



Fire in the Ice

THE NATIONAL ENERGY TECHNOLOGY LABORATORY METHANE HYDRATE NEWSLETTER



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REMOTE OBSERVATORY TO PROVIDE DETAILED DATA ON NEAR-SEA-FLOOR FLUID DYNAMICS

By Carol Lutken and Tom McGee, Center for Marine Resources and Environmental Technology (CMRET) of the University of Mississippi

The Gulf of Mexico will soon be the home of a unique observatory designed to monitor the water column and sediments of the near-sea-floor environment. The design of the observatory has evolved over the past four years as preliminary data gathering and component testing has progressed. With initial deployment of the first sensing elements scheduled for 2005, here is an update on the current objectives and the system designed to achieve them.

Background

The Gulf of Mexico-Hydrate Research Consortium was organized in 1999 by the Center for Marine Resources and Environmental Technology (CMRET) at the University of Mississippi to develop and install a remote sea-floor observatory within the hydrate stability zone of the continental slope of the northern Gulf of Mexico. Its primary scientific objective is to study the cause and effects of the migration of hydrocarbon fluids into and out of the hydrate stability zone, as well as associated chemical interactions.



A prototype of the vertical acoustic array was tested in 2002 using a watergun energy source.



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INTENT

Fire in the Ice is published by the National Energy Technology Laboratory to promote the exchange of information among those involved in the research and development of gas hydrates as a resource.

Interested in contributing an article to *Fire in the Ice*?

This newsletter now reaches nearly 480 scientists and other individuals interested in hydrates in sixteen countries. If you would like to submit an article about the progress of your methane hydrates research project, please contact Frances Toro at 304-285-4107.

Data collected by the observatory will promote a better understanding of the near-sea-floor hydrocarbon system, including hydrate formation/dissociation, fluid venting into the water column, and the relationships between these activities and the associated microbial/chemosynthetic communities. Study results should provide improved understanding of the role of gas hydrates and associated free gas in regard to: 1) geo-hazards to sea-floor installations; 2) the significance to potential energy resources; and 3) the global climate implications of hydrocarbon gasses venting into the water column and, eventually, the atmosphere.

Because hydrocarbons in the water-column and the sub-bottom are involved, the observatory will be equipped with sensors in the seawater, on the bottom, and within bottom sediments. Moreover, because the flow of gas and other fluids is not constant in time, an effort will be made to accomplish more-or-less continuous monitoring of the sub-bottom by utilizing the sound of passing ships and/or wind-blown waves at the water surface as sources of acoustic energy.

Presently, the Consortium includes six private corporations and seventeen universities at various levels of involvement. Over the past four years consortium achievements have included:

- the first laboratory demonstrations that bacterially-produced surfactants have significant impact on hydrate formation (Mississippi State University),
- the first vertical line array designed expressly for high-resolution acoustic imaging (University of Mississippi, University of Victoria and Specialty Devices, Inc. of Plano, Texas),
- the development of pore-water samplers for recovery of pore-water under *in situ* conditions (University of North Carolina and Florida State University), and
- the development of spectrographic sensors for detecting and quantifying concentrations of methane in sea water (Georgia Institute of Technology, Wood's Hole Oceanographic Institute and WellDog, Inc., of Laramie, Wyoming)

The monitoring station project has received funding from three sources. Initial funding was from the Department of Interior's Minerals Management Service (MMS) in FY1998. MMS funds were augmented by the Department of Energy's National Energy Technology Laboratory beginning in FY 2000 and by the Department of Commerce's NOAA-NURP beginning in 2002.

The Sensor Arrays

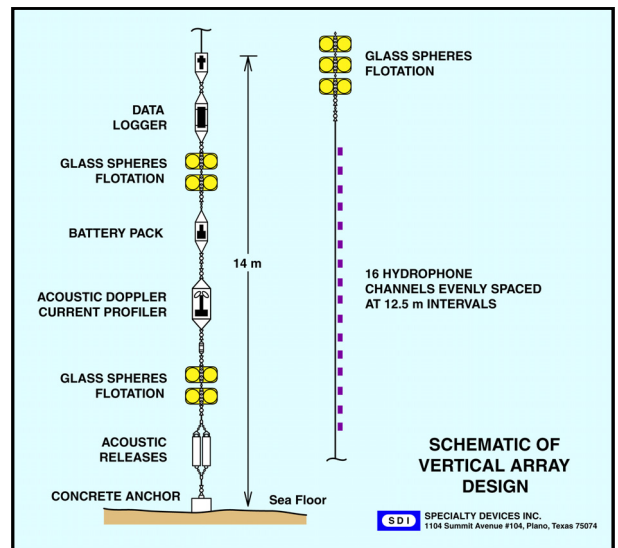
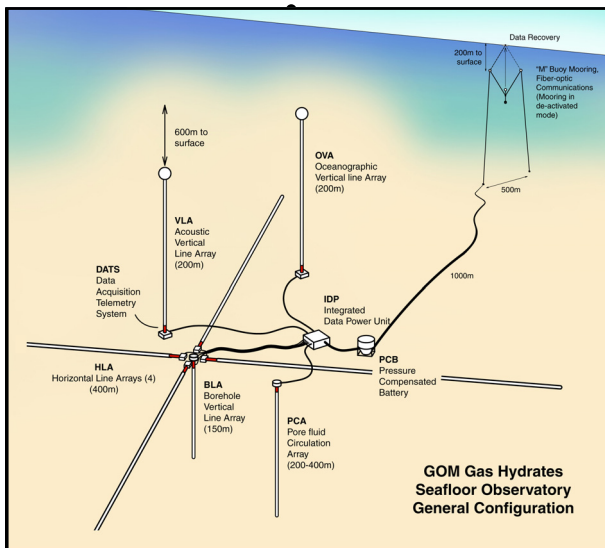
When completed, the observatory will consist of linear arrays of sensors connected to peripheral systems that provide electrical power, collect data, and provide the means by which data are recovered. The arrays will be deployed above, on, and below the seabed. Two arrays, one acoustic and the other oceanographic, will occupy the lower portion of the water column. Four seismo-acoustic arrays will be laid horizontally on the water bottom. Two arrays, one seismo-acoustic/thermal-gradient and the other for monitoring pore fluids, will be deployed in boreholes drilled into the upper sea-floor sediments.

