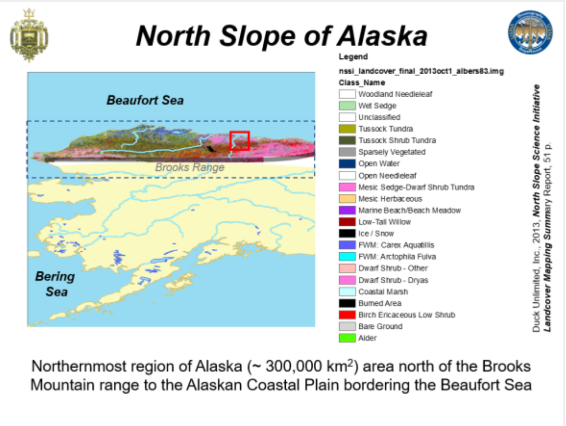
Dr. Tom Douglas, U.S. Army ERDC- Cold Regions Research and Engineering Laboratory, Fairbanks, AK USA
Dr. Tom Boyd, Marine Biogeochemistry (Code 6114), U. S. Naval Research Laboratory, Washington, DC USA
Mr. John Woods, Oceanography Department, U. S. Naval Academy, Annapolis, MD USA

FIERY ICE 2017 -



Background

- Arctic tundra **~ 8%** of global land surface and permafrost soils contain ***vast amount of OM*** (est. 1672 Pg-C; *Tamocai et al., 2009*)
- Increased thaw period and/or melting of tundra permafrost ***could release large amounts of CO_2 and CH_4*** (*McGuire et al., 2012*)
- Artic (tundra) wetlands ***contribute ~23 Tg-CH_4/y (est.) to atmosphere (~10-20% of total annual global contribution*** (*Zhuang et al., 2004*))
- Arctic tundra wetland ***landscapes are heterogeneous***
- In order to quantify present and future tundra wetland CH_4 flux, ***need to constrain spatial variability in CH_4 fluxes across a diverse, heterogenous tundra landscape***
- Some studies investigate ***spatial variability in tundra CH_4 flux on small scales & influence of local geophysical and geochemical conditions*** (*Morrissey and Livingston, 1992; Sturtevant et al., 2012; Kim, 2015*)



North Slope of Alaska

Legend

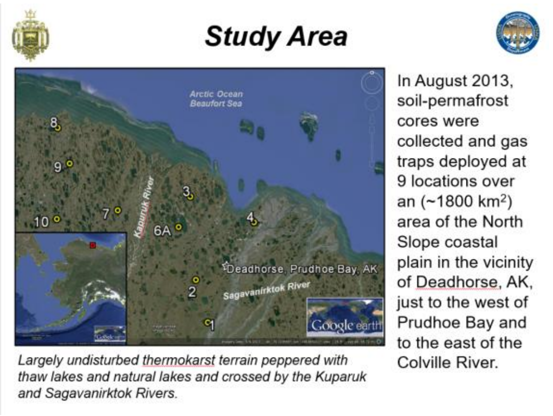
nssi_landcover_final_2013oct1_albers83.img

Class_Name

- Woodland Needleleaf
- Wet Sedge
- Unclassified
- Tussock Tundra
- Tussock Shrub Tundra
- Sparsely Vegetated
- Open Water
- Open Needleleaf
- Mesic Sedge-Dwarf Shrub Tundra
- Mesic Herbaceous
- Marine Beach/Beach Meadow
- Low-Tall Willow
- Ice / Snow
- FWM: Carex Aquatilis
- FWM: Arctophila Fulva
- Dwarf Shrub - Other
- Dwarf Shrub - Dryas
- Coastal Marsh
- Burned Area
- Birch Ericaceous Low Shrub
- Bare Ground
- Alder

Duck Unlimited, Inc., 2013, ***North Slope Science Initiative Landcover Mapping Summary*** Report, 51 p.

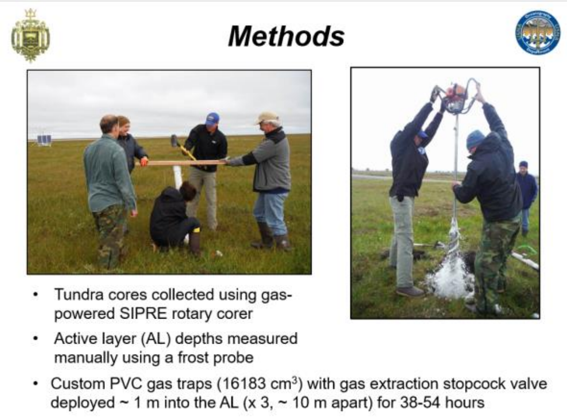
Northernmost region of Alaska (~ 300,000 km²) area north of the Brooks Mountain range to the Alaskan Coastal Plain bordering the Beaufort Sea



Study Area

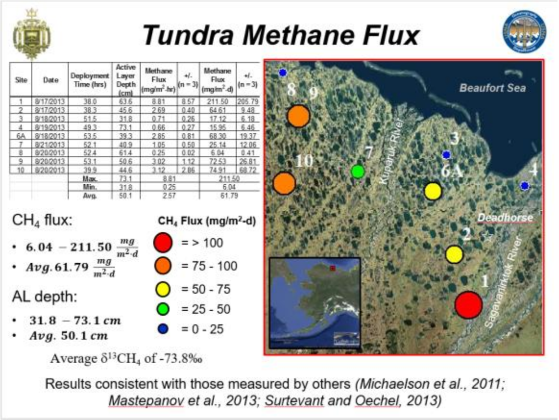
Largely undisturbed thermokarst terrain peppered with thaw lakes and natural lakes and crossed by the Kuparuk and Sagavanirktok Rivers.

In August 2013, soil-permafrost cores were collected and gas traps deployed at 9 locations over an (~1800 km²) area of the North Slope coastal plain in the vicinity of Deadhorse, AK, just to the west of Prudhoe Bay and to the east of the Colville River.



Methods

- Tundra cores collected using gas-powered SIPRE rotary corer
- Active layer (AL) depths measured manually using a frost probe
- Custom PVC gas traps (16183 cm³) with gas extraction stopcock valve deployed ~ 1 m into the AL (x 3, ~ 10 m apart) for 38-54 hours



Tundra Methane Flux

Site	Date	Deployment Time (hrs)	Active Layer Depth (cm)	Methane Flux (mg/m²-hr)	+/- (n = 3)	Methane Flux (mg/m²-d)	+/- (n = 3)
1	8/17/2013	38.0	63.6	8.81	8.57	211.50	205.79
2	8/17/2013	38.3	45.6	2.69	0.40	64.61	9.48
3	8/18/2013	51.5	31.8	0.71	0.26	17.12	6.18
4	8/19/2013	49.3	73.1	0.66	0.27	15.95	6.46
6A	8/18/2013	53.5	39.3	2.85	0.81	68.30	19.37
7	8/21/2013	52.1	40.9	1.05	0.50	25.14	12.06
8	8/20/2013	52.4	61.4	0.25	0.02	6.04	0.41
9	8/20/2013	53.1	50.6	3.02	1.12	72.53	26.81
10	8/20/2013	39.9	44.6	3.12	2.86	74.91	68.72
		Max.	73.1	8.81		211.50	
		Min.	31.8	0.25		6.04	
		Avg.	50.1	2.57		61.79	

CH_4 flux:

- $6.04 - 211.50 \frac{mg}{m^2 \cdot d}$
- $Avg. 61.79 \frac{mg}{m^2 \cdot d}$

AL depth:

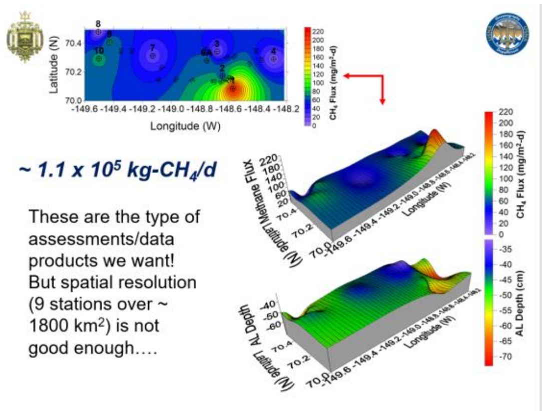
- $31.8 - 73.1\ cm$
- $Avg.\ 50.1\ cm$

CH_4 Flux (mg/m²-d)

- 🔴 = > 100
- 🟠 = 75 - 100
- 🟡 = 50 - 75
- 🟢 = 25 - 50
- 🔵 = 0 - 25

Average $\delta^{13}CH_4$ of -73.8‰

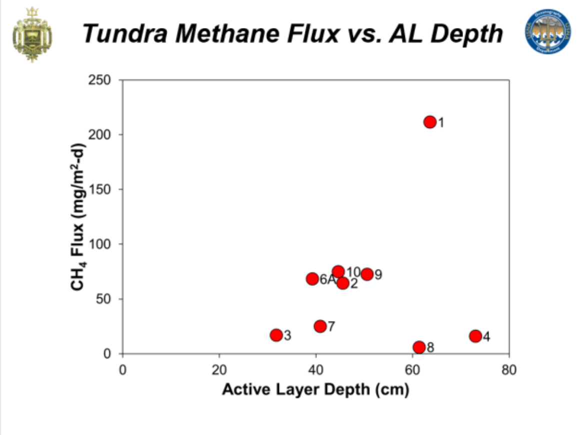
Results consistent with those measured by others (*Michaelson et al., 2011; Mastepanov et al., 2013; Surtevant and Oechel, 2013*)



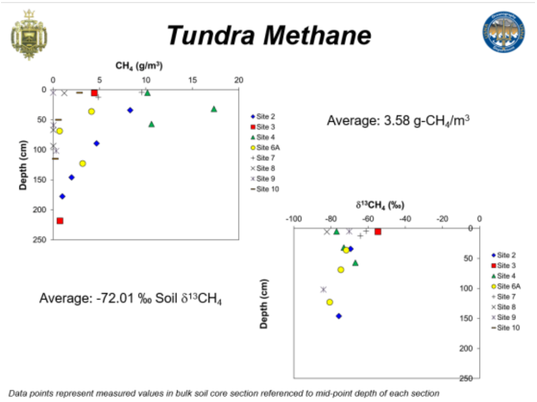
~ 1.1 x 10^5 kg-CH_4/d

These are the type of assessments/data products we want! But spatial resolution (9 stations over ~ 1800 km^2) is not good enough….

