

Gas Hydrates: A Cleaner Source of Energy and Opportunity for Innovative Technologies

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Abstract—The global energy system is characterized by a gradual de-carbonization and move to cleaner burning technologies: from wood to coal to oil and to natural gas. A final destination characterized by the term “hydrogen economy” is desired. Gas hydrate found in the earth’s crust is considered a source of natural gas that is essentially 100% methane (CH₄) gas. Natural gas hydrate estimates worldwide range from 10,000 to 40,000 trillion cubic meters (TCM). Efforts are underway to exploit this resource. These methane hydrates in the earth’s crust also have the potential to be a significant factor in global climate change. Moreover, gas hydrates offer opportunities for the development of innovative technologies (separation of CO₂ from CO₂/N₂ and CO₂/H₂ mixtures, CO₂ sequestration, natural gas transportation and storage and H₂ storage). In this work we assess the progress towards exploitation of gas hydrates as a resource for methane (cleaner energy) and summarize the state of the art with respect to the role of gas hydrates in the development of innovative technologies.

Key words: Gas Hydrate, Energy Source, Natural Gas Transport/Storage, Hydrogen Storage, Gas Separation

INTRODUCTION

Prior to industrial revolution the world’s population was approximately 1 billion and the energy needs were satisfied primarily by using wood. Another supply of power was of course the muscles of people and horses or oxen. The increased energy needs due to rapid industrialization were met initially by using coal and later oil and natural gas [Bacher, 2002; Hall et al., 2003]. Various conversion factors are used to express the amount of carbon emitted per unit energy of different fuels. These are 27 kgC/GJ of coal, 21 kgC/GJ for oil and 15 kgC/GJ for natural gas [Gough et al., 2002]. Thus, our global energy system is characterized by a gradual de-carbonization since it moved from wood to coal to oil and to natural gas. This is a positive trend considering that the production and use of energy lead to local, regional and global environmental problems [Bacher, 2002]. While local and regional problems are amenable to solutions that have already been implemented, particularly in wealthy nations, the global problem known as “greenhouse effect” is still open.

The atmosphere’s near transparency to visible radiation and strong trapping of infrared energy is often referred to as the greenhouse effect. The average temperature on the surface of the earth would be 33 K lower if the greenhouse effect was absent. While this phenomenon appears to be beneficial for life, human activities during the past 150 years have led to the concern that the global climate will undergo significant change. It is known that the concentration of CO₂ in the atmosphere has increased from 280 to 350 ppmv since the industrial revolution. Methane’s concentration has also increased from 0.8 to 1.72 ppmv since the industrial revolution [Taylor, 1991]. The continuous increase in the concentration of these gases is expected to enable the atmosphere to trap more infrared energy and

subsequently re-radiate it, causing global warming near the earth’s surface. Energy-related activities are by far the largest source of greenhouse gas emissions. The annual global emission of carbon from the consumption of fossil fuels is 5 Gt or 5×10^{12} kg [Shindo and Komiyama, 1994]. In another study the annual global CO₂ emissions are considered to be equivalent to 22 Gt of carbon [Herzog et al., 1997]. It is noted that fossil fuels (oil, natural gas and coal) supply 80% of the world’s energy needs. Obviously, preventing catastrophic climate change is essentially an energy challenge [Loiseaux, 2002; Wirth et al., 2003].

Ultimately, what is sought is a clean source of energy that will replace hydrocarbons and will alleviate the environmental problem associated with emissions. Hydrogen is a clean burning fuel that does not produce carbon dioxide. This has led to the concept of a hydrogen economy and hydrogen being the last stop in the pathway from wood to coal to natural gas to hydrogen. However, before hydrogen can be used as fuel it must first be extracted from other compounds (water, coal, natural gas). Unfortunately, the extraction process generates emissions.

