

Fire in the Ice



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METHANOGENESIS IN HYDRATE-BEARING SEDIMENTS: INTEGRATION OF EXPERIMENTAL AND THEORETICAL APPROACHES

F. S. Colwell (Idaho National Laboratory), W. Ussler (Monterey Bay Aquarium Research Institute), G. Dickens (Rice University)

Estimates of the quantity of gas hydrates and associated free gas in the Earth's subsurface vary considerably. Regardless of the calculation, the values are usually in the gigaton (billion metric ton) range, which translates to a lot of methane! Critically, this immense pool of methane is intimately connected to the rest of the global carbon cycle. Although some methane in sediments is thermogenic, most derives from anaerobic methanogenic microorganisms (i.e., methanogens), as evidenced in part by its extreme ¹³C depletion.

The amount, distribution and behavior of gas hydrates and dissolved gas in sediments throughout time, including the present-day, can best be understood from a dynamic perspective, with methane entering and leaving the sediment system over time. Researchers have begun to explain the presence of gas hydrates using numerical models that recognize this dynamic perspective. However, while "methane outputs" have reasonably good constraints, the indispensable "methane inputs" remain problematic (see Figure 1). Methanogens have been found near and within hydrate-bearing sediments in marine continental margins

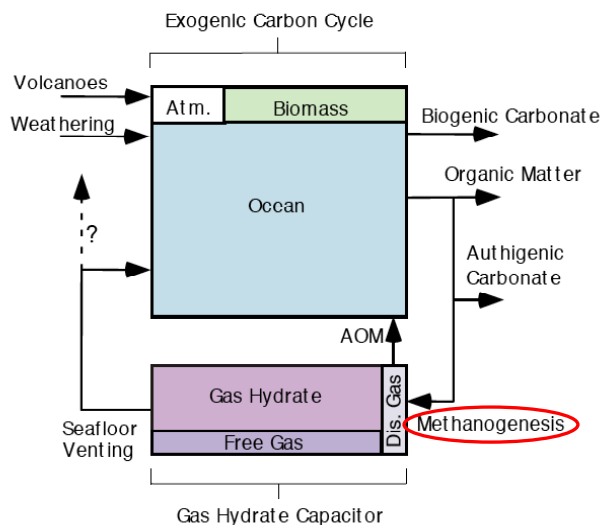


Figure 1. A basic, steady state view of the exogenic global carbon cycle (ocean, atmosphere and biomass) with postulated connections to gas hydrates and free gas (from Dickens, 2003. *Earth Planet. Sci. Lett.* 213:169-183). AOM = anaerobic oxidation of methane. The methane input term denoted by the red circle is the focus of the experiments and thermodynamic modeling in this research.

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This newsletter now reaches nearly 500 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 Karl Lang at 301-670-6390 ext. 129 (klang@tms-hq.com)

as well as in Arctic permafrost regions, although they do not seem to occur in great numbers in either of these environments. Significantly, the biological production rates of methane in the sediments are difficult to obtain and have not been well established. Thus, numerical models may ignore methanogenesis by invoking an external methane source, or assuming a “methanogenic activity term” from the literature.

To obtain and use refined estimates of the methanogenic activity term, our team is combining lab studies and modeling to: 1) experimentally derive a range of methanogenic rates for a starved model methanogen (see Figure 2) that has been subjected to seafloor conditions (temperature, pressure, dissolved methane and formate - a methanogenic growth substrate), 2) produce coupled thermodynamic and kinetic models for methanogenic metabolism that represent expected conditions under which microbes may be active in subsurface sediments, and 3) place these biological methane inputs into straightforward numerical models that describe the systematics of gas hydrate in marine sediments.

For the experimental work we assume that these methanogens, as for microbes in most subsurface environments, are starved, barely sustaining their existence at exceedingly low activities. Such low rates of microbial activity are hard to measure directly on sediment samples with acceptable accuracy. However, by growing the cells in a biomass recycle reactor we can starve these methanogens and then glean the per-cell methane production rate when they are just active enough to stay alive. Using these rates along with molecular determinations of the numbers of methanogens in deep sediments from Hydrate Ridge (see Figure 3) we have obtained a first estimate that most of the sediments in that location may yield no more than 2×10^{-6} nmoles of methane/g sediment/day. This rate of methanogenesis is lower than that described in many previous studies and appears to be low enough that it would not exhaust the buried organic carbon in the sediments upon which the methanogens ultimately depend. Our next experimental step involves restricting the starved methanogens further by imposing upon them the pressure, temperature, and pore water chemistry conditions of their sedimentary habitat. In these studies, we may detect levels of methanogenesis that are lower still.

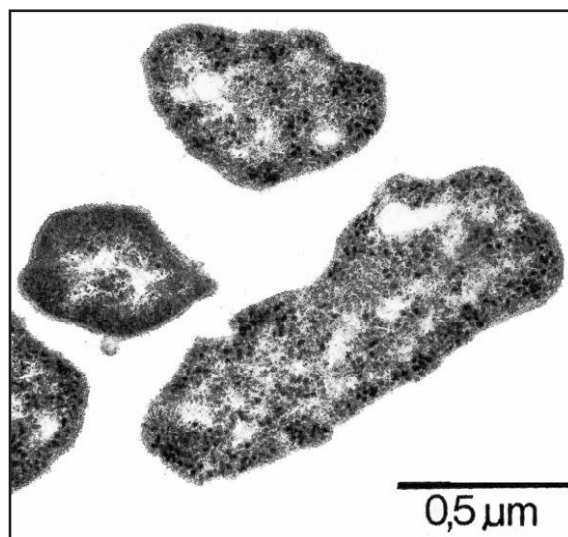
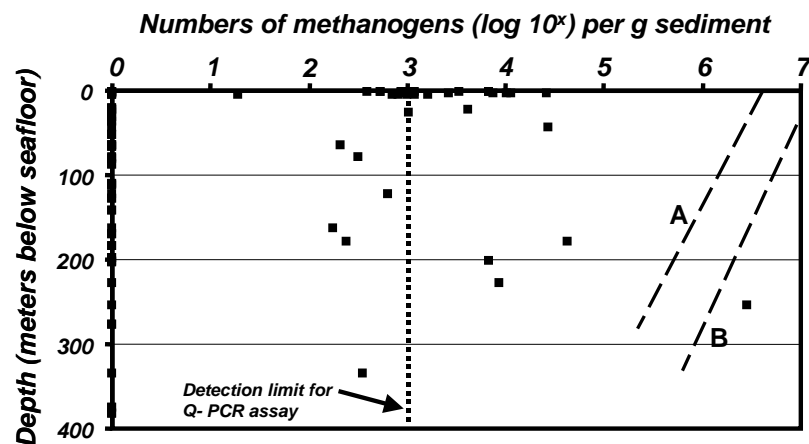


