AIChE WILEY InterScience® DISCOVER SOMETHING GREAT

Perspective

Natural Gas Hydrates: Recent Advances and Challenges in Energy and Environmental Applications

Carolyn A. Koh and E. Dendy Sloan
Center for Hydrate Research, Colorado School of Mines, Golden, CO 80401

DOI 10.1002/aic.11219

Keywords: gas hydrate, clathrate, natural gas, energy, environment

Introduction

This work shows gas hydrates to be fascinating Euclidean solids, with the potential for significant impact on world energy and the environment. With as much as 164 volumes of gas contained per volume of gas hydrate, these concentrated energy solids are found in nature containing an estimated 700,000 trillion cubic feet of gas world-wide. If only a fraction of this hydrated gas is recoverable, hydrates constitute a substantial unconventional source of energy, as well as significant concern for their impact on climate change and sea-floor stability.

After the discovery of gas hydrates in 1810,[1] which some suggest may have been preceded by Priestly in 1778, it was over a century before these compounds were recognized as industrially significant, rather than merely of scientific curiosity. In 1934, Hammerschmidt[2] was the first to report that gas hydrates rather than ice caused blockages of gas pipelines. Three decades later, researchers began investigating hydrates occurring in nature.[3,4] Since the early 1990s there has been a proliferation of research efforts on the effects of gas hydrates in the broad areas of energy and environmental applications. These broad applications include: production and transportation of gas and oil in subsea flowlines (flow assurance), the potential energy recovery from naturally occurring hydrate deposits, the role of gas hydrates in climate change and sea-floor stability, and the storage of fuel (natural gas or hydrogen) in hydrate materials.

Technological advancements on the control of hydrate formation and decomposition are critical to enabling the economic and ecologically safe production of energy from natural hydrate deposits, storing energy in hydrates, and preventing hydrate blockages in pipelines.[4] The state-of-the-art of hydrate research and development and key challenges for the future are summarized as follows:

- In flow assurance the use of conventional methods such as thermodynamic chemical inhibitor injection is becoming increasingly uneconomic as well as of ecological concern. Therefore, a new approach, known as risk management is being developed in which hydrate formation is no longer avoided. Instead flowline hydrate blockages must be prevented by manipulating the time-dependent properties of hydrate formation and agglomeration.
- Hydrates in nature have about twice the amount of energy compared to the total fossil fuel resource. Hydrates in nature are at the tipping point of turning to a permafrost production paradigm, from an exploration mapping paradigm. The key need for assessing the feasibility of recovering hydrated energy is long-term (6–12 months to several years) permafrost production tests. In the oceans, it may be several years before it is determined whether hydrates are an economically viable resource. International collaboration will be critical in developing the technology associated with exploration/production tests.
- The environmental impact of naturally occurring hydrates is still unknown. Therefore, further research is required to aid our understanding of the effect decomposing natural hydrates may have on global warming and sea-floor stability.
- The use of hydrates to store fuel is an exciting prospect that has potential advantages over other storage materials. However, development of these materials requires an improved understanding of the structure-stability relationships of these guest-host systems.

This article will provide an overview of the structural properties of gas hydrates. Perspectives will be discussed on the state-of-the-art of gas hydrates in flow assurance, energy recovery and production, the environment, and energy storage.

Hydrate Structural Properties

Gas hydrates (also known as clathrate hydrates) are formed when water and small gas molecules (<0.9 nm) come into contact at high-pressures and low-temperatures (e.g., 3–10 MPa and 275–285 K for methane hydrate). Gas hydrates are solid solutions comprised of a lattice of polyhedral water cages (host) which trap small gas molecules (guests), such as methane, carbon dioxide, or propane. The guest molecules stabilize

---

Correspondence concerning this article should be addressed to E. D. Sloan esloan@mines.edu or to C. A. Koh at ckoh@mines.edu.

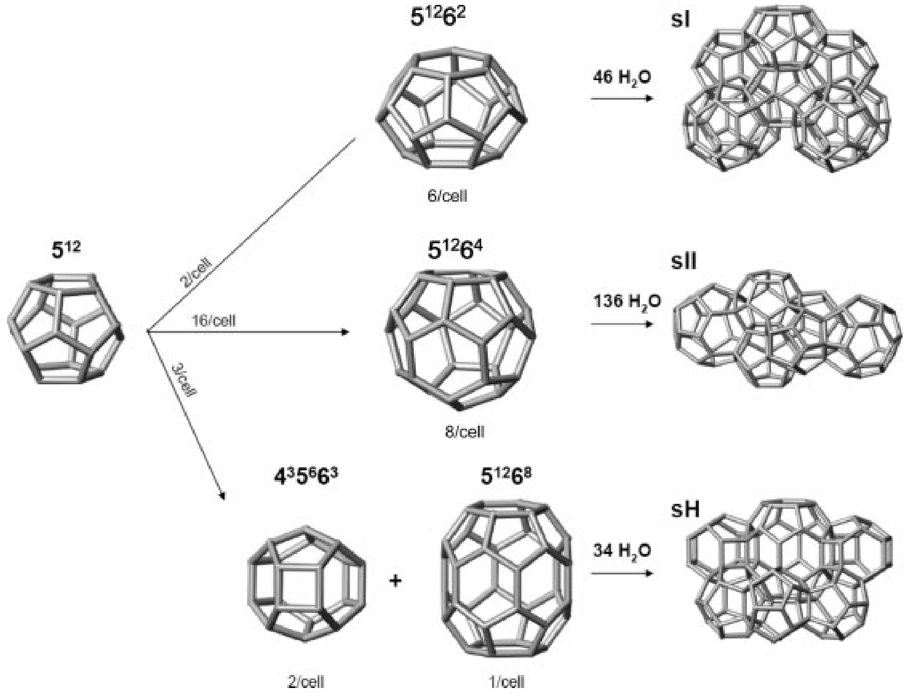

Figure 1. Polyhedral water cavities comprising sI, sII, and sH hydrates.