Four broad options are typically considered for reducing anthropogenic emissions of greenhouse gases and CO₂ in particular (carbon management): (a) improvement in energy efficiency in power generation or in end-use; (b) switching to fuels containing less carbon (e.g. natural gas or coal); (c) substitution of electricity from carbon-free sources (e.g. renewable or nuclear); (d) capture and storage of carbon dioxide. Realistically, it is unlikely that any single approach would be used alone. A combination of these four options will most likely be adopted to meet particular needs. It is also noted that by using CO₂ removal and storage technology it is conceivable that hydrogen (a clean energy carrier or fuel) can be produced almost free of emissions from fossil fuels. The idea is illustrated in Fig. 1. The advantage of removing carbon dioxide from flue gases is that it will enable society to continue using fossil fuels and enjoy the standard of living that was attained over the years while minimiz-

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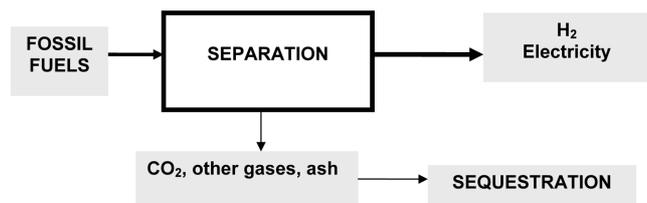


Fig. 1. Generation of H₂ and electricity with capture and storage of CO₂ (sequestration).

ing the impact on the environment.

Conventional fossil fuel resources are finite, and hence an active search for new sources is underway. One such source is the vast quantity of methane gas hydrate found in the earth [Kvenvolden, 1999, 2000; Bacher, 2002]. Russian researchers were the first to confirm that methane gas hydrates were formed naturally within and below the permafrost zone and in sub sea sediments [Makogon et al., 1972; Suess et al., 1999; Kvenvolden 1999, 2000]. Samples recovered from the earth during Leg 164 of the Ocean Drilling Program were decomposed into mostly methane (99.9% volume) plus some C₂ to C₅ hydrocarbons [Dickens et al., 1997; Holbrook et al., 1996]. In addition, samples from the Mallik 2L-38 gas hydrate research well showed 98-100% methane. The balance in some of the samples was propane and carbon dioxide [Tulk et al., 1999]. Bottom simulated reflectors (BSR) on seismic reflection profiles have provided a means for identifying hydrate reservoirs. However, this has proven to be a not so robust indicator [Paull, 1999].

While this methane also known as frozen energy represents a future resource it may also be a source of methane (a greenhouse gas) in the atmosphere if it is released in an uncontrolled manner (runaway greenhouse effect). The objective of this paper is to briefly review gas hydrates and then describe their potential as a new energy source and a factor in global climate change. Furthermore, gas hydrates are considered an opportunity to develop innovative clean energy technologies [Englezos, 1993; Mori, 2003]. The latter include methods for natural gas transport and storage; storage of hydrogen; CO₂ sequestration and CO₂/N₂ and CO₂/H₂ separation technologies. Thus, the status of these technologies will also be discussed. Finally, some aspects of the role of gas hydrates in ocean disposal of CO₂ or geological sequestration will also be covered.

GAS HYDRATES

Gas hydrates are nonstoichiometric crystalline inclusion compounds formed by water and a number of small molecules at suitable temperature and pressure conditions. For example, water can be mixed with methane or carbon dioxide and form hydrate crystals. Pressure-temperature formation conditions for hydrate formation from these two gases and binary mixtures are shown in Fig. 2. Such a figure is known as a partial phase diagram. Seo and Lee [2001a] have also studied the methane-carbon dioxide-water ternary system and reported hydrate formation conditions.

Traditionally, gas hydrates have been a problem in the oil and gas industry because they may block transportation lines. Gas hydrates may also be a hazard during oil and gas drilling and a geohazard [Sloan, 1998; Kvenvolden, 1993, 1999]. The gas hydrate crystal

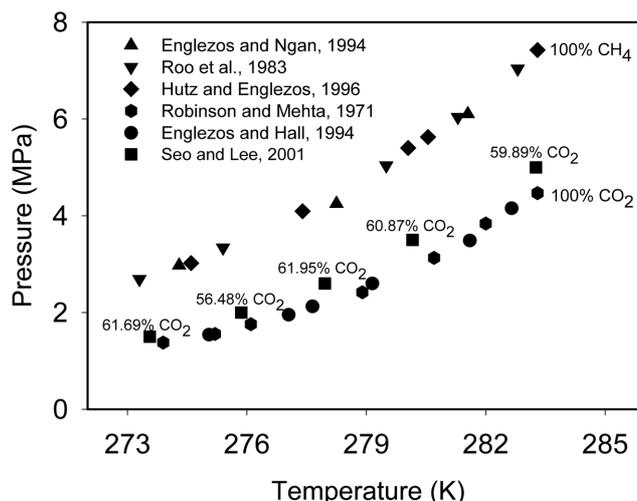


Fig. 2. Experimental conditions for methane and carbon dioxide hydrate formation.