Each of the arrays in the water column will be 200 m in length. The acoustic array will consist primarily of hydrophones to record water-borne acoustic energy, but it will also contain thermistors to record water temperature and tilt meters with compasses to ascertain array geometry in the presence of water currents. A prototype of this array has been constructed and was tested in 2002 using a watergun energy source. A comparison of the test data to a simultaneously recorded reflection profile illustrates the functionality of the array.

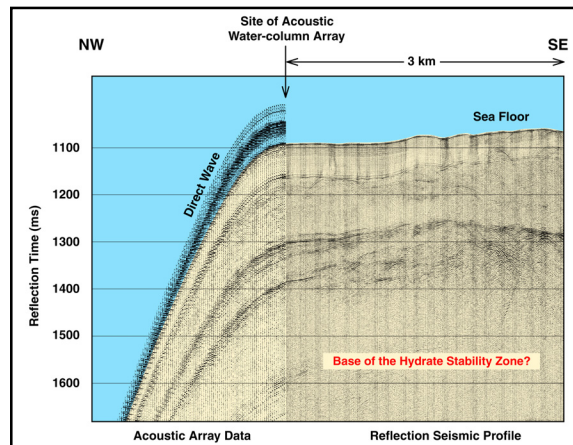
The oceanographic water-column array will consist of sensors to measure physical parameters such as conductivity, temperature, and depth. It will also contain fluorimeters to detect the chemical characteristics of hydrocarbon fluids venting from the sea bed.

The four seafloor arrays (horizontal line arrays), each 400 m long and consisting of hydrophones and 3-component accelerometers, will be laid upon, and pressed into, the soft sediment of the sea floor. They will be arranged in the shape of a cross to simulate two perpendicular 800 m arrays. This deployment will be accomplished by means of a sea-floor sled designed to lay cable and deploy probes into shallow, unconsolidated sediments. This sled will also be used as a seismic source of compressional and shear waves for calibrating the subsurface seismo-acoustic array.

The two sub-bottom arrays (Borehole Vertical Line Array and Pore Fluid Circulation Array) will be installed in boreholes drilled into the upper unconsolidated sea-floor sediments. The seismo-acoustic array will consist of hydrophones, 3-component accelerometers, and thermistors for monitoring thermal gradient. The pore-fluid array will consist of tubular osmosamplers designed to draw fluid samples from several depths and store them in a seafloor apparatus that can be recovered under *in situ* pressure. Pressure sensors will also be included to monitor pore-fluid pressure at depths of interest. Eventually, a spectrometer will be added to identify and quantify pore fluids and hydrocarbon gases in the sediment section.



Six linear arrays deployed above, on, and below the sea-bed will be connected to systems that provide electrical power, collect data, and provide the means to recover the data.



The acoustic array will include hydrophones, thermistors to record water temperature, and tilt meters with compasses to ascertain array geometry.

Vertical acoustic array test data compared to conventional seismic profile recorded simultaneously.

Data Recovery

Retrieving data from offshore sensors across large distances is not a trivial problem. A number of possibilities have been considered: telemetry from a production platform, telemetry from a buoy, and near-to-real-time transmission to shore via a commercial optic-fiber service. The optic-fiber link appears to be the preferable solution, but the service will not be available until 2006 or later. Therefore, until the optic-fiber link becomes available, data will be accessed at the sea surface on acoustic command.

The arrays will be connected to an integrated data/power (IDP) unit designed to collect data from and supply power to the arrays. The design is such that the IDP will be capable of streaming the data onto an optic-fiber link when it becomes available. In the meantime, the IDP unit will be connected to an optic-fiber data recovery system. A configuration of buoys will bring the data recovery system to the surface on command, and data can be downloaded to a boat.

Since the IDP module also supplies electrical power to the station, it will be necessary to replace the pressure-compensated battery periodically. The exchange of batteries will be accomplished remotely by a station service device. When the sea-floor battery is depleted, a ship will lower a cable with the station service device, a replacement battery, and a fresh pore-fluid sampler. Upon reaching the IDP, the station service device will disconnect the arrays from the depleted battery, connect them to the replacement battery, and operate valves to exchange the used sample collector for the unused one. The station service device, depleted battery, and pore fluid samples under in *situ* pressure will then be winched to the surface.

Deployment Plans

Several factors affect the maximum depth at which the monitoring station can be deployed. The geochemical sensors, in particular the spectrometer, is presently rated to 1,000 m and strengthening the housing for greater depths would seriously degrade the sensitivity of the instrument.

The use of wind-driven wave noise at the water surface as an acoustic source for monitoring the sub-bottom requires horizontal arrays with lengths about the same as the water depth. At present, each sea-floor array is planned to be 400 m long and they will be deployed as a cross that simulates two perpendicular 800 m arrays. This design would limit the water depth to about 800 m.