the hydrate cages by van der Waals interaction forces. There are no chemical bonds between host and guest molecules. Typically, a water cage has a maximum occupancy of one guest molecule at normal pressure conditions (i.e., less than 0.5 GPa at ambient temperature). It is not necessary for all the cages in the gas hydrate structure to be occupied, e.g. methane hydrate is typically formed with only about 96% of the cages (i.e., about 80–90% and 95–99% filling of the small and large cages, respectively) occupied by methane.[4] The cage filling depends on pressure, temperature, and the nature of the guest species. Hence, these structures are often referred to as "non-stoichiometric hydrates".

The three most common gas hydrate structures are sI, sII, and sH hydrate. Both sI and sII hydrates have cubic crystal structures, while sH hydrate has a hexagonal crystal structure (Figure 1). Hydrates of sI and sII contain two different types of water cages, while sH hydrate contains three different types of water cages. The water cages are described by the general notation X^n, where X = the number of sides of a cage face, n = the number of cage faces having these X sides. For example, the 5^{12} pentagonal dodecahedral water cage is comprised of 12 five-membered water rings. Table 1 summarizes the structure and cage types of sI, sII, and sH hydrates.

In general, the type of gas hydrate structure that forms depends on the size of the guest molecule, e.g. CH_4, C_2H_6, and CO_2 all form sI hydrates as single guests, and C_3H_8 forms sII hydrate, while a larger guest molecule such as methylcyclohexane in the presence of CH_4 forms sH hydrate. However, a combination of two simple sI hydrate formers, such as CH_4 and C_2H_6, can result in sII hydrate formation depending on the composition and/or pressure.[5]

Between the time when clathrate hydrates were first discovered in 1810 and 1996, only three main structures were identified. Yet, within the last decade, at least three new clathrate hydrate structures have been discovered, including high pressure (in the GPa range) phases which contain more than one guest in a hydrate cage. For example, nitrogen and oxygen hydrates have been shown to exhibit double occupancy of the large cavity of sII hydrate at higher pressures from neutron diffraction.[6] Similarly, multiple occupancy of water cavities in hydrogen, methane, argon, and xenon hydrates have been confirmed at high-pressure using neutron and X-ray

Table 1. Structure and Cage Types of the Common Clathrate Hydrate Structures

Property	sI	sII	sH
Lattice type	Primitive cubic	Face centered cubic	Hexagonal
Space group	Pm3n	Fd3m	P6/mmm
Unit cell parameters (nm)	a = 1.20	a = 1.70	A = 1.21, c = 1.01
Average cavity radius (nm) [no. cavities per unit cell (cavity type)]	$0.395[2(5^{12})]$(S) $0.433[6(5^{12}6^2)]$(L)	$0.391[16(5^{12})]$(S) $0.473[8(5^{12}6^4)]$(L)	$0.391[3(5^{12})]$(S) $0.406[2(4^35^66^3)]$(S) $0.571[1(5^{12}6^8)]$(L)
Number of water molecules per unit cell	46	136	34
General unit cell formula	$X \cdot 5.75H_2O$	$X \cdot 17H_2O$	$(5X,Y) \cdot 34H_2O$

L= large cage, S = small cage, X,Y= guest molecules diffraction.[7,8] New hydrate structures also include a complex clathrate hydrate structure, containing 1.67 choline hydroxide-tetra-n-propylammonium fluoride· $30.33H_2O$, which was identified in 1999 using single crystal X-ray diffraction.[9] This complex structure consists of alternating stacks of sH and sII hydrates. Other clathrate hydrate structures include the tetragonal structure (space group $P4_2/mmm$) of bromine hydrate[10] and trigonal sT hydrate structure (space group $P321$), formed with dimethyl ether guest molecules.[11]

Gas and Oil Production and Transportation (Flow Assurance)

Gas and oil production and transportation in subsea flow lines is moving to deeper water depths (>6000 ft), hence more extreme temperature and pressure conditions. These conditions are highly favorable for hydrates to form within the flow line, which can result in blockages, and as a consequence economic loss accompanied by ecological and safety risks.[4] The typical method used to prevent hydrate formation within subsea flow lines is to add a thermodynamic inhibitor (such as methanol or monoethylene glycol), which shifts the hydrate formation conditions to lower temperatures and/or higher pressures.[4] Other thermodynamic methods of avoiding hydrate formation include: heating the system to above the hydrate formation conditions, insulating the flow line, separating the free water, and drying the gas.