Tundra Methane Flux vs. AL Depth



Tundra Methane

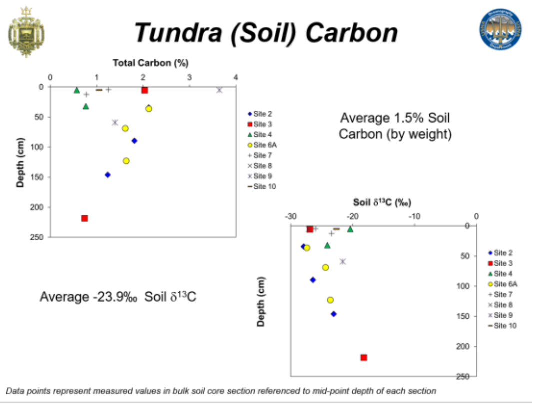


Average: 3.58 g-CH_4/m^3

Average: -72.01 ‰ Soil δ^{13}CH_4

Data points represent measured values in bulk soil core section referenced to mid-point depth of each section

Tundra (Soil) Carbon

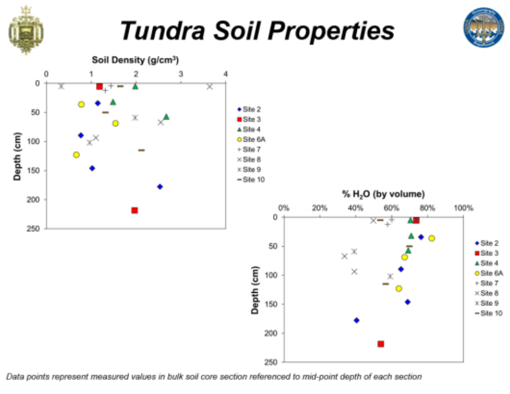


Average 1.5% Soil Carbon (by weight)

Average -23.9‰ Soil δ^{13}C

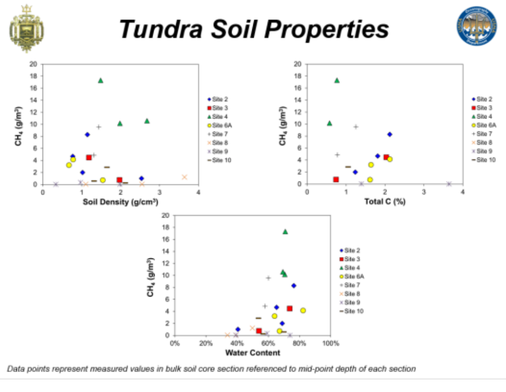
Data points represent measured values in bulk soil core section referenced to mid-point depth of each section

Tundra Soil Properties

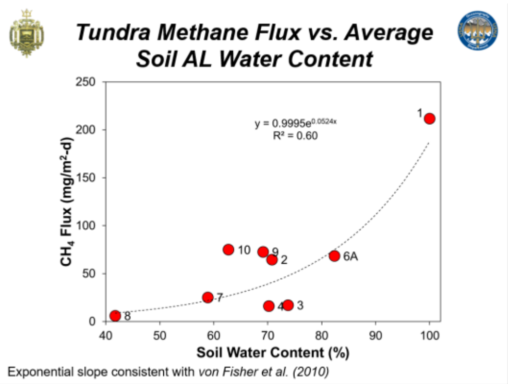


Data points represent measured values in bulk soil core section referenced to mid-point depth of each section

Tundra Soil Properties

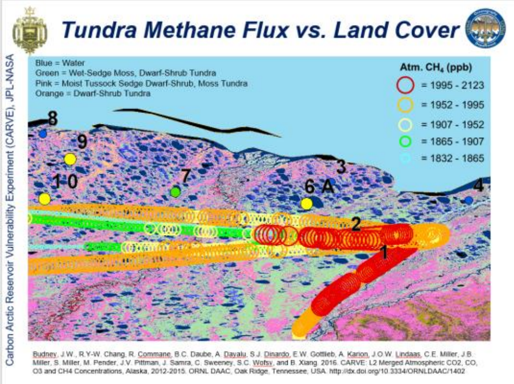


Data points represent measured values in bulk soil core section referenced to mid-point depth of each section



Tundra Methane Flux vs. Average Soil AL Water Content

Exponential slope consistent with *von Fisher et al. (2010)*



Tundra Methane Flux vs. Land Cover

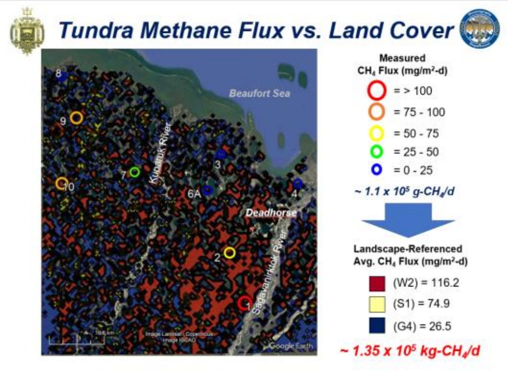
Blue = Water
Green = Wet-Sedge Moss, Dwarf-Shrub Tundra
Pink = Moist Tussock Sedge Dwarf-Shrub, Moss Tundra
Orange = Dwarf-Shrub Tundra

Atm. CH_4 (ppb)

- ○ = 1995 - 2123
- ○ = 1952 - 1995
- ○ = 1907 - 1952
- ○ = 1865 - 1907
- ○ = 1832 - 1865

Carbon Arctic Reservoir Vulnerability Experiment (CARVE), JPL-NASA

Budney, J.W., R.Y-W. Chang, R. Commane, B.C. Daube, A. Dayalu, S.J. Dinardo, E.W. Gottlieb, A. Karion, J.O.W. Lindaas, C.E. Miller, J.B. Miller, S. Miller, M. Pender, J.V. Pittman, J. Samra, C. Sweeney, S.C. Wofsy, and B. Xiang. 2016. CARVE: L2 Merged Atmospheric CO2, CO, O3 and CH4 Concentrations, Alaska, 2012-2015. ORNL DAAC, Oak Ridge, Tennessee, USA. http://dx.doi.org/10.3334/ORNLDAAC/1402



Tundra Methane Flux vs. Land Cover

Measured CH_4 Flux (mg/m²-d)

- ○ = > 100
- ○ = 75 - 100
- ○ = 50 - 75
- ○ = 25 - 50
- ○ = 0 - 25

~ 1.1 x 10^5 g-CH_4/d

Landscape-Referenced Avg. CH_4 Flux (mg/m²-d)

- 🟥 (W2) = 116.2
- 🟨 (S1) = 74.9
- 🟦 (G4) = 26.5

~ 1.35 x 10^5 kg-CH_4/d

Conclusions

- *Significant,* ***small-scale variability in daily CH_4 flux*** *through the soil AL in the late-summer on the North Slope*
- ***Variations in biogeochemical, geophysical parameters*** *such as soil composition,* ***water content, and AL depth*** *from site-to-site* ***control the CH_4 flux*** *regime along with* ***vegetation*** *and the* ***hydrogeological setting***
- ***Need to better constrain variability for remote sensing of CH_4 flux***

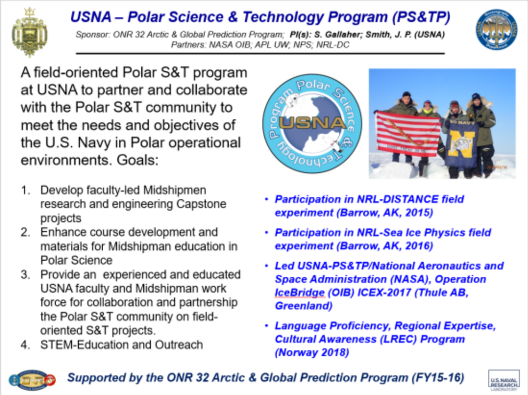
Methanotrophy vs. Methanogenesis?

Von Fisher et al. (2010)

Jet Propulsion Laboratory
California Institute of Technology

NEWS | NOVEMBER 12, 2014
NASA: Alaska Shows No Signs of Rising Arctic Methane

https://www.jpl.nasa.gov/news/news.php?CFID=a22a5b97-db36-4c04-8c1e-d0907f875052&CFTOKEN=0&feature=4376



USNA – Polar Science & Technology Program (PS&TP)

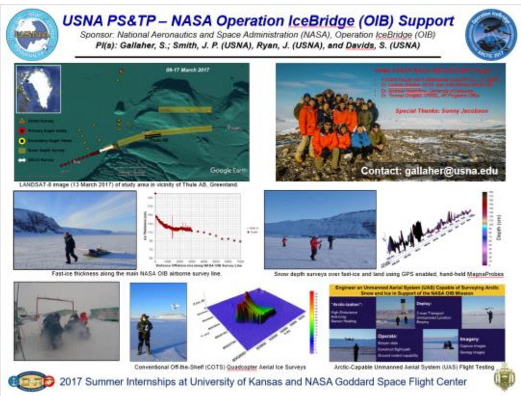
Sponsor: ONR 32 Arctic & Global Prediction Program; ***PI(s): S. Gallaher; Smith, J. P. (USNA)***
Partners: NASA OIB; APL UW; NPS; NRL-DC

A field-oriented Polar S&T program at USNA to partner and collaborate with the Polar S&T community to meet the needs and objectives of the U.S. Navy in Polar operational environments. Goals:

1. Develop faculty-led Midshipmen research and engineering Capstone projects
2. Enhance course development and materials for Midshipman education in Polar Science
3. Provide an experienced and educated USNA faculty and Midshipman work force for collaboration and partnership the Polar S&T community on field-oriented S&T projects.
4. STEM-Education and Outreach

- ***Participation in NRL-DISTANCE field experiment (Barrow, AK, 2015)***
- ***Participation in NRL-Sea Ice Physics field experiment (Barrow, AK, 2016)***
- ***Led USNA-PS&TP/National Aeronautics and Space Administration (NASA), Operation IceBridge (OIB) ICEX-2017 (Thule AB, Greenland)***
- ***Language Proficiency, Regional Expertise, Cultural Awareness (LREC) Program (Norway 2018)***

Supported by the ONR 32 Arctic & Global Prediction Program (FY15-16)



USNA PS&TP – NASA Operation IceBridge (OIB) Support

Sponsor: National Aeronautics and Space Administration (NASA), Operation IceBridge (OIB)
PI(s): Gallaher, S.; Smith, J. P. (USNA), Ryan, J. (USNA), and Davids, S. (USNA)

LANDSAT-8 image (13 March 2017) of study area in vicinity of Thule AB, Greenland.

Contact: gallaher@usna.edu

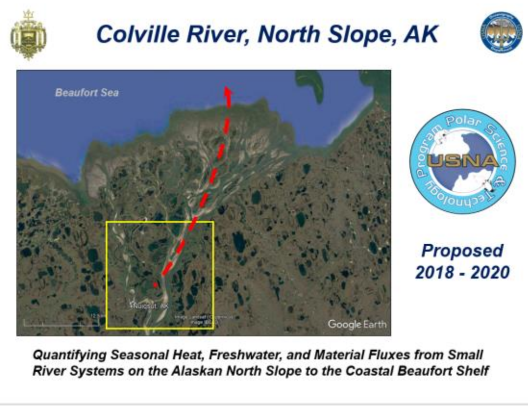
Fast-ice thickness along the main NASA OIB airborne survey line.