Once a suitable site is selected, the plan is to deploy the seismo-acoustic array and have it fully operational by summer 2005. It is expected that the complete seafloor observatory will be deployed and fully operational by the end of 2007.

Data Architecture, Management, and Processing

The architecture of the data set produced by the observatory and overall data management is being handled by Barrodale Computing Services Ltd. of Victoria, B.C. They are recognized experts in large, diverse data sets and recently were awarded a contract to perform similar functions for the Neptune-Venus Project that is instrumenting the Juan de Fuca Plate offshore of Washington and British Columbia (visit www.neptune.washington.edu for more information on this effort).

Specific methods of processing seismo-acoustic data are being studied by three graduate students. At the University of Victoria, a Ph.D. student is working with procedures to produce 3-D sub-bottom images, and an M.S. student is working with the utilization of ship noise and wave sounds. Also, a Ph.D. student at the University of South Carolina is investigating the use of conventional petroleum industry processing systems for processing observatory data.

For more information on the Gulf of Mexico seafloor observatory, contact Carol Lutken at cbl@olemiss.edu or 662-915-5598.

USGS LABORATORY STUDIES SHED LIGHT ON HYDRATE DECOMPOSITION BEHAVIOR UNDER POSSIBLE GAS PRODUCTION SCENARIOS

by Stephen H. Kirby, Susan Circone, Laura A. Stern, and John Pinkston, U.S. Geological Survey, Menlo Park, CA

Producing natural gas from a conventional reservoir requires an understanding of how gas flow changes with reservoir pressure; flow does not depend strongly on reservoir temperature. Producing natural gas by hydrate decomposition depends not only on the *in-situ* pressures and temperatures, but also on the thermodynamic and other properties of the hydrate system. Methane hydrate decomposition experiments performed at the U.S. Geological Survey show that, because hydrate decomposition requires heat to proceed, reservoir temperatures can drop significantly and ice can form under certain conditions. A fundamental low-temperature limit is imposed on hydrate decomposition by the phase equilibria of the hydrate/ice/water system.

Naturally occurring gas clathrate hydrates are found where low temperature, elevated pressure, and a supply of hydrocarbons exist together. Their limited range of stability makes them prone to decomposition when natural or man-made perturbations occur in their environment (e.g., climate or sea level changes, drilling activity, exposure to warm fluids, or depressurization). Hydrates usually occur in sediments at temperatures of 0 to 20 degrees C. If perturbed in place, hydrate usually decomposes to constituent natural gas and water. Partial decomposition of hydrate often occurs during recovery of hydrate-bearing cores, as pressure and temperature conditions move outside the limits of hydrate stability. Interestingly, recovered hydrate-bearing marine sediment cores are often colder than any temperature encountered *in situ* or during retrieval (this phenomenon was observed during Ocean Drilling Project legs 146, 201, and 204), and some cores contained ice. Thermal depressions can be several degrees and are employed to infer the presence of hydrate and identify sections for further inspection. They occur because hydrate decomposition reactions involve absorption of heat, as well as large volume increases, which can cause these reactions to be self-regulating. This thermal response, though not unexpected, expresses itself in interesting ways that are potentially important for natural-gas production from hydrates.

Once pressure/temperature conditions are outside the hydrate stability field, decomposition requires heat to proceed. Either sufficient heat must flow from the surroundings to maintain isothermal conditions (the low thermal conductivity of methane hydrate works against this), or the temperature must fall. In settings where the proportion of hydrate relative to free water and sediments is low, all of the hydrate will decompose before pressure and temperature conditions reach the hydrate phase boundary. However, in hydrate-rich settings, temperature in the vicinity of the decomposing hydrate will decrease and may become temporarily fixed at the phase boundary conditions during decomposition. In this case, self-regulation will occur as the decomposition rate is balanced against the heat flow from the surroundings.

Understanding this behavior is important because it affects the *in situ* environmental conditions during hydrate decomposition, and thus must be incorporated into models for predicting gas production rates from decomposing hydrate. These models are important tools for analyzing proposed schemes for natural gas production from hydrates, either by depressurization or thermal stimulation.

We have observed several aspects of self-regulation during hydrate decomposition in laboratory experiments conducted on pure methane hydrate. In particular, we have investigated hydrate decomposition near the quadruple point—the pressure, temperature condition at which the hydrate phase boundary intersects the ice/water phase boundary—where hydrate, gas, ice and water coexist. In the CH₄-H₂O system, this point is at 0°C and a methane pressure of 2.6 MPa. An important factor concerns whether pressure remains constant as decomposition proceeds—by allowing released gas to escape—or does pressure climb? Some of the results of our studies follow, with technical details and an in-depth discussion of the experimental results to be found in the references listed at the end of this article.

Decomposition by depressurization to conditions above the quadruple point

A pressure-temperature phase diagram for methane hydrate can be used to illustrate the changes that occur during decomposition. On this diagram (Figure 1) Q₁ is the quadruple point located at the intersection of the hydrate phase boundary (blue curve) with the ice/water boundary (vertical dotted black line). The solid vertical arrows show the path of depressurization from starting conditions to Point A. The horizontal dashed arrow shows the initial thermal response (cooling) as decomposition begins following depressurization, while the red box shows the conditions at which subsequent decomposition proceeds. When pressure drops below the equilibrium boundary to point A, decomposition starts immediately, and the temperature of the hydrate drops (horizontal dashed segment) until the conditions of the hydrate phase boundary are reached (red box). If pressure is decreased further, the hydrate temperature continues to decrease to maintain pressure/temperature conditions along the equilibrium boundary, and the decomposition rate increases.

