#### **Supplementary Paper 4**

## Methane Hydrates and the Future of Natural Gas

Carolyn Ruppel (cruppel@usgs.gov) Gas Hydrates Project U.S. Geological Survey, Woods Hole, MA

#### Introduction

For decades, gas hydrates have been discussed as a potential resource, particularly for countries with limited access to conventional hydrocarbons or a strategic interest in establishing alternative, unconventional gas reserves. Methane has never been produced from gas hydrates at a commercial scale and, barring major changes in the economics of natural gas supply and demand, commercial production at a large scale is considered unlikely to commence within the next 15 years. Given the overall uncertainty still associated with gas hydrates as a potential resource, they have not been included in the EPPA model in MITEI's *Future of Natural Gas* report. Still, gas hydrates remain a potentially large methane resource and must necessarily be included in any consideration of the natural gas supply beyond two decades from now.

Despite the relative immaturity of gas hydrates R&D compared to that for other unconventional gas resources, the accomplishments of the past decade, summarized in detail by Collett et al. (2009), have advanced gas hydrates along the path towards eventual commercial production. The U.S. Department of Energy (DOE), as directed by the Methane Hydrates R&D Act of 2000 and the subsequent Energy Act of 2005, has partnered with other government agencies, academe, and industry in field, modeling, and laboratory programs that have produced numerous successes (Doyle et al., 2004; Paull et al., 2010). These accomplishments have included the refinement of methods for pre-drill estimation of hydrate saturations and safe completion of logging and coring programs in gas hydrate-bearing sediments in both deepwater marine and permafrost environments. Within the next 4 years, US federal-industry partnerships are scheduled to oversee advanced logging and direct sampling of resource-grade (high saturation) gas hydrates in sand deposits in the deepwater Gulf of Mexico and completion of a long-term test of production methods on the Alaskan North Slope. In Japan, the government-supported methane hydrates program (now called MH21; Tsuji et al., 2009) has also relied on cooperation among the private, public, and academic sectors over past decade and plans to conduct an initial production testing of resource-grade gas hydrates in the deepwater Nankai Trough in 2012. The current MH21 effort has grown out of earlier advanced borehole logging and deep coring in 1999-2000 (MITI) and in 2004 (METI), as described by Tsuji et al. (2004, 2009) and Fujii et al. (2009). Canada has also worked with a consortium of partners to complete three major drilling programs in the permafrost of the Mackenzie Delta (e.g., Dallimore et al., 1999; Dallimore and Collett, 2005; Dallimore et al., 2008). Canada was the first country to ever produce small volumes of gas from hydrates during short duration (up to a few days) production tests at these wells. Since 2005, India (e.g., Collett et al., 2008; M. Lee and Collett, 2009; Yun et al., 2010), Korea (Park et al., 2008; Ryu et al., 2009), China (Zhang et al., 2007; Wu et al., 2008), and private sector interests operating offshore Malaysia (Hadley et al., 2008) have also launched major, successful

deepwater hydrate drilling expeditions, and Korea drilled the Ulleung Basin again in the second half of 2010 (S.R. Lee et al., 2011).

As befits costly exploration projects with uncertain short-term payoffs, the global effort to investigate the potential of gas hydrates as a resource has often been carried out with significant cooperation among countries, substantial support from governments, and major leadership from both the government and academic research sectors. Even after more research, key challenges are likely to remain in locating gas hydrates, assessing the size of the resource, developing viable production strategies, and understanding the economics of eventual gas production from gas hydrates within the context of natural gas supply as a whole.

#### Background

Sometimes dubbed "methane ice", methane hydrate is a naturally-occurring frozen compound formed when water and methane combine at moderate pressure and relatively low temperature conditions. Methane hydrates represent a highly concentrated form of methane, with a cubic meter of idealized methane hydrate containing 0.8 m<sup>3</sup> of water and more than 160 m<sup>3</sup> of methane at standard temperature-pressure conditions. Ethane, propane, and carbon dioxide, and similar gases can also form gas hydrates, and individual molecules of these gases are often incorporated into gas hydrates that contain predominantly methane. Both on a global volumetric basis and in terms of areal distribution, methane hydrates are the most important type of natural gas hydrate.



Figure 1. The stability of an idealized methane hydrate in nature (area to the left of the red phase boundary) in nominal marine (A) and permafrost (B) cases, modified from *Ruppel* (2007). These diagrams show only where gas hydrate is stable in ocean water and/or sediments, not where it actually occurs in nature. A. For the marine case at an arbitrary water depth of 1200 m, gas hydrate is in theory stable in the lower part of the water column (where the ocean water temperature curve dips below the stability curve) and in the uppermost ~200 m of the seafloor sediments (where the blue geotherm overlaps the yellow stability zone). The possible configuration of gas hydrate-

bearing sediments over free gas is shown in the column at the right. Depending on the sediment geotherm and the ocean temperature structure, the gas hydrate stability zone thins to vanishing at ~300 to 500 m water depth on the continental margins and can thicken to include more than 1000 meters of seafloor sediments at great water depths. B. For a nominal permafrost thermal gradient (geotherm), gas hydrate is theoretically stable starting within the bottom part of permafrost-bound sediments and extending to several hundred meters below the base of permafrost, as indicated by the depths over which the geotherm (blue) is cooler than the temperature of the phase transition (red).

In contrast to conventional natural gas, methane hydrates occur only in sediments characterized by well-known pressure and temperature conditions, meaning that exploration activities can be strictly limited to specific zones. The pressure-temperature conditions consistent with methane hydrate stability are widespread on Earth. At pressure-temperature conditions outside the stability zone, methane is no longer bound in "methane ice" and exists only as free gas or gas dissolved in pore waters.

An estimated 99% of worldwide gas hydrate occurs in ocean sediments, and the appropriate temperature and pressure conditions predominate within the upper tens to hundreds of meters of seafloor sediments at water depths ranging from 300 to 500 m on the shallow end to greater than 4000 m. In theory, methane hydrates are also stable on the seafloor and in the water column in large swaths of the world's oceans. Gas hydrates do not persist long in the water column, and seafloor gas hydrates are not significant as a resource. Neither type of gas hydrate will be discussed in detail here.

Onshore, methane hydrates occur almost exclusively in areas with thick permafrost. The appropriate temperature and pressure conditions can occur over a zone that is typically several hundreds of meters thick and that encompasses the bottom part of the permafrost-bearing section and the top of the subpermafrost sedimentary section.



Figure 2. Global map of recovered and inferred gas hydrates, modified from Collett et al. (2009). The color coding refers to drilling programs highlighted in the gas hydrates research timeline shown in Figure 5. This map includes gas hydrates recovered from both shallow depths, which are generally not considered relevant for resource studies, and greater depths. For full discussion see Ruppel et al. (2011).

Despite the widespread occurrence of gas hydrate, the deposits are not ubiquitous within the gas hydrate stability zone. The key factor limiting gas hydrate formation in most locations is the lack of sufficient gas. A lack of free water in sediments can also limit gas hydrate formation, but this situation occurs almost exclusively in specific geologic settings (very low permeability formations) or possibly near the base of the stability zone.

The amount of methane trapped in gas hydrates remains uncertain. In pre-1990 studies, estimates of the amount of methane trapped in global gas hydrate deposits varied by many orders of magnitude from  $\sim 10^{17}$  ft<sup>3</sup> or  $10^5$  trillion cubic feet (TCF; McIver, 1981) to  $10^8$  TCF (Trofimuk, 1973). During the same period, Kvenvolden (1988), Gornitz and Fung (1994), and Harvey and Huang (1995) produced oft-cited and independently-determined intermediate values. Even with the substantial increase in data about gas hydrate occurrences since the mid-1990s and more

sophisticated numerical modeling, estimates of the total volume of gas sequestered in gas hydrates have continued to vary, ranging from 1.4 to  $1.7 \times 10^5$  TCF (Milkov, 2004; Buffett and Archer, 2004) to  $4.2 \times 10^6$  TCF (Klauda and Sandler, 2003) with some intermediate estimates ( $1.4 \times 10^6$  TCF; Wood and Jung, 2008) over the past decade. In the most recent review of this subject, Boswell and Collett (2011) concluded that an estimate of  $10^5$  TCF of methane trapped in gas hydrates (gas-in-place or GIP) is a reasonable figure, but they strongly emphasize that the GIP number is not meaningful for resource-based studies.