Snow depth surveys over fast-ice and land using GPS enabled, hand-held MagnaProbes

Conventional Off-the-Shelf (COTS) Quadcopter Aerial Ice Surveys

Arctic-Capable Unmanned Aerial System (UAS) Flight Testing

2017 Summer Internships at University of Kansas and NASA Goddard Space Flight Center



Colville River, North Slope, AK

Proposed 2018 - 2020

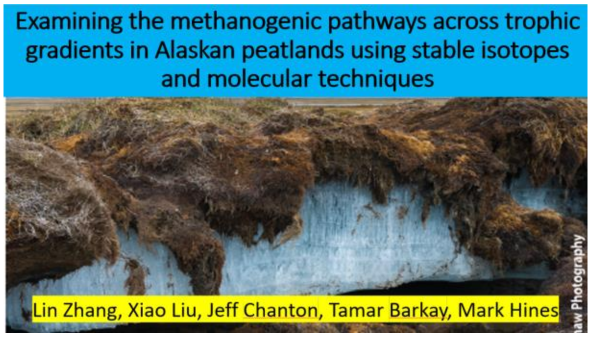
Quantifying Seasonal Heat, Freshwater, and Material Fluxes from Small River Systems on the Alaskan North Slope to the Coastal Beaufort Shelf

Questions?
Joseph P. Smith
Tel: +1-410-293-6568
Email: jpsmith@usna.edu

Methanogenic pathways in Alaskan peatlands at different trophic levels with evidence from stable isotope ratios and metagenomics

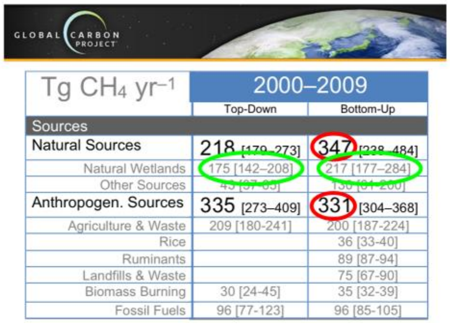
Lin Zhang, Xiao Liu, Lauren Langford, Jeff Chanton, Spencer Roth, Jeffra Schaefer, Tamar Barkay Mark E Hines

To better constrain the large uncertainties in emission fluxes, it is necessary to improve the understanding of methanogenic pathways in northern peatlands with heterogeneous surface vegetation and pH. Surface vegetation is an excellent indicator of porewater pH, which heavily influences the microbial communities in peatlands. Stable C isotope ratios ($\delta^{13}C$) have been used as a robust tool to distinguish methanogenic pathways, especially in conjunction with metagenomic analysis of the microbial communities. To link surface vegetation species compositions, pH, microbial communities, and methanogenic pathways, 15 peatland sites were studied in Fairbanks and Anchorage, Alaska in the summer of 2014. These sites were ordinated using multiple factor analysis into 3 clusters based on pH, temp, CH_4 and volatile fatty acid production rates, $\delta^{13}C$ values, and surface vegetation composition. In the ombrotrophic group (pH~3.3), various *Sphagna* species dominanted, but included shrubs *Ledum decumbens* and *Eriophorum vaginatum*. Primary fermentation rates were slow with no CH_4 detected. The fen cluster (pH~5.3) was dominated by various *Carex* species, and CH_4 production rates were lower than those in the intermediate cluster but more enriched in ^{13}C (-49‰). *Methanosaeta* and *Methanosarcina* were the dominant methanogens. In the intermediate trophic level (pH~4.7), *Sphagnum squarrosum* and *Carex aquatilis* were abundant. The same methanogens as in fen cluster also dominated this group, but with higher abundances, which, in part, lead to the higher CH_4 production rates in this cluster. The syntrophs *Syntrophobacter* and *Pelobacter* were also more abundant than the fen sites, which may explain the $\delta^{13}CH_4$ values that were the lighetest among the three clusters (-54‰). The high methanogenic potential in the intermediate trophic sites warrant further study since they are not only present in large areas currently, but also represent the transient stage during the evolution from bog to fen in projected climate change scenarios.

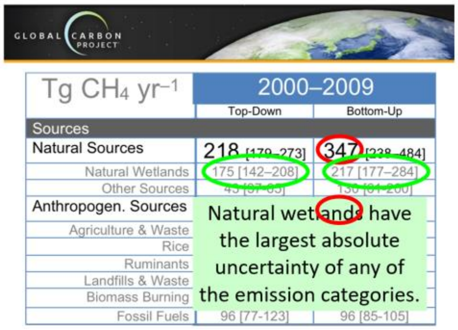


Examining the methanogenic pathways across trophic gradients in Alaskan peatlands using stable isotopes and molecular techniques

Lin Zhang, Xiao Liu, Jeff Chanton, Tamar Barkay, Mark Hines



Tg CH_4 yr^{-1}	2000–2009	
	Top-Down	Bottom-Up
Sources		
Natural Sources	218 [179–273]	347 [238–484]
Natural Wetlands	175 [142–208]	217 [177–284]
Other Sources	43 [37–65]	130 [61–200]
Anthropogen. Sources	335 [273–409]	331 [304–368]
Agriculture & Waste	209 [180-241]	200 [187-224]
Rice		36 [33-40]
Ruminants		89 [87-94]
Landfills & Waste		75 [67-90]
Biomass Burning	30 [24-45]	35 [32-39]
Fossil Fuels	96 [77-123]	96 [85-105]



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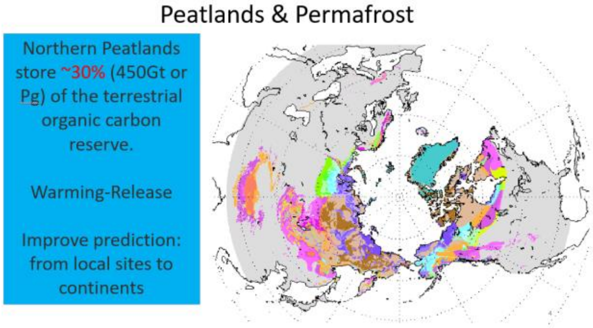
Biomass Burning		
Fossil Fuels	96 [77-123]	96 [85-105]

Natural wetlands have the largest absolute uncertainty of any of the emission categories.

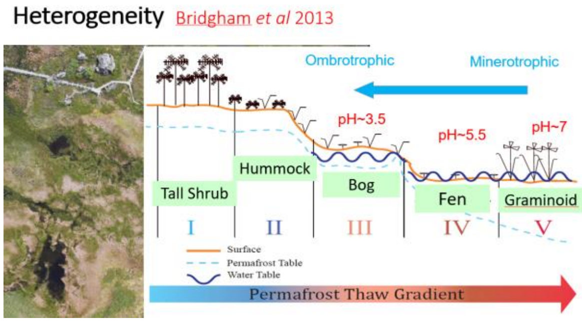


Peatlands & Permafrost

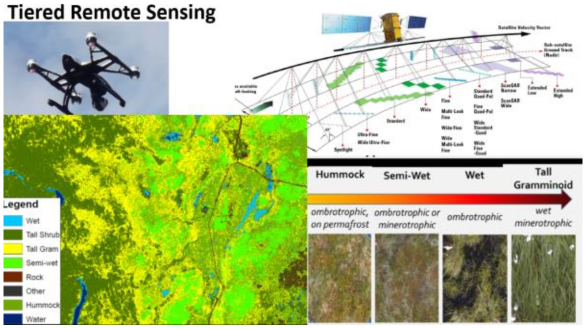
Northern Peatlands store ~30% (450Gt or Pg) of the terrestrial organic carbon reserve.

Warming-Release

Improve prediction: from local sites to continents

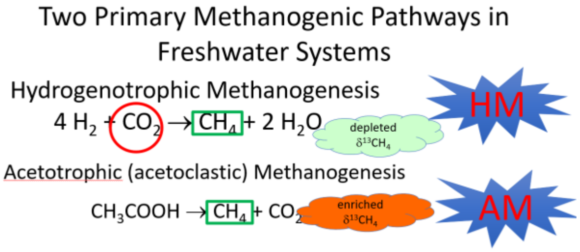


Heterogeneity Bridgham *et al* 2013



Tiered Remote Sensing

Ground truth work: connect vegetation (trophic level) with methanogenic potentials and pathways.



Two Primary Methanogenic Pathways in Freshwater Systems

Hydrogenotrophic Methanogenesis

$4\ H_2 + CO_2 \rightarrow CH_4 + 2\ H_2O$

depleted $\delta^{13}CH_4$

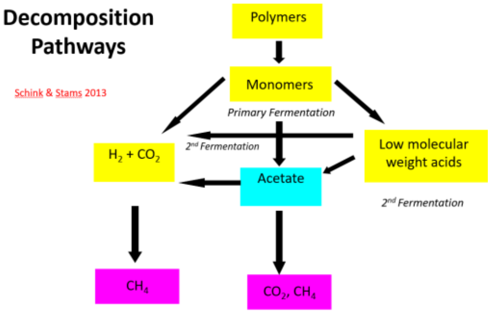
HM

Acetotrophic (acetoclastic) Methanogenesis

$CH_3COOH \rightarrow CH_4 + CO_2$

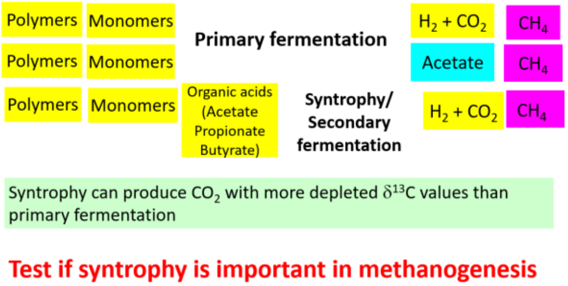
enriched $\delta^{13}CH_4$

AM



Decomposition Pathways

Schink & Stams 2013



Syntrophy can produce CO_2 with more depleted $\delta^{13}C$ values than primary fermentation

Test if syntrophy is important in methanogenesis

Sampling locations in Alaska

Measured Parameters:

1. Biogeochemical Function
   Production Rates (µM/day) CH_4, CO_2, H_2, Acetate, Propionate, and Butyrate, Sulfate, Nitrate, and $\delta^{13}C$ of CH_4 and CO_2
2. Vegetation: non-vascular, vascular 35 different species
3. Environment: pH Temp

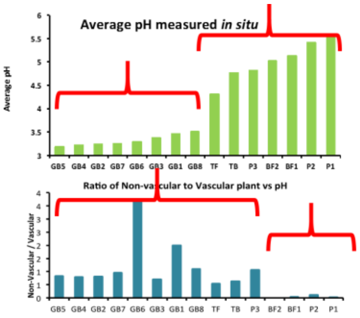
Multiple Factor Analysis Clustering Sites into Groups

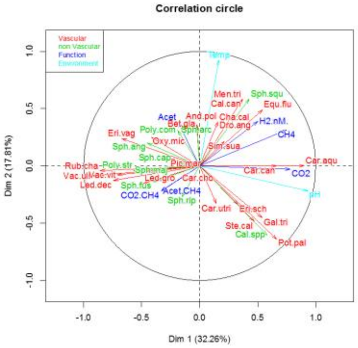
pH Gradients

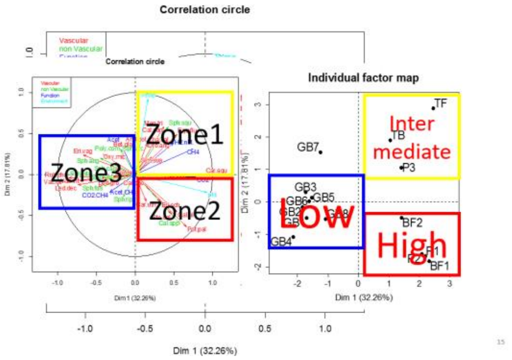
Vegetation Gradients

non-vascular coverage

vascular coverage





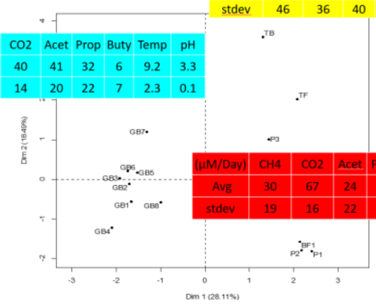


Production Rates (Biogeochem. Func.)
Incubations

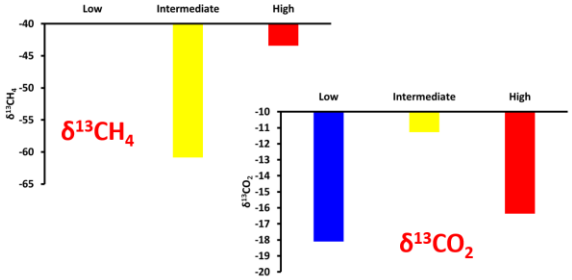
(µM/Day)	CH4	CO2	Acet	Prop	Buty	Temp	pH
Avg	50	68	41	22	8	14.2	4.7
stdev	46	36	40	21	7	2.5	0.3

