# HYDRATE FORMATION AND DISSOCIATION IN FIELD SAMPLES

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## INTRODUCTION

The goal of this two-year research project is to characterize the thermodynamics and kinetics of natural gas hydrate formation and dissociation and biogeochemically characterize MH containing sediments. Characterization of samples from ODP Leg 204 and associated hydrated stability of drilling additives is the primary focus with minor efforts on analysis of coring from Mallik. Experiments are being conducted in the ORNL Seafloor Process Simulator at the ORNL hydrate research facility. Microbiological enrichments and time course characterizations are being conducted with properties correlated with hydrate thermodynamic and kinetic properties.

## GOALS AND EXPERIMENTAL APPROACH

The goal of this project is to characterize the thermodynamics and kinetics of natural gas hydrate formation and dissociation and to biogeochemically characterize MH containing sediments. The approach will be to utilize the extraordinary potentials of the ORNL 70 liter SPS hydrate facility as well as smaller vessels to examine microbial, mineralogical, chemical and physical characteristics of host sediments. These characteristics will be correlated with hydrate thermodynamic and kinetic properties. Aspects of this work will be to characterize the ODP-Leg-204 cores as well as to develop an understanding of hydrate formation and stability in the sediments and a more applied aspect of this project is to examine hydrate nucleation and inhibition agents that are an ongoing concern to the safety of hydrate exploration. In that vein most of the second year effort in late FY 2003–2004 will examine hydrate formation and stability in sediment/drilling fluid/adjuvant mixtures to assess the ability of drilling fluid additives to enhance or inhibit hydrate nucleation in sedimentary environments.

## TECHNICAL PROGRESS

**Results from Mallik cores.** Biological methane production from Mallik cores could not be detected even after more than three months of incubation under ambient conditions, enriched with acetate, hydrogen and or methanol. Despite analysis of more than 100 tubes, each containing 3–5 g of sediment from a time course study revealed considerable production of carbon dioxide from radiolabeled 14C-2-acetate but no radioactive methane (sensitivity of 200 dpm from 10,000,000 dpm of added 14CO2 or 14-acetate). Similarly, no increase in the methane concentrations within the headspace of test tubes were

detected (sensitivity of ~0.1%) during the >3 month time course experiment. Results corroborated those of R. Colwell (INEEL) and other investigators.

**Analysis of cores from ODP.** Successful core recovery, storing, shipping and handling procedures were developed and used for ODP Leg 204. Our on shore laboratories received at least 5 shipments of cored materials from the cruise, with most being received within days of recovery. Types of samples included ~20 small (<100 g) of samples frozen under liquid nitrogen that are currently stored at –80C, several kg of samples frozen samples stored at –20C, and several kg of fresh sediments used for time course activity and microbial enrichment experiments and some of which is stored at 4C. The first set of test samples were delayed a day in delivery and ship-board researchers quickly fixed the hurdles and subsequent shipments arrived in good time and in good quality. The Leg and the science were a huge success and we have had a very good response from DOE involvement in the cruise. Experiments are currently in progress. This constituted the successful accomplishment of the fall 2002 milestone.

Biological methane production from ODP Leg 202 cores past their final incubation point after more than three months with one set of incubations under ambient conditions, and two at near in situ temperatures of 4C. Some are enriched with acetate, hydrogen and or methanol. These tubes may be in stark contrast to those from Mallik where results revealed considerable production of carbon dioxide from radiolabeled 14C-2-acetate but no radioactive methane (sensitivity of 200 dpm from 10,000,000 dpm of added 14CO2 or 14-acetate). Similarly, no increase in the methane concentrations within the headspace of test tubes were detected (sensitivity of ~0.1%) during the >3 month time course experiment of the Mallik samples but considerable methane and radioactive methane are anticipated form the ODP cores. Results are being corroborated those of R. Colwell and M. Delwiche (INEEL) and other investigators. Now that Dr. Zatsepina is oriented to the ORNL laboratory system analyses of the samples will proceed promptly.