Most of the methane included in the GIP estimate is probably trapped in gas hydrates that are present in low saturations (<10% of pore space) in fine-grained, low permeability marine sediments. Such disseminated, low-saturation gas hydrate is nearly impossible to detect without drilling and is unlikely to ever produce commercial quantities of gas. From an energy perspective, a more important figure is the amount of methane trapped in resource-grade deposits, estimated at  $10^4$  TCF in marine settings and several hundred TCF in permafrost-associated deposits (Boswell and Collett, 2011). This estimate of GIP in resource-grade methane hydrates is ~35% more than the 2010 estimate for global natural gas reserves (~6600 TCF; EIA, 2010) and nearly 100 times greater than the annual global consumption of gas. It is important to note that there are as yet no proved reserves of gas hydrate since gas has never been produced from gas hydrate for more than a few days in research tests.

#### **Gas Hydrate Resources**

The hydrate resource pyramid (Boswell and Collett, 2006), shown in modified form in Figure 3, captures the distribution of sequestered methane among the major types of global gas hydrate deposits. The pyramid also demonstrates that only a small subset of these deposits is likely to be considered viable as a source of commercial quantities of natural gas and serves as a convenient way to understand the probable chronology for development of gas hydrates as a resource.



Figure 3. The hydrate resource pyramid modified from Boswell and Collett (2006).

#### Arctic sand reservoirs

At the top of the pyramid lie high permeability sediments in permafrost areas. Despite the relatively small amount of gas hydrate in these settings globally, permafrost-associated gas hydrates will probably be the first to be commercialized, particularly in areas with well-developed infrastructure for conventional hydrocarbon extraction (e.g., Alaskan North Slope). The gas produced in these settings would most likely be used to meet on-site power needs (Howe, 2004; Hancock et al., 2004). To date, these permafrost-associated deposits are the only places where production of gas from verifiable dissociation of gas hydrates has ever been documented. Short-term (i.e., several days) production tests were carried out at the Mallik well in the Mackenzie Delta area of Canada in 2002 and 2007 (Dallimore and Collett, 2005; Hancock et al., 2005; Takahisa, 2005; Kurihara et al., 2008) and at the Mt. Elbert (Milne Point) site on the Alaskan North Slope in 2008 (e.g., Hunter et al., 2011). Within the next few years, DOE and its partners plan a longer-term (i.e., probably longer than a year) research test to determine appropriate conditions for gas production from methane hydrates in permafrost-associated sediments in Prudhoe Bay, Alaska.

## Marine sand reservoirs

Permeable marine sediments appear below permeable permafrost-associated sands on the gas hydrate pyramid and are considered the major target for long-term development of gas hydrates as a resource. Resource-grade gas hydrate deposits are delineated based on a combination of reservoir quality and saturation. Highly permeable marine sands with moderate gas hydrate

saturations are considered the best targets for wide-scale resource development. Recent loggingwhile-drilling in the Gulf of Mexico has identified geologic units with inferred hydrate saturations as high as 80% (Boswell et al., 2009).

High saturation gas hydrate deposits in marine sands were first explored in a Japanese test well in the Nankai Trough in 1999 and were subsequently sampled during a drilling expedition in 2004 (e.g., Tsuji et al., 2009). Since then, coarse-grained sediments with significant saturations of gas hydrates have been studied by the international academic drilling program (Integrated Ocean Drilling Program or IODP) in thin stringers within the sedimentary section on the Vancouver margin (Riedel et al., 2006), by drilling on the Indian margin (e.g., Collett et al., 2008) and the Malaysian margin (Hadley et al., 2008), and by a 2009 logging-while-drilling expedition (e.g., Boswell et al., 2009) targeting such gas hydrate occurrences in various parts of the deepwater northern Gulf of Mexico under the auspices of a DOE/Chevron Joint Industry Project (JIP). The second Korean drilling expedition (UGBH2) also found gas hydrate in turbiditic sands (S.R. Lee et al., 2011).

The next step for proving that gas hydrates in permeable marine sediments can be a resource for natural gas is testing to determine the optimal processes and conditions for extracting the gas. There are few technical barriers to conducting such a test, but the cost and relative immaturity of routine deepwater operations mean that it will probably be at least a few years before even a short-term test can be undertaken. Japan's national methane hydrates R&D program (MH21) currently plans to conduct one to two such tests on Nankai Trough gas hydrates by 2014 and is on track to be the first to demonstrate gas production from deepwater marine hydrate deposits. The U.S. R&D program, through the DOE/Chevron Joint Industry Project, plans pressure coring (i.e., coring that retains the sediments at in situ pressure conditions) of gas hydrate-rich sandy sediments in the northern Gulf of Mexico in 2012. Such a program would be the next step along the trajectory towards a U.S. deepwater research production test within the next decade.

## Non-sand marine sediment

The category for non-sand marine sediment just below marine sands in the gas hydrate resource pyramid can be best interpreted as less permeable (usually smaller grained) sediments that might host gas hydrate in fracture-related permeability (e.g., Cook, 2010). Drilling on the Indian and Korean margins (e.g., Cook and Goldberg, 2008; M. Lee and Collett, 2009; Cook et al., 2010) and in the Gulf of Mexico (Cook et al., 2008) has found gas hydrate filling pervasive fractures within low permeability sediments (e.g., silts and clays). Taken in bulk, such sediments may not have a high average saturation of gas hydrate, but targeted production from gas hydrates within the fractures could theoretically yield significant gas. As with shale gas, the fractures themselves might also be exploited as conduits for rapidly extracting gas through otherwise low permeability sediments.

## Low permeability marine sediments

At the base of the resource pyramid lie low permeability marine sediments. As noted above, such sediments host most of the global GIP in methane hydrates and are unlikely to become a target for commercial production of gas from methane hydrates.

## Alternate Classification Scheme

Besides the gas hydrate resource pyramid, another categorization scheme is commonly applied to resource-grade hydrates and has importance for classifying potential reservoirs. Moridis and Collett (2004) originated this classification system, which has found acceptance mostly in reservoir simulation literature. The classification scheme does not distinguish between marine and permafrost-associated gas hydrates, focusing instead on whether the deposits are highly concentrated and associated with mobile gas and/or fluids. Class 1 and 2 gas hydrate deposits have high saturation and underlying mobile gas and fluid and mobile fluid, respectively. Class 3 deposits a gas hydrate-bearing layer with no mobile fluid beneath. Class 4 deposits correspond to both permafrost-associated and marine gas hydrates that are disseminated and occur in low saturations within sediments. The classification system reflects the multiphase (gas hydrate, free gas, and pore fluid) nature of real gas hydrate reservoirs and, importantly, accounts for the characteristics of pore-filling materials (fluid or gas) in sediments underlying gas hydrate-bearing layers. Mobile water is an advantage for most production scenarios, while associated free gas can be produced before and during production from gas hydrate in some cases (Moridis et al., 2008c), making the overall prospect of gas hydrate commercialization more feasible.

## **Locating High-Saturation Gas Hydrates**

One of the biggest challenges for development of gas hydrates as a resource is the difficulty of finding the deposits. This challenge is exacerbated by the lack of exhaustive laboratory and field data that can be used to calibrate geophysical parameters as a function of the saturation of gas hydrates in porous sediments.

For many years, marine gas hydrates were believed to occur only where exploration seismic data detect a so-called bottom simulating reflector (BSR; see Figure 1a), which marks the base of the gas hydrate stability zone in some places. This reflector generally indicates that overlying sediments host some gas hydrate, although often at a saturation of less than 10%. Gas hydrates have now been sampled in many places lacking a BSR, rendering the presence of a BSR a sufficient, but not necessary, one for gas hydrate occurrence. In permafrost areas, the difficulty of using reconnaissance seismic imaging to locate gas hydrates is even more acute since BSR-type features have never been observed.

A step beyond direct detection of the base of the gas hydrate stability zone is inferring gas hydrate distributions and concentrations based on analysis of seismic data. Occasionally, it is possible to detect gas hydrates directly based on velocity anomalies in sediments containing high hydrate saturations (e.g., Holbrook et al., 2002). More often, sophisticated analyses are required. On the Japanese margin, the Indian margin, and the Alaskan North Slope, attribute analysis of 3D seismic data, coupled with information from borehole logs, has been used to delineate the extent of hydrate deposits (Hato et al., 2006; Satyavani et al., 2008; Inks et al., 2009; M. Lee et al., 2009). A full waveform inversion method that can be readily applied to industry-quality marine seismic data, calibrated with available borehole logs, and interpreted in terms of gas hydrate saturation by the application of rock physics models has been used to predict the occurrence and saturation of hydrate in disparate geologic settings in the northern Gulf of Mexico (Dai et al., 2008a, 2008b; Shelander et al., 2010).