Figure 2. Photomicrograph of *Methanoculleus submarinus*, a methanogen that was isolated from 247 meters below the seafloor in the Nankai Trough (see Mikucki et al. 2003. *Appl. Environ. Microbiol.* 69: 3311-3316). Photo courtesy of H. Aldrich, University of Florida.

- Coincident with the experimental studies, we will produce coupled thermodynamic and kinetic models for methanogenic metabolism in subseafloor sediments. These models will address the biogeochemical reactions associated with microbial methane production and oxidation in deep-sea sediments. The models will be tailored to the specific laboratory conditions in which *M. submarinus* is tested, with attention towards determining the theoretical threshold at which methanogenesis can occur and simulating the effects that pressure, temperature, and substrate availability have on microbial metabolism. Realistic kinetic models for high pressure microbial metabolism will be developed and coupled with the thermodynamic models to produce a better framework for designing and evaluating the laboratory incubations and for application of these results to gas hydrate formation and stability, and carbon cycling in the geologic environment on geologic time-scales.

- We are also beginning to place these experimentally derived and simulated biological methane inputs into numerical models that describe the systematics of gas hydrates in marine sediments systems that have been drilled to date (e.g., Hydrate Ridge, Blake Ridge). For these locations, the downhole pore water chemical profiles allow us to develop basic numerical models for how methane cycles over time, based principally from methane outputs. In each case, however, the assumed methanogenic input term varies significantly. Our plan is to take the results from our previous experimental and modeling tasks and drive numerical models for gas hydrate systems from the methane inputs, establishing if and how the outputs might vary over time.

- This integration of experimental and theoretical science will assist our understanding of gas hydrates by determining more accurate terms for in situ methanogenesis rates and the thermodynamic controls on the process models, and in turn, contribute better values for the system models that describe global carbon cycling. These new data will increase the level of certainty for predictions of the occurrence, distribution, and volume of methane gas hydrate in marine sediments. This higher level of certainty will lead to a better understanding of how hydrates influence global carbon cycling and climate.



- **Figure 3.** Numbers of methanogens in all Hydrate Ridge sediments sampled as a part of ODP Leg 204 plotted versus depth. Methanogens were enumerated by quantitative polymerase chain reaction (Q-PCR) using primers directed at the methyl-CoM-reductase gene in DNA extracted from the sediments. Symbols shown are means of triplicate Q-PCR runs performed on a single DNA extract from sediment samples acquired from ODP Sites 1244, 1245, and 1251. DNA was extracted twice from each sample. The dotted line (at 10³ methanogens per g) represents the limit of detection for the Q-PCR assay below which our estimates of methanogen numbers are uncertain. Dashed lines represent the approximate numbers of total cells in the sediments for Sites 1244 and 1245 (A) and 1251 (B) (from Inagaki et al. 2006. Proc. Nat. Acad. Sci. USA 103: 2815-2820).

GEOMECHANICAL IMPLICATIONS OF THERMAL STRESSES ON HYDRATE-BEARING SEDIMENTS

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The placement of wells, production platforms and pipelines associated with offshore oil and gas production is influenced by the presence of gas hydrate on the sea floor or within the sediment lithology. This is primarily due to concerns about the geomechanical stability of hydrate-bearing sediments (HBS). Warm fluids rising in the wellbore from deeper reservoirs may cause gas hydrate in the neighborhood of a well or pipeline to dissociate, reducing the stability of the supporting sediments and placing significant investments at risk. Such concerns would only increase if the hydrate accumulations are themselves the target of development operations. Locating platforms at sites dictated by the need to avoid hydrates rather than optimize production operations (as is the current practice) increases the cost of production and impedes the commercial development of such deposits.

Currently, there is a lack of understanding of the mechanical and thermal properties of sediments containing gas hydrates, especially in marine deposits. The general perception of instability of hydrate-bearing sediments, coupled with this lack of knowledge, have resulted in a general strategy of avoidance. The main objective of the study described here was to evaluate the response of marine HBS to thermal loading using computer simulations. Such thermal loading occurs when heat from hot reservoir fluids (produced from deeper reservoirs) flows through marine HBS via uninsulated pipes. The results confirm that significant concerns regarding the geomechanical behavior of such a system need to be alleviated if wells are to be installed under such conditions.

Physical Changes Associated with Hydrate Dissociation and Their Effects

Even before dissociation is attained, a rising temperature can be expected to affect the mechanical strength of hydrate-bearing sediments—possibly severely—given the narrow temperature range between hydrate stability and dissociation. When the temperature reaches the hydrate equilibrium temperature, hydrate dissociation occurs by thermal stimulation. This leads to the rapid release of large amounts of gas, which can in turn result in the evolution of high pressures. This higher pressure can result in formation fracturing, with potentially serious consequences if the fracture plane crosses the confining (impermeable) top boundary of an underlying reservoir and allows the escape of reservoir fluids. It is also possible that the increase in pressure could cause damage to a wellbore assembly, including cement failure and wellbore collapse.