lattice consists of polyhedral water cavities that are stabilized by the inclusion of molecules like natural gas components [Davidson, 1973; Makogon, 1981; Berez and Balla-Achs, 1983; Englezos, 1993; Ripmeester et al., 1994; Sloan, 1998, 2003a, b; Ripmeester, 2000]. The interaction between the gas (guest) and water (host) molecules is due to weak van der Waals forces. Chlorine hydrate was the first hydrate that was formed in the laboratory by Sir Humphry Davy in 1810. Faraday confirmed Davy's experiments in 1823. Hydrates crystallize in two cubic structures known as I and II and a hexagonal one known as structure H [Ripmeester et al., 1987; Ripmeester and Ratcliffe, 1990]. Structure H requires the presence of a small guest (like methane) and a large molecule guest substance (LMGS) as it is called [Tsuji et al., 2004]. It should be noted that structure investigations are ongoing since new but rather rare structures continue to be reported [Seo et al., 2003]. There is also an interplay between structure and kinetics or structure and hydrate forming gas composition [Schicks and Ripmeester, 2004].

The basic cavity formed by water molecules through hydrogen bonding is the pentagonal dodecahedron (5^{12}). A unit cell of structure I hydrate has 46 water molecules forming two (5^{12}) and six ($5^{12}6^2$) cavities. The latter is the tetrakaidecahedron, a polyhedron with 12 pentagonal and 2 hexagonal faces ($5^{12}6^2$). Methane, ethane and carbon dioxide form structure I hydrate. The unit cell of structure II has 136 water molecules forming 16 (5^{12}) and eight ($5^{12}6^4$) cavities. The latter polyhedron has 12 pentagonal and 4 hexagonal faces. Propane, Ar, Kr, O₂ and N₂ form structure II crystals [Kuhns et al., 1997; Schicks and Ripmeester, 2004]. Structure H hydrate has two more cavities in addition to the 5^{12} one. The medium cavity is the irregular dodecahedron, which has three-square faces, six-pentagonal faces and three-hexagonal faces ($4^35^66^3$). The largest cavity has 12 pentagonal faces and six hexagonal faces ($5^{12}6^8$). Due to the bigger cavity size, approximately 24 compounds have been identified as the guest molecule. A unit cell of structure H has 34 water molecules and 3-small (5^{12}), 2-medium ($4^35^66^3$) and 1-large ($5^{12}6^8$) cavities.

The ratio of the number of water to the number of gas molecules (*hydration number*) is a function of the formation conditions and several values ranging from 5.77 to 7.4 have been reported for

methane hydrate [van der Waals and Platteeuw, 1959]. Gas hydrate formation is an exothermic process. The enthalpy change is approximately 64 kJ/mole of hydrate formed or 8.8 kJ per mole of water assuming the following hydrate formula: $\text{CH}_4 \cdot 7.2\text{H}_2\text{O}$. The enthalpy of fusion of water is 6.01 kJ/mol. The enthalpy change of 56.84 kJ/mol for the formula $\text{CH}_4 \cdot 6.0\text{H}_2\text{O}$ was also reported [Kang et al., 2001b]. The CO_2 molecules occupy primarily the large cavities and some small ones [Udachin et al., 2001; Ripmeester and Ratcliffe, 1990]. The hydration number ranges from 5.8 to 7.68 [Uchida, 1997]. The enthalpy change of 65.2 kJ/mol for the formula $\text{CO}_2 \cdot 7.23\text{H}_2\text{O}$ was reported by Kang et al. [2001a].

METHANE GAS HYDRATE IN THE EARTH

Methane gas hydrates in the earth are located within the pores of sediment within or below permafrost or below the ocean floor. Methane hydrate may exist within a zone known as the theoretical methane hydrate stability zone (TMHSZ). One may convert the pressure-temperature (equilibrium) diagram for methane from Fig. 2 to a temperature-depth diagram. This diagram is then superimposed on the geothermal gradient, i.e., the temperature profile $T(X, t)$ in a particular location to obtain the TMHSZ. Such diagrams are shown in Figs. 3 and 4 where the dotted line is the geothermal gradient and the dotted-dashed line is the equilibrium line. The two lines in Figs. 3 and 4 define the upper (X_U) and the lower (X_L) bounds of the methane hydrate stability zone. It should be kept in mind that