Some types of geophysical measurements—particularly shear wave velocity and electrical properties--are far more sensitive to the presence of gas hydrate than the more routinely

measured compressional wave velocity. This is particularly true at relatively low gas hydrate saturations (e.g., Yun et al., 2005; J.Y. Lee et al., 2010a, 2010b). Unfortunately, shear wave data are more difficult to record and more rarely obtained than compressional wave data, both for regional exploration surveys and for borehole logs. Owing to the marked increase in electrical resistivity with even modest gas hydrate saturations (e.g., Collett and Ladd, 2000; Goldberg and Saito, 1998), electrical resistivity anomalies have long been considered the best method for locating gas hydrate-bearing units in borehole logs in marine and subpermafrost settings. For regional scale exploration, use of electromagnetic methods to locate resource-grade hydrates still remains largely unproven though. Controlled source electromagnetic (CSEM) methods that have been widely applied by the private sector for locating deep (particularly subsalt) conventional targets in marine settings (Constable, 2010) have been modified by academic researchers to explore shallower gas hydrate-bearing sediments, as have some other EM/electrical methods (Schwalenberg et al., 2005; Weitemeyer et al., 2006a, b; Weitemeyer and Constable, 2010; Ellis et al., 2008). Such data may have the most promise not as a primary exploration technique, but when used in conjunction with seismic data. Indeed, joint inversion of seismic and EM data (e.g., Chen et al., 2007) may provide one hope for a new, non-invasive exploration approach for locating high-saturation gas hydrates in porous (not fractured) sediments.

A holistic petroleum systems analysis is among the newest tools adapted by gas hydrates researchers for inferring the location resource-grade deposits. This approach uses all available geophysical and geologic information to identify a source of methane gas, migration pathways linking the gas source to the hydrate stability zone, a reservoir unit (e.g., coarse-grained sands) to trap the methane as hydrate within the stability zone, and sometimes a structural or stratigraphic cap/trap for the hydrate-bearing unit. The petroleum systems approach for inferring the distribution of gas hydrate was first articulated and applied to permafrost-associated gas hydrates above conventional hydrocarbon reservoirs on the Alaskan North Slope (Hunter et al., 2004) and the Canadian Beaufort's Mackenzie Delta (Osadetz and Chen, 2004). The first full-scale application of the petroleum systems framework for locating marine gas hydrate deposits was during the site selection process for the 2009 northern Gulf of Mexico methane hydrates LWD campaign led by the DOE/Chevron JIP (Hutchinson et al., 2008). By (a) focusing on sedimentary environments that should be associated with coarse-grained sedimentation, (b) perusing well logs for indicators of hydrate charging in sand units, (c) interpreting seismic data both qualitatively and quantitatively, and (d) identifying the various components of the petroleum system at each site, researchers successfully chose deepwater drilling targets where high saturation gas hydrate deposits were later located (Boswell et al., 2009) based on a relatively routine suite of a priori information and limited well logs.

## **Formal Assessments**

The three modern quantitative in-place regional assessments of gas hydrates that have been completed to date are for part of the Nankai Trough (Fujii et al., 2008), for the northern Gulf of Mexico (Frye, 2008), and for the U.S. (Collett, 1995). In addition, the US Geological Survey (USGS) has completed the first-ever technically recoverable assessment of gas hydrate resources for part of the Alaskan North Slope (Collett et al., 2008). While there is no standard methodology for conducting gas hydrate assessments, many of the principles that apply to conventional hydrocarbon assessments carry over to gas hydrates. One key difference is that the pressure-temperature stability constraints for gas hydrates and the necessity of having a large

enough supply of gas to enable hydrate formation in the first place add an overprint of complexity to gas hydrate assessments.

The three modern in-place gas hydrate assessments use detailed interpretations of the threedimensional distribution of likely reservoir units (e.g., high permeability sands) and adopt the probabilistic approach common in resource assessments. For many years, the only quantitative assessment was the U.S. gas-in-place as gas hydrate assessment for the onshore US and the offshore waters within the Exclusive Economic Zone (Collett, 1995). The median value produced by this assessment was 320,222 TCF, with 5% and 95% confidence limits of ~112,700 TCF and ~676,000 TCF, respectively. The northern Gulf of Mexico assessment completed by the US Minerals Management Service (now Bureau of Ocean Energy Management, Regulation and Enforcement or BOEMRE) produced median values of 21,444 TCF GIP overall (Frye, 2008), compared to the earlier value of ~38,000 TCF determined by Collett (1995). From a resource perspective, the more important outcome of the Gulf of Mexico assessment was the determination of a median of 6717 TCF of in-place gas in methane hydrate located in sands (Frye, 2008). Within the next 2 years, BOERME is expected to release gas-in-place assessments for gas hydrates on the U.S. Atlantic margin and the U.S. Beaufort Shelf offshore Alaska. For the Nankai Trough, the published assessment (Fujii et al., 2008) covers 10% of the area associated with a BSR and yields 20 TCF in high-saturation zones and 40 TCF in the full section.

The first-ever assessment of undiscovered technically-recoverable gas contained within gas hydrate was completed by the USGS in 2008 for central and eastern parts of the Alaskan North Slope, including the offshore area out to the 3-mile limit. Full details of the assessment are still being published, but the median for gas that could be recovered using current technology is 85.4 TCF (Collett et al., 2008), compared to 590 TCF estimated for the in-place gas in the earlier assessment (Collett, 1995).

# Production

It is widely agreed that existing technology can be used to produce gas hydrates. The production methods being evaluated now have changed little since the early 1980s, when Holder et al. (1984) discussed the technical merit and economic feasibility of thermal stimulation, depressurization, and chemical inhibition for the production of gas from hydrates. This section reviews production methods, discusses some production scenarios, and briefly mentions potential hazards associated with gas production from methane hydrates.

## Methods

Short-term production tests at the permafrost Mallik (e.g., Dallimore and Collett, 2005; Hancock et al., 2005; Kurihara et al., 2008) and Mt. Elbert (Hunter et al., 2011) wells and laboratory simulations on sediment cores (Kwon et al., 2008; Yun et al., 2010, 2011) have produced important data on gas production via depressurization and/or thermal stimulation. Here we consider each of the primary production methods in turn:

A) Thermal stimulation refers to warming the formation through the injection of heated fluid or potentially direct heating of the formation, as shown schematically in Figure 4a. Thermal stimulation is energy intensive and will lead to relatively slow, conductionlimited dissociation of gas hydrates unless warmer pore fluids become mobilized and increase the volume of the formation exposed to higher temperatures. The endothermic nature of gas hydrate dissociation also presents a challenge to thermal stimulation; the cooling associated with dissociation (and, in some cases, gas expansion) will partially offset artificial warming of the formation, meaning that more heat must be introduced to drive continued dissociation and prevent formation of new gas hydrate. In terrestrial settings thermal stimulation must be carefully controlled to minimize permafrost thawing (Henninges et al, 2005), which might lead to unintended environmental consequences and alter the permeability seal for the underlying gas hydrate deposits.

- B) Depressurization, shown schematically in Figure 4b, has emerged as the preferred and more economical means of producing gas from methane hydrates during most of a well's life. Depressurization does not require large energy expenditure and can be used to drive dissociation of a significant volume of gas hydrate relatively rapidly.
- C) Chemical inhibition exploits the fact that gas hydrate stability is inhibited in the presence of certain organic (e.g., glycol) or ionic (seawater or brine) compounds. Seawater or other inhibitors might be needed during some stages of production (e.g., Bai et al., 2008) of gas from methane hydrate deposits, but would not be the primary means of dissociating gas hydrate nor used for an extended period or on a large scale.

Moridis et al. (2008a) provide the most extensive overview to date of reservoir simulation results using single (either depressurization or thermal stimulation) and mixed production methods for various classes of gas hydrate reservoirs. While production of gas from methane hydrates is not yet a reality on a large scale, an international reservoir simulation code comparison effort (e.g., Wilder et al., 2008) led by the US DOE has allowed researchers to calibrate their models using data obtained during short-term production tests in permafrost settings.



Figure 4. Possible methods for producing gas from a marine Class 1 gas hydrate deposit, which is characterized by methane hydrate-bearing sediments (yellow granular media labeled GHBS) overlying sediments with free gas (brown channeled sediments). Production techniques are shown in the left panels, modified from Collett (2002), and the impacts of the production methods on reservoir conditions are portrayed on the right. Sediments in which gas hydrate is dissociating are denoted in shaded yellow to orange. In real settings, the same well would not always be used to perturb the gas hydrate stability field and to extract the gas released by hydrate dissociation. (a) Thermal stimulation introduces heat or warm fluids into the gas hydrate stability zone and dissociates gas hydrate. As shown on the right, the original geotherm (blue) will warm and dissociate gas hydrate in part of the reservoir. (b) Depressurization lowers the pressure in the GHBS. The diagram at the right shows that the part of the stability curve (green solid segment) that originally extended to pressures lower (shallower depths) than those at the seafloor applies to the gas hydrate reservoir after depressurization (dashed green). The pressure perturbation is shown schematically as the black dashed curve. (c) Inhibitors like seawater generally shift the gas hydrate stability boundary towards lower temperatures, as shown on the right with the difference between the red stability boundary and the dashed curve for stability with inhibitor. Injection of an inhibitor will dissociate gas hydrate in the vicinity of the well and result in mixed stability conditions (parts of the reservoir with and without the inhibitor), as shown by the red dashed "perturbed" stability boundary.