Figure 1. Dissociating sample of a marine HBS core. (Deep Sea Drilling Program, Leg 67, courtesy of C.K Paull of the Monterey Bay Research Institute).

Another problem that can potentially result from thermal loading is the deterioration of the structural stability of the sediments in the vicinity of the wellbore; sediments that may be supporting not only the well assembly itself but also pipelines, subsea equipment and platforms. Hydrates are very effective cementing agents, and their dissociation can lead to significant geomechanical changes in the thermally affected region (including substantial subsidence), that can pose a hazard to the structural stability of the wellbore assembly or other equipment. The reason for the concern is demonstrated in the photograph of Figure 1, which shows a dissociating core of a marine HBS. While the more isolated inner portion of the core (where hydrate still remains) appears “solid” and structurally strong, the medium in the outer annular space (where hydrate dissociation is in progress or has already occurred) displays a fluid-like consistency because of the loss of the cementing hydrate and shows evidence of escaping gases (bubbling). Because of its consistency, the remaining watery mud is characterized as “soupy sediment.” The impact of its evolution on the structural stability of marine HBS demands evaluation, especially in the case of compressible sediments such as muds and clays.

In addition to the temperature-driven changes that occur during dissociation, the basal zone of the gas hydrate becomes under-consolidated and possibly over-pressurized because of the newly released gas, leading to a zone of weakness (i.e., low shear strength) where failure could be triggered by gravitational loading or seismic disturbances, resulting in submarine landslides.

The task of our study was to look at the problem using a two-dimensional simulation with realistic representations of the geology and conditions occurring in natural oceanic HBS.

Simulation Design

In the simulation, the geological system of interest was represented as a layered sequence of five formations (A through E), confined at the top and bottom by impermeable (or nearly-impermeable) shale layers (designated as formations U and L, respectively). There was a downward trend of the intrinsic permeability with depth, declining from 10^{-15} m^2 (1 mD) in the shallower formation A to $5 \times 10^{-18} \text{ m}^2$ (0.005 mD) in the deepest formation E. Similarly, the porosity decreased from 0.50 in formation A to 0.40 in formation E. Conversely, the initial hydrate saturation generally increased with depth from 0.15 in formation A to 0.50 in formation E, within the reported range of similar systems. These variations in permeability, porosity and hydrate saturation with depth were consistent with field observations.

In the simulation, heat from the rising hot fluids (at a temperature of $90 \text{ }^\circ\text{C}$) in the inner tubing flows through the well assembly to the hydrate-bearing formations, causing a temperature rise and resulting in hydrate dissociation. The confining formations (top and bottom boundaries) are impermeable, but allow heat exchange with sediments both the above and below the five-layer system. Consequently, the gas released from dissociation cannot escape upward into the ocean, but remains trapped in the system and leads (inevitably) to higher pressures. With a geothermal gradient of $0.0332 \text{ }^\circ\text{C/m}$, the base of the hydrate coincided with the bottom of the hydrate stability zone, at which elevation the initial pressure was 12.4 MPa.

Simulation Results and Observations

The pressure distribution in the reference case (Figure 2) indicates that the region of maximum pressure is observed in the lowermost hydrate-bearing formations where the lowest permeability and porosity, and the highest hydrate saturation, occur. A very important observation is that while the pressure rise is very significant (about 9 MPa, a 70% increase at the bottom of formation E), the high-pressure region is confined to a small volume in the vicinity of the well and does not appear to extend significantly beyond a radius of 25 to 30 m (in a domain with an maximum radius of 1000 m), even after 30 years of continued heating. The high-pressure region is restricted to formations C through E (with pressure increasing with depth), and does not appear to extend to the upper formations A and B. This is due to the relatively high permeabilities and low initial hydrate saturations in formations A and B. It is evident that the majority of significant geomechanical change will occur in the high-pressure region. However, despite its limited extent, it is reasonable to expect that the significant pressure change we observed can have substantial impact in weak marine sediments. Because no information is currently available on the geomechanical behavior of HBS, it is not possible to predict whether these pressure changes are sufficient to effect fracturing of the HBS or of the adjacent shale layers.

The most important observation from review of the hydrate saturation distribution in the reference case is the limited extent of the hydrate dissociation zone (Figure 3). This zone, where dissociation has decreased hydrate saturation to zero, decreases with depth. It extends from a maximum radius of barely more than 15 m (after 30 years of heating) in the uppermost formation A to 10 m in the lowermost formation E, and is very small compared to the 1000 m radius of the simulated domain.

The limited extent of the hydrate dissociation zone is consistent with expectations because the cylindrical configuration of the system results in rapidly increasing volumes (as the radius increases) supplied with heat by a constant-temperature boundary (the inner tubing). Thus, a progressively decreasing fraction of the released heat reaches the dissociation front, the rest being consumed to maintain the temperature of the increasing volume of the hydrate-free (after dissociation) cylindrical zone around the well. Additionally, the heat flux from the constant-temperature boundary continuously decreases because of the increasing formation temperature,