**SPS hydrate formation results.** A new procedure/method for enhancing the nucleation of hydrates that was recently discovered as part of this work was mentioned in the last quarterly report. After lengthy discussions with our intellectual property experts we determined that while the technology was indeed patentable in the classic sense of claims and exclusionary rights, it was impossible to detect its unauthorized utilization in its most sensitive mode. In other words, a simple ice machine could suffice for the enablement of the technology and no clear indication of its unauthorized use would be indicated. Instead of the patent disclosure we are advised and concur that we will share the technology with sponsors and through publications.

Nevertheless the discovery of cool water formerly present as ice, even if the cool waters are days removed from the frozen state leads to a 10–20-fold improvement in the amount of overpressure required for nucleation, from ~600 psi to ~30 psi. The new procedure was not expected from a review of the literature and the results were startling. In the range of 3–6C nucleation pressures greater than 1200 psi

are customary for nucleation to occur in the SPS. Similar to smaller vessels as noted in the literature there a significant memory effect is noted upon repeated formation of hydrates. If hydrates are dissociated and then reformed within hours a memory effect is observed and nucleation often occurs at far less overpressure. For example, in fresh water nucleation overpressures of ~600 psi are typical whereas if hydrates are formed again using the same water (even if there is a 24 hr lag time) the overpressure required to form hydrates is typically 200–300 psi. This memory effect represents a substantial energy savings from initial hydrate formation equilibria. Consequently any nucleation enhancer should lower the required overpressure far more than any observed memory effect. Our new process resulted in required overpressures of only 22 and 33 psi in two separate attempts with fresh water. This is nearly an order of magnitude better than nucleation enhancement of the well known memory effect. This phenomenal successful nucleation enhancement procedure may be more scalable and less expensive though at least as effective as our procedure documented previously that relied on chemical additives enhancing ice nucleation.

## EFFECTS OF THAWED WATER, AGITATION, AND BUBBLES ON HYDRATE FORMATION

The formation of hydrates of gasses is an attractive process to several industries such as natural gas storage and transportation, as well as in separation technologies. The hydrated form of methane concentrates the gas approximately 160 times the concentration of gas phase methane per unit volume. An ability to concentrate fuels, therefore, makes an economic way to form hydrates an area of active research. Additionally, when water is taken up into the hydrate structure, dissolved ions are excluded, so hydrate formation is considered a possible desalinization technique. It has been published that the use of previously frozen water in experiments significantly lowers the hydrate nucleation overpressure (i.e., the amount of pressure above beyond the 3-phase equilibrium point necessary to form hydrate) (Vysniauskas et al., 1983; Takeya et al., 2000). In those experiments, however, the entire volume of water used in the experimental reactor was frozen and thawed. This method would be uneconomical for an industrial scale hydrate reactor. We have demonstrated experimentally that even if a relatively small amount of the reactor water was previously frozen, and if left in a cool thawed state for many hours, the overpressure required for hydrate formation is significantly lowered in the large volume SPS (Table 1). Additionally, our results demonstrated that the thawed water could be stored at room temperature (~25C) for 48 hours and the effect is preserved.

Nucleation experiments were performed by pressurizing the SPS reactor with the hydrate forming gas (in this case, methane), to a pressure below the hydrate equilibrium pressure and cooling the reactor to ~4–6C for several hours to saturate the water with gas. Gas is then injected into the water through a