A novel potential production method slated to undergo initial field testing in the Prudhoe Bay area of Alaska in 2012 (Farrell et al., 2010) involves injection of  $CO_2$  into sediments containing methane hydrates. In the laboratory, the injected  $CO_2$  has been shown to replace the methane in the gas hydrate lattice without measurable dissociation of gas hydrate (e.g., H. Lee et al., 2003; Ota et al., 2005; Graue et al., 2008; Ersland et al., 2010). Modeling studies have confirmed the viability of such a replacement phenomenon (Tegze et al., 2007; White and McGrail, 2008). If this approach is successful at a field scale, methane could potentially be extracted from gas hydrate without co-production of significant volumes of water. Furthermore, the injected  $CO_2$  hydrate (e.g., Yezdimer et al., 2002; Park et al., 2006). In spring 2011, DOE and ConocoPhillips conducted preliminary drilling and emplaced borehole instrument packages that will be required for monitoring the  $CO_2$  injection test in the Prudhoe Bay area on the Alaskan North Slope in spring 2012 (Schoderbek and Boswell, 2011).

#### **Production Scenarios**

Peak production for conventional gas usually occurs soon after a well is established. In contrast, reaching peak production of gas from gas hydrate deposits alone (i.e., those not associated with free gas) may take several years (Hancock et al., 2004; Moridis et al., 2008a; Walsh et al., 2009), largely due to the time required for a dissociation front to propagate through the hydrate-bearing sediments. As noted above, both the rapid expansion of gas and the endothermic heat of hydrate dissociation might cool sediments and lead to the formation of secondary gas hydrate or ice (Shahbazi and Pooladi-Darvish, 2009), a notion challenged by recent results of Anderson et al. (2011). If such cooling processes occur and are not properly controlled, they have the potential to dramatically reduce net production and production rates. In practice, the anticipated reduced production from a gas hydrate well during various parts of its life cycle will probably dictate the use of mixed production scenarios characterized by long depressurization intervals and brief, interspersed thermal stimulation events or even inhibitor injection.

Production from methane hydrate deposits does pose special challenges for commercialization. For example, hydrate dissociation frees significant volumes of free water, and the study by Walsh et al. (2009) shows nearly 2500 bbl of water produced for every million cubic feet of gas produced from deepwater methane hydrate early in the development of a hypothetical deepwater reservoir. This figure drops to ~100-200 bbl water produced per million cubic feet of gas produced during much of the life of the well before climbing rapidly after more than a decade into the hypothetical production scenario.

Another issue that distinguishes gas hydrate production from production of conventional gas is that gas hydrate reservoirs occur at significantly lower pressure than conventional gas reservoirs. This means less pressure is available to drive gas flow into the production well and more energy will likely need to be expended to lift gas from the formation. On the other hand, the lower pressure of the formation means that there is less potential for gas expansion or uncontrolled flow of gas during production, somewhat lowering the risk of a catastrophic event.

## Hazards

There have sometimes been concerns that the production of gas from gas hydrate is inherently risky and could pose unique or unknown dangers for infrastructure or personnel (e.g., Hovland et

al., 2001), beyond those associated with conventional hydrocarbon production. It is possible that destabilization of natural hydrates (as opposed to those that form in pipelines and conduits) has occasionally affected the integrity of the seafloor or boreholes, led to well control problems, or contributed to shallow water flows (e.g., Dutta et al., 2010), but there is scant published evidence. The long-time industry practice of simply avoiding areas with known gas hydrates during production activities that target deeper, conventional hydrocarbons has become increasingly impractical with the push for more deepwater operations. The issue of risk related to drilling through gas hydrates, no less production of gas from methane hydrates, must therefore be directly addressed.

The first stage of the DOE/Chevron JIP drilling in the northern Gulf of Mexico was partially designed to determine whether drilling of low saturation gas hydrates, like those commonly encountered in the shallow subseafloor for deepwater environments, posed a manageable risk to drilling activities and borehole/seafloor stability (Ruppel et al., 2008). More than ten major deepwater drilling expeditions have now successfully targeted gas hydrates and experienced no major safety issues. Borehole stability modeling (e.g., Birchwood et al., 2007), careful drilling fluid management (i.e., temperature, weight of drilling mud), and planning for possible formation overpressures are critical for ensuring safe operations in gas hydrate wells, as in normal wells. Reservoir simulations for production of gas from even the highest saturation hydrate deposits have repeatedly shown that runaway dissociation, rapid gas migration, and even blowouts are not typically concerns for gas hydrate wells. In fact, gas production from methane hydrate is always predicted to occur at a rate lower than the peak rate from a comparable conventional well, and the key challenge in production from gas hydrates is ensuring that dissociation continues even while the endothermic heat of dissociation and other processes cool the formation. Reservoir simulation for gas hydrates does not yet accurately incorporate advanced geomechanics concepts. Thus, one risk factor that remains to be assessed is the potential for gas migrating away from a dissociating, high saturation gas hydrate deposit to find an existing fracture or to cause a new fracture to form in an overlying, relatively impermeable layer. Such a scenario might lead to unintended leakage of methane into other sediments or even emission of methane at the surface (Rutqvist and Moridis, 2010).

## **Economics**

Without data from a long-term production test like the one that DOE plans to undertake with private sector partners within the next few years, the economics of gas production from gas hydrate deposits has been difficult to analyze. Until recently, the studies by Howe (2004) and Hancock et al. (2004) were among the few economic analyses to have been completed for gas hydrate production. A recent study by Walsh et al. (2009) now stands as the most exhaustive analysis of the economics of gas production from gas hydrates and (in some cases) associated free gas to become available in the public domain. Building on the earlier work by Hancock et al. (2004) and unpublished research by Hancock, the Walsh et al. (2009) study uses CMG-STARS for reservoir simulation of permafrost-associated gas hydrate production and Que\$tor for determining costs. They report that the price of gas would have to reach \$7.50 Canadian (2005 dollars) per Mcf for production from permafrost-associated gas hydrates overlying producible free gas to be economically viable. This estimate and others that follow include pipeline tariffs, but not local taxes and tariffs. If there is no underlying free gas that can be produced during the

life of the well, then the gas price would have to reach \$12 Canadian (2005 dollars) per Mcf for production from hydrates to become viable.

To assess the production characteristics and economics of marine gas hydrates, Walsh et al. (2009) used the TOUGH+HYDRATE reservoir simulation (Moridis et al., 2008b) results published by Moridis and Reagan (2007) and Que\$tor for cost analyses in comparing production from gas hydrates to that from a conventional gas reservoir. The costs estimates include a pipeline, production facility, and subsea development for both conventional and gas hydrate production and the extra costs (e.g., additional wells, artificial lift to manage water production) associated with gas production from hydrate. At the 50% confidence level, the additional cost associated with production from deepwater gas hydrates vs. conventional gas deposits is \$3.50 to \$4.00 (U.S. dollars) per Mcf.

The economic evaluations discussed above incorporate some of the prospective costs associated with pipelines. It is important to note that transportation issues probably pose an even greater economic challenge for gas hydrates than for many conventional gas reservoirs or for some other forms of unconventional gas. The primary reason is geographic: Many conventional and unconventional (e.g., shale, coalbed) deposits are closer to production and distribution infrastructure than the deepwater marine and permafrost areas where resource-grade gas hydrates are concentrated. This is one factor motivating researchers to maintain that initial commercial-scale production of gas from hydrate will probably occur on the Alaskan North Slope near existing infrastructure that can immediately exploit the gas to run on-site operations.

## Timeline

The timeline for commercialization of gas hydrate deposits depends most critically on two factors: (1) research and development advances to prove the resource and to surmount some of the other key obstacles and (2) an economic, political, or natural gas supply climate in which there is urgency to develop the resource potential of gas hydrates. Gas hydrates, despite the amount of methane they sequester, are probably the least likely of unconventional resources to be tapped for natural gas within the next few decades, even if the economics or supply model changes dramatically. Still, there are strong arguments to be made for a continuing R&D effort to address the remaining challenges in advancing gas hydrates along a trajectory towards viability as a resource. Activities undertaken now will be critical for ensuring the availability of this gas twenty or more years in the future and for improving the energy security of nations currently lacking access to a domestic gas supply.