(µM/Day)	CH4	CO2	Acet	Prop	Buty	Temp	pH
Avg	1.1	40	41	32	6	9.2	3.3
stdev	1.3	14	20	22	7	2.3	0.1

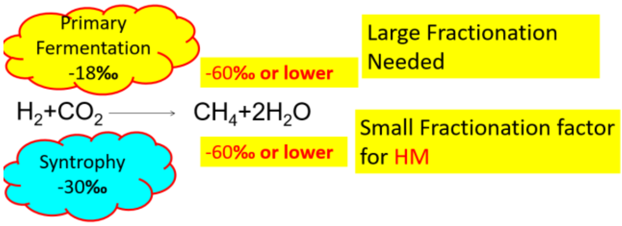
(µM/Day)	CH4	CO2	Acet	Prop	Buty	Temp	pH
Avg	30	67	24	23	6	7.7	5.3
stdev	19	16	22	10	4	0.7	0.3



$\delta^{13}CH_4$ & $\delta^{13}CO_2$ at different trophic groups



Syntrophy- $\delta^{13}C$



-60‰ or lower

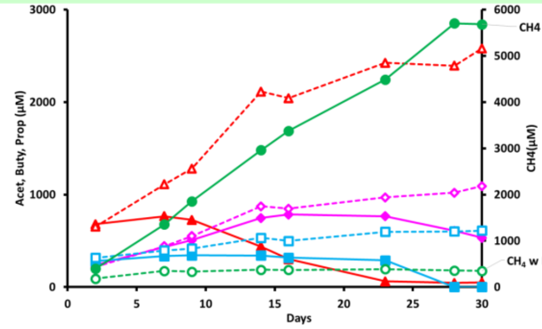
Large Fractionation Needed

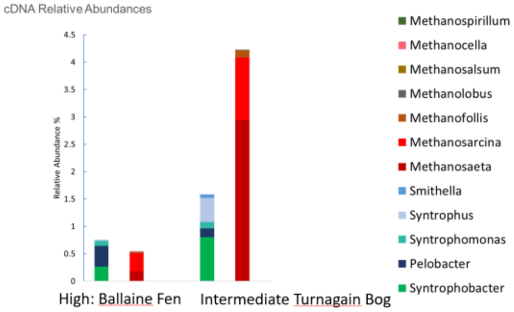
$H_2+CO_2 \longrightarrow CH_4+2H_2O$

-60‰ or lower

Small Fractionation factor for HM

Finding Syntrophy: Incubation with Methanogenesis inhibitors





High: Ballaine Fen Intermediate Turnagain Bog

Summary

Low Trophic Level
Eriophorum vaginatum; Ledum decumbens; Sphagnum majus
No CH_4, Low pH
Small methanogen community

Intermediate Trophic
Sphagnum squarrosum; Sphagnum magellanicum;
Carex aquatilis
Lots CH_4, Acet, Prop, Buty, Intermediate pH
Lots methanogens, fermenters, syntrophs

High Trophic
Carex aquatilis; Very little moss
Some CH_4, High pH
Less methanogens, fermenters, syntrophs than the intermediate group

Thank You!

- NSF Macrosystem Biology 1241937 and ARC1304804

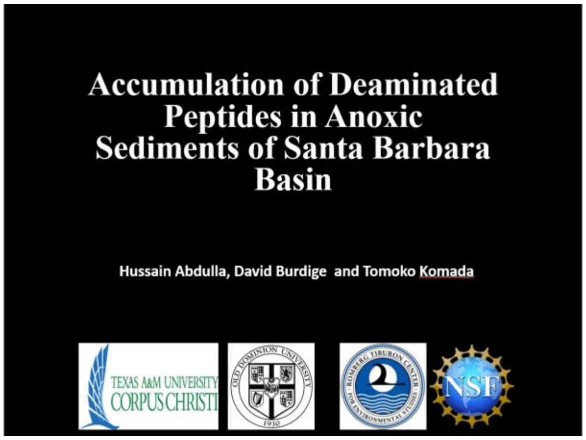
Accumulation of Deaminated Peptides in Anoxic Sediments of Santa Barbara Basin

Hussain A. Abdulla[a*], David J. Burdige[b], Tomoko Komada[c]

a. Department of Physical and Environmental Sciences, Texas A&M University-Corpus Christi, 6300 Ocean Drive, Corpus Christi, TX 78412, USA.
b. Department of Ocean, Earth and Atmospheric Sciences, Old Dominion University, 4600 Elkhorn Ave., Norfolk, VA 23529, USA.
c. Romberg Tiburon Center, San Francisco State University, 3150 Paradise Drive, Tiburon CA 94920, USA.

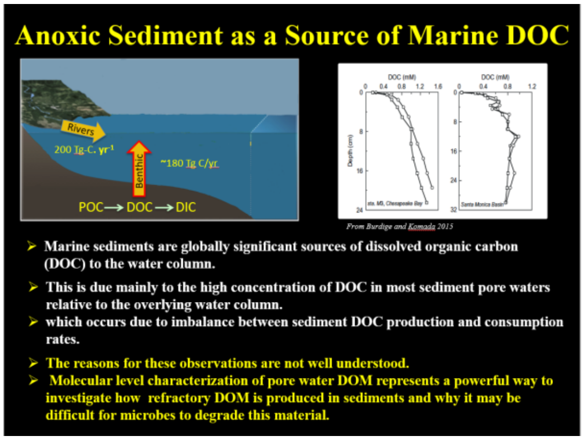
Proteins represent the most abundant class of biomolecules in marine sinking particles and microbial biomass, yet their cycling in marine sediments is not fully understood. To investigate whether some portion of hydrolyzed proteins escapes complete remineralization and accumulate in the pore waters, we analyzed dissolved organic matter from the anoxic sediments of Santa Barbara Basin, California, by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS). The results showed an increase in the molecular diversity and abundance of dissolved organic nitrogen (DON) formulas with depth. A comparison of the detected DON formulas to a database of small peptides (2-4 amino acid sequences) returned 119 matches, and these formulas were most abundant near the sediment surface. When we compared our detected formulas to all possible structures that would result from deamination of peptides in the database, we found 680 formula matches. However, these molecular formulas can represent hundreds of different structural isomers (in the present case as many as 3,257 different deaminated peptide structures), which cannot be distinguished by the FTICR-MS settings that were used. Analysis of amino acid sequences suggests that these deaminated peptides may be the products of selective degradation of source proteins in marine sediments. We hypothesize that these deaminated peptides accumulate in the pore waters due to extracellular proteinases being inhibited from completely hydrolyzing specific peptides to free amino acids. We suggest that anaerobic microbes deaminate peptides largely to produce H_2, which is ultimately used as a reducing agent by other sediment microbes (e.g. CO_2 reduction by methanogens). Simple calculations suggest that deaminated peptides may represent ~ 25-45% of DOC accumulating in these sediment pore waters. Unlike rapid remineralization of free amino acids, peptide deamination leaves behind the peptide carbon skeleton. Molecular structures of these remnant carbon skeletons may hold important clues about specific microbial processes influencing organic matter remineralization and accumulation.

ASK if this IS ALL



Accumulation of Deaminated Peptides in Anoxic Sediments of Santa Barbara Basin

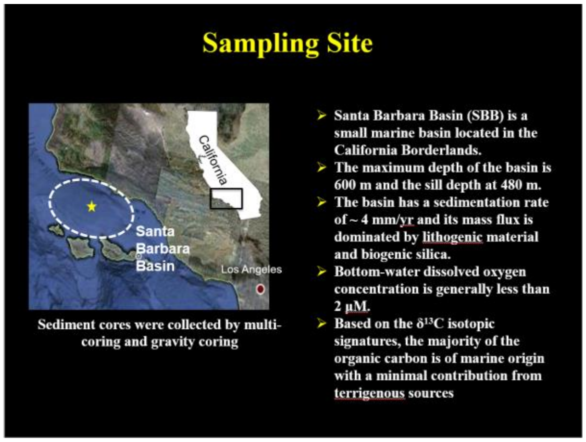
Hussain Abdulla, David Burdige and Tomoko Komada



Anoxic Sediment as a Source of Marine DOC

From Burdige and Komada 2015

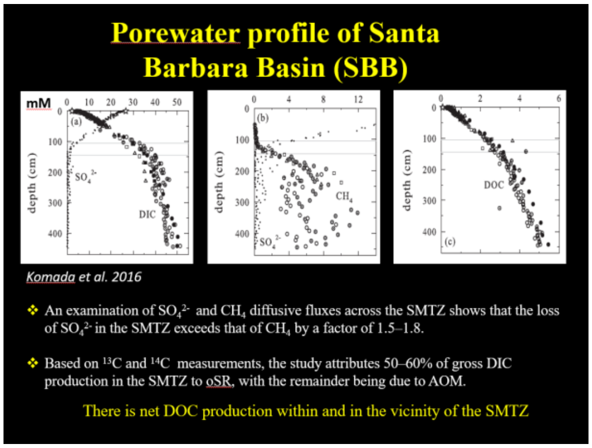
- Marine sediments are globally significant sources of dissolved organic carbon (DOC) to the water column.
- This is due mainly to the high concentration of DOC in most sediment pore waters relative to the overlying water column.
- which occurs due to imbalance between sediment DOC production and consumption rates.
- The reasons for these observations are not well understood.
- Molecular level characterization of pore water DOM represents a powerful way to investigate how refractory DOM is produced in sediments and why it may be difficult for microbes to degrade this material.



Sampling Site

Sediment cores were collected by multi-coring and gravity coring

- Santa Barbara Basin (SBB) is a small marine basin located in the California Borderlands.
- The maximum depth of the basin is 600 m and the sill depth at 480 m.
- The basin has a sedimentation rate of ~ 4 mm/yr and its mass flux is dominated by lithogenic material and biogenic silica.
- Bottom-water dissolved oxygen concentration is generally less than 2 µM.
- Based on the $\delta^{13}C$ isotopic signatures, the majority of the organic carbon is of marine origin with a minimal contribution from terrigenous sources

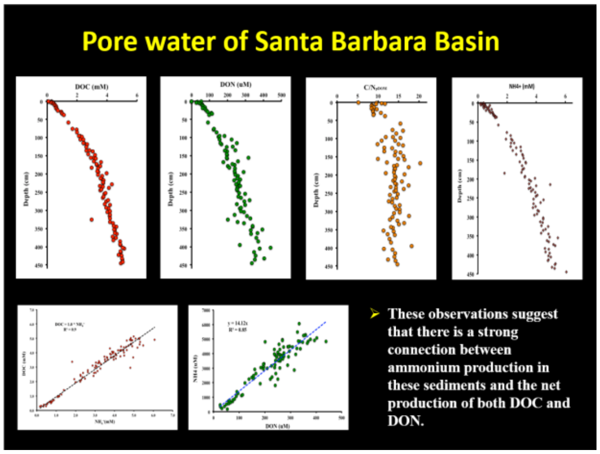


Porewater profile of Santa Barbara Basin (SBB)

Komada et al. 2016

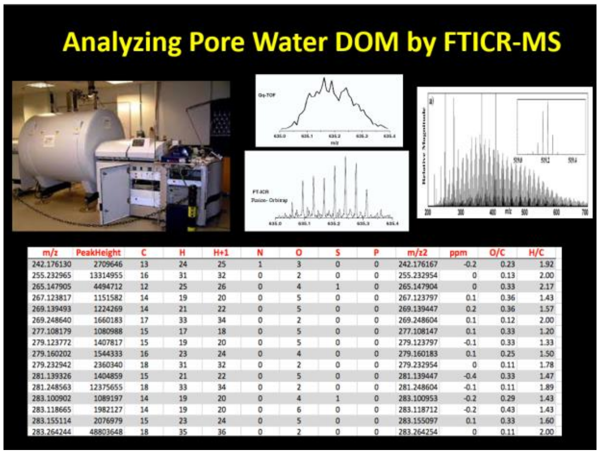
- ❖ An examination of SO_4^{2-} and CH_4 diffusive fluxes across the SMTZ shows that the loss of SO_4^{2-} in the SMTZ exceeds that of CH_4 by a factor of 1.5–1.8.
- ❖ Based on ^{13}C and ^{14}C measurements, the study attributes 50–60% of gross DIC production in the SMTZ to oSR, with the remainder being due to AOM.