However, in many deepwater production scenarios, thermodynamic inhibition can become uneconomical and even prohibitive due to the high concentrations of inhibitor required. Therefore, flow assurance is progressively moving away from *avoidance* (thermodynamic control) of hydrate formation toward *risk management* (kinetic control) which may allow hydrates to form, while preventing a hydrate blockage.[4]

Hydrate plugs are not typically formed during normal flow line operation by design. However, plugs can occur due to the following abnormal flow line operations:

1. When the water phase is uninhibited as a result of inhibitor injection failure, dehydrator failure, or the production of excess water,
2. During startup following an emergency shut-in performed due to system failure or adverse weather conditions, such as a hurricane, or
3. When water-wet gas expands rapidly through a valve, orifice or other restriction, resulting in significant Joule-Thomson cooling at under-inhibited conditions.

New technologies currently[4] being developed to control hydrate formation within deepwater flowlines during normal and abnormal operations include:

1. The addition of low dosage hydrate inhibitors (LDHIs) that are effective at concentrations below about 1 wt. %.[12] There are two broad classes of LDHIs: kinetic hydrate inhibitors (KHIs) and antiagglomerants (AAs). KHIs (e.g. poly-N-vinylcaprolactam) operate by delaying nucleation and/or crystal growth. AAs (e.g., quaternary ammonium salts) prevent hydrate crystals from agglomerating to form a blockage, by maintaining the hydrates in the form of a suspended slurry which allows fluid flow to occur unimpeded.
2. "Cold flow", denotes the process, whereby hydrates could be pumped as a slurry through the flow line without the need for chemical inhibitors. Sintef-BP researchers[13] have reported that the addition of water to a flow of dry hydrate results in the formation of further dry hydrate. It is suggested that capillary attractive forces between dry hydrates are low; hence, these particles should not agglomerate to form a plug. This economic technique of risk-management appears promising.
3. Hydrate plug remediation methods include depressurizing the line, injecting a thermodynamic inhibitor, or electrical heating. Plug dissociation occurs radially, and dissociation times can be predicted using a Fourier's Law model (e.g., CSMPlug).[4] However, single-sided plug depressurization can be life-threatening due to the potential for a pressure-driven projectile, and, therefore, safety should be a major consideration. Unlike one-sided dissociation, careful two-sided dissociation normally eliminates the concern of having a projectile in the pipeline.

The thermodynamics of hydrate formation is well-established, with a number of reliable and adequately accurate prediction programs available (e.g., PVTSim, Multiflash, DBR Hydrate, CSMGem). However, the time-dependent processes of hydrate formation and decomposition are still poorly understood. A major challenge is predicting the time required for hydrate crystals to nucleate, grow, agglomerate and eventually form a hydrate plug in a transient, multiphase flow line.

Hydrate nucleation studies are particularly challenging due to the stochastic, microscopic nature of the nucleation process, which involves 10s to 1,000s of molecules. Nucleation and hydrate induction (formation) times are affected by a number of variables, including: apparatus geometry, surface area, water contaminants and history, and the degree of agitation or turbulence. This makes it very difficult to transfer the results from one laboratory or flow loop facility to another. The question of transferability and scale-up to field conditions is even more daunting. Therefore, being able to predict when hydrates will nucleate and grow is a major challenge which is critical to assessing the risk of hydrate formation.

For hydrate formation in liquid hydrocarbon systems, fundamental understanding of the chemistry of the system (water-in-oil and oil-in-water emulsion chemistry, and interfacial interactions) coupled with multiphase flow is needed. The phenomenon of hydrate particle agglomeration is key to determining the risk of hydrate plug formation.

Energy Recovery and Production of Natural Hydrates

Gas hydrates occur naturally within and under permafrost in arctic regions and within ocean sediments.[4] The most recent estimates of the total amount of methane (STP) in these hydrated gas deposits vary from 0.2×10^{15} to 12×10^{16} m^3 (see references listed in 7.1 of [4]). Despite this wide range of estimated gas, all estimates are significant when compared to evaluations of the conventional gas reserve of 0.15×10^{15} m^3 methane (STP).[14] In the United States the mean hydrate value indicates 300 times more hydrated gas than the gas in the total remaining recoverable conventional reserves. Hydrate reservoirs are considered a substantial future energy resource due