Figure 5. Timeline of major post-1990 gas hydrate field programs and future activities. Circles correspond to logging and/or coring, while squares/rectangles denote activities that included/will include production testing. Solid symbols denote completed activities, and open symbols are potential or planned activities. Rectangles filled with shaded pattern refer to longer term production activities that remain prospective. The deepwater marine programs are delineated by country and program name, with components of the Japanese activities labeled with their respective acronyms for easy cross-referencing with the literature. JIP denotes the DOE/Chevron Joint Industry Project. Permafrost activities are labeled by location, not by participants in the activities. For example, Japanese entities have been major participants and co-sponsors of some of the Mallik drilling. The DOE programs are labeled for ease of searching the associated literature, and CP and BP refer to ConocoPhillips and British Petroleum, respectively. Only the three academic drilling expeditions with an exclusive gas hydrates focus are shown in the bottom panel. Ocean Drilling Program (ODP) Legs 164 (Paull et al., 1996) and 204 (Trehu et al., 2003) investigated gas hydrates on passive and active margins, respectively. Integrated Ocean Drilling Program (IODP) Expedition 311 (Riedel et al., 2006) drilled a transect to research gas hydrate occurrences across the Vancouver margin. In the coming years, academic groups are likely to succeed in installing subseafloor gas hydrate observatories linked to seafloor cables with sufficient bandwidth to provide real-time data access to researchers.

The timeline shown in Figure 5 summarizes the post-1990 global drilling efforts that have propelled gas hydrates resource studies to their present-day state. The timeline provides few predictions about the future, other than the likely development of commercial scale production

first in permafrost-associated gas hydrates in the Arctic and then in the gas hydrates hosted in sands in the deepwater Pacific. A summary of the activities expected in the coming two or more decades is given below.

Before 2015 (relatively certain):

- Second-stage drilling in the deepwater Gulf of Mexico (DOE/Chevron JIP) and possibly other locations, most likely in the Pacific or Indian Ocean
- Tests of production scenarios over many months to more than a year on the Alaskan North Slope (DOE and private sector partners)
- Test of the CO<sub>2</sub> injection method of gas production (DOE/ConocoPhillips in 2012)
- First production tests (2012 and 2014) for deepwater gas hydrates (Japan's MH21 effort)
- In-place assessments for the remainder of the US EEZ (BOEMRE)
- Release of full study related to technically-recoverable assessment of Alaskan North Slope gas hydrates (USGS)
- First assessment of technically-recoverable marine gas hydrates
- First major experiment designed to test joint application of EM and seismic methods for finding resource-grade hydrates

Before 2020 (less certain)

- First-stage research drilling of deepwater marine gas hydrates by countries not currently active in this area
- More deepwater (Japan MH21? Other countries?) and permafrost (US and Canadian Arctic?) production tests
- Wider application (e.g., to different basins) of petroleum system approaches for locating resource-grade gas hydrates
- Wider publication of quantitative technically recoverable resource assessments for different basins
- First quantitative, probabilistic assessment of economically recoverable gas hydrates in a well-studied area where a production test has already been conducted, leading to the first articulation of a gas hydrate "reserve"
- Further development of  $CO_2$  method for simultaneous gas hydrate production and  $CO_2$  sequestration
- Local production of gas from methane hydrates to meet energy needs in remote communities (e.g., Alaskan North Slope; T. Walsh et al., 2008)
- Tapping of gas hydrate as an ancillary production target in conventional hydrocarbon wells (Holder et al., 1984)

Before 2025 to 2030:

- First attempt at small-scale commercialization, most likely in permafrost settings to provide power for existing infrastructure engaged in conventional hydrocarbon production (US or Canadian Arctic)
- Depending on gas supply, needs, and economic demands, initial commercialization of deepwater gas hydrates, probably by nations seeking a domestic source of natural gas

#### References

- Bai, Y., Q. Li, X. Li, and Y. Du, 2008. The simulation of nature gas production from ocean gas hydrate reservoir via depressurization, Science in China Series E: Technological Sciences, 51, 1272-1282. (doi: 10.1007/s11431-008-0146-1)
- Birchwood, R.A., Noeth, S., Tjengdrawira, M. A., Kisra, S. M., Elisabeth, F. L., Sayers, C. M., Singh, R., Hooyman, P. J., Plumb, R. A., Jones, E., Bloys, J. B., 2007. Modeling the mechanical and phase change stability of wellbores drilled in gas hydrates by the Joint Industry Participation Program (JIP) Gas Hydrates Project Phase II, SPE Ann. Tech. Conf., 11-14 November, 2007, SPE 110796.
- Boswell, R., and T. Collett, 2006. The gas hydrates resource pyramid, Fire in the Ice, US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, 6(3), p. 5-7.

http://www.netl.doe.gov/technologies/oil-gas/publications/hydrates/2009Reports/FITI06\_Pyramid.pdf

- Boswell, R. and Collett, T.S., 2011. Current perspectives on gas hydrate resources. Energy and Environmental Science, 4, 1206-1215.
- Boswell, R., Collett, T., McConnell, D., Frye, M., Shedd, B., Mrozewski, S., Guerin, G., Cook, A., Godfriaux, P., Dufrene, R., Roy, R., and E. Jones, 2009. Joint Industry Project Leg II discovers rich gas hydrate accumulations in sand reservoirs in the Gulf of Mexico, Fire in the Ice, US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, 9(3), 1-5.

http://www.netl.doe.gov/technologies/oil-gas/publications/Hydrates/Newsletter/MHNewsSummer09.pdf

- Buffett, B., and Archer, D., 2004. Global inventory of methane clathrate: sensitivity to changes in environmental conditions, Earth and Planetary Science Letters 227, 185-199.
- Chen, J., G.M. Hoversten, D. Vasco, Y. Rubin, and Z. Hou, A Bayesian model for gas saturation estimation using marine seismic AVA and CSEM, Geophysics, 72, WA85. (doi:10.1190/1.2435082).
- Collett, T.S., 1995. Gas hydrate resources of the United States. In: Gautier DL, Dolton GL, Takahasi KI, Varnes KL (eds) National Assessment of United States Oil and Gas Resources on CD-ROM: U.S. Geological Survey Digital Data Series 30.
- Collett, T.S., 2002. Energy resource potential of natural gas hydrate, American Association of Petroleum Geologists Bulletin, 86, 1971-1992
- Collett, T.S., and Ladd, J., 2000. Detection of gas hydrate with downhole logs and assessment of gas hydrate concentrations (saturations) and gas volumes on the Blake Ridge with electrical resistivity log data, in: Paull, C.K., Matsumoto, R., Wallace, P.J., and Dillion, W.P. (Eds.), Proc. ODP, Sci. Results, 164, 179-191.
- Collett, T., Agena, W., Lee, M., Zyrianova, M., Bird, K., Charpentier, T., Houseknecht, D., Klett, T., Pollastro, R., Schenk, C., 2008. Assessment of gas hydrate resources on the North Slope, Alaska, 2008: U.S. Geological Survey Fact Sheet 2008-3073, 4 pp.
- Collett, T.S., Lee, M.W., *et al.*, 2011. Permafrost associated natural gas hydrate occurrences on the Alaskan North Slope. Marine and Petroleum Geology, 28, 279-294.
- Collett, T., Riedel, M., Cochran, J.R., Boswell, R., Kumar, P., and Sathe, A.V., 2008. Indian continental margin gas hydrate prospects: results of the Indian National Gas Hydrate Program (NGHP) expedition 01, Proc. 6<sup>th</sup> Int. Conf. Gas Hydrates,Vancouver. https://circle.ubc.ca/bitstream/handle/2429/1035/5365.pdf?sequence=1
- Collett, T. S., A. H. Johnson, C. C. Knapp, and R. Boswell, 2009, Natural Gas Hydrates: A Review, in T. Collett, A. Johnson, C. Knapp, and R. Boswell, eds., Natural gas hydrates— Energy resource potential and associated geologic hazards: AAPG Memoir 89, p. 146–219.