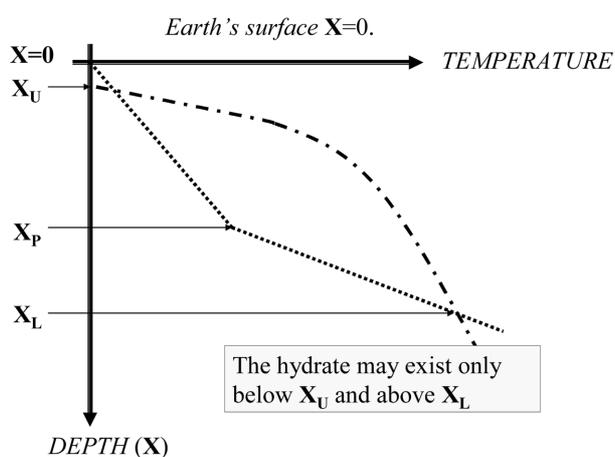


Fig. 3. Theoretical methane hydrate stability zone (TMHSZ) in permafrost.

the T-X profile varies from location to location, whereas the T-X curve corresponding to methane hydrate equilibrium is affected by the presence of salts in the pore waters and the porous medium. These effects can be calculated if we know the salt type and concentration and the pore size.

Methane hydrate may form if sufficient amounts of gas and water exist at a point whose the T-X coordinates are between the upper (X_U) and lower (X_L) bounds of the TMHSZ. It is noted that in Fig. 3 the temperature profile changes slope at X_p because it corresponds to a permafrost layer that is assumed to extend from the earth's surface down to point X_p . Below X_p the properties are those of sediment and the temperature drops at a smaller rate with depth.

1. Resource Assessment

It is noted that 1 m^3 of methane hydrate will release approximately 170 m^3 of methane gas at Standard Temperature and Pressure (STP) conditions or 0.55 m^3 of methane gas at 30 MPa. Thus, one recognizes immediately the potential of methane hydrate in the earth to become a source of natural gas. Methane hydrates contain more methane per unit volume than do rocks in conventional natural gas deposits [MacDonald, 1983]. It should also be kept in mind that approximately 0.8 m^3 of water are also released when 1 m^3 of methane hydrate dissociates.

Estimates of the amount of *in-situ* gas hydrates vary considerably [Ginsburg and Soloviev, 1998]. A consensus value of $20.5 \times 10^{15} \text{ m}^3$ or 21,000 Trillion cubic meters (TCM) of methane has emerged [Sloan, 1998, 2003b; Kerr, 2004]. However, any value between 10,000 and 40,000 TCM is considered acceptable. Any estimate

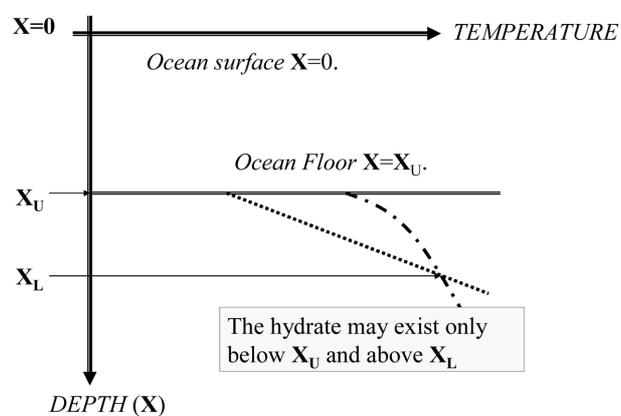


Fig. 4. Theoretical methane hydrate stability zone (TMHSZ) below ocean floor.

Table 1. Natural gas hydrate resource estimates and conventional natural gas reserves

| Country or region | Minimum estimate of natural gas hydrate (TCM) | Maximum estimate of natural gas hydrate (TCM) | Mean estimate of natural gas hydrate (TCM) | Known conventional natural gas reserves (TCM) |
|-------------------------------------|---|---|--|---|
| Canada ^(a) | 25 | 730 | | 11 |
| US ^(b) | - | - | 8,500 | 5-6 |
| China & Central Asia ^(c) | - | - | 430 | 10 |
| Japan ^(d) | 7.4 | - | - | - |
| World | 10,000 | 40,000 | 20,500 | 370 |

(a) Scott Dallimore, Natural Resources Canada, Personal communication, April 2004; (b) Kleinberg and Brewer, 2001; (c) Sloan, 2003b; (d) Ryo Ohmura, AIST, Hokkaido, Japan, personal communication, April 2004.