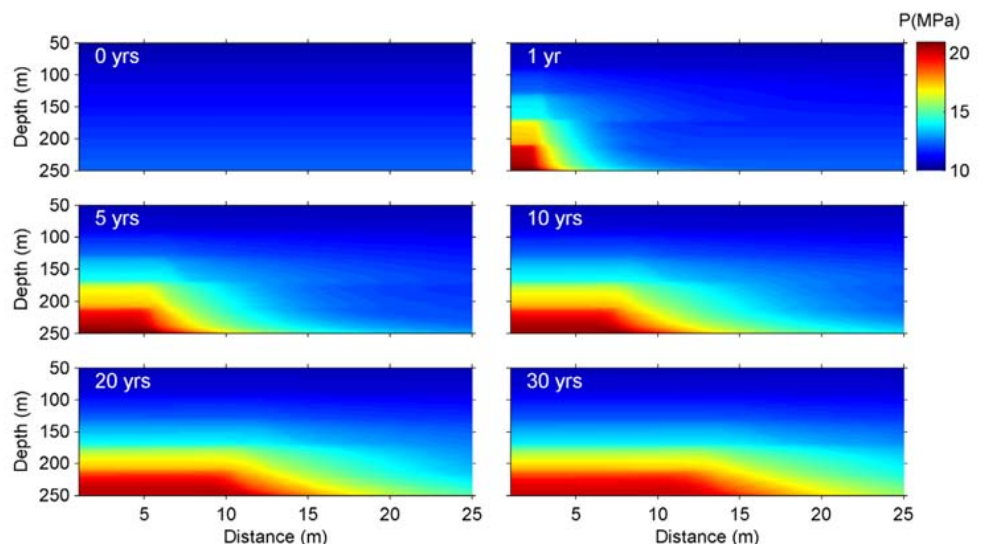


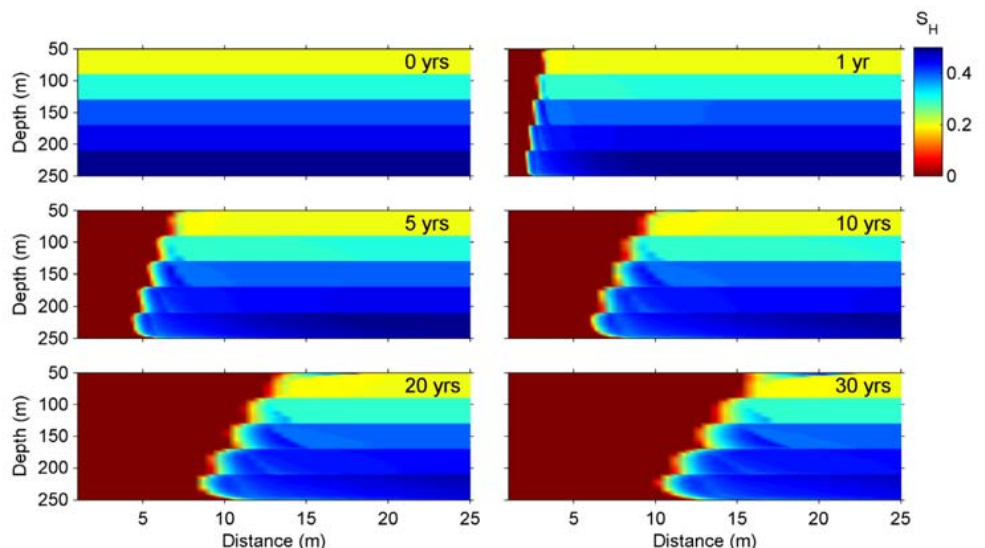
Figure 2. Evolution of spatial distribution of pressure in the HBS of Case A (reference case).

- leading to smaller temperature differentials and weakening the driving force of heat transfer. Note in Figure 3 the creation of a thin zone of “new” hydrate in the uppermost region of layer A, where the released gas accumulates (because of buoyancy) and where the temperature is relatively low. Formation of new hydrates can also be observed ahead of the dissociation fronts in each of the various layers (indicated by the slightly darker color at these locations in layers B and C, for example).

- The “staircase” appearance of hydrate saturation distributions is attributable to the layered pattern of decreasing permeability and increasing hydrate saturation with depth. While the higher hydrate saturation results in a lower composite heat capacity of the HBS (and, thus, in a faster response to heating), the effect is outweighed by the reduction in the relative permeability of fluids. Consequently, the advection of warm fluids (an effective mechanism of heat transfer) moving radially outward from the well is increasingly restricted with depth, while the contribution of the far more inefficient conduction increases. This results in heat transport and hydrate dissociation that increase with the effective permeability of the system, and the staircase pattern. An additional reason for the dissociation zone radius decreasing with depth is the higher pressure that results from the gas release in the lower formations (Figure 2), which acts as an impediment to dissociation. Conversely, the higher permeability and lower hydrate saturations in the upper formations allow gas flow toward the outer radius of the reservoir, prevent pressure build-up, and result in easier dissociation.

Fundamental Knowledge Still Lacking

- This relatively simple simulation serves to highlight the complexity of hydrate behavior in sediments under dynamic temperature and pressure conditions. While the zone of dissociation may be limited, significant concerns regarding the geomechanical behavior of this system need to be alleviated if wells are to be installed under such conditions. The question that begs to be answered is whether the zone of dissociation (at the center of which lies the well) can continue to provide support for the considerable weight of the wellbore assembly if a weak unconsolidated porous sediment becomes “soupy” after dissociation of the hydrate. The issue becomes even more critical if the production system design involves close spacing of multiple wells. Lack of fundamental knowledge precludes any reliable predictions at this time.



• **Figure 3.** Evolution of spatial distribution of the hydrate saturation in the HBS.

HERIOT-WATT UNIVERSITY'S CENTRE FOR GAS HYDRATE RESEARCH REFLECTS GROWING INTEREST IN HYDRATES

Bahman Tohidi, Centre for Gas Hydrate Research, Institute of Petroleum Engineering/Heriot-Watt University, Edinburgh, UK

In 1986, Heriot-Watt University began research into gas hydrates, primarily in response to industry interest in gas hydrate problems in subsea pipelines. Activities were extended to gas hydrates in sediments in 1996 and in 1999 an experimental set-up for pore-scale visual observation of gas hydrate formation and dissociation in porous media was funded. The Centre for Gas Hydrate Research was formally established in 2001, and today a 17-strong (staff and students) hydrate research group is active in a number of research areas including flow assurance and hydrate inhibition design, kinetics of hydrate formation and dissociation, storage and transport of oil and gas using hydrate technology, hydrates in CO₂ capture and storage, and gas hydrates in marine sediments. This article provides a brief overview of the Centre's current activities and capabilities.