This behavior is illustrated by an experiment in which pressure was decreased in stepwise increments and then held constant for several minutes, while the temperature of the surroundings (T_{surr}) was maintained constant by a controlled low temperature bath. After each stepwise pressure decrease, the pressure was held constant by releasing the gas via a back pressure regulator. The temperature of the gas hydrate sample decreased immediately following each pressure decrease, following the hydrate phase boundary. Figure 2 illustrates this experiment; the known methane hydrate phase equilibria data are shown as red solid circles and a blue line; the external bath conditions are shown as black open circles (temperature equivalent to T_{surr}); and the hydrate temperature during decomposition is shown as purple circles. Bath and hydrate temperatures at a given pressure are observed at the same time. The black vertical arrows show the externally imposed path of depressurization (segments 2 and 4 show decreasing pressure steps followed by constant pressure holds) and the horizontal black line (segment 3) shows cooling at constant pressure during decomposition.

During this stepwise pressure decrease, the temperature of the surroundings (T_{surr}) was maintained constant by the controlled low temperature bath, first at 11.5°C, and then at 7°C (steps 2 and 4, respectively, with cooling at step 3). Hydrate decomposition occurred continuously, except when the bath temperature briefly crossed below the hydrate equilibrium phase boundary at 5.5 MPa. The hydrate sample responded to depressurization by following the pressure/temperature pathway indicated by the purple arrows, as predicted by the phase equilibria data. The internal temperature rebounded to T_{surr} (horizontal purple line at 1.5 MPa) once all of the hydrate had decomposed.

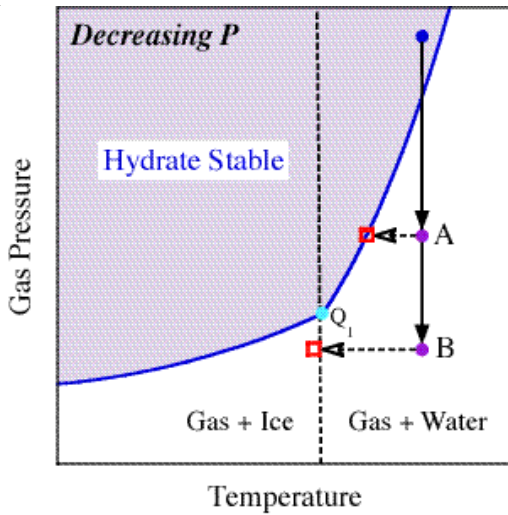


Figure 1: Schematic pressure/temperature phase diagram for methane hydrate illustrating relative positions of quadruple point (Q_1), hydrate phase equilibrium boundary (blue curve), ice/water phase boundary (dotted black line), and isothermal depressurization pathways.

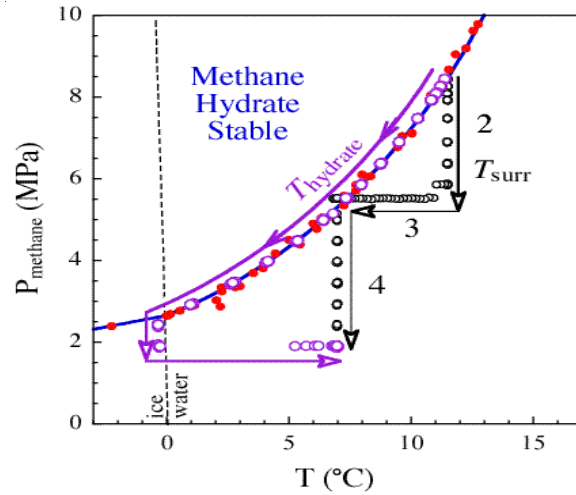


Figure 2: Plot of experimental conditions during methane hydrate decomposition, showing phase equilibria data (red solid circles, blue line), external bath conditions (black open circles, equivalent to T_{surr}), and hydrate temperature during decomposition (purple circles).

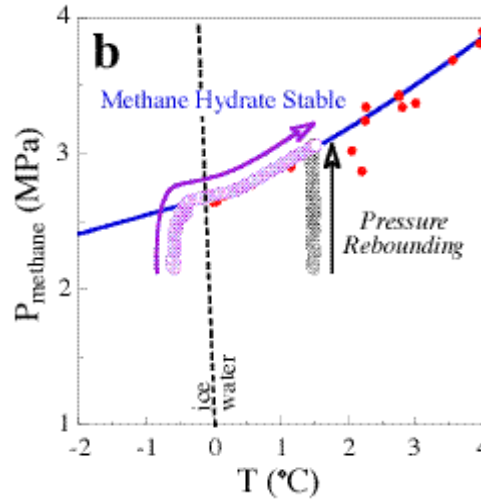
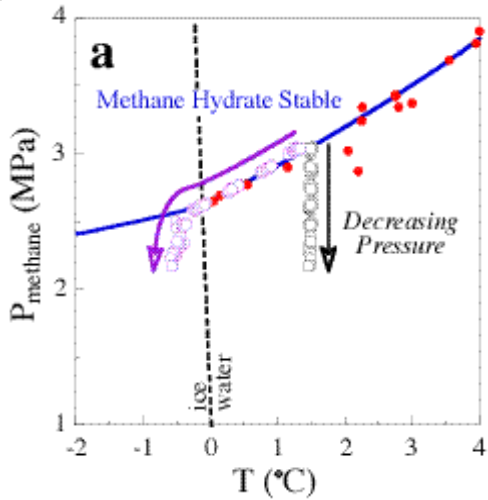


Figure 3: Plots of experimental conditions during methane hydrate decomposition below the quadruple point showing evidence of internal temperature regulation.