**Table 1. Methane Hydrate Nucleation Experiments With and Without the Use of Thawed Water**

| Description of experiment | Nucleation pressure (psi) | Nucleation temperature (°C) | Equilibrium pressure (psi) | Nucleation overpressure (psi) |
|---|---|---|---|---|
| 1st nucleation no thawed water | 1338 | 5.9 | 674 | 663 |
| 1st nucleation no thawed water | 1195 | 4.5 | 584 | 610 |
| 2nd nucleation, no thawed water | 951 | 5.3 | 631 | 320 |
| 2nd nucleation, no thawed water | 740 | 3.9 | 552 | 188 |
| 1st nucleation, all thawed water | 630 | 4.7 | 597 | 33 |
| 1st nucleation, 20% thawed water | 557 | 4.0 | 555 | 22 |

diffuser and the gas bubbles rise through the water and terminate at the gas/water interface. The pressure relief valve on the vessel is closed during injection, so the vessel pressure increases at a rate of ~8 psi/min. Hydrate formation is detected visually by the presence of opaque hydrate-covered gas bubbles collecting and persisting at the gas-water interface. The pressure at which this occurs is called the nucleation pressure. For the experiments involving thawed water, the water was allowed to warm up to room temperature (~25C) after thawing for approximately 48 hours. In one experiment, all of the water in the vessel (~60 L) was frozen and thawed. In the other, approximately 20% of the water added to the vessel was previously frozen. In all of the 1st nucleation experiments, all of the water in the vessel was drained out to prevent any hydrate "memory effect." This memory effect is apparent by comparing the reduction in overpressure in the 2nd nucleation experiments (experiments where the water was not changed between hydrate nucleation experiments) with the 1st nucleation experiments.

Using the commercially available hydrate equilibrium program CSMHYD (Sloan, 1998), the equilibrium pressure can be calculated for the experimental temperature. The difference between the actual nucleation pressure and the equilibrium pressure is called the overpressure (Table 1). Several additives have been tested which also have been found to lower the hydrate nucleation overpressure, but none were found to be as effective as the use of thawed water. Example from our laboratory include the use of SNOMAX, a bacterially derived protein use commercially as a snow nucleator, as a possible hydrate nucleation promoter. It was found to lower the nucleation overpressure to an average of 182 ± 21 psi at concentrations of 20–30 mg/L. These results are similar to those found by Morgan et al. (1997). Bentonite, a clay mineral which is a common component of drilling muds was found to lower the overpressure to an average of 96 ± 11 psi at a concentration of 200 mg/L. While these additives do significantly lower the nucleation overpressure as compared to bulk water, neither are as effective or as economical as the use of recently thawed water.

Experiments are currently being conducted in a small pressure vessel (450-ml volume) to determine whether there is a volume dependent effect of the thawed water on nucleation (Fig. 1). Experiments are also being conducted on the effect of agitation and bubble formation on hydrate formation. Preliminary