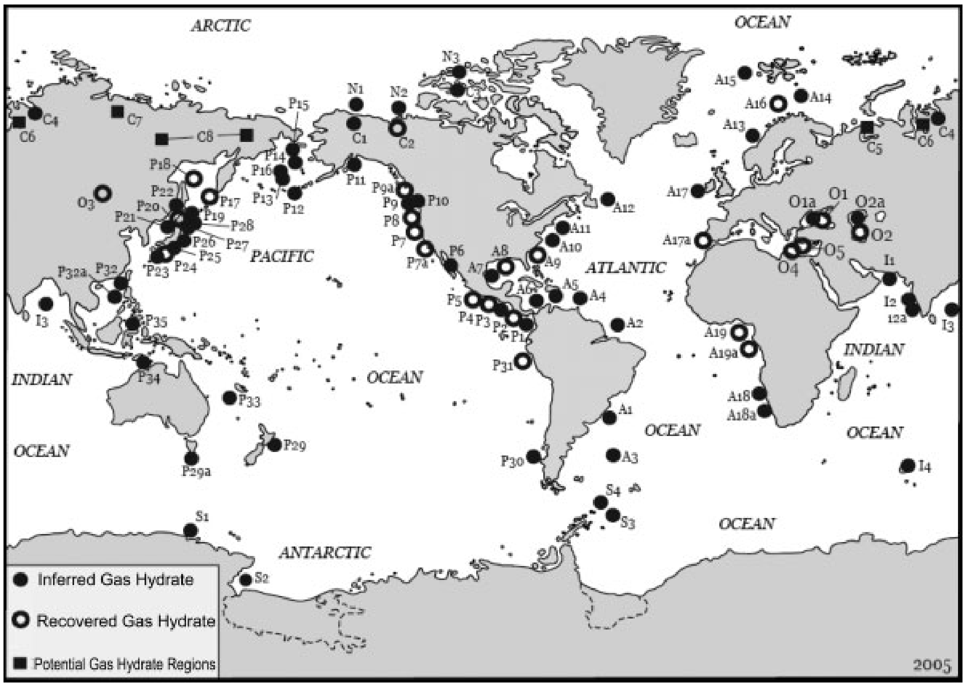

Figure 2. World map showing the locations of natural gas hydrate deposits on-shore (within and beneath permafrost), and off-shore (within a few 100 m of the seafloor on continental slopes, in deep seas and lakes): (courtesy K. Kvenvolden, Nov. 2005).

to the large amount of hydrated gas in these deposits, coupled with hydrates concentrating methane (at STP) by as much as a factor of 164, and requiring less than 15% of the recovered energy for dissociation. However, energy recovery is an engineering challenge.

Three general heuristics[15] for naturally occurring ocean hydrates are:

1. Water depths of 300–800 m (depending on the local bottom water temperature) are sufficient to stabilize the upper hydrate boundary.
2. Biogenic hydrates predominate, with only a few sites comprising thermogenic hydrates (containing CH_4 and higher hydrocarbons), such as in the Gulf of Mexico, Cascadia, and in the Caspian Sea. These thermogenic deposits tend to comprise large accumulations near the sea floor.
3. Hydrates are typically found where organic carbon accumulates rapidly, mainly in continental shelves and enclosed seas. These are biogenic hydrates (containing CH_4, formed from bacterial methanogenesis). (Further details of the mechanism of generation of biogenic and thermogenic gas hydrates can be found in [4]).

Figure 2 shows the on-shore and off-shore locations in which gas hydrates have been confirmed from recovered hydrate cores, or inferred from drillings and associated well log data, and seismic (e.g. bottom simulating reflectors (BSR)) data. BSRs related to hydrates are normally taken as indications of velocity contrasts between the velocity in hydrated sediments and a gas, marked by a sharp decrease in sonic compressional velocity (Vp), and a sharp increase in shear velocity (Vs). However, it should be noted that BSRs are not reliable as sole indicators of hydrates. For example, hydrates were recovered from the Middle America Trench[16] without BSRs present, while in other cases, BSRs existed yet no hydrates were recovered by coring to within 200 m (vertical) of the BSR. Therefore, there is the need for a much better remote prospecting tool than BSR due to reliability issues.[15]

Locations of natural deposits of gas hydrates in Russia include: the Okhotsk Sea (proposed based on seismic and core sampling measurements), the Messoyakha field permafrost deposit which was discovered by the Soviets in 1967,[17] also the Black Sea, Caspian Sea, and Lake Baikal, where evidence for hydrates has been provided from sample recovery or BSR data.[4] Natural gas hydrates have been also identified in core samples (21 out of more than 800 cores) recovered offshore West Africa on the Nigerian continental slope.[18] The hydrate samples were collected during surface geochemical exploration surveys in the deep and ultradeep waters of Nigeria during 1991, 1996, and 1998.

In the Western Hemisphere, hydrate cores were recovered in 1972 from the ARCO-Exxon Northwestern Eileen Well Number Two in West Prudhoe Bay, Alaska. Also in 1972, hydrates were found when drilling an imperial well in Canada's MacKenzie Delta.[4] Using logs from the ARCO-Exxon well, Collett[19] evaluated possible hydrate occurrences in 125 wells in the North Slope of Alaska. The most notable hydrate accumulations in the North Slope of Alaska are in the Prudhoe Bay-Kuparuk River area, which contain around 1 trillion standard cubic meters of gas, which is about twice the volume of conventional gas found in the Prudhoe Bay field.[20] The Prudhoe Bay-Kuparuk accumulation is particularly appealing due to its proximity to highly developed oilfield infrastructure; however, without a gas pipeline to market the gas is currently stranded.

The most systematic evaluation of oceanic hydrate deposits has been performed by the Deep Sea Drilling Project (DSDP), the Ocean Drilling Program (ODP), and currently the Integrated Ocean Drilling Program (IODP).[4,21] Logging while drilling (LWD) was combined with recovered hydrate cores in the deep oceans from both coasts of the U.S. (e.g., Blake-Bahama Ridge, Hydrate Ridge), from the Mid-America Trench off Guatemala, and off the coast of Peru. Significant advances have been made to further understand hydrate system controls, such as lithography and fluid flow by application of techniques, including: LWD, enhanced pressure coring, laboratory-based pressure core imaging, and high pressure physical testing. The hydrate ocean drilling programs have indicated that a combination of high-quality geophysical and geochemical data are key to a successful hydrate exploration and characterization study.