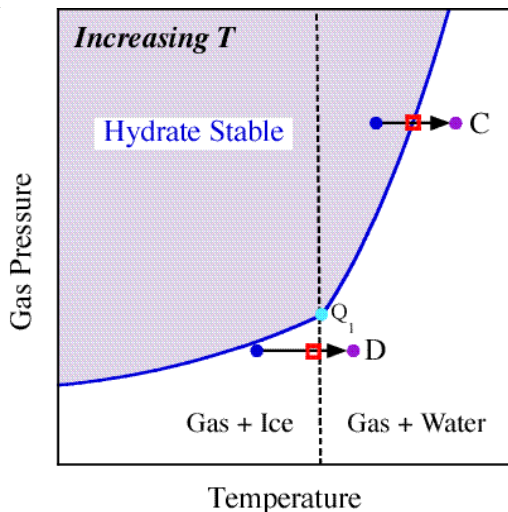


Figure 4: Schematic pressure/temperature phase diagram for methane hydrate illustrating constant pressure thermal stimulation pathways.

LARGE-VOLUME, HIGH-PRESSURE VIEW CELL HELPS FILL GAPS IN UNDERSTANDING OF METHANE HYDRATE BEHAVIOR

By Charles E. Taylor, U.S. DOE/NETL

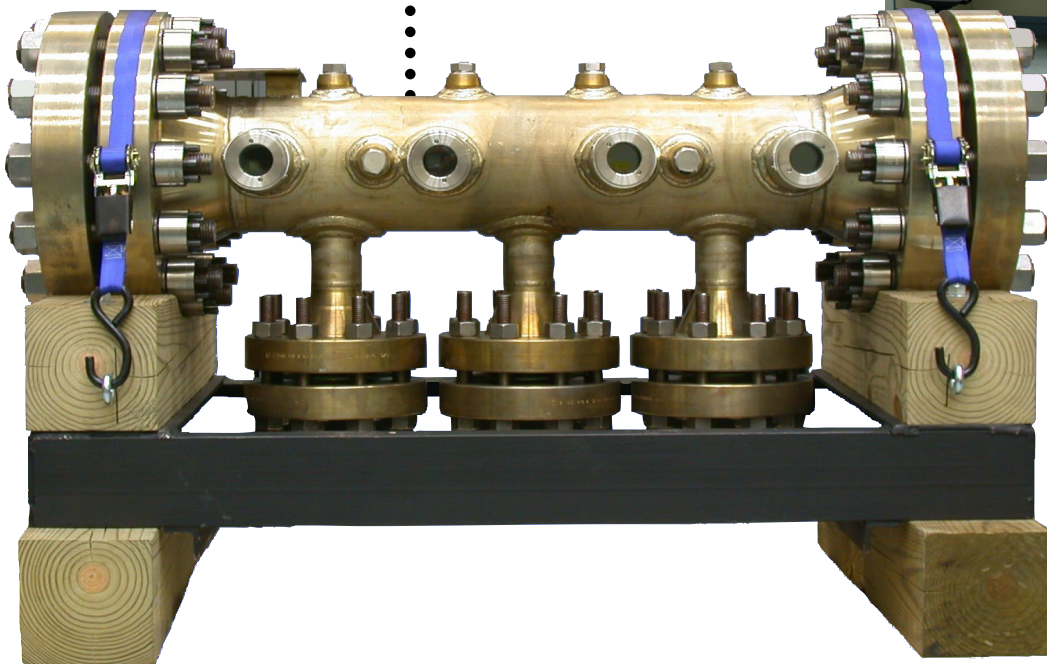
The National Energy Technology Laboratory's Office of Science and Technology conducts research to fill key gaps in the basic data available regarding methane hydrates. Five such data gaps have been identified and targeted by the Methane Hydrate Research Group at NETL: thermal properties of hydrates in sediments, kinetics of natural hydrate dissociation, hysteresis effects during methane hydrate formation and dissociation, permeability to gas and capillary pressures within the fine sediments where marine hydrates are found, and hydrate distribution on the pore scale. Research at NETL is focused on both physical and computational studies related to these five areas.

In order to fill these gaps, NETL has expanded its onsite hydrate research capabilities during the last three years. An important part of this effort relates to the laboratory apparatus required to create and study hydrates. Currently, we have six dedicated methane hydrate cells in operation: two identical 40-milliliter high pressure (20,000 psi) view cells, a single 1-liter (L) cell, a variable volume thermoconductivity cell, a view cell situated within the sample compartment of a Raman spectrometer, and the newest addition, a 15 L high-pressure (1500 psi) view cell. Operation of this larger-volume cell marks an important step in the NETL methane hydrate research program.

Control housing allows total environmental control of cell with observation via multiple video cameras.



Side view of 15-liter, high-pressure hydrate view cell prior to installation shows multiple viewing windows along the horizontal axis with access ports above and below.



New view cell enhances experimental options

The 15 L view cell was designed at NETL to accommodate a much wider range of experimental conditions and data collection capabilities than any of the then-current pressure cells. By significantly increasing both the volume and the instrumentation capability, a new level of resolution is possible in monitoring the behavior of hydrates during their formation and dissociation.