- Constable, S., 2010, Ten years of marine CSEM for hydrocarbon exploration, Geophysics 75, 75A67-75A81. Doi: 10.1190/1.3483451.
- Cook, A.E., 2010. Gas hydrate filled fractures on continental margins, Ph.D. thesis, Columbia University, 215 pp. <u>http://gradworks.umi.com/3400636.pdf</u>
- Cook, A.E. and D. Goldberg, 2008. Extent of gas hydrate filled fracture planes: implications of in situ methanogenesis and resource potential, Geophysical Research Letters 35, L15302, doi:10.1029/2008GL034587.
- Cook, A.E., Anderson, B.I., Malinverno, A., Mrozewski, S., and D.S. Goldberg, 2010. Electrical anisotropy due to gas hydrate-filled fractures, Geophysics, 75, F173. doi: 10.1190/1.3506530.
- Cook, A., Goldberg, D., Kleinberg, R., 2008. Fracture-controlled gas hydrate systems in the Gulf of Mexico. Marine and Petroleum Geology 25 (9), 932–941.
- Dai, J., Snyder, F., Gillespie, D., Koesoemadinata, A., and Dutta, N., 2008a. Exploration for gas hydrates in the deepwater northern Gulf of Mexico: Part I. A seismic approach based on geologic model, inversion, and rock physics principles, Marine and Petroleum Geology, 25, 830-844. doi: 10.1016/j.marpetgeo.2008.02.006
- Dai, J., Banik, N., Gillespie, D. and N. Dutta, 2008b. Exploration for gas hydrates in the deepwater northern Gulf of Mexico: Part II. Model validation by drilling, Marine and Petroleum Geology, 25, 845-859. doi:10.1016/j.marpetgeo.2008.02.005
- Dallimore, S.R., Uchida, T., and Collett, T.S., eds., 1999. Scientific Results from the JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada Bulletin 544.
- Dallimore S.R., Collett T. S., editors, 2005. Scientific Results from the Mallik 2002 Gas Hydrate Production Research Well Program, MacKenzie Delta, Northwest Territories, Canada, Geological Survey of Canada Bulletin 585.
- Dallimore, S R; Collett, T. S., Uchida, T, Weber, M, Takahashi, H, 2002, Mallik Gas Hydrate Research Team; Overview of the 2002 Mallik Gas Hydrate Production Research Well Program ; in, Proceedings of the Fourth International Conference on Gas Hydrates. vol. 1, 36-39.
- Dallimore, S. R., J. F. Wright, F. M. Nixon, M. Kurihara, K. Yamamoto, T. Fujii, K. Fujii, M. Numasawa, M. Yasuda, and Y. Imasato, 2008a, Geologic and porous media factors affecting the 2007 production response characteristics of the JOGMEC/NRCAN/AURORA Mallik Gas Hydrate Production Research Well, Proceedings of the 6th International Conference on Gas Hydrates, 10 p.
- Doyle, E.H., S.R. Dallimore, R.A. Fine, A.M. Nur, M.E.Q. Pilson, W.S. Reeburgh, E.D.Sloan Jr., A.M. Tréhu, J. Bintz, J. Merrill, and N. Caputo, 2004. Charting the Future of Methane Hydrate Research in the United States. National Academies Press, Washington D.C., 192 pp.
- Dutta, N.C., R.W. Utech, and D. Shelander, 2010. Role of 3D seismic for quantitative shallow hazard assessment in deepwater sediments, The Leading Edge, 930-942.
- Ellis, M., R.L. Evans, D. Hutchinson, P. Hart, J. Gardner, and R. Hagen, 2008. Electromagnetic surveying of seafloor mounds in the northern Gulf of Mexico, Marine Pet. Geol., 25, 969-968 doi: 10.1016/j.marpetgeo.2007.12.006
- Energy Information Administration (EIA), 2010. Natural gas, in: International Energy Outlook 2010, U.S. Dept. of Energy, Washington DC. <u>http://www.eia.doe.gov/oiaf/ieo/pdf/0484(2010).pdf</u>
- Ersland, G., Husebo, J., Graue, A., Baldwin, B., Howard, J.J., and Stevens, J.C., 2010. Measuring gas hydrate formation and exchange with CO<sub>2</sub> in Bentheim sandstone using MRI tomography, Chem. Eng. J., 158, 25-31.

Farrell, H., Boswell, R., Howard, J., and Baker, R., 2010, CO<sub>2</sub>-CH<sub>4</sub> exchange in natural gas hydrate reservoirs: potential and challenges, Fire in the Ice, US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, 10(1), 19-21. <u>http://www.netl.doe.gov/technologies/oil-</u>

gas/publications/Hydrates/Newsletter/MHNews 2010 03.pdf#page=19

- Frye, M., 2008. Preliminary evaluation of in-place gas hydrate resources: Gulf of Mexico Outer Continental Shelf: Minerals Management Service Report 2008-004.
- Fujii, T., T. Saeiki, T. Kobayashi, T. Inamori, M. Hayashi, O. Takano, T. Takayama, T. Kawasaki, S. Nagakubo, M. Nakamizu, and K. Yokoi, 2008. Resource assessment of methane hydrate in the Nankai Trough, Japan, Offshore Technology Conference, Houston, TX, Paper 19310.
- Goldberg, D., and S. Saito, 1998, Detection of gas hydrates using downhole logs, *in* J.-P. Henriet, and J. Mienert, eds., Gas Hydrates Relevance to World Margin Stability and Climate Change: London, The Geological Society, p. 129-132.
- Gornitz, V., Fung, I., 1994. Potential distribution of methane hydrates in the world's oceans, Global Biogeochemical Cycles, 8, 225-347.
- Graue, A., Kvamme, B., Baldwin, B.A., Steven, J., Howard, J., Aspenes, E., Ersland, G., Husebo, J., and Zornes, D. 2008. MRI visualization of spontaneous methane production from hydrates in sandstone core plugs when exposed to CO<sub>2</sub>. SPE Journal, 13, 146-152.
- Hadley, C., D. Peters, A. Vaughan, 2008. Gumusut-Kakap project: Geohazard characterisation and impact on field development plans, International Petroleum Technology Conference, 12554, 15 pp.
- Hancock, S., Collett, T.S., Dallimore, S.R., Satoh, T., Huenges, E., Henninges, J. 2005. Overview of thermal stimulation production test results for the Japex/JNOC/GSC Mallik 5L-38 Gas Hydrate Research Well; in: Dallimore, S.R., and Collett, T.S. (eds.), Scientific Results from Mallik 2002 Gas Hydrate Production Research Well Program, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada Bulletin 585
- Hancock S, Collett T, Pooladi-Darvish M, Gerami S, Moridis G, Okazawa T, Osadetz K, Dallimore S, Weatherill B., 2004. A preliminary investigation on the economics of onshore gas hydrate production based on the Mallik Field discovery, American Association of Petroleum Geologists Hedberg Conference Proceedings, Vancouver, CA. <u>http://www.searchanddiscovery.net/documents/abstracts/2004hedberg\_vancouver/short/hancock02.htm</u>
- Harvey, L. D. D. and Huang, Z., 1995. Evaluation of potential impact of methane clathrate destabilization on future global warming. J. Geophys. Res., 100, 2905–2926.
- Hato M, Matsuoka T, Inamori T, Saeki T., 2006. Detection of methane-hydrate-bearing zones using seismic attributes analysis, The Leading Edge, 25, 607-609.
- Henninges, J., Schrotter, J., Erbas, K., and Huenges, E., 2005. Temperature field of the Mallik gas hydrate occurrence—implications on phase changes and thermal properties, in: Dallimore, S.R., and Collett, T.S. (eds.), Scientific Results from Mallik 2002 Gas Hydrate Production Research Well Program, Mackenzie Delta, Northwest Territories, Canada, Geological Survey of Canada Bulletin 585, 14 pp.
- Holbrook, W.S., Gorman, A.R., Hornbach, M., Hackwith, K.L., and J. Nealon, 2002. Direct seismic detection of methane hydrate, The Leading Edge, 21, 686-689. (doi: 10.1190/1.1497325)
- Holder G.D., Kamath, V.A., and S.P. Godbole 1984. The potential of natural gas hydrates as an energy resource, Annual Review of Energy, 9, 427-445.
- Hovland M, Gudmestad, OV (2001) Potential influence of gas hydrates on seabed installations.

In: Paull CK, Dillon, WP (Eds.) Natural Gas Hydrates-Occurrence, Distribution, and Detection, American Geophysical Union, Washington DC, 307-315.