Improved pressure coring techniques, combined with laboratory-based spectroscopic and diffraction measurements, in addition to *in situ* Raman measurements of seafloor hydrates (pioneered by the Monterey Bay Aquarium Research Institute) have advanced the identification and characterization of natural hydrates. Analysis of hydrate deposits at Hydrate Ridge on the Cascadia Margin, off the coast of Oregon showed that sI methane hydrate predominated, with small quantities of other guests, such as H_2S.[4,22] In contrast, sI, sII, and sH gas hydrates were detected in deposits analyzed at Barkley Canyon.[22,23] Barkley Canyon is one of the only thermogenic hydrate sites found on a convergent continental margin, and represents a potential "sweet spot" (i.e., accessible, high concentrations of hydrate) of ocean hydrate accumulations. This site is rich in sea floor hydrates which exist as mounds (up to 8 m in length and 2–3 m in height) penetrating into the ocean sediments. The depths below which these massive seafloor hydrate accumulations protrude into the sediments are currently unknown. The irony of this discovery is that it was made by a fishing trawler which accidentally captured in the nets over 1 ton of gas hydrate. Clearly, in order to discover other ocean "sweet spots", more sophisticated and reliable detection tools need to be developed.

The above hydrate prospecting programs have indicated that the amount of hydrated gas in oceanic deposits is at least two-orders of magnitude greater than that in permafrost regions. Oceanic gas hydrate deposits are typically (with the exception of sweet spots, such as those found in Barkley Canyon) too disperse (average 3.5% of the pore space) to warrant near-term exploration.[4] Conversely, permafrost deposits have significantly higher porosity and higher gas hydrate saturations than most hydrates found in ocean sediments, and have an effective reservoir seal comprising overlying permafrost, making production more viable. As a consequence, pilot drilling has been performed in the permafrost in the Mallik well in Canada (30% gas hydrate saturation[24]), and at Milne Point, Alaska North Slope,[25] and a short-term (five days) production test was performed at the Mallik site (Mallik 2002 at a cost of U.S.$22 million[24]). The successful drilling programs performed at Mallik and Milne Point result from a culmination of several years of research into the geology and geophysics of the areas, and also detailed engineering evaluations. Many suggest the Messoyakha Field in Russia provided proof of long-term production,[17] however, while hydrates likely played a part at Messoyakha, the exact role of hydrates is under some scientific dispute. Longer-term production tests are planned at Mallik, Canada, and Milne Point, Alaska; these tests are required for better assessment of the reservoir production models. Planning for these production tests is being led by the Japanese Oil, Gas, and Metals National Corp. (JOGMEC) in Canada, and by BP/DOE in Alaska.

Clearly, the permafrost hydrate deposits are far less technologically challenging than hydrate accumulations in the ocean sediments. Hence, these permafrost hydrates are being considered first for production tests in the U.S., with the U.S. DOE hydrate program funded at around $12 million/year. However, countries outside the U.S. are actively performing and planning ocean drilling and production tests within the next decade. Specifically, the Japanese have initiated a National Project to drill hydrates in the Nankai Trough, offshore Japan, which includes coring and seismic to assess the resource (Ministry of Economy, Trade and Industry, METI-sponsored project in 1999-2000; Japan National Oil Company, JNOC and Japan Petroleum Exploration Corporation, JPEX studies in 1997–2000). The drilling program in 2003 was funded at $100 million, and drilling in the Sea of Kumano in 2006-7 is budgeted at $68.5 million. Exploitation is planned for 2009, with commercial production planned in 2017. The Indian National Gas Hydrate Program (NGHP) expedition of ocean hydrates has been also initiated. In the 2006 expedition offshore India, over 494 cores were recovered at depths ranging from 952 to 2674 mbsf (meters below sea floor).[26] The cost of this expedition is estimated at $36 million. A production test is planned by the Indian NGHP in 2009. Recently, China has initiated a major hydrate exploration program, and Malaysian and Korean state-owned oil companies have indicated interests in exploring hydrates in their territories.

The technologies for gas production from hydrate deposits need to be further developed and coupled closely with state-of-the-art reservoir numerical models. Recent experimental and modeling studies indicate that hydrate dissociation is heat transfer limited.[4] The methods that can be used to destabilize hydrates for gas production include: heating, depressurization, and chemical inhibitor injection. For example, reservoir simulations of a model test well indicated that depressurization combined with well-heating is the most effective method for producing gas from hydrate deposits.[27] If only depressurization is used, heat must be supplied internally (reservoir rock or boundary) or externally (hot water injection) to sustain the endothermic process of hydrate dissociation.[27] A number of long-term production tests (6–12 months for each test) need to be performed to evaluate production techniques and their combinations.