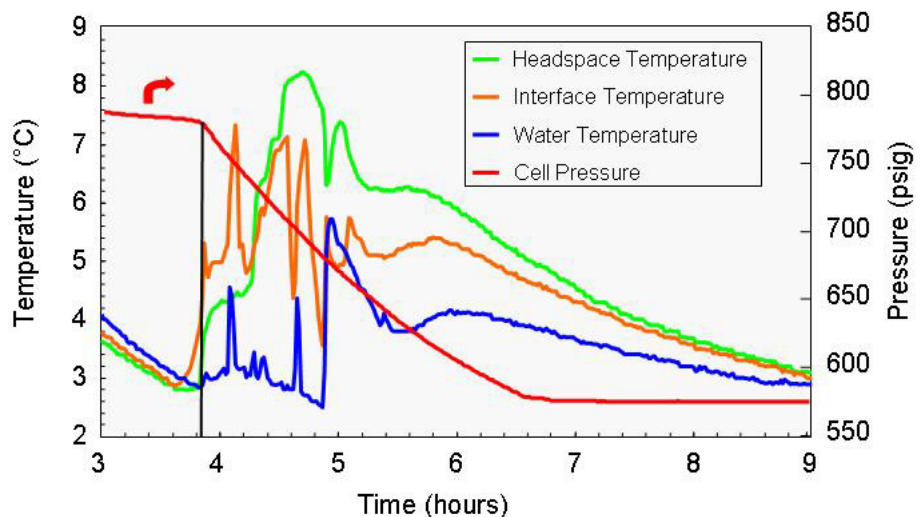
Constructed of 316 stainless steel, the cell measures 1 meter in length and has a 15.2 centimeter (cm) inside diameter. Either horizontal or vertical operation of the cell is possible. The interior of the cell is coated with Teflon® to minimize wall effects. Seven 3.8 cm glass view ports are arranged along the central axis of the cell — four on the front side, and three on the back. Three additional ports along one side of the cell act as stir ports when the cell is operated in the horizontal position. In addition, seven threaded ports are situated along the cell's circumference and on the end caps.

The assembly is housed in an environmental chamber that is used to control the temperature. Closed circuit cameras can be placed in front of any of the view ports to visually observe and record conditions within the cell.

Thermocouple bundles are positioned along the length of the cell such that the temperature in the methane headspace, at the methane-water interface, and within a water-hydrate mixture can be recorded. Additional thermocouples record the temperature of the environmental chamber. Mass flow meters monitor the uptake of methane during cell charging and hydrate formation, while vented methane or dissociated methane from hydrates is measured by a downstream wet test meter. Pressure within the cell is monitored by a pressure transducer.

First experiments provide details of hydrate formation

The cell became operational in May, 2004 when the first series of tests were performed. This inaugural test provided a good example of the enhanced observational capabilities made possible through multiple temperature probes. With the cell in the horizontal position, 9.2 L of distilled water and 2.0265 grams of sodium dodecylsulfate were added (a 225 parts-per-million solution). The cell was connected to a high-pressure nitrogen line, pressurized to 900 psig and vented. This pressure/vent procedure was repeated three times to



Temperature profiles for three individual thermocouples in 15 L cell during methane hydrate formation illustrate exothermic nature of hydrate formation while pressure probe records accompanying pressure decline.

make certain that any dissolved oxygen had been removed from the liquid and to ensure that the cell's many fittings were not leaking. With this stage completed, the cell was connected to a high-pressure methane supply (99.9 percent pure methane) and the pressurizing/venting procedure repeated three times. The cell was finally pressurized to 900 psig and then sealed off from the high-pressure methane feed.

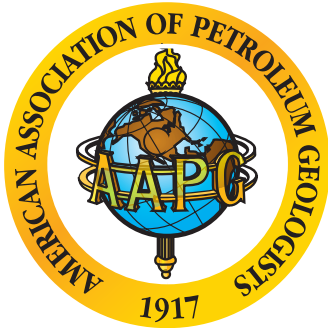
Data collection began with the video recording of activity within the cell as the temperature within the environmental chamber was reduced to 1.5°C over a one-hour period. After approximately 3.75 hours, the camera captured the first signs of methane hydrate formation at the water/gas interface. This activity was accompanied by an increase in the temperature and a decrease in the pressure within the cell. Of note was the fact that the exotherm associated with methane hydrate formation was recorded first by the thermocouple at the water/methane interface (the location where hydrate formation first occurs), followed by a temperature increase in the methane gas space, and finally by an increase in the liquid. Also of note was a rapid decrease in methane pressure associated with the exotherm recorded by the thermocouple positioned in the liquid. The temperature measurements at various points within the system provided a new level of understanding that was not possible with earlier, less sophisticated cells.

Within one hour after hydrate formation began, the inside of the entire view port was covered with hydrate. The cell was maintained at 1.5°C over night, and the next morning the temperature in the environmental chamber was raised to 30°C to dissociate the hydrate. This formation/dissociation procedure was repeated four times with identical results.

Future experiments planned for the 15 L cell include studies of methane hydrate formation under a constant methane head pressure and studies simulating the natural formation of methane hydrates within sediments. Once the cell is fully operational, NETL will invite other hydrate researchers to perform experiments that combine the new cell's capabilities with their own unique hydrate monitoring equipment.

Modeling efforts progress along with physical experiments

In addition to the research conducted with methane hydrate samples prepared in our laboratory, NETL also has a number of computational/modeling efforts underway. We are currently developing theoretical models to describe the kinetics of hydrate formation and dissociation, using equilibrium and non-equilibrium approaches; developing fundamental insights into hydrate growth, dissociation, and stability using a first principles molecular dynamics approach; performing Monte Carlo simulations of hydrate formation/dissociation; and performing Beta-testing for a methane hydrate reservoir simulator based on the TOUGH (Transport of Unsaturated Groundwater and Heat) family of simulators. TOUGH is a general-purpose numerical simulation program for multi-phase fluid and heat flow in porous and fractured media. TOUGH-Fx, a new and improved version, was developed in the Earth Sciences Division of Lawrence Berkeley National Laboratory. Although primarily designed for geothermal reservoir studies and high-level nuclear waste isolation, TOUGH-Fx can be applied to a wider range of problems in heat and moisture transfer, including methane hydrate dissociation.