- Howe, S.J., 2004. Production modeling and economic evaluation of a potential gas hydrate pilot production program on the North Slope of Alaska. M.S. Thesis, University of Alaska Fairbanks, 138 pp.
- Hunter, R.B., Collett, T.S., Patil, S.L., Casavant, R.R., and Mroz, T.H., 2004. Characterization, appraisal, and economic viability of Alaska North Slope gas hydrate accumulations, AAPG Hedberg Conference, Vancouver, Canada.

http://www.searchanddiscovery.net/documents/abstracts/2004hedberg\_vancouver/extended/hunter/hunter.htm

- Hutchinson, D., Shelander, D., Dai, J., McConnell, D., Shedd, W., Frye, M., Ruppel, C., Boswell, R., Jones, E., Collett, T., Rose, K., Dugan, B., Wood, W., and T. Latham, 2008, Site selection for DOE/JIP gas hydrate drilling in the northern Gulf of Mexico, Proceedings of the 6th International Conference on Gas Hydrates (ICGH), Vancouver, Canada, 6-10 July, 12 pp. https://circle.ubc.ca/handle/2429/1165
- Inks, T. L., M. W. Lee, W. F. Agena, D. J. Taylor, T. S. Collett, M. V. Zyrianova, and R. B. Hunter, 2009. Seismic prospecting for gas hydrate and associated free gas prospects in the Milne Point area of northern Alaska, in T. Collett, A. Johnson, C. Knapp, and R. Boswell, eds., Natural gas hydrates -- Energy resource potential and associated geologic hazards: AAPG Memoir 89, p. 555–583.
- Jung, J. W., D. N. Espinoza, and J. C. Santamarina, 2010. Properties and phenomena relevant to CH<sub>4</sub>-CO<sub>2</sub> replacement in hydrate-bearing sediments, J. Geophys. Res., 115, B10102, doi:10.1029/2009JB000812.
- Klauda, J.B. and S.I. Sandler, 2003. Predictions of gas hydrate phase equilibria and amounts in natural sediment porous media, Mar. Pet. Geo., 20, 459-470.
- Konno, Y., Y. Masuda, Y. Hariguchi, M. Kurinara, and H. Ouchi, 2010. Energy Fuels, 24(3), 1736-1744.
- Kurihara, M., Funatsu, K., Ouchi, H., Masuda, Y., Yasuda, M., Yamamoto, K., Numasawa, M., Fujii, T., Narita, H., Dallimore, S., and F. Wright, 2008. Analysis of the JOGMEC/NRCAN/Aurora Mallik gas hydrate production test through numerical simulation, Proc. 6<sup>th</sup> Int. Conf. Gas Hydrates, Vancouver.

https://circle.ubc.ca/bitstream/handle/2429/2234/5831\_1.pdf?sequence=1

- Kwon, T.-H.; Cho, G.-C.; Santamarina, J. C. Gas hydrate dissociation in sediments: Pressuretemperature evolution. Geochem., Geophys., Geosyst. 2008, 9, No. Q03019.
- Kvenvolden, K.A., 1988. Methane hydrate-a major reservoir of carbon in the shallow geosphere? Chemical Geology, 71, 41-51.
- Lee, H., Seo, Y., Seo, Y., Moudrakovski, I., Ripmeester, J. 2003. Recovering methane from solid methane hydrate with carbon dioxide, Angewandte Chemie-International Edition. 42(41), 5048-5051.
- Lee, J. Y., J. C. Santamarina, and C. Ruppel, 2010a, Parametric study of the physical properties of hydrate-bearing sand, silt, and clay sediments: 1. Electromagnetic properties, J. Geophys. Res., 115, B11104, doi:10.1029/2009JB006669.
- Lee, J. Y., F. M. Francisca, J. C. Santamarina, and C. Ruppel, 2010b, Parametric study of the physical properties of hydrate-bearing sand, silt, and clay sediments: 2. Small-strain mechanical properties, J. Geophys. Res., 115, B11105, doi:10.1029/2009JB006670.
- Lee, M.W. and T.S. Collett, 2009. Gas hydrate saturations estimated from fractured reservoir at Site NGHP-01-10, Krishna-Godavari Basin, India, J. Geophys. Res., 114, B07102, doi: 10.1029/2008JB006237.

- Lee, M. W., T. S. Collett, and T. L. Inks, 2009. Seismic-attribute analysis for gas-hydrate and free gas prospects on the North Slope of Alaska, in T. Collett, A. Johnson, C. Knapp, and R. Boswell, eds., Natural gas hydrates-Energy resource potential and associated geologic hazards: AAPG Memoir 89, p. 541-554.
- Lee, S.R. and UBGH2 Science Party, 2011. Second Ulleung Basin gas hydrate expedition (UBGH2): Findings and implications, Fire in the Ice, US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, 11(1), 5-9.

http://www.netl.doe.gov/technologies/oil-gas/futuresupply/methanehydrates/newsletter/newsletter.htm

- McIver, R., 1981, Gas hydrates: in R. Meyer and J. Olson, eds., Long-term Energy Resources: Pitman, Boston, MA, pp. 713-726.
- Milkov, A., 2004, Global estimates of hydrate-bound gas in marine sediments: how much is really out there? Earth-Science Reviews, 66, 183-197.
- Moridis, G.J., Collett, T.S., 2004. Strategies for gas production from hydrate accumulations under various geologic conditions. Report LBNL-52568. Lawrence Berkeley National Laboratory, Berkeley, CA.
- Moridis, G., Collett, T.S., Boswell, R., Kurihara, M., Reagan, M., Koh, C., and E. D. Sloan, 2008a. Toward production from gas hydrates: current status, assessment of resources, and simulation-based evaluation of technology and potential, SPE Unconventional Reservoirs Conference, SPE 114163.
- Moridis, G.J., Kowalsky, M.B., Pruess, K., 2008b. TOUGH+HYDRATE v1.0 User's Manual: a code for the simulation of system behaviour in hydrate-bearing porous media. Report LBNL-149E. Lawrence Berkeley National Laboratory, Berkeley, CA.
- Moridis, G.J., Reagan, M.T., and K. Zheng, 2008c, On the performance of Class 2 and Class 3 hydrate deposits during co-production with conventional gas, Offshore Technology Conference, OTC 19435-MS.
- Moridis, G.J., and M. Reagan, 2007. Strategies for production from oceanic Class 3 hydrate accumulations. OTC paper 18865.
- Osadetz, K.G. and Z. Chen, 2004. Progress toward a petroleum system approach to gas hydrate resource assessment, AAPG Hedberg Conference, 2004.

http://www.searchanddiscovery.net/documents/abstracts/2004hedberg\_vancouver/extended/osadetz/osadetz.htm

- Ota, M., Morohashi, K., Abe, Y., Watanabe, M., Smith, R., and H. Inomata, 2005. Replacement of  $CH_4$  in the hydrate by use of liquid  $CO_2$ . Energy Conversion and Management, 46(11-12), 1680-1691.
- Park, Y., Kim, D., Lee, J., Huh, D., Park, K., Lee, J., Lee, H., 2006, Sequestering carbon dioxide into complex structures of naturally occurring gas hydrates. Proc. National Academy of Sciences, 103-34, 12690- 12694.
- Park, K.P., Bahk, J.J., et al. 2008. Korean National Program expedition confirms rich gas hydrate deposits in the Ulleung Basin, East Sea. Fire in the Ice, US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, 8(2), 6-9.

http://www.netl.doe.gov/technologies/oil-gas/publications/Hydrates/Newsletter/HMNewsSpring08.pdf#page=6

- Paull, C.K., Matsumoto, R., et al. Proceedings of the Ocean Drilling Program, Initial Reports 164, College Station: Ocean Drilling Program (1996).
- Paull, C., W.S. Reeburgh, S.R. Dallimore, G. Enciso, S. Green, C.A. Koh, K.A. Kvenvolden, C. Mankin, and M. Riedel, 2010. Realizing the energy potential of methane hydrate for the United States, National Research Council Report.