Flow Assurance is Major Topic of Study

The Centre's longest running Joint Industry Project (JIP) addresses mainly thermodynamic issues associated with gas hydrates in relation to flow assurance in subsea pipelines. In previous phases of this JIP, gas hydrate phase equilibria for various fluid systems (e.g. single, double and multi-component systems, synthetic and real gases, condensate and oil systems) have been studied, resulting in the generation of a large quantity of data on hydrate dissociation conditions and the amount and composition of various phases under equilibrium conditions. The investigation has also covered the inhibition characteristics of various alcohols and salts.

The JIP has resulted in the development and validation of a new technique for the optimisation of Kihara potential parameters, and an investigation of the characteristics of inhibitors used in drilling and completion fluids. An integrated wax-hydrate model was also developed and used to gain a better understanding of wax equilibria and the effect of wax on gas hydrates and vice versa. The current phase of the project, which began in December 2005, covers a number of topics, including gas hydrates in low water content gases, inhibitor distribution in various fluid phases, hydrate equilibrium measurements for multi-component systems at very high pressure conditions, and a hydrate phase equilibria database.

Evaluation of low-dosage hydrate inhibitors (LDHI) began in 2000 under another joint project, in this case with the University of Warwick. This project resulted in the development of new experimental equipment and test procedures and was followed by a JIP where high pressure glass micromodels were used for investigating gas hydrate formation and inhibition at the micro-scale, with results being up-scaled to high pressure kinetic rig tests. A variety of LDHI formulations were investigated, including assessment of their compatibility with scale and corrosion inhibitors using an array of novel experimental techniques that included ultrasonic methods. A new phase of the project, due to start in May 2006, will address kinetic hydrate inhibitors (KHI) in particular.

A further new project focuses on developing hydrate monitoring and early warning systems. Currently, hydrate inhibitors are injected at the upstream end of pipelines, with dosage based on a number of calculated parameters and “worst case” assumptions. Because there are generally no means of monitoring and controlling inhibitor performance along the pipeline, high safety margins are used to minimise the risk of gas hydrate formation. In spite of these efforts, hydrates can still form, causing considerable economic and safety impacts. This project has been launched with the objectives of (1) developing online methods for more accurately determining safety margins and optimizing inhibitor use, and (2) developing techniques for detecting initial hydrate formation in pipelines and alerting operators prior to hydrate build up and pipeline blockage. The current phase of the project, which began in August 2005, is supported by seven major oil and gas production companies.

Other Topics of Study Span the Spectrum of Hydrate Science

In addition to flow assurance, the Centre is involved in a wide variety of hydrate research. For example, with the petroleum industry developing fields in increasingly deeper waters, there is an increasing need to quantify the hazards to drilling operations posed by gas hydrates, in particular, situations where dissociation of gas hydrates in near-wellbore or load-bearing sediments may lead to instability, wellbore collapse, and loss of well control. The Centre is part of an integrated experimental, modelling and field evaluation joint venture with CSIRO Petroleum Australia, supported by four major E&P companies, that is focused on this topic.

Yet another project involves the investigation of a new concept where hydrates are encouraged to form and the solid hydrates transported as a stabilised slurry (i.e. cold flow). Additives may be used to control the hydrate crystal size and prevent their agglomeration to avoid pipeline blockage. This cold flow approach could potentially reduce the costs of operating pipelines by reducing the need for insulation and inhibitors, while increasing pipeline capacity and reducing operating risks. This two-year project, which began in September 2005, is being supported by the Scottish Enterprise Proof of Concept Programme.

A further three-year project that began in March 2006 will look into one potential role of hydrates related to CO₂ sequestration in offshore environments. Depending on the sediment temperature, CO₂ can form gas hydrate at water depths greater than 200 m. Therefore, any CO₂ escaping from a subsea formation used for CO₂ sequestration could be converted into CO₂ hydrate in seafloor sediments, providing an additional seal and safety factor against CO₂ leakage to ocean/atmosphere. If proved, this phenomenon could provide a criterion for the choice of suitable storage sites.

A second three-year project, started in February 2006, will focus on determining the relationship between pore size, geometry, capillary pressures and gas hydrate growth and dissociation conditions in synthetic and natural porous media, and assessing the extent to which capillary inhibition is a factor in seafloor/permafrost hydrate systems. Specific objectives include clarifying the origins of the observed hysteresis between hydrate growth and dissociation in porous media, investigating the effect of free gas in the pore space on hydrate growth, exploring the effects of wettability (hydrophilic versus hydrophobic pores), quantifying the relationship between confining stresses and capillary inhibition for unconsolidated media, and extending an existing thermodynamic model to the prediction of hydrate growth and dissociation behaviour in porous media based on pore size distribution (PSD) and pore geometry data.

Finally, a three-year project started in April 2004, in collaboration with GZG Abt. Kristallographie University (Göttingen, Germany), Ecole de Mines (Sainte Etienne, France), Moscow State University (Moscow, Russia), and VNII GAZ (Russia), is developing physically realistic models of the formation and decomposition of gas hydrates in natural sediments. This model will be based on experimental laboratory work combined with physico-chemical modelling.

Technical Consulting Group Provides Support Services to Industry

The Centre also provides technical support to major oil and gas production and service companies, and recently formed a spin-off company, HYDRAFACT Ltd, with the four primary objectives of (1) undertaking consultancy studies for the industry, (2) building experimental equipment, (3) providing training in the use of this equipment, and (4) further developing commercial software.

The Centre is equipped to perform tasks that address various technical problems associated with gas hydrates and flow assurance, including:

- Measurement and prediction of the hydrate stability zones for various hydrocarbons with and without formation water and/or organic inhibitors,
- Measurement of the amount and composition of various phases in the presence of gas hydrates,
- Determination of the hydrate stability zone in porous media,
- Assessment of the kinetics of hydrate formation,
- Assessment of the performance of LDHIs,
- Determination of the transportability of fluid systems containing gas hydrates,
- Measurement of wax-hydrate equilibria,
- Development of best practices for pipeline operations involving hydrates,
- Simulation of various gas hydrate formation and production scenarios,
- Characterization of aqueous solutions of organic inhibitors and/or electrolytes.