Announcements

AAPG HEDBERG RESEARCH CONFERENCE ON GAS HYDRATES, SEPTEMBER 12-16

The American Association of Petroleum Geologists (AAPG) is sponsoring a Hedberg Research Conference, with supplemental support from the DOE's National Energy Technology Laboratory, on "*Gas Hydrates: Energy Resource Potential and Associated Geologic Hazards*," to be held in Vancouver, BC, Canada on September 12-16, 2004.

Co-conveners Tim Collett (USGS) and Art Johnson (Hydrate Energy International) have organized this meeting to discuss state-of-the-art concepts, methodologies, case histories, and the future of gas hydrates as an energy resource. The four-day meeting promises to be packed with information. Attendees will hear a total of 45 oral presentations on recent and ongoing research efforts, while another 42 poster presentations will be available over breaks and during evening sessions. The keynote address, "*Important Problems for Methane Hydrate Commercialization*," will be presented Tuesday evening by Marlan Downey, past President of ARCO International, past Bartell Professor of Geosciences at the University of Oklahoma, and current Chief Scientist of the Sarkey's Energy Center at University of Oklahoma.

The presentations are grouped under five topics: *Gas Hydrate Resources Development Research; Resource Potential and Geology of Marine Gas Hydrates; Resource Potential and Geology of Terrestrial Arctic Gas Hydrates; Geologic Controls on the Occurrence of Gas Hydrate; and Gas Hydrate Resource Production Testing and Modeling*. An opening session titled *Challenges of Unconventional Resources* will address methane hydrates alongside several unconventional hydrocarbon resources. Oral presentations will be 30 minutes in length, with topical group discussions by all attendees at the end of each afternoon, and the poster sessions linked to the oral presentations. The afternoon session on the last day will be comprised of a panel discussion focused on the current status of gas hydrate knowledge, R&D needs, and research partnership issues. Results of the conference will be published in a compendium research volume. For information contact Debbi Boonstra, at debbi@aapg.org or via fax at 918-560-2678.

GULF OF MEXICO HYDRATES JIP DRILLING DELAYED UNTIL SPRING 2005

The original plan to drill several methane hydrate test wells at Atwater Valley Block 14 in the Gulf of Mexico (GOM) has been further delayed. An EPA General Discharge Permit required under the Clean Water Act could not be issued in time for the original spring 2003 drilling cruise timeframe. Rules governing the issuance of General Discharge Permits expired in November 2003 and have not yet been renewed, but it was earlier hoped that the EPA process could be completed in August or September 2004. Unfortunately, this will not be possible. Plans now call for the drill ship selected for the cruise, the *Fugro Explorer*, to begin operations in the spring 2005 timeframe.

Announcements

TOUGH-Fx/HYDRATE v1.0 - A NEW SIMULATOR FOR MODELING HYDRATE-BEARING GEOLOGIC SYSTEMS, RELEASED JUNE 2004

At a June 24th and 25th workshop hosted by NETL-Morgantown, the TOUGH-Fx/HYDRATE v1.0 hydrate formation & dissociation model was released for beta-testing to a small group of government, industry, and university hydrate researchers. This newly released code was developed by George Moridis at the Lawrence Berkeley National Laboratory (LBNL), for simulating the behavior of hydrate-bearing geologic systems. TOUGH-Fx/HYDRATE v1.0 is capable of modeling both kinetic and equilibrium hydrate formation and dissociation.

The model accounts for heat and up to four mass components: water, CH₄, hydrate, and water-soluble inhibitors, such as salts or alcohols, as well as four possible phases: gas, liquid, ice, and hydrate. Hydrate dissociation or formation, phase changes, the corresponding thermal affects, and the effects of the inhibitors are also described, allowing the model to examine the range of hydrate dissociation mechanisms.

TOUGH-Fx/HYDRATE is the first member of TOUGH-Fx, successor to the TOUGH2 family of codes developed at LBNL. TOUGH-Fx is fully backward compatible with the TOUGH2 generation of code, was written in standard FORTRAN 95, and can be run on any computational platform for which appropriate compilers are available.

For more information about the new TOUGH-Fx/HYDRATE model, please contact Kelly Rose by email at kelly.rose@netl.doe.gov or by phone at 304-285-4157.

DOE ADVISORY COMMITTEE TO MEET IN SEPTEMBER

The Department of Energy (DOE) Methane Hydrates Advisory Committee meeting is scheduled for September 21-22, 2004, at the Sea Lodge in La Jolla, California near Scripps Institution of Oceanography. James Slutz, the Deputy Assistant Secretary for Oil and Natural Gas, will be hosting the meeting. Mr. Slutz and other DOE representatives will hear the observations and recommendations of the Committee as they continue to plan for the future in hydrate research. The meeting is open to the public.

On Tuesday, September 21, the meeting will begin at 8:00 a.m. and adjourn at 5:00 p.m. and on Wednesday, September 22, the meeting will again begin at 8:00 a.m. and adjourn at 3 p.m., to be followed by an optional tour of Scripps Institution of Oceanography. The meeting is expected to include:

1) presentations on the activities and results of projects supported by the program; 2) presentation and discussion of the National Research Council study of the program; and, 3) discussion of the draft revised strategic plan.