There is net DOC production within and in the vicinity of the SMTZ



Pore water of Santa Barbara Basin

- These observations suggest that there is a strong connection between ammonium production in these sediments and the net production of both DOC and DON.



Analyzing Pore Water DOM by FTICR-MS

m/z	PeakHeight	C	H	H+1	N	O	S	P	m/z2	ppm	O/C	H/C
242.176130	2709646	13	24	25	1	3	0	0	242.176167	-0.2	0.23	1.92
255.232965	13314955	16	31	32	0	2	0	0	255.232954	0	0.13	2.00
265.147905	4494712	12	25	26	0	4	1	0	265.147904	0	0.33	2.17
267.123817	1151582	14	19	20	0	5	0	0	267.123797	0.1	0.36	1.43
269.139493	1224269	14	21	22	0	5	0	0	269.139447	0.2	0.36	1.57
269.248640	1660183	17	33	34	0	2	0	0	269.248604	0.1	0.12	2.00
277.108179	1080988	15	17	18	0	5	0	0	277.108147	0.1	0.33	1.20
279.123772	1407817	15	19	20	0	5	0	0	279.123797	-0.1	0.33	1.33
279.160202	1544333	16	23	24	0	4	0	0	279.160183	0.1	0.25	1.50
279.232942	2360340	18	31	32	0	2	0	0	279.232954	0	0.11	1.78
281.139326	1404859	15	21	22	0	5	0	0	281.139447	-0.4	0.33	1.47
281.248563	12375655	18	33	34	0	2	0	0	281.248604	-0.1	0.11	1.89
283.100902	1089197	14	19	20	0	4	1	0	283.100953	-0.2	0.29	1.43
283.118665	1982127	14	19	20	0	6	0	0	283.118712	-0.2	0.43	1.43
283.155114	2076979	15	23	24	0	5	0	0	283.155097	0.1	0.33	1.60
283.264244	48803648	18	35	36	0	2	0	0	283.264254	0	0.11	2.00

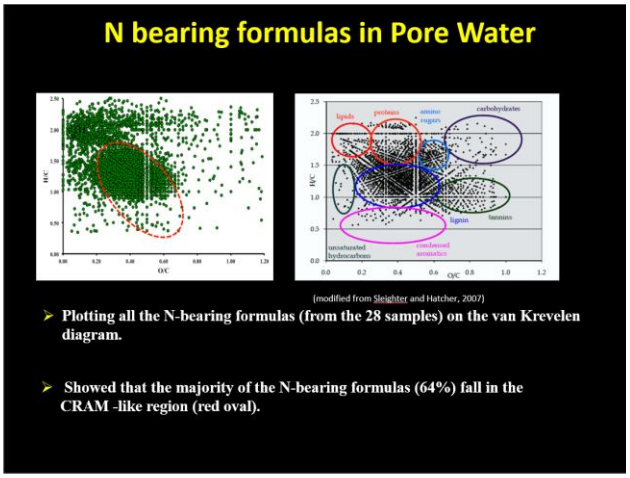
Analyzing Pore Water DOM by FTICR-MS

- Using FTICR-MS we were able to identify 8,843 unique molecular formulas in all of the 28 pore water samples.

Out of these:

- 2726 molecular formulas contain only carbon, hydrogen and Oxygen, CHO compounds (~31% of the total formulas)
- 3091 molecular formulas contain sulfur heteroatom (~35% of the total molecular formulas)
- 3971 molecular formulas contain nitrogen heteroatom (~ 45% of the total molecular formulas)

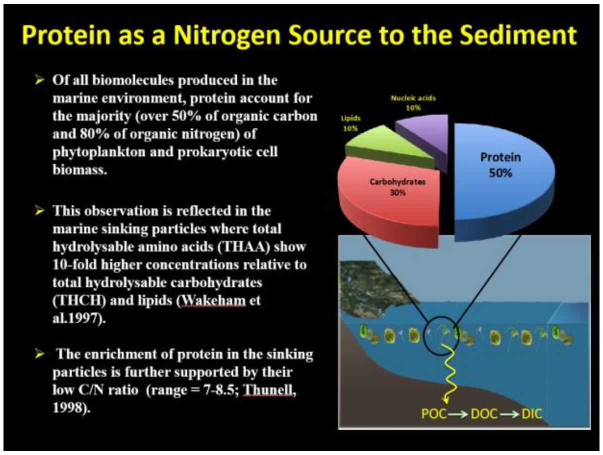
These samples has almost 4x more nitrogen and sulfur molecular formulas relative to open ocean and terrestrial DOM samples.



N bearing formulas in Pore Water

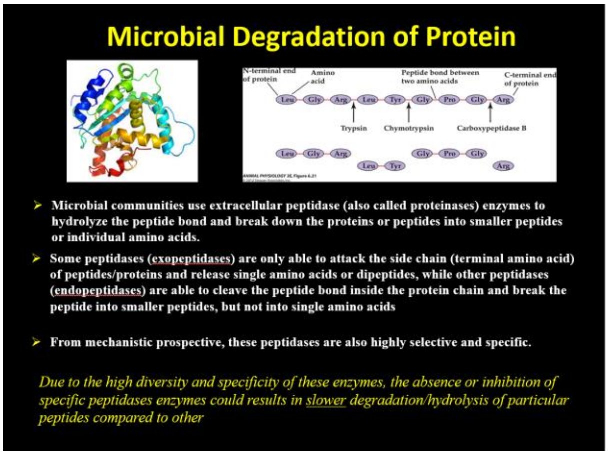
(modified from Sleighter and Hatcher, 2007)

- Plotting all the N-bearing formulas (from the 28 samples) on the van Krevelen diagram.
- Showed that the majority of the N-bearing formulas (64%) fall in the CRAM -like region (red oval).



Protein as a Nitrogen Source to the Sediment

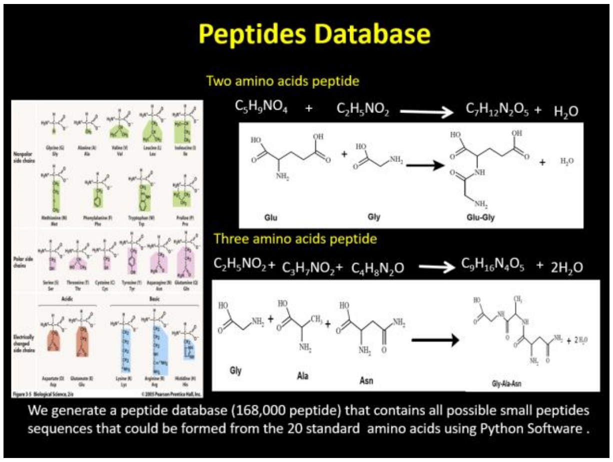
- Of all biomolecules produced in the marine environment, protein account for the majority (over 50% of organic carbon and 80% of organic nitrogen) of phytoplankton and prokaryotic cell biomass.
- This observation is reflected in the marine sinking particles where total hydrolysable amino acids (THAA) show 10-fold higher concentrations relative to total hydrolysable carbohydrates (THCH) and lipids (Wakeham et al.1997).
- The enrichment of protein in the sinking particles is further supported by their low C/N ratio (range = 7-8.5; Thunell, 1998).



Microbial Degradation of Protein

- Microbial communities use extracellular peptidase (also called proteinases) enzymes to hydrolyze the peptide bond and break down the proteins or peptides into smaller peptides or individual amino acids.
- Some peptidases (exopeptidases) are only able to attack the side chain (terminal amino acid) of peptides/proteins and release single amino acids or dipeptides, while other peptidases (endopeptidases) are able to cleave the peptide bond inside the protein chain and break the peptide into smaller peptides, but not into single amino acids
- From mechanistic prospective, these peptidases are also highly selective and specific.

Due to the high diversity and specificity of these enzymes, the absence or inhibition of specific peptidases enzymes could results in slower degradation/hydrolysis of particular peptides compared to other



Peptides Database

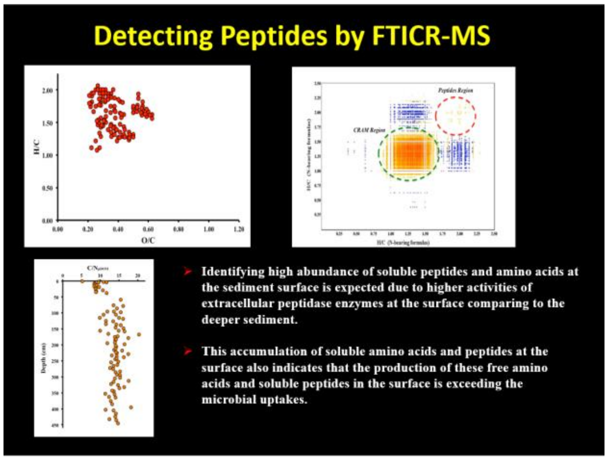
Two amino acids peptide

$C_5H_9NO_4 + C_2H_5NO_2 \longrightarrow C_7H_{12}N_2O_5 + H_2O$

Three amino acids peptide

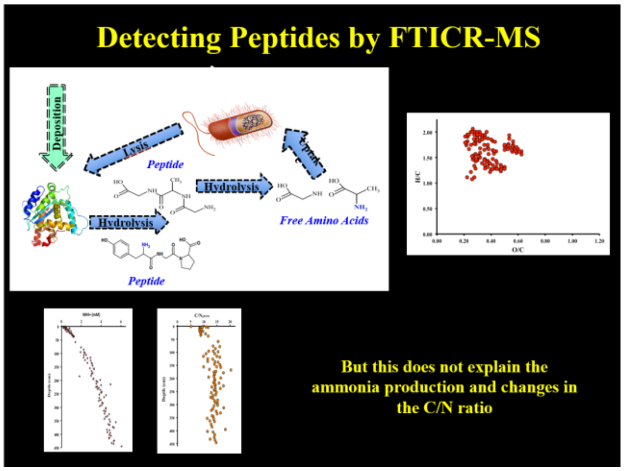
$C_2H_5NO_2 + C_3H_7NO_2 + C_4H_8N_2O \longrightarrow C_9H_{16}N_4O_5 + 2H_2O$

We generate a peptide database (168,000 peptide) that contains all possible small peptides sequences that could be formed from the 20 standard amino acids using Python Software .



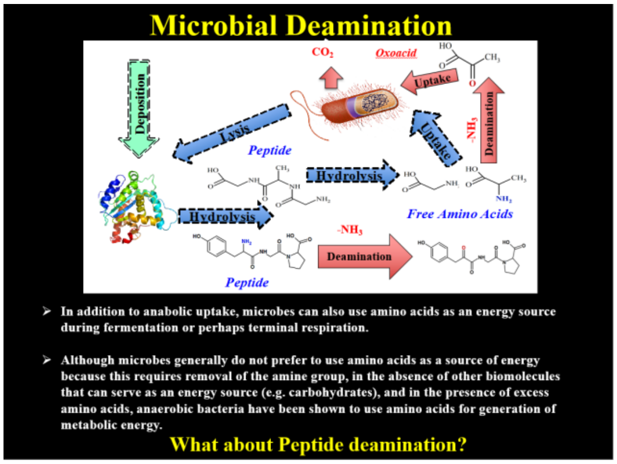
Detecting Peptides by FTICR-MS

- Identifying high abundance of soluble peptides and amino acids at the sediment surface is expected due to higher activities of extracellular peptidase enzymes at the surface comparing to the deeper sediment.
- This accumulation of soluble amino acids and peptides at the surface also indicates that the production of these free amino acids and soluble peptides in the surface is exceeding the microbial uptakes.