The Centre also offers training programmes and short courses, including a five-day course intended for petroleum, production, process and drilling engineers that is designed to give an insight into gas hydrates, their properties, their formation in transmission lines, drilling fluids and process facilities, and methods for predicting the hydrate phase boundary in the absence or presence of inhibitors. A further advanced five-day course focuses on the practical aspects of flow assurance and gas hydrates, covering hydrate formation conditions, inhibitor design strategies, the application of hydrate inhibitors, and hydrate blockage removal techniques.

Unique Laboratory Resources Support Research and Consulting Efforts

The experimental equipment in the Centre's two laboratories consists of more than 25 experimental rigs for investigating various aspects of gas hydrates and flow assurance, including:

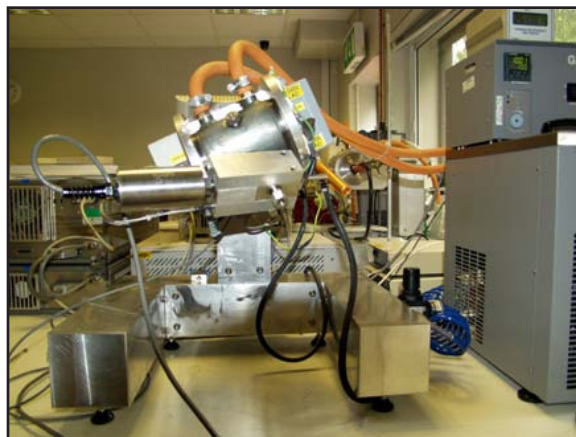
- Eleven autoclave type reactors with stirrers and torque measuring capabilities for measuring hydrate phase equilibria, kinetics of hydrate formation/dissociation, and evaluation of kinetic hydrate inhibitors/anti-agglomerants over a wide range of temperature and pressure conditions (-60 °C to +70 °C, up to 10,000 psia)

- Two rocking cells, with pressure ratings of 10,000 and 30,000 psia, for investigating hydrate phase equilibria and kinetics for various fluid systems (see photo in Figure 1),
- Two glass micromodel set-ups, with pressure ratings of 1200 and 6000 psia, for visual observation of gas hydrate formation, dissociation and distribution at the microscale (used for investigating hydrate formation in porous media and/or the effect of various chemicals on gas hydrate crystal size and morphology) (see photo in Figure 2, showing hydrate formation and distribution in porous media),
- One porous media rig (6000 psia) for investigating the effect of pore size, saturation and wettability on gas hydrate phase boundary and the kinetics of gas hydrate formation in sediments,
- Three ultrasonic rigs (6000 psia) for investigating hydrate formation in various natural and synthetic sediments, each of which has one moving and one stationary piston to simulate various overburden pressures and for assessing the effect of hydrate formation/dissociation on sediments' geomechanical properties (see photo in Figure 3).

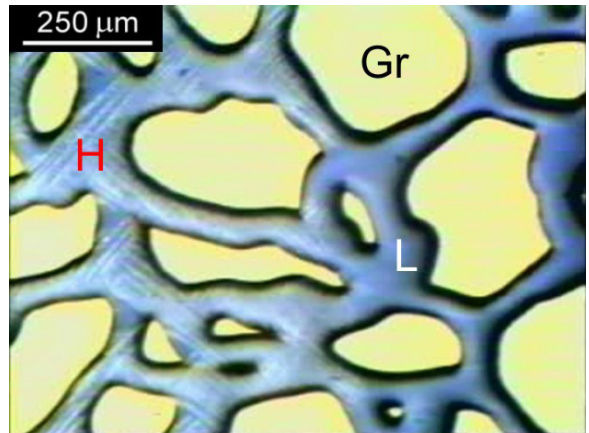
Hydrate Predictive Software

The Centre also authors computer software packages for use in modelling hydrate and wax behaviour. These include the Heriot-Watt Hydrate (HWHYD) and Heriot-Watt Wax (HWWAX) packages. The first is a thermodynamic model capable of predicting hydrate phase behaviour, including phase boundaries and flash calculations. In addition to conventional PVT calculations, the HWHYD model can simulate many operational scenarios, e.g., the presence of methanol, formation water, formation water plus methanol, salt deposition, and the effect of heavy hydrate formers. The second is a thermodynamic wax model for predicting the wax phase boundary and the amount of wax formed at various pressure and temperature conditions for multi-component systems. The wax model has recently been integrated into the HWHYD model and a commercial version will be released shortly.

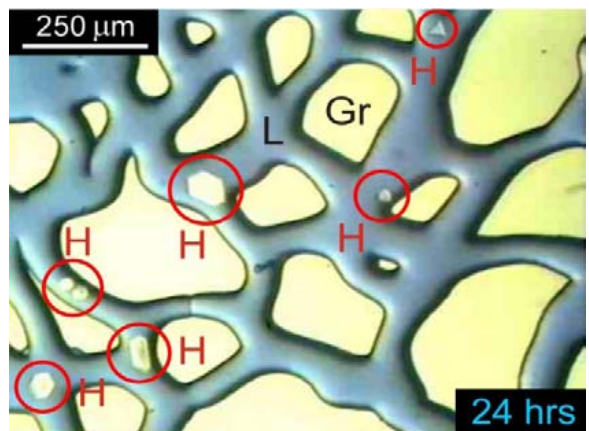
The Centre also has developed various empirical correlations for predicting the hydrate phase boundary and the effect of single and mixed electrolytes/organic inhibitors. Some of the above correlations, as well as a free demo version of HWHYD, are available on the Centre website (www.pet.hw.ac.uk/research/hydrate). For further information contact Professor Bahman Tohidi at B.Tohidi@hw.ac.uk.