Given the enormous technological and economic challenges involved in production testing, international collaborations will significantly enhance and fast-track the development of the technologies required to produce gas from permafrost and oceanic deposits. It is not clear whether marine hydrates will be economically viable. This question is central to hydrate development in nature because the amount of marine hydrates surpasses those in the permafrost by several orders of magnitude. The path to marine hydrate development leads through permafrost hydrate development.

Environmental Impact of Gas Hydrates

Methane hydrate has been also considered a potential source for climate change.[3,15] The clathrate gun hypothesis

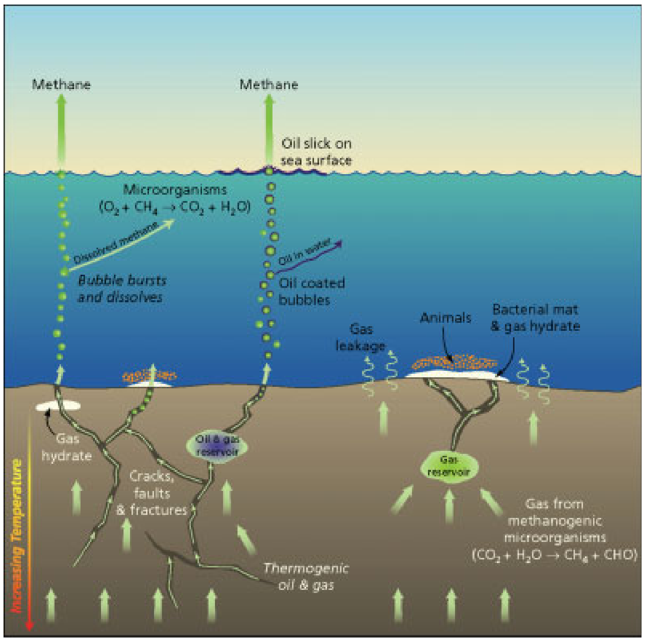

Figure 3. Suggested mechanisms by which methane can be emitted to the atmosphere.[31]

(also known as the "late Quaternary climate change") suggests that methane released from methane hydrate around 15,000 years ago caused immense global warming.[28] However, this hypothesis remains controversial. A recent review by Reeburgh[29] indicates the rate of methane hydrate decomposition is a key missing piece of information central to understanding the methane global budget.

Research expeditions to Hydrate Ridge (e.g., expeditions by ODP, Geomar, and MBARI) have demonstrated that natural seafloor hydrates are significantly dynamic in nature. Similarly, methane hydrates in ocean sediments represent a dynamic reservoir and decomposition of these hydrates may be an important source of methane emissions from convergent margins,[29] and, hence, global warming. A key challenge in assessing the methane hydrate dissociation rates is distinguishing hydrated methane from thermogenic or petroleum-derived methane since this is difficult to perform with isotopic measurements of ^{14}C–CH_4. Direct measurements of hydrate dissociation rates are difficult and so the most viable approach may involve estimating the basal hydrate decomposition rate by development of heat-transfer models.[29] One unique dataset[30] on the dissociation of natural seafloor hydrates at Barkley Canyon gives surface dissolution rates of 22.5 and 33.9 nm/s (depending on the hydrate texture). Assessing the impact of dissociating methane hydrate deposits to climate change requires the geochemical budget, which is a flux or mass balance, to estimate the magnitudes of sources and sinks. Figure 3[31] gives an illustration of suggested mechanisms of methane emissions from dissociating hydrate deposits and leakage from gas and oil reservoirs.

Mitigation strategies for carbon dioxide emissions have been suggested, based on sequestering carbon dioxide in hydrates which would be stored in the ocean, or replacing methane with carbon dioxide during energy production from natural hydrate deposits. These strategies are still under debate and require further investigation. The dissolution rate of carbon dioxide hydrate on the seafloor has been found to be significantly faster than that for methane hydrate due to the higher solubility in water of CO_2 compared to CH_4.[32]

Dissociation of natural hydrates has been also implicated in continental margin sediment instability.[33] When hydrates are destabilized and decompose to water and gas, this transformation can decrease the shear strength in sediments, making the sediments more prone to failure. There have been a number of reports implicating hydrate dissociation in major slumps on continental margins, however, this link remains controversial. These reports are based on BSRs, which remotely detect the presence of gas hydrate in the sediments around the erosion/eruption. For example, seismic data from Blake Bahama Ridge indicates a seafloor erosion/eruption associated with a BSR gas/hydrate boundary.[33]

It is clear that further research is needed to better assess the environmental impacts of hydrate dissociation, since these impacts may include both global climate change and submarine sediment stability, the latter of which can affect subsea industrial exploration and production facilities and infrastructure.

Energy Storage in Gas Hydrates

Energy storage in gas hydrates presents an attractive solution to the transportation of stranded gas in hydrated form or to provide fuel to ships, with hydrate requiring a low-storage space and low-pressures. Methane hydrate has an energy density equivalent to a highly compressed gas, but is less energy dense than liquefied natural gas (LNG). Gudmundsson and Borrehaug[34] proposed to ship natural gas in hydrated form, rather than in LNG tankers, suggesting the economics were favorable. This basic concept has been extended by researchers from Mitsui Shipbuilding in conjunction with the Japanese Maritime Research Institute.[35] The hydrated gas is stored in pellet form at low-temperatures. The stability of these pellets can be enhanced by exploiting the concept of anomalous preservation first reported by Stern and coworkers.[36]

Efforts to develop clathrate hydrate materials for hydrogen storage followed the reports that hydrogen could be stored in pure hydrogen hydrate at high-pressures,[37] and stored at lower pressures by adding THF as a promoter molecule.[38] The key challenge for hydrogen storage in hydrates is to balance the storage capacity with the requirement for mild pressure and temperature conditions for storage. The development of fuel storage materials (both for natural gas and hydrogen) requires an improved understanding of the structure-stability relations of these host-guest systems.