Detecting Peptides by FTICR-MS

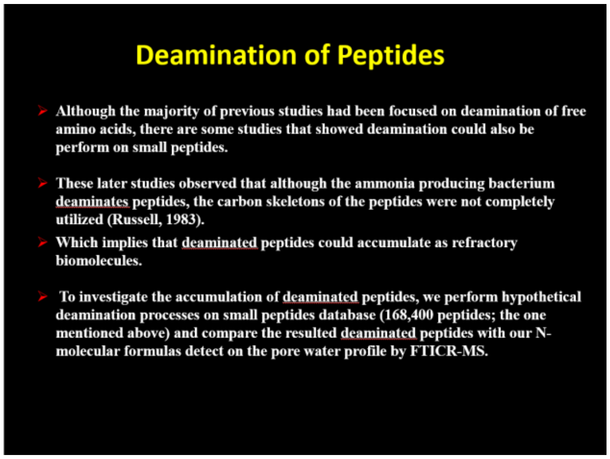
But this does not explain the ammonia production and changes in the C/N ratio



Microbial Deamination

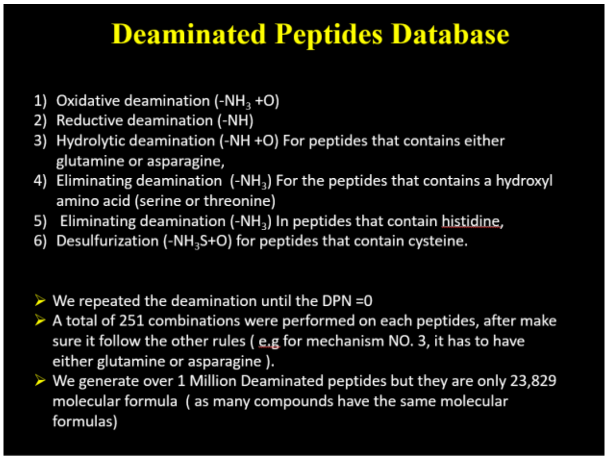
- In addition to anabolic uptake, microbes can also use amino acids as an energy source during fermentation or perhaps terminal respiration.
- Although microbes generally do not prefer to use amino acids as a source of energy because this requires removal of the amine group, in the absence of other biomolecules that can serve as an energy source (e.g. carbohydrates), and in the presence of excess amino acids, anaerobic bacteria have been shown to use amino acids for generation of metabolic energy.

What about Peptide deamination?



Deamination of Peptides

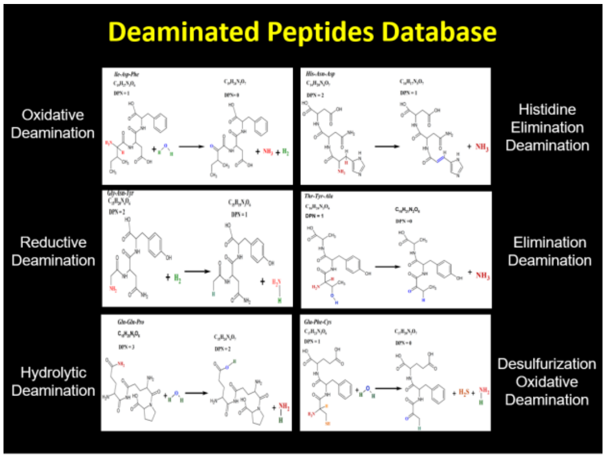
- Although the majority of previous studies had been focused on deamination of free amino acids, there are some studies that showed deamination could also be perform on small peptides.
- These later studies observed that although the ammonia producing bacterium deaminates peptides, the carbon skeletons of the peptides were not completely utilized (Russell, 1983).
- Which implies that deaminated peptides could accumulate as refractory biomolecules.
- To investigate the accumulation of deaminated peptides, we perform hypothetical deamination processes on small peptides database (168,400 peptides; the one mentioned above) and compare the resulted deaminated peptides with our N-molecular formulas detect on the pore water profile by FTICR-MS.



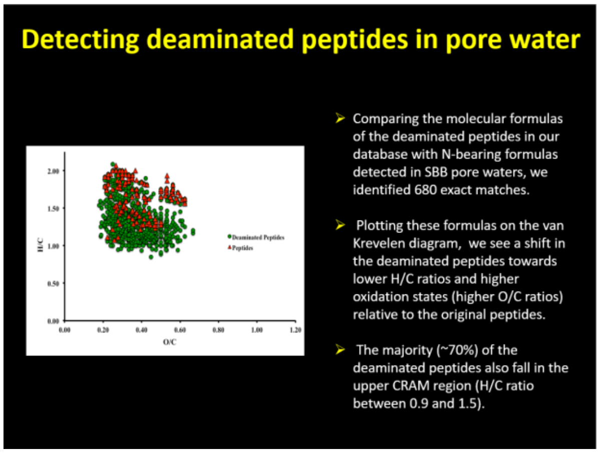
Deaminated Peptides Database

1) Oxidative deamination (-NH_3 +O)
2) Reductive deamination (-NH)
3) Hydrolytic deamination (-NH +O) For peptides that contains either glutamine or asparagine,
4) Eliminating deamination (-NH_3) For the peptides that contains a hydroxyl amino acid (serine or threonine)
5) Eliminating deamination (-NH_3) In peptides that contain histidine,
6) Desulfurization (-NH_3S+O) for peptides that contain cysteine.

- We repeated the deamination until the DPN =0
- A total of 251 combinations were performed on each peptides, after make sure it follow the other rules (e.g for mechanism NO. 3, it has to have either glutamine or asparagine).
- We generate over 1 Million Deaminated peptides but they are only 23,829 molecular formula (as many compounds have the same molecular formulas)

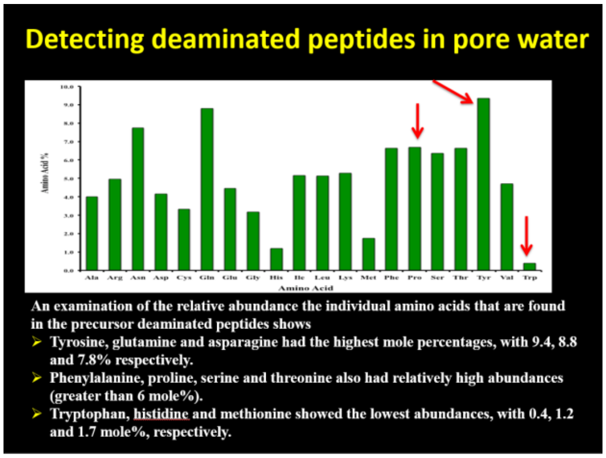


Deaminated Peptides Database



Detecting deaminated peptides in pore water

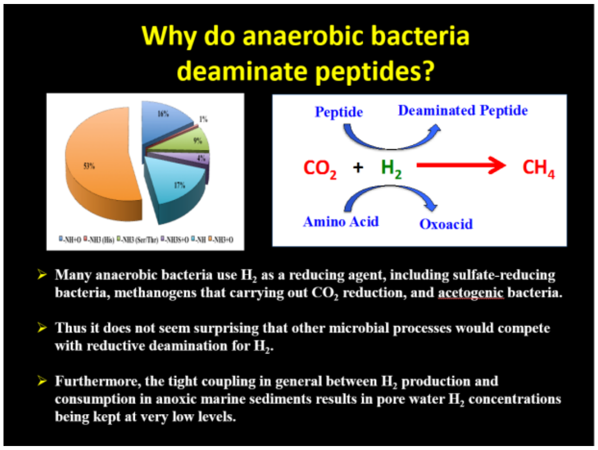
- Comparing the molecular formulas of the deaminated peptides in our database with N-bearing formulas detected in SBB pore waters, we identified 680 exact matches.
- Plotting these formulas on the van Krevelen diagram, we see a shift in the deaminated peptides towards lower H/C ratios and higher oxidation states (higher O/C ratios) relative to the original peptides.
- The majority (~70%) of the deaminated peptides also fall in the upper CRAM region (H/C ratio between 0.9 and 1.5).



Detecting deaminated peptides in pore water

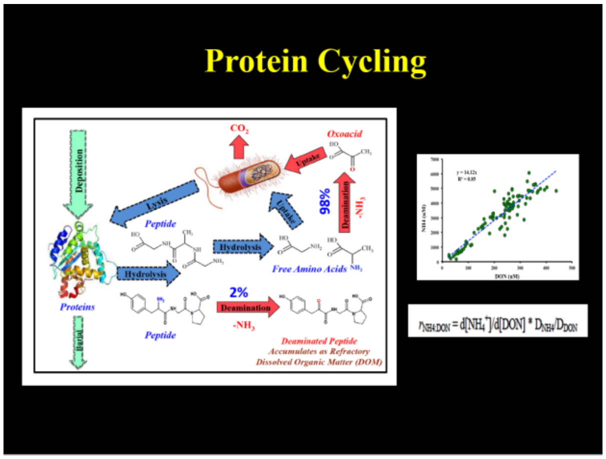
An examination of the relative abundance the individual amino acids that are found in the precursor deaminated peptides shows

- Tyrosine, glutamine and asparagine had the highest mole percentages, with 9.4, 8.8 and 7.8% respectively.
- Phenylalanine, proline, serine and threonine also had relatively high abundances (greater than 6 mole%).
- Tryptophan, histidine and methionine showed the lowest abundances, with 0.4, 1.2 and 1.7 mole%, respectively.



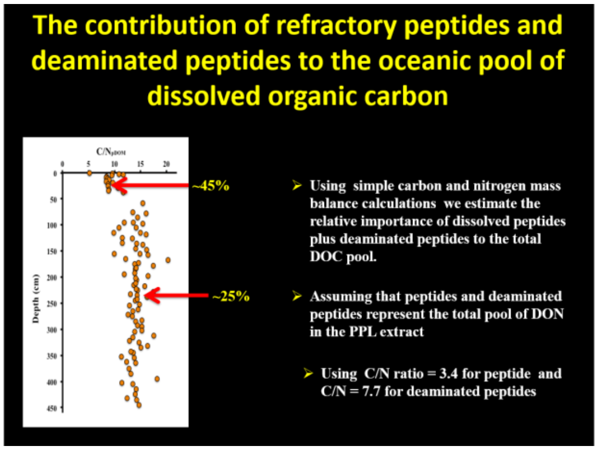
Why do anaerobic bacteria deaminate peptides?

- Many anaerobic bacteria use H_2 as a reducing agent, including sulfate-reducing bacteria, methanogens that carrying out CO_2 reduction, and acetogenic bacteria.
- Thus it does not seem surprising that other microbial processes would compete with reductive deamination for H_2.
- Furthermore, the tight coupling in general between H_2 production and consumption in anoxic marine sediments results in pore water H_2 concentrations being kept at very low levels.