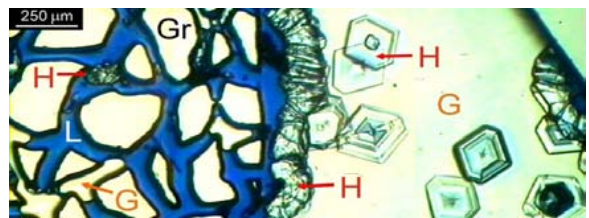
• **Figure 1.** High pressure (30,000 psia) rocking cell



CO₂ hydrate formation from dissolved gas (i.e., no free gas phase) under high degree of subcooling



Hydrates formed from dissolved gas (C₁-CO₂ system)



Methane hydrates formed in the vapour and gas-water interface.

Figure 2. Hydrate formation in glass micromodel simulating porous media. (G=Gas, L=Aqueous Phase, H=Hydrate, and Gr=Grain)

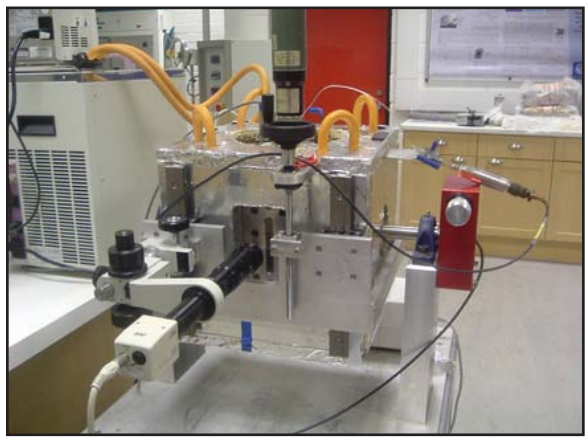


Figure 3. Integrated rig (6000 psia)

• **Announcements**

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• **OPEN MEETING OF THE METHANE HYDRATE
ADVISORY COMMITTEE**

• There will be an open meeting of the Methane Hydrate Federal Advisory
• Committee, April 24 and 25, at the L'Enfant Plaza Hotel in downtown
• Washington DC. The Advisory Committee provides advice to the Secretary
• of Energy and assists in developing recommendations and priorities for the
• Department of Energy's methane hydrate research and development program.
• The meeting will be the first to occur following the reauthorization of the
• Methane Hydrate Research and Development Act of 2000. The revised
• membership of the committee is as follows:

• **Returning members:**

• Art Johnson Hydrate Exploration International
• Bob Woolsey University of Mississippi
• Emrys Jones Chevron
• Miriam Kastner Scripps Institute of Oceanography
• Peter Brewer Monterey Bay Aquarium Research Institute
• Devinder Mahajan Brookhaven National Laboratory
• Richard Charter Environmental Defense

• **New members:**

• E. Dendy Sloan Colorado School of Mines
• Kim Juenger ConocoPhillips
• Jean Whelan Woods Hole Oceanographic Institute
• Nader Dutta WesternGeco/Schlumberger
• Robert Swenson Alaska Department of Natural Resources
• Scott Wilson Ryder Scott
• Steve Masutani University of Hawaii

• For further information, or if you would like to provide information to the
• committee, please contact Edith Allison, U.S. Department of Energy, Office
• of Oil and Natural Gas, Washington, DC 20585. Phone: 202 586 1023.

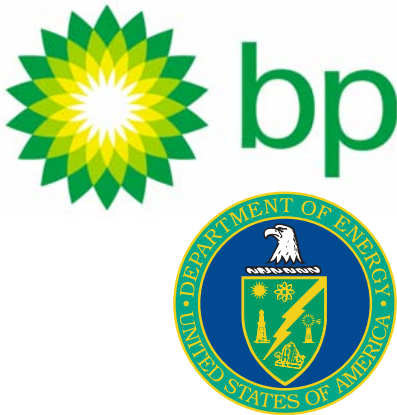
• **Announcements**



• **5TH INTERNATIONAL WORKSHOP ON METHANE HYDRATE R&D SCHEDULED FOR FALL**

• The 5th International Workshop on Methane Hydrate Research and Development will take place at the Marriot Dalmahoy Hotel and Country Club, Edinburgh, Scotland, between the 9th and 12th of October 2006. The objective is to foster collaboration among international scientists engaged in methane hydrate research and the emphasis will be on overcoming the barriers to hydrate research that have been experienced in the past.

• The program will include opportunities for invited national and international program coordinators to introduce their research priorities (to date, the US, India, Korea, Russia and Portugal are represented). These will be backed up by break-out sessions to discuss opportunities for collaboration, with emphasis on global climate change, geohazards and energy. An icebreaker reception on the evening of Monday, October 9th will kick off the workshop, which will run through mid-day Thursday, October 12th. Posters for daily sessions can be submitted through registration. A pre-registration form is available at http://www.noc.soton.ac.uk/CHD/fluidflow/fiery_ice/.



• **BP-DOE COOPERATIVE ALASKA GAS HYDRATE RESEARCH PROJECT UPDATE**

• The cooperative research project between BP Exploration (Alaska), Inc. (BPXA) and the U.S. Department of Energy (DOE) is characterizing and assessing the Alaska North Slope (ANS) methane hydrate resource potential that is located within existing industry infrastructure. Identification of leveraging technical and commercial factors could help determine if gas hydrate could become a future gas resource. ANS gas hydrate has been known primarily as a drilling hazard rather than a resource due to the lack of a market and unknown potential productivity. However, over 33 TCF gas-in-place (GIP) potential gas hydrate resource has been interpreted within shallow sand reservoirs beneath ANS production infrastructure within the Prudhoe Bay, Kuparuk River, and Milne Point production units. Estimates of technically recoverable gas, based on reservoir modeling, range from 0 to 12 TCF of the GIP. Interpretation and modeling of 3D seismic data within the Milne Point unit has identified multiple probable gas hydrate-bearing prospects containing over 600 BCF GIP. Based on this information, BPXA has approved proceeding into an initial data acquisition phase with a stratigraphic test planned in 2006. This stratigraphic test will include drilling to a depth of approximately 4000 feet and acquiring up to 400 feet of core samples, wireline log data, and wireline flow testing to help resolve reservoir permeability and saturations. A drillsite had been selected and fully permitted at an ice pad/road near the Milne Point production facility within the northern portion of the Eileen gas hydrate trend and drilling was to occur in Spring 2006 using the Doyon-Akita Arctic Fox, a newly built small profile drill rig. However, rig delays on prior third-party exploration wells led to the well's deferral. The drilling and data acquisition stratigraphic test program is scheduled to take 20 - 25 days.