New Paradigms in Gas Hydrate Technology

In all the gas hydrate technological applications, it is clear that the paradigm has shifted from thermodynamics (time-independent properties) to hydrate formation and dissociation kinetics. Improved understanding and control of the kinetics of these processes are key to advancing the technologies required in:

- Maintaining flow in pipelines by assessing the kinetics of hydrate formation, e.g. determining when and where a hydrate plug will occur, or whether the cold flow technology can be reliably implemented.
- Gas recovery from hydrate deposits by assessing the techniques needed to dissociate and release the gas from the deposit.
- Assessing submarine hydrate dissolution rates, and the impact of this dissociation to the environment.

For energy production, it is clear that more investment needs to be made for long term field production tests. Better detection tools are also required since the main BSR technique is often unreliable. As we start to consider energy production from hydrate deposits the impact of gas release from the deposit to the environment needs to be seriously evaluated, as well as the impact of the release technology to the stability of the permafrost or ocean sediments. Improved fundamental understanding of the nucleation, growth and agglomeration processes will enhance the development of flow assurance tools. This is also important to the development of energy storage materials which require effective synthesis and stability technologies.

Acknowledgments

The authors acknowledge support from the CHR Hydrate Consortium (BP, Chevron Energy Technology Company, ConocoPhillips, ExxonMobil, Halliburton, Petrobras, Schlumberger, Shell, Statoil), the US Department of Energy (DE-FG02-05ER46242), National Science Foundation (CTS-0419204), National Oceanic and Atmospheric Administration/University of Alaska-Fairbanks (NA030AR4300104/UAF 06-0097), American Chemical Society-PRF fund (42254-AC2). Thanks also to Dr. K.C. Hester for his help with this work.

Literature Cited

1. Davy H. The Bakerian Lecture. On some of the combinations of oxymuriatic gas and oxygene, and on the chemical relations of these principles to inflammatory bodies. *Philos Trans R Soc London*. 1811;101:1.
2. Hammerschmidt EG. Formation of gas hydrates in natural gas transmission lines. *Ind and Eng Chem*. 1934;26:851.
3. Makogon YF. *Gazov Promst*. Hydrate formation in the gas-bearing beds under permafrost conditions. 1965;5:14; Ginsburg GD. *Hydrogeology of the North Yenisei Region*. 1969;109.
4. Sloan ED, Koh CA. Clathrate hydrates of natural gases. 3rd Edition, Taylor & Francis CRC Press; 2007.
5. Subramanian S, Kini R, Dec S, Sloan E. Annals of the New York Academy of Sciences. Structural transition studies in methane + ethane hydrates using Raman and NMR. in *Proc. Gas Hydrates, Challenges for the Future*. 2000;912:873.
6. Chazallon B, Kuhs WF. In situ structural properties of N_2-, O_2-, and air-clathrates by neutron diffraction. *J. Chem Phys*. 2002;117:308.
7. Loveday JS, Nelmes RJ, Guthrie M, Klug DD, Tse JS. Transition from cage clathrate to filled ice: The structure of methane hydrate III. *Phys Rev Lett*. 2001;87:215501.
8. Hirai H, Tanaka H, Kawamura K, Yamamoto Y, Yagi T. Structural changes in gas hydrates and existence of a filled ice structure of methane hydrate above 40 GPa. *J Phys Chem Solids*. 65,1555 (2004).
9. Udachin KU, Ripmeester JA. A complex clathrate hydrate structure showing bimodal guest hydration. *Nature*. 1999;397:420.
10. Udachin KA, Enright GD, Ratcliffe CI, Ripmeester JA. Structure, stoichiometry, and morphology of bromine hydrate. *J Am Chem Soc*. 1997;119:11481.
11. Udachin KA, Ratcliffe CI, Ripmeester JA. A dense and efficient clathrate hydrate structure with unusual cages. *Angew Chem Int Ed*. 2001;40:1303.
12. Kelland MA. History of the development of low dosage hydrate inhibitors. *Energy & Fuels*. 2006;20:825.
13. Wolden M, Lund A, Oza N, Makogon T, Argo CB, Larsen R. Cold flow black oil slurry transport of suspended hydrate and wax solids. in Proc. *Fifth International Conference on Gas Hydrates*. T. Austvik, ed. Trondheim, Norway. June 13–16, 2006;1101. Paper 4002.
14. Radler M. World crude and natural gas reserves rebound in 2000. *Oil and Gas J*. 2000;98(51):121.
15. Tréhu AM, Ruppel C, Holland M, Dickens GR, Torres ME, Collett TS, Goldberg DS, Riedel M, Schultheiss P. Gas hydrates in marine sediments – lessons from scientific ocean drilling. *Oceanography*. 2006;19:124.
16. Finley P, Krason J. *Geological Evolution and Analysis of Confirmed or Suspected Gas Hydrate Localities: Basin Analysis, Formation and Stability of Gas Hydrates in the Middle America Trench*. 1986. U.S. Dept of Energy. DOE/MC/21181–1950: Vol 9.
17. Makogon YF. *Hydrates of Hydrocarbons*. PennWell Books: Tulsa, OK; 1997.
18. Brooks JM, Bryant WR, Bernard BB, Cameron NR. *Gas Hydrates: Challenges for the Future*. Annals New York Academy of Sciences. The nature of gas hydrates on the Nigerian continental slope. 2000;912:76.
19. Collett TS. *Detection and Evaluation of Natural Gas Hydrates from Well Logs*. Prudhoe Bay, AK: University of Alaska; 1983. M.S. Thesis.
20. Collett TS. Energy resource potential of natural gas hydrates. *AAPG Bulletin*. 2002;86:1971–1992.
21. Paull CK, Lorenson TD, Boroworski WS, Ussler W, Olsen K, Rodriguez NM, Wehner H. Isotopic composition of CH_4, CO_2 species, and sedimentary organic matter within samples from the Blake Ridge: gas source implications. *Proc Ocean Drill Program, Sci Results*. 2000;164:67.
22. Hester KC. Spectroscopic Investigations In *Clathrate Hydrates in Both the Field and Laboratory*. Colorado School of Mines, Golden, CO; 2007. PhD Thesis.
23. Lu H, Seo Y, Lee J, Moudrakovski I, Ripmeester JA, Chapman NR, Gardner RB, Pohlman, J. Complex gas hydrate from the Cascadia Margin. *Nature*. 2007; 445: 303.
24. Colwell FS, Nunoura T, Delwiche MF, Boyd S, Bolton R, Reed DW, Takai K, Lehman RM, Horikoshi K, Dlias