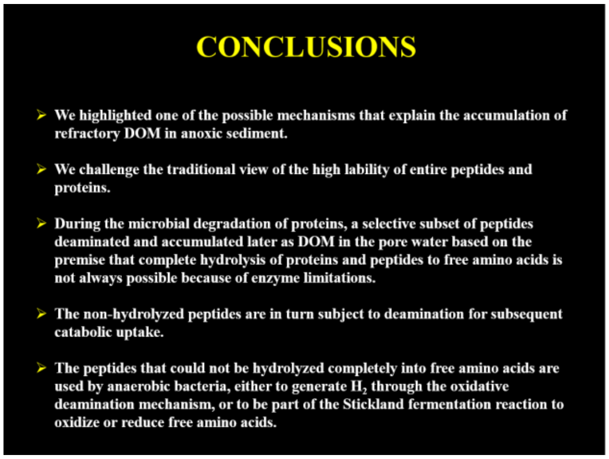
Protein Cycling

$r_{NH4:DON} = d[NH_4^+]/d[DON] * D_{NH4}/D_{DON}$



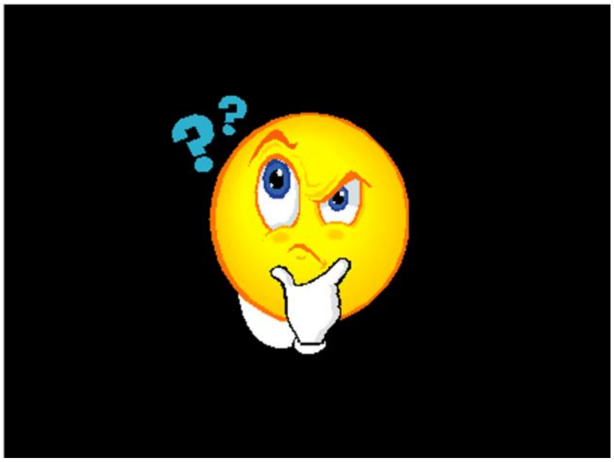
The contribution of refractory peptides and deaminated peptides to the oceanic pool of dissolved organic carbon

- Using simple carbon and nitrogen mass balance calculations we estimate the relative importance of dissolved peptides plus deaminated peptides to the total DOC pool.
- Assuming that peptides and deaminated peptides represent the total pool of DON in the PPL extract
  - Using C/N ratio = 3.4 for peptide and C/N = 7.7 for deaminated peptides



CONCLUSIONS

- We highlighted one of the possible mechanisms that explain the accumulation of refractory DOM in anoxic sediment.
- We challenge the traditional view of the high lability of entire peptides and proteins.
- During the microbial degradation of proteins, a selective subset of peptides deaminated and accumulated later as DOM in the pore water based on the premise that complete hydrolysis of proteins and peptides to free amino acids is not always possible because of enzyme limitations.
- The non-hydrolyzed peptides are in turn subject to deamination for subsequent catabolic uptake.
- The peptides that could not be hydrolyzed completely into free amino acids are used by anaerobic bacteria, either to generate H_2 through the oxidative deamination mechanism, or to be part of the Stickland fermentation reaction to oxidize or reduce free amino acids.



Breakout Sessions

TEXAS A&M UNIVERSITY CORPUS CHRISTI

HOKKAIDO UNIVERSITY

UNIVERSITAS BERGENSIS

HNEI

AIST
NATIONAL INSTITUTE OF
ADVANCED INDUSTRIAL SCIENCE
AND TECHNOLOGY (AIST)

Objective

This 3 day workshop was attended by 55 scientists from 12 countries. The text through this document is an overview of the presentations and discussions during the workshop. Following this summary key note speaker presentations, summaries of research discussions, and posters are presented. The key issues addressed during the workshop included the following:

1. Future Arctic Ocean research plans need to be developed with a long term field and laboratory research and monitoring plan. As a result of the discussions an international workshop to focus on development of an international Arctic Ocean methane hydrate research program will be planned for the fall of 2008. Topics that will be addressed in the workshop will include an overview of the current Arctic Ocean data, new seismic and pressure core sampling protocol, application of general ocean circulation models coupled with methane data and applied to the Arctic Ocean, and determination of the methane assimilation in the water column relative to the flux into the atmosphere.
2. Methane hydrate drilling needs a more thorough evaluation of well production rates that are coupled with production models. There is also a need for exploration protocol and models.
3. Higher resolution seismic profiling needs to be developed and applied. The seismic data need to be coupled with CSEM, shallow sediment porewater geochemistry profiles, and heatflow data for a more thorough evaluation of deep sediment hydrate deposits. Coupling these parameters is intended to provide pre-drilling site evaluation.
4. Laboratory and pilot scale experiments need to focus on geologic accumulation of hydrates, production testing, geomechanic sediment properties, biogeochemical influence on hydrate formation and stability, and sediment thermodynamics.
5. Theoretical modeling needs further development in rock physics flow simulations, geomechanical sediment properties, and environmental system cycling.
6. Production testing needs small scale evaluation to address, environmental impact assessment and regulation, efficiency of hydrate dissociation protocols in terms of pressure and temperature, and flow assurance.

The following is a review of the discussion sessions, as presented by the session chairs and rapporteurs.

Chair: **Prof. Bjørn Kvamme** **Rapporteur:** **Prof. Na Wei**	Laboratory Experimentation: 1) Limitations on experimentation relative to the environment. 2) Mineral/hydrate/ Fluid interactions focus on porous non steady stat conditions

Recorded by Kevin Supak

Microbiology and Hydrates

- We don’t know much about the individual microbial cell methane consumption.
- Not all species behave the same and need to understand the genes that control processes
- Understand the cell behavior of methane production and consumption
- Comment: In-Situ monitoring is gaining attention because labs cannot adequately grow the proper organisms. Another comment from Brandi Reese: Start with model organisms

  to better understand the processes before looking at the field. Temperature affects the metabolism of these organisms.
- We don't have experiments with joint CH4 consumption/production.

Multiscale Modeling

- Verify modeling of how mineral surfaces work
- Between the reservoir surface and the mudline we know there is a thermogenic layer but we don't know much between the thermogenic layer and the reservoir in BSR formations (ethane/propane hydrocarbon layer?)
- Many different technical disciplines required to model/understand these different surfaces
- Requires state-of-the-art microbiology modeling to assist in the effort
- There is a need to simulate the cold conditions bacteria?
- There are competing phase transitions that are not well understood.

Non-Equilibrium Systems

- Water leaking in or gas from other structures
- Gas hydrate generation and distribution throughout the world – they all act differently
- Pressure and temperature changes affect the formation differently

Basic question: What is the age of the gas hydrate in the different regions of the world?

CO2 / Methane Exchange

- Solid state mechanism is too slow

It was suggested to go around the room and share their biggest experimental challenges.
Questions from around the room:

- Understand gas seep methane releases to climate – what is the sedimentary record (bio markers or chemical)?
- Scientists around the world use different standards for measuring sediment solutions and it is difficult to compare results
    - Comment from audience – not easy to make laboratory samples standardized; but care should be taken in how to make and care for samples.
    - The same happens when you take a core sample – you effectively shut off the flow and reservoir effects
- Is there a uniform way to form hydrate bearing sediments to standardize the way we study them (shear rates, dissociation processes, etc.)
- Too little funding is spent in benchmarking reservoir simulators
- How can we improve the speed of forming hydrate bearing sediments in static experiments to get more experiment frequency.
    - Comment – have a circulation rate of fluid to enhance homogeneity
    - Comment – homogeneity is a relative term
- Can we incorporate field production data (engineering data) to develop feedback to laboratory experiment? Too much time is spent on controlling the experiment and they aren't controlled perfectly.
    - Comment – not enough field data, never got into an actual production mode, mineral and mineral distribution in the field is not the same as the laboratory mineral simulants
- Question from the industry: Further investigate practical applications and industrial collaboration.

    - Comment – what is the true energy potential of these hydrates reserves? What is the value of producing this for industry?
- What engineering is needed in drilling technology to recover from hydrate reserves?
- Better understanding phase change properties/kinetics is still challenging for hydrate simulations. This could be the reason there is a difference between the model and experiment.

Chair: **Prof. Joo Yong Lee** **Rapporteur:** **Mr. Zhenyuan Yin**	Gas Hydrate Related Modelling: Load Predictions, Coastal - Platform Stability, Environmental Safety

Topic of the session: Gas hydrate related modelling: Load Predications, Coastal - Platform Stability, Environmental Safety

Session Chair:

Lee Joo Yong

Rapporteur:

Yin Zhenyuan

1.1 Reservoir Stability

- Fluids from reservoir, rate and property
- Stability of reservoir and related Geomechanics
- Leakages of fluids
- Reservoir deformation
- Rock mechanics should be included

1.2 Wellbore stability

- Cementing and Casing
- Platform stability
- Sliding upon methane hydrate bearing sediment dissociation
- Subsidence
- Devise optimum Completion technology

1.3 Geomechanics code on methane hydrate

- The effect of depressurization effect should be fully understood
- Coupling between reservoir modeling and geomechnics modelling codes
- Validation between experimental data and simulation results are strongly needed
- Geomechanics code depended on constitutional relationships, linear elasticity model
- Very complicated process due to the two-way coupling of the flow and geomechincs processes
- Develop implicate geomechanics code to take account of the quick phase transition behavior happened during MH dissociation

1.4 Seismic aspects of MH

- The identification of BSR and its week indication of hydrate bearing layer
- Slow failure due to hydrate dissociation with pore pressure increase

  - Contrast in strain due to slide plane
  - Step-wise depressurization rather than sudden depressurization

After the short discussion, the group merged with the other group discussing on the laboratory experiments.

Chair: **Prof. Subbarao Yelisetti** **Rapporteur:** **Ms. Hao Yu**	Gas Hydrate Deep Drilling: Technology, Recent Data

- How many of you are involved with drilling studies? And how many with hydrate drilling?

A: 11 members joined the discussion. Four of us are involved with drilling studies and two with hydrate drilling.

- Many drilling studies around the world in the past two decades (northern Cascadia, southern Cascadia, US east coast (Blake Ridge), offshore India, Korea, South China Sea, Nankai margin off Japan, Chile, Peru, Costa Rica, Gulf of Mexico, and Borneo). What have we learned from these? What are the main technological problems for methane hydrate production? and how can we overcome these?

A: The most challenging issues are drilling under pressure and storing core samples. There are some methods to maintain pressure. For example, UT Austin uses new pressure coring tool.
New development of technologies:
1) Geotech (whole system); 2) Georgia Tech; 3) AIST; 4) UT Austin's new pressure coring tool. All systems are supported by Geotech. However, maintaining pressure in transportation is still a big challenge. Also, time is a big factor- samples need to be studied immediately

- What about the status of hydrate funding in various countries? For example Canada reduced funding for hydrate research…but we ask funding for studying geohazards/climatic effects and some how relate those to hydrate studies.

A: Japan currently has funding.

Korea's funding primarily comes from the government. US plans to spend 20 million dollars on this for next 5 years, 70% from government.
IODP offers funding for drilling proposals.
US DoE – is funding UT led hydrate drilling efforts in the GoM, ~$40 million
Developing artificial sand pack hydrate deposits in laboratory and comparing the mechanical, physical, geochemical, and petrophysical properties with drilling samples from the GoM.

- Many production methods discussed (for example, depressurization, Hot water circulation, solid fluidization, thermal stimulation and gas swapping). What is the most economically feasible production method?

A: It is uncertain, and depends on the depth and characteristics of the system. For example, methane hydrates exploited in South China Sea are in the shallow shelf of about 20 mbsf, while methane hydrates off Indian and Japan are in deep waters. Hence the production methods are different.

- Previous production tests were carried out only for few days (1-3 weeks). Is it possible to establish a technological base that can produce gas for the long-term?