A block of rooms is being held at the Sea Lodge Hotel until August 30. The hotel is located just 12 miles and 15 minutes north of San Diego International Airport/Lindberg Field. Visit www.sealodge.com or call 800-237-5211 for details. If you have any questions about attending the meeting, please contact Edith Allison (202-586-1023 or edith.allison@hq.doe.gov).

Announcements



The Greek 61 m-long R/V 'AEGAEO' used for the May 2003 Anaximander-I cruise, also scheduled for the September 2004 Anaximander-II cruise

ANAXIMANDER PROJECT TARGETS EASTERN MEDITERRANEAN GAS HYDRATES

A research cruise to study gas hydrate accumulations off the coast of southern Turkey in the Eastern Mediterranean Sea will take place this fall. This is the second and final research cruise (September 30 to October 14, 2004) that will be carried out for the Anaximander project, which is funded by the 5th Framework Program of the European Union. It includes participants from eight universities and research institutes from Greece, Germany, The Netherlands and Spain. The AEGAEO, a research vessel operated by Greece's National Center for Marine Research, will carry out the cruise.

The Anaximander project during this cruise will sample methane-containing sediments and associated gas hydrate sites with state-of-the-art instrumentation, and investigate the deep biosphere as it relates to the presence of methane and/or the formation/dissociation of gas hydrates. The Anaximander* Mountains, a subsea feature east of the Rhodes Basin, is the site of the cruise. This site has been sampled by conventional methods in the past, but not with advanced technologies that could provide pristine cores and preserved gas hydrate samples.

The project began with an earlier cruise (May 12 to 24, 2003), which included detailed mapping (including swath bathymetry) of the gas hydrate environment and identification of promising sampling sites. These sites will be sampled and cored during the second cruise, and the researchers will study the formation and distribution of gas hydrates in the pore space under *in situ* conditions; characterize the microbial communities in the sediments; define the tectono-sedimentary framework where the gas hydrate is found; and study methanogenesis and the composition of gas hydrates. The end result will be a comprehensive picture of the methane hydrate environment in the Mediterranean Sea. Additional details related to the cruise can be found at <http://www.igme.gr/anaximander/>.

** Anaximander of Miletus was an early Greek philosopher who worked in the fields of what we now call geography and biology, among others. He was the leader of a philosophical school that included also Anaximenes and Anaxagoras, both from Asia Minor, after which two mud volcanoes in the area were named.*



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Keith sees the future for gas hydrate science as bright. *“The groundwork has been laid and we now need to work out the details, using the information we’ve collected to carefully determine what remains to be done.”*

When not researching hydrates, Keith enjoys his family, including three grandchildren, and pursuing several hobbies. These range from playing the recorder to garden railroading.

Spotlight on Research

DR. KEITH KVENVOLDEN, USGS

“I’m an organic geochemist who just happened to stumble into the field of naturally occurring gas hydrates,” laughs Keith Kvenvolden. But after spending the last 25 years studying them, Keith is certain that *“Methane hydrates may be more important than anyone yet realizes in terms of their impact on near-surface geologic processes and global change.”*

You might say he stumbled into organic geochemistry as well. *“After high school my interest was in biomedicine,”* says Kvenvolden, *“but then I went to Colorado School of Mines, got hooked on earth sciences, and never looked back.”* After graduating with a degree in geophysical engineering, working two years with Mobil Oil Co. in Venezuela, and spending two years in the Army, Keith went to California where he found himself studying the hydrocarbons in San Francisco Bay sediments in the 1950s as a graduate student. After obtaining his Ph.D. in geology from Stanford, he embarked on a career in research, first with Mobil Oil Company in Dallas, then with NASA, and finally with the United States Geological Survey (USGS). At NASA he worked on the organic chemistry of extraterrestrial materials, contamination-free methodologies for dealing with lunar samples, and research on the origin of life.

Arriving at the USGS, Kvenvolden soon became instrumental in developing a program in marine organic geochemistry. *“In 1975 we initiated a program to begin to understand the occurrence of hydrocarbon gas in the shallow marine sediments of continental margins. This included surveys off the western U.S. coast, off southern and western Alaska, and in the South Pacific. We learned that hydrocarbon gases are ubiquitous in shallow marine sediments, and then we began to realize, based on what we learned and what we were reading, that a much larger source of hydrocarbon gases, mainly methane, was to be found in deeper sediments as gas hydrates.”* Keith participated in several deep sea drilling efforts with the specific goal of sampling and studying naturally occurring marine gas hydrates. Based on the results of these surveys, he was able to articulate the enormous importance of gas hydrates, both in terms of their volume and the possible impact on global climate.

“I believe my proudest moment was the publication of a paper in Reviews of Geophysics in 1993,” adds Keith. *“I think this was the first time someone had tied all the pieces together to characterize just what naturally occurring gas hydrates could mean in an earth science context.”* This paper has been highly cited in the gas hydrate literature.

When asked what he has found most rewarding in his hydrate career, Kvenvolden cites *“...being part of a blossoming of scientific interest in a topic—from a point of little knowledge and few investigators, to a point where knowledge is growing exponentially and many investigators are involved.”* He adds that, *“sharing that interest with individuals like George Claypool, Dendy Sloan, Tim Collet, Bill Dillon, and Tom Lorenson is also part of the reward.”*

What is the primary challenge facing gas hydrate research today? *“Turning the speculation into real understanding that results in better detection and better quantification,”* he remarks quickly. *“This will be challenging because of the interdisciplinary nature of gas hydrate research...geologists, geophysicists, geochemists, geomicrobiologists...we all need to work together to achieve a synthesis of the information available, and the results may be surprising to everyone.”*