• Announcements



Cal Dive DSV Uncle John

• **GULF OF MEXICO HYDRATE JIP/DOE WORKSHOP TO BE HELD THIS MONTH**

• On April 13th and 14th the Chevron/DOE Naturally Occurring Gas Hydrates JIP will host an important workshop to report data findings from the 2005 GOM drilling and to discuss future developments and opportunities. The Workshop is open to JIP members and all others interested in the latest developments regarding the characterization and commercialization of naturally occurring gas hydrates. The objectives of the workshop are to provide a summary of the data collected in 2005, and to also discuss and recommend: geologic settings for additional drilling, development of coring tools used for evaluating hydrates in sediments, improvements for seismic protocols for predicting hydrate occurrence, and improvements for testing protocols and equipment for evaluating hydrates in the field and lab. The venue is the Hilton Houston Westchase, 9999 Westheimer, Houston, Texas. All attendees (and presenters) are asked to pay \$100 to help offset the cost of the workshop. Included are breakfasts, breaks and lunch for both days. To register, log on to http://www.theenergyforum.com/hydrates_2006/main.asp or contact Sara at 281-578-2011 or Sara@TheEnergyForum.com/.

• **PROGRESS ON DEVELOPMENT OF AN INTERNATIONAL GAS HYDRATES DATA SYSTEM**

• CODATA (www.codata.org) is a non-profit, Interdisciplinary Scientific Committee of the International Council for Science [ICSU]. CODATA was established in 1966 by ICSU to promote and encourage, on a world-wide basis, the compilation, evaluation and dissemination of reliable numerical data of importance to science and technology. Presently, Dr. E. Dendy Sloan of the Colorado School of Mines is leading an international committee charged to develop a hydrate database component for CODATA. At a March 2006, meeting in Kauai, Hawaii, the group reviewed progress on the first step towards achieving this goal: development of a Gas Hydrates Markup Language. The official publication of the GHML is expected to occur at special hydrates session at the 20th International CODATA conference in Beijing, China, October 23-25, 2006. Future efforts of the committee will address creation of a database portal linking various national databases, encouragement for development of additional national databases, and creation of various tools to ease data entry and use. The hydrates international Task Group consists of the following:

• Canada – John Ripmeester

• China – Xiao Yun, Wen Hao, and Zhang Hui

• France – Jean-Jacques Royer

• Germany – Ralf Loewner

• India – K. Lal

• Japan – Tsutomu Uchida

• Russia – F. Kuznetsov

• UK – Bahman Tohidi

• USA – Dendy Sloan



• Spotlight on Research



TIMOTHY KNEAFSEY

Scientist
Earth Sciences Division, Lawrence
Berkeley National Laboratory
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LBNL SCIENTIST SCANS HYDRATE TO LEARN THE DYNAMIC PROCESS OF METHANE PRODUCTION

Several years ago, a colleague at Lawrence Livermore National Laboratory showed Tim Kneafsey a methane hydrate sample created by Laura Stern in a U.S. Geological Survey laboratory. Tim was afraid to touch it. But he was intrigued, and following some additional education on the topic by Stern and her colleagues, Tim recognized that few researchers were working on the problem of how to extract natural gas from hydrate in the porous media where it is found. Prior to coming to LBNL in 1996, Kneafsey worked as an environmental engineer performing hazardous waste site cleanup, so the study of multiphase flow and transport through porous and fractured media had always been an interest. Working on the question of how these issues will ultimately determine the potential of gas hydrate as an energy source seemed to be a natural combination of interest and past experience.

Tim currently works as a member of the LBNL team that is focused on improving our ability to numerically simulate the process of natural gas production from hydrates. “Our most significant contributions are related to applying imaging techniques to observe the spatial occurrence of hydrate-related processes and interpreting the processes we see,” says Kneafsey. “For example, we used x-ray computed tomography scanning ...CT scans ... to look at hydrate formation and dissociation in sand and learned that hydrate formation and dissociation strongly influence the water saturation.”

The aspect of his work that he finds most rewarding is the opportunity to work with the world-class researchers at LBNL (and elsewhere) on hydrate related problems. “These colleagues have supported my approaches to the study of a variety of processes and continue to teach me about hydrates every day,” says Tim. As might be expected for someone with a degree in Civil and Environmental Engineering, he particularly enjoys designing ways to test hypotheses related to hydrates, watching the changes that occur during CT experiments, and trying to explain these changes to himself and others.

Tim believes that exploitation of methane hydrates is likely to occur within the next decade or so if information gaps can be filled and an effective infrastructure built. “Research will continue to be needed during development of technologies to produce hydrate-derived gas in both arctic and marine environments,” he adds. “Significant remaining problems include how changes in the amount of hydrate during production affect both the mobility of the gas and water in the sediment and the mechanical strength of the sediment. These issues directly affect not only the potential production rate but also the stability of the wells and surface production equipment.”

When not studying hydrates Tim likes to investigate similar topics related to multiphase heat and mass transfer in porous and fractured media, for example, those pertaining to geothermal energy, heavy oil, coal bed methane, carbon sequestration, and nuclear waste disposal. More importantly, outside of work he is an active family member in an active family. Tim also aspires to be a guitarist “when he grows up.” One can imagine him in a band with a more organic sound ... no heavy metals ... perhaps Tim K. and the Klathrates?