DA, Phelps TJ. In: Dallimore SR, Collett TS, eds. Scientific Results from the Mallik 2002 Gas Hydrate Production Research Well Program. Mackenzie Delta, Northwest Territories, Canada. Geological Survey of Canada Bulletin 585, including CD. 2005; p 102.

25. Vendl L, Weeks M, Digert S, Hunter B, Collett T, Winters B, Waite W, Lorenson T, Agena W, Lee M, Miller J, Boswell R, Rose K, Rosenbaum E, Torres M, Colwell R, Hancock S, Inks T, Wilson S. *Fire in the Ice*. U.S. Dept of Energy, Office of Fossil Energy, NETL. 2007;1. http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/newsletter/newsletter.htm. Winter 2007.
26. Collett T, Boswell R. personal communication. Aug. 31, 2006.
27. Gupta A. *Methane Hydrate Dissociation Experiments and Modeling: The Role of Heat Transfer and Reaction Kinetics*. Colorado School of Mines, Golden, CO; 2007. Ph.D. Thesis.
28. Kennett JP, Cannariato KG, Hendy IL, Behl RJ. Methane Hydrates in Quaternary Climate Change: The Clathrate Gun Hypothesis. *Special Publications Series*, AGU. 2002; vol. 54.
29. Reeburgh WS. Oceanic methane biogeochemistry. *Chemical Reviews*. 2007;107:486.
30. Peltzer E. MBARI. Personal Communication. 2007.
31. Whelan J. Woods Hole Oceanographic Institution. personal communication; March 22, 2007.
32. Rehder G, Kirby SH, Durhan WB, Stern LA, Peltzer ET, Pinkston J, Brewer PG. Dissolution rates of pure methane hydrate and carbon-dioxide hydrate in undersaturated seawater at 1000-m depth. *Geochim Cosmochim Acta*. 2003;68:285. doi:10.1016/j.gca.2003.07.001.
33. Paull CK, Dillon WP. eds. Natural Gas Hydrates: Occurrence, Distribution and Detection, Geophysical Monograph Series, Am. Geophysical Union, Washington DC; 2001.
34. Gudmundsson JS, Borrehaug A. In Proc. Second International Conference on Gas Hydrates; Frozen hydrate for transport of natural gas. June 2–6. Monfort JP. ed. Toulouse, France; 1996:415.
35. Takaoki T, Hirai K, Kamei M, Kanda H. In Proc. Fifth International Conference on Natural Gas Hydrates, Study of natural gas hydrate (NGH) carriers. June 13–16. Trondheim, Norway. Paper 4021. 2005.
36. Stern LA, Circone S, Kirby SH, Durham WB. Anomalous preservation of pure methane hydrate at 1 atm. *J Phys Chem*. 2001;105:1756.
37. Mao WL, Mao HK, Goncharov AF, Struzhkin VV, Guo QZ, Hu JZ, Shu JF, Hemley RJ, Somayazulu M, Zhao YS. Hydrogen clusters in clathrate hydrate. *Science*. 2002;297:2247.
38. Florusse LJ, Peters CJ, Schoonman J, Hester KC, Koh CA, Dec SF, Marsh KN, Sloan ED. Stable low-pressure hydrogen clusters stored in a binary clathrate hydrate. *Science*. 2004;306:469.