A: Cost is the most important problem in deciding the production test period. Environmental factors also prevents this. For example, it is difficult to get access to Mallik gas hydrate drilling site in Canada.
US plans to drill North Slope of Alaska in this or next year.
Japan doesn't have fixed plan in production tests, because the methane hydrate storage area has many holders, which needs coordination.

- We have seen sand entering production wells from drilling in Canada, Japan and Korea. How can we prevent this?

A: It is hard. Filtering techniques maybe helpful. China is developing a method to separate sand from methane gas in South China Sea using cyclone separator.

- What are the environmental risk factors associated with hydrate drilling? Gas pipe blowouts? Effect of natural hazards on drilling platforms? Earthquakes, typhoons? Does gas production from methane hydrate induce a large-scale seafloor slide or earthquake?

A: Environmental risks include landslides and seafloor subsidence. Landslides reported earlier at the IODP drilling off New Zealand. Seafloor subsidence has been discussed in some conference held in Japan. In deep waters, platform is relatively safe. At present short term production tests doesn't worry too much about earthquakes.

- What about international collaboration for deep-sea drilling?

A: India, US and Japan successfully collaborated in drilling in the Bay of Bengal.
USGS is trying to collaborate with India now.
These are good cases. Political factors and funding prevent this.
We need to find better ways to have more such collaborations at the international level involving many countries.

- Does commercial gas production from methane hydrate appears feasible in the near future?

A: Japan: 2027, China: 2030

- Where does your research fall interns of deep-sea hydrate drilling? What are your thoughts about the future of hydrate drilling?

A: Cheap drilling technology is much needed. Currently the technology primarily comes from the oil and gas exploitation.
Island offshore company provides cheap drilling facilities

New drilling proposals:

Proposal to drill over chatham rise off New Zealand looking for geochemical profiles to interpret vertical fluid and gas migration-Richard Coffin and Ingo Pecher+others?
Proposal to drill in the hikurangi margin hydrate system -Richard Coffin and Ingo Pecher+others?
Proposal to drill in the Rio Grande fan off the coast of southern Brazil
Proposal to drill in the northwest Atlantic

Chair: **Dr. Kelly Rose** **Rapporteur:** **Dr. Xin Lu**	Carbon Sequestration Related to Gas Hydrate Mining: Pla

There was a general discussion on can you do CO2/CH4 exchange to CCS? Offshore shallow water EOR with CO2 is likely leading the charge. Kelly indicated that this is likely a risky move due to shelf stability and high sands permeability.

Steve asked a bold question regarding CCS: “Are we past the tipping point?” He indicated that his personal opinion is yes and maybe we should focus research on adaptation strategies rather than CCS.

Rick said land based studies should be the place to start CO2 storage/EOR because it’s easier/cheaper.

Bjorn indicated that GasNova funds big gas storage projects. Bjorn said that Europe has mandated that CO2 injection into deepwater water-flooded wells is the CCS solution and Norway is following suit – and not encouraging CO2/CH4 hydrate exchange.

Kelly inquired to the Integrity of hydrate seals/layers and how that might work for CO2 sequestration. Can you make a hydrate cement with CO2? Bjorn says thermodynamically probably not.

Is there a difference between shallow versus deepwater CO2 water columns being able to handle the acidification?

Will the ocean be a toxic soup by adding a lot of CO2 whether in hydrates or as free gas?
Kevin asked the question has there been any large-scale test to verify sedimentary stability with CH4/CO2 exchange? There doesn’t seem to be.

Rick asked if there is value in injection N2 and CO2 together?

How do you make this attractive in deepwater GoM or arctic – especially for the operators/services companies, DOE, etc.?

Chair: **Prof. Richard Coffin** **Rapporteur:** **Mr. Sajjad Abdullajintakam**	Initial Site Assessment: Seismic and Geochemical Evaluation, Recent Data (Positive and Negative), Additional Approaches.

Summary of Discussion: Site Assessment

Perspective:

- Instrumentation
- Sampling
- Seismic Data

Sampling Perspective

- Sample collection to lab – changes the thermodynamics
- Problems with assessment of in-situ methane concentration
- Isotope mass balance offers back calculations
- ONBOARD/in-situ data is more effective

Instrumentation perspective:

- Pressure cores – excellent but expensive

Economically feasible approaches..?

- Calibration of methane and pressure cores with sulfate-DIC prediction
- Alternate/developing techniques - Raman spectroscopy

Needs:

- High resolution data sets on seismics
- Estimate fracture system – to back calculate reservoir – include in modelling parameters
- Inversion of seismics in elasticity and geo-mechanics

Seismic Data Perspective:

- Limitations:
  - Resolution is limited
  - BSR can not necessarily indicate GH; GH may/may not have BSR
- Control Source Electromagnetics – in compliment with BSR – Provides higher resolution
- For shallow GH system, fishery echo-sounding data is useful –offer potential collaborations with fisheries research

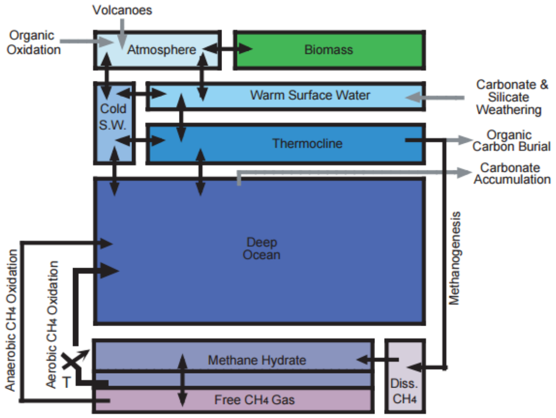
Geochemistry Perspective:

- Elements other than C and O.. Non traditional geochemical proxies
- How sulfate profiles are used for back-calculation by different groups?
- Redefine carbon budgets with methane-carbon energy included

- **Gather data from different proxies/methods used world wide margins and compare more/most effective methods**
- **International attempt to share data/protocols for this initiative**

Modelling Perspective:

- **Initial site assessment data needs to be going into modelling**
- **Next generation reservoir simulations – need collaboration between modelling community**
- Estimate fracture system – to back calculate reservoir – include in modelling parameters
- Inversion of seismics in elasticity and geo-mechanics



Practical Strategies to Make this a Reality

- **Next generation reservoir simulations – need collaboration between modelling community**
- **International participation is necessary**
- **International funding base for this educational source – seed funding for many prospectus endeavors**

- Teaching/Educational aspect is fundamental
- **Establish an international school – community**
  - **need to profile it in an appropriate manner (diplomatic issues)**
  - **Expand to next generation scientists**
  - **Expand/bridge with non-GH systems – e.g oil and gas.. multidisciplinary approach**
  - **Two future international proposals – NSF, EU, DOE, Horizon 2020, other..**
    - **i) for education**
    - **ii) for a cruise - black sea**

Next IMHRD

- Compile work groups and science focus by different participants and then establish an comprehensive effort
- Advertise to all participating countries in advance
- Next workshop – focus on better arranging breakup groups
- Need a survey/questionnaire before the workshop to set better breakup groups

Chair: **Prof. Brandi Reese** **Rapporteur:** **Prof. Joseph Smith**	Biogeochemical Assessments of Gas Hydrate Loading and Monitoring Environmental Health

Attendees

ATTENDEES

	Name	Email	Affiliation	Nation	Presenting	Poster	Talk	Registered
1	Abdulla, Hussain	hussian.abdulla@tamucc.edu	TAMU-CC	US	Y		X	Y
2	Abdullajintakam, Sajjad	sajjad.abdullajintakam@tamucc.edu	TAMU-CC	US	Y	X		Y
3	Chee, Soon Seong	schee@slb.com	Schlumberger	Malaysia	N			Y
4	Ciferno, Jared	Jared.Ciferno@NETL.DOE.GOV	DOE-NETL	US	Y		X	Y
5	Cifuentes, Luis	luis.cifuentes@tamucc.edu	TAMU-CC	US	N			
6	Cooper, Jenna	Jenna.Cooper@tamucc.edu	TAMU-CC	US	Y	X		Y
7	Coffin, Richard	Richard.coffin@tamucc.edu	TAMU-CC	US	Y		X	Y
8	Chen,Wei	zhonglin858296@163.com	CNOOC	China	N			Y
9	Clark, Corrie	cllanes@islander.tamucc.edu	TAMU-CC	US	Y	X		Y
10	Cui, Jingyuan	Jingyuan.cui@cnpcusa.com	CNPC	US	N			Y
11	Ersland, Geir	Geir.Ersland@uib.no	University of Bergen	Norway	Y		X	Y
12	Furui, Kenji	furui@waseda.jp	Waseda University	Japan	N			Y
13	Kanno, Takayuki	tkanno@slb.com	Schlumberger K.K.	Japan	N			Y
14	Konno, Yoshihiro	Yoshihiro-konno@edu.k.u-tokyo.ac.jp	University of Tokyo	Japan	Y		X	Y
15	Kvamme, Bjørn	bjorn.kvamme@ift.uib.no	University of Bergen	Norway	Y		X	Y
16	Lee, Joo Yong	jyl@kigam.re.kr	KIGAM	S. Korea	Y		X	Y
17	Lu, Xin	lvxin@cnooc.com.cn	CNOOC	China	Y		X	Y
18	Qiang, Fu	zhonglin858296@163.com	CNOOC	China	N			Y
19	Qinping, Li	zhonglin858296@163.com	CNOOC	China	Y			Y
20	Masutani, Stephen	stephenm@hawaii.edu	University of Hawaii	US	N			Y
21	Oyama, Ai	aioyama@hawaii.edu	University of Hawaii	US	N			Y
22	Reese, Brandi	Brandi.reese@tamucc.edu	TAMU-CC	USA	Y		X	Y
23	Mienert, Jurgen	jurgen.mienert@uit.no	University of Tromsoe	Norway	Y		X	Y
24	Murgulet, Val	Valeriu.Murgulet@tamucc.edu	TAMU-CC	US	N			Y
25	Shouwei, Zhou	zhonglin858296@163.com	CNOOC	China	N			Y
26	Smith, Joe	jpsmith@usna.edu	USNA	US	X		X	
27	Szczerbinska, B	barbara.szczerbinska@tamucc.edu	TAMU-CC	US	N			Y
28	Tamborello, Brittney		University of Oklahoma	US				Y
29	Tenma, Norio	tenma-n@aist.go.jp	AIST	Japan	N			Y
30	Tomaru, Hitoshi	tomaru@chiba-u.jp	University of Chiba	Japan	Y	X		Y
31	Uchida, Tsutomu	t-uchida@eng.hokudai.ac.jp	University of Hokkaido	Japan	N			Y

32	Wang, Guorong	swpi2002@163.com	SWPU	China	Y		X	Y
33	Wang, Xu	Kelly.Parker@cnpcuse.com	CNPC	USA	N			YY
34	Wei, Na	weina8081@163.com	SWPU	China	Y		X	Y
35	Yanzhen, Liu	chemliu@yeah.net	Dalian University of Technology	China	Y	X		Y
36	Yang, Tang	tangyanggreat@126.com	SWPU	China	Y		X	Y
37	Yelisetti, Subbarao	Subbarao.Yelisetti@tamuk.edu	TAMU-K	US	Y		X	
38	Yin, Zhenyuan	E0013211@u.nus.edu	National University of Singapore	Singapore	Y		X	Y
39	Yu,Hao	hao.yu@tamucc.edu	TAMU-CC	US	Y	X		Y
40	Zhang, Lin	lin.zhang@tamucc.edu	TAMU-CC	US				Y
41	Zhong, Lin	zhonglin858296@163.com	CNOOC	China	Y		X	Y