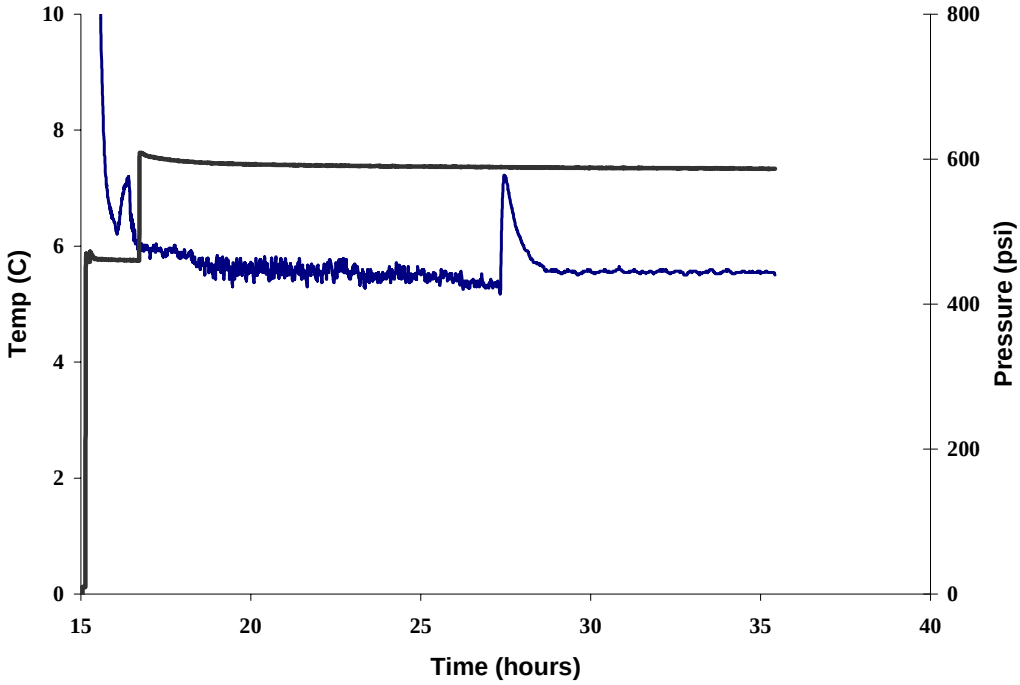


**Fig. 1. Hydrate formation in the 450 ml vessel using distilled water (without thawed water, agitation, or bubble formation).** Hydrate formation was detected approximately 10 hours after the vessel was pressurized to about 200 psi overpressure. Hydrate formation is detected by a spike in the vessel temperature, which is due to the exothermic nature of hydrate formation. Experiments are being conducted on the effects of thawed water, water agitation, as bubble formation on the onset of hydrate formation.

results have shown that the rapid agitation of the vessel fluid (via a spinning propeller at about 400 rpm) may decrease the induction time for hydrate formation and increase the amount of hydrate formed. Experiments have also been conducted in which the vessel was rapidly depressurized a small amount (but still within the hydrate 3-phase equilibrium pressure and temperature) after some hydrate had formed in the water phase. The depressurization causes the formation of small bubbles as gas is releases from solution. Hydrates rapidly form on the interfacial surface of the bubbles and the vessel was rapidly filled entirely with hydrate.

There are several potential uses for simple, inexpensive methods for the formation of hydrates. For example, when drilling through gas-rich sediments during oil and gas exploration, thawed water could be used to form hydrate and sequester the potentially explosive gasses that are transported to the surface through the drill hole. Another example is in the use of hydrate formation as a desalinization or dissolved chemical concentration method (dissolved species will become concentrated in the aqueous phase that has not been incorporated into the hydrate structure). The simple addition of thawed water would be cheaper and cleaner than the use of any additives to promote hydrate formation.

## IMPLICATIONS

Implications of this research are directly related to hydrate occurrence and mechanism of accumulation; hydrate stability and uses in third party technologies; and maintaining hydrate stability during sub seafloor hydrocarbon exploration.

The lack of methanogenesis in Mallik cores is another line of evidence that hydrate accumulation in sediments may well be the result of transport, even if of biological origin. Biogenic methane will transport in subsurface environments such that hydrate accumulation may be spatially separated several km from the initial methane source and temporally separated by millions of years from the time the methane was produced. Accordingly the spatially and temporally separated methane production need have been subjected to the ~1/3 energetic penalty imposed by producing methane against a >100 partial pressure methane gradient nor would the methanogens need to have proliferated to a massive extent in low permeability silts formations. ODP cores are being examined to see if the hypothesis follows in these similarly silt environments poorly-hospitable for massive methanogenesis. Testing these hypotheses are important for methane hydrate exploration, explaining their occurrence and understanding their significance in U.S. energy derivation.