http://books.nap.edu/openbook.php?record\_id=12831&page=R1

- Riedel, M., Collett, T. et al. Gas hydrate drilling transect across northern Cascadia maring— IODP Expedition 311. In Sediment-hosted Gas Hydrates: New Insights on the Natural and Synthetic Systems. Geological Society of London, Special Publications, 319, 11-19 (2009).
- Riedel, M., Collett, T.S., Malone, M.J., and the Expedition 311 Scientists, 2006. Proc. IODP, 311: Washington, DC (Integrated Ocean Drilling Program Management International, Inc.). doi:10.2204/iodp.proc.311.101.2006 <u>http://publications.iodp.org/proceedings/311/</u>
- Ruppel, C., 2007, Tapping methane hydrates for unconventional natural gas, Elements, 3 (3), 193-199.
- Ruppel, C., Boswell, R., and E. Jones, 2008, Scientific results from Gulf of Mexico gas hydrates joint industry project Leg 1 drilling: Introduction and overview, Mar. Pet. Geology, 25 (doi:10.1016/j.marpetgeo.2008.02.007)
- Ruppel, C., Collett, T., Boswell, R., Lorenson, T., Buckzowski, B., and W. Waite, 2011, A new global gas hydrate drilling map based on reservoir type, Fire in the Ice, US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, 11(1), 15-19. http://www.netl.doe.gov/technologies/oil-gas/futuresupply/methanehydrates/newsletter/newsletter.htm
- Rutqvist, J. and G. Moridis, 2010. Evaluation of geohazards of in situ gas hydrates related to oil and gas operations, Fire in the Ice, US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, 10(2), 1-4. <u>http://www.netl.doe.gov/technologies/oil-gas/publications/Hydrates/Newsletter/MHNews 2010 08.pdf#Page=1</u>
- Ryu, B.-J., Riedel, M, Kim, J-H, Hyndman, R.D., Lee, Y-J., Chung, B-H., and I.S. Kim, 2009. Gas hydrates in the western deep-water Ulleung Basin, East Sea of Korea. Marine and Petroleum Geology, 26, 1483-1498. Doi:10.1016/j.marpetgeo.2009.02.004.
- Satyavani, N., Sain, K., Lall, M., and B.J.P. Kumar, 2008. Seismic attribute study of gas hydrates in the Andaman, offshore India, Mar. Geophys. Res., 29, 167-175. (doi: 10.1007/s11001-008-9053-x)
- Schoderbek, D. and R. Boswell, 2011. Ignik Sikumi #1, gas hydrate test well, successfully installed on the Alaska North Slope, Fire in the Ice, US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, 11(1), 1-4. http://www.netl.doe.gov/technologies/oil-gas/futuresupply/methanehydrates/newsletter/newsletter.htm
- Schwalenberg, K., E. Willoughby, R. Mir, N. R. Edwards, 2005. Marine gas hydrate electromagnetic signatures in Cascadia and their correlation with seismic blank zones. *First Break*, 23, 57–63.
- Shahbazi, A., and M. Pooladi-Darvish, 2009. Modeling of ice formation in gas hydrate reservoirs, CSPG CSEG CWLS Convention, 594-596.
- Shelander, D., J. Dai, and G. Bunge, 2010. Predicting saturation of gas hydrates using pres-stack seismic data, Gulf of Mexico. Marine Geophysical Research, 31, 39-57. doi:10.1007/s11001-010-9087-8.
- Takahashi, H., T. Yonezawa, T., and Y. Takedomi, 2001. Exploration for natural hydrate in the Nankai-Trough well offshore Japan, Offshore Technology Conference, Paper OTC13040, Houston, TX. Resource Geology, 54
- Takahisa, I., 2005. Overview of production test results for the Mallik 2002 gas hydrate production research well program, J. Japan Inst. Energy, 84, 106-111.
- Tegze, G., Gránásy, L., and B. Kvamme, 2007. Phase field modeling of CH4 hydrate conversion into CO2 hydrate in the presence of liquid CO2. Physical Chemistry Chemical Physics, 9(24), 3104-3111.

- Trofimuk, A., Cherskiy, N, Tsarev, V., 1973. Accumulation of natural gases in zones of hydrate—formation in the hydrosphere. Doklady Akademii Nauk SSR 212, 931-934 (in Russian).
- Tsuji, Y., Ishida, H., Nakamizu, M., Matsumoto, R. and Shimizu, S., 2004. Overview of the MITI Nankai Trough wells: a milestone in the evaluation of methane hydrate resources. Resource Geology, 54, 3–10. doi: 10.1111/j.1751-3928.2004.tb00182.x
- Tsuji, Y., T. Fujii, M. Hayashi, R. Kitamura, M. Nakamizu, K. Ohbi, T. Saeki, K. Yamamoto, T. Namikawa, T. Inamori, N. Oikawa, S. Shimizu, M. Kawasaki, S. Nagakubo, J. Matsushima, K. Ochiai, T. Okui, 2009. Methane-hydrate Occurrence and Distribution in the Eastern Nankai Trough, Japan: Findings of the Tokai-oki to Kumano-nada Methane-hydrate Drilling Program, in: T. Collett, A. Johnson, C. Knapp, and R. Boswell, eds., Natural gas hydrates— Energy resource potential and associated geologic hazards: AAPG Memoir 89, 228-249.
- Walsh, M.R., S.H. Hancock, S.J. Wilson, S.L. Patil, G.J. Moridis, R. Boswell, T.S. Collett, C.A. Koh, and E.D. Sloan, Preliminary report on the commercial viability of gas production from natural gas hydrates, Energy Economics, 31, 815-823, 2009.
- Walsh, T., Stokes, P., Panda, M., Morahan, T., Greet, D., MacRae, S., Singh, P., and S. Patil, 2008, Characterization and quantification of the methane hydrate resource potential associated with the Barrow Gas Field, Proceedings of the 6<sup>th</sup> International Conference on Gas Hydrates (ICGH 2008), Vancouver, British Columbia.
- Weitemeyer, K., Constable S., Key K., 2006a. Marine EM techniques for gas-hydrate detection and hazard mitigation. The Leading Edge, 25 (5), 629–632.
- Weitemeyer, K.A., S.C. Constable, K.W.Key, and J.P. Behrens, 2006b. First results from a marine controlled source electromagnetic survey to detect gas hydrates offshore Oregon. Geophys. Res. Lett., 33, L03304, doi:10.1029/2005GL024896.
- Weitemeyer, K., and S. Constable, 2010. Mapping shallow seafloor structure with marine CSEM, examples from the Gulf of Mexico gas hydrate experiment. First Break, 6 (28), 97-102.
- White, M., and P. McGrail, 2008. Numerical simulation of methane hydrate production from geologic formations via Carbon Dioxide injection. Soc. Pet. Eng., Offshore Technology Conference, Paper # OTC-19458.
- Wilder, J.W., Moridis, G.J., Wilson, S.J., Kurihara, M., White, M., Masuda, Y., Anderson, B.J., Collett, T.S., Hunter, R.B., Narita, H., Pooladi-Darvish, M., Rose, K., and R. Boswell, 2008.
  An international effort to compare gas hydrate reservoir simulators, Proceedings of the 6<sup>th</sup> International Conference on Gas Hydrates (ICGH 2008), Vancouver, British Columbia.
- Wood, W., Jung, W., 2008, Modeling the extent of Earth's marine methane hydrate cryosphere, Proceedings of the 6th International Conference on Gas Hydrates (ICGH 2008), July 6-10, 2008, Vancouver, British Columbia, Canada, 8 p.
- Wu, N., Yang, S., et al. 2008, Preliminary discussion on gas hydrate reservoir system of Shenhu area, north slope of South China Sea. Proceedings, of the 6th International Conference on Gas Hydrates (ICGH 2008), July 6-10, 2008, Vancouver, British Columbia, Canada, 8 pp.
- Yang, S., Zhang, H., Wu, N., Su, X., Schultheiss, P., Holland, M., Zhang, G., Liang, J., Lu, J., Rose, K., 2008. High concentration of hydrate in disseminated forms obtained in Shenhu area, North Slope of South China Sea., Proceedings, of the 6th International Conference on Gas Hydrates (ICGH 2008), July 6-10, 2008, Vancouver, British Columbia, Canada, 8 pp. <u>https://dspace.library.ubc.ca/bitstream/handle/2429/1178/5701.pdf?sequence=1</u>
- Yezdimer, E., Cummings, P., Chalvo, A., 2002. Extraction of methane from its gas clathrate by carbon dioxide sequestration – determination of the Gibbs Free Energy of gas replacement and molecular simulation. J. Phys. Chem A., 106, 7982-7987.

- Yun, T. S., F. M. Francisca, J. C. Santamarina, and C. Ruppel, 2005. Compressional and shear wave velocities in uncemented sediment containing gas hydrate, Geophys. Res. Lett., 32, L10609, doi:10.1029/2005GL022607.
- Yun, T.S., D. Fratta, and J.C. Santamarina, 2010. Hydrate-bearing sediments from the Krishan-Godavari Basin: physical characterization, pressure core testing, and scaled production monitoring, Energy Fuels 24, 5972-5983. Doi: 10.1021/ef100821t.
- Yun, T. S., C. Lee, J.-S. Lee, J. J. Bahk, and J. C. Santamarina, 2011. A pressure core based characterization of hydrate-bearing sediments in the Ulleung Basin, Sea of Japan (East Sea), J. Geophys. Res., 116, B02204, doi:10.1029/2010JB007468.
- Zhang, H., Yang, S., Wu, N., Su, X, Holland, M., Schultheiss, P., Rose, K., Butler, H., Humphrey, G., and GMGS-1 Science Team, 2007. Successful and surprising results for China's first gas hydrate drilling expedition, US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, 7(3), 6-9.

http://www.netl.doe.gov/technologies/oil-gas/publications/Hydrates/Newsletter/HMNewsFall07.pdf#page=6