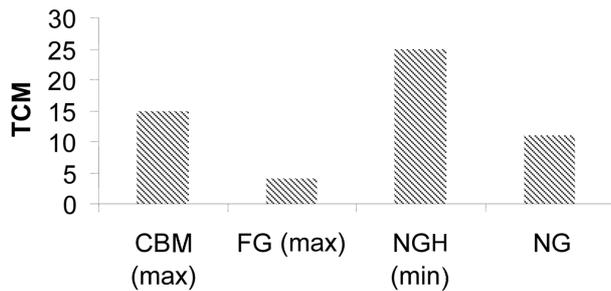


Fig. 5. Unconventional gas resources and conventional gas reserves in Canada.

should be viewed with extreme caution due to the porous nature of the hydrate. Hydrates have the tendency to occlude significant amounts of water and thus the amount of water converted to hydrate is significantly overestimated [Englezos, 1996]. Table 1 shows estimates of natural gas hydrates and known conventional natural gas reserves. It is believed that 1 TCM of natural gas from hydrate will be made available in US over the next 25 years. In Japan recovery of methane from hydrate is expected to begin in 2017. Fig. 5 pertains to Canada. It shows a comparison of the minimum amount of natural gas as gas hydrate, the conventional gas reserves, the amount of natural gas in coal bed methane (CBM) and in frontier gas (deep offshore and in Arctic islands). Finally, it is estimated that there are about 370 TCM of conventional natural gas available in the world. The annual world consumption of natural gas is 2.4 TCM. Natural gas hydrates are therefore considered to be a huge energy resource.

It is also noted that the energy density of gas hydrate is 10 times greater than CBM and 2-5 times greater than that of conventional natural gas. The energy density is the volume of CH_4 at standard conditions per volume of sediment. Moreover, while conventional fossil fuel resources are not evenly distributed gas hydrates are found everywhere on the planet [Kleinberg and Brewer, 2001]. *Whether these methane hydrates are a recoverable reserve or an expected resource remains to be resolved.* Finally, this is exactly the methane that is linked to past and future global climate changes. This aspect will be discussed later.

2. Methane Hydrate Energy Recovery

BeMent et al. [1998] discussed several technical issues that need to be resolved before production could begin. For example, one should know the spatial distribution of hydrate within a reservoir and be able to deal with water production and disposal. Obviously, sufficient gas either as a hydrate and/or trapped as free gas in a conventional reservoir beneath a seal of a hydrate bearing sediment should exist. Kvenvolden [1999] also discussed the difficulties in recovering gas from hydrates. The qualitative methane hydrate partial phase diagram seen in Fig. 6 shows that methane gas hydrate may decompose to methane gas and water by pressure reduction or thermal stimulation. Also, injection of inhibitors like methanol, glycols or electrolyte solutions shifts the phase boundary to the left and thus offers another possibility for hydrate decomposition. Based on experience from oil and gas reservoirs and knowledge of the methane hydrate partial phase diagram the following three conceptual/laboratory tested models have emerged [Sloan, 1998].

(a) *Thermal stimulation*: The objective is to raise the temperature

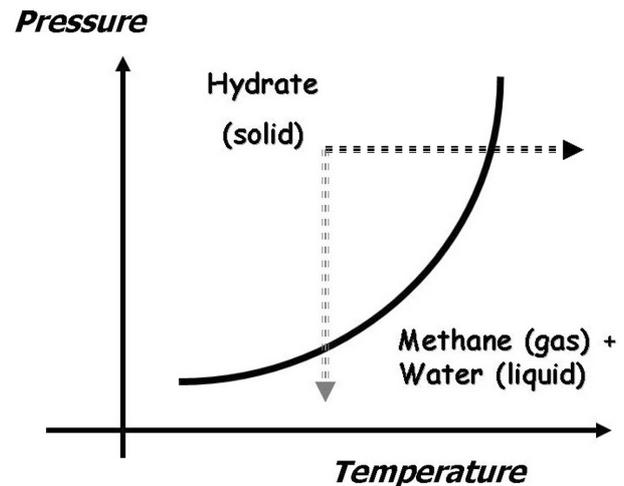


Fig. 6. Illustration of hydrate recovery methods on the partial phase diagram.

by steam injection to a level sufficient for hydrate to decompose. Large heat inputs are required.