Another major implication of this work is the formation of hydrates as an attractive process to several industries such as natural gas storage and transportation, as well as in separation technologies. When water is taken up into the hydrate structure, dissolved ions are excluded, so hydrate formation is considered a possible desalinization technique, as exemplified in the seven patents of Michael Max). Interestingly, use of previously frozen water in experiments significantly lowers the hydrate nucleation overpressure (i.e., the amount of pressure above beyond the 3-phase equilibrium point necessary to form hydrate) (Vysniauskas et al., 1983; Takeya et al., 2000). In those experiments, however, the entire volume of water used in the experimental reactor was frozen and thawed and would be uneconomical for an industrial scale hydrate reactor. We have demonstrated experimentally that even if a relatively small amount of the reactor water was previously frozen, and if left in a cool thawed state for many hours, the overpressure required for hydrate formation is significantly lowered in the large volume SPS (Table 1). Additionally, our results demonstrated that the thawed water could be stored at room temperature (~25C) for 48 hours and the effect is preserved. This newly found process for routinely forming massive hydrates at low overpressures is spawning a new interest in using hydrates in separations chemistry and we are drafting another patent disclosure for improved CO2 separations using hydrates. Processes considered too energy intensive have now seen a 50% reduction in energy requirements making their reevaluation timely.

The major implication of this work will likely be in hydrate stability during hydrocarbon exploration in hydrate stability regions. We are collaborating with the JIP, ODP, NETL, and others to evaluate

hydrate nucleation and inhibition additives in the 70 liter SPS. Using the techniques described above we are uniquely suited for these large volume tests examining the ability of additives to enhance, forestall or inhibit nucleation processes. We will also examine characteristics of any formed hydrates and controls on their size, be they dispersed slurries or massive solids posing safety and pipeline clogging hazards.

## FUTURE RESARCH

Biogeochemical and microbiological characterization of the ODP-LEG 204 samples is progressing well with future experiments to be directed at hydrate formation and stability.

ODP cores studies examining thermodynamic and hydrate kinetic experiments are being in progress. Sufficient materials or high quality are preserved for the planned experiments and other core materials are available from ODP.

Experiments are also in progress for the enhanced hydrate nucleation and inhibition materials. During the spring and summer 2002 DOE-GH workshops interest was expressed in the enhanced nucleation and in the inhibition of hydrates, particularly low cost additives for drilling fluids. Experiments are in progress with additives to bentonite drilling fluids and see if they enhance/inhibit hydrate formation. Based on our knowledge of hydrate nucleation we have reason to suspect that our additives may perform better and at lower or comparable costs to lecithin additives currently used in the drilling industry. Fluids and adjuvants were received by Phelps and experiments are planned for late FY 2003–2004 on the formation and inhibition/enhancement characteristics of drilling fluid components and determine if our procedures or simple adjuvants may better serve the drilling community. Experiments to date are already leading to at least one paper on enhanced hydrate nucleation materials, and papers on hydrate inhibition are to follow from planned experiments. These experiments are planned on hydrate inhibition/enhancement studies of drilling fluids and their additives from the in progress artic drilling campaign

## PUBLICATIONS/PRESENTATIONS

Phelps was an invited participant in the International Pressure Coring Workshop sponsored by the ODP. The conference was in College Station, TX, February 5–7, 2003 and the topic of the presentation was on the SPS being an integral link to the accessing and R&D on cores recovered at temperature and pressure, exuded at temp and pressure and then examined in the native temperature and pressure regime. Work is underway between agencies to foster collaborations in pressure and temperature experiments.

The Marine Geology paper entitled, “Sediment Surface Effects on Methane Hydrate Formation and Dissociation,” authored by David Riestenberg, Olivia West, Sangyong Lee, Scott McCallum, and Tommy J. Phelps is officially in Press and galley proofs were returned to the editor in March 2003.

Publication is planned for a special Issue entitled, “Geosphere-Bioshpere,” hopefully in the April–May issue of Marine Geology.

A second paper on hydrate nucleation at low overpressures is currently being drafted.

Though the patent disclosure on improved procedures of hydrate formation has been stopped due to an inability to verify the use of a water cooling device (patent would not enforceable) we are instead refocusing DOE intellectual property efforts on enhanced chemical separations by hydrates, gaining advantage of the low overpressures required for hydrate formation.