(b) *Depressurization*: Pressure reduction that enables hydrate decomposition.

(c) *Injection of inhibitors* (methanol and/or electrolytes): Injection of inhibitors alters the methane hydrate phase diagram, i.e., hydrate equilibrium curve shifts to higher pressures.

The performance of the methods and the economics will depend on local reservoir conditions. For example, a hydrate reservoir must have high in-situ *permeability* or be located above a free gas zone or near geothermal aquifers. It is noted that hydrate decomposition is an endothermic process and hence rapid decomposition could cause such a temperature drop that would allow water from the decomposing hydrate to form ice. In this case, decomposition will practically stop. Water disposal is another consideration since hydrate dissociation generates 0.8 m^3 of water from 1 m^3 of hydrate.

Based on information from Makogon's extensive work, Sloan reviewed the history surrounding the gas recovery from the Messoyakha gas hydrate field [Sloan, 1998]. This field in Siberia is believed to be the only example up to date of methane recovery from the decomposition of in situ hydrates. The production was based on hydrate inhibitor injection. It is estimated that about 36% of the gas recovered from this field came from hydrate decomposition. It should be noted, however, that the data from this reservoir have been viewed with caution. Hyndman and Dallimore [2001] discussed recovery from hydrates and focused on two Canadian study areas (Arctic and Offshore western Canada). Finally, it is noted that addition of CO_2 to convert methane hydrate to CO_2 hydrate has been proposed and is being investigated [Hirohama et al., 1996; Lee et al., 2003].

A gas hydrate reservoir simulation model is a suitable tool to evaluate gas recovery schemes. This model should incorporate the intrinsic rate of dissociation together with heat and mass transfer phenomena relevant to a particular system as well as the sediment and hydrate reservoir properties. Such a comprehensive reservoir simulation model will facilitate the assessment of the bounds of the energy

efficiency of a gas recovery process. However, such a simulator is not available yet in spite of considerable progress [Masuda et al., 2002; Sung et al., 2002; Moridis, 2003, 2004; Hong et al., 2003; Pooladi-Darvish, 2004; Pooladi-Darvish and Hong, 2004].

The development of hydrate resources is believed to follow the technology development roadmap of coal bed methane or other resources [Hyndman and Dallimore, 2001]. It took about 30 years to achieve commercial production from coal bed methane [Kerr, 2004]. More importantly, the significance experience has been gained from the fact that a 1,150-m deep gas hydrate research well known as JAPEX/JNOC/GSC Mallik 2L-38 was completed in the Mackenzie Delta, Northwest Territories of Canada. This was a collaborative effort from Canada, Japan and United States. This scientific effort is well documented in a volume produced by the Geological Survey of Canada [Dallimore et al., 1999, 2002]. The results obtained from the Mallik drilling program indicated the occurrence of concentrated hydrate accumulations. Extrapolations indicated that 0.17 trillion standard m³ of gas may be present. Simulation results for Mallik indicated that the amount of methane released from the dissociating hydrate deposits is sensitive to the hydrate saturation, the initial temperature, the specific enthalpy, and the flow rate of the circulating fluids [Moridis, 2004]. In addition, the reservoir properties were characterized as favorable for production. Thus, these results are rather optimistic as opposed to those from the Ocean Drilling Program's legs 146 and 164 off the coast of Vancouver Island and North Carolina respectively. Three observation wells as well as a production well have already been completed. Gas was continuously produced from a hydrate reservoir that was thermally stimulated [Kerr, 2004]. Experience and data from the Mallik project fuels the optimism of the Japanese to begin exploiting Gas hydrates in the Nankai trough area (off southeast Japan) around 2017.

3. Methane Hydrate and Global Climate Change

Although the physical processes involved in the phenomenon known as *greenhouse effect* are well validated, the anticipated global temperature rise cannot be easily estimated. However, annual temperature rises of 0.006 °C (*low-impact* global warming scenario), 0.03 °C (*moderate* scenario) and 0.08 °C (*catastrophic* scenario) were proposed [Schneider, 1990]. If this warming causes decomposition of the earth's hydrates, then the "runaway" greenhouse effect (RGE) shown in Fig. 7 is possible to occur. Hatzikiriakos and Englezos [1993] assessed the possibility of the above RGE. It was

found that under the catastrophic scenario, the temperature at the top of a typical methane hydrate zone will begin to rise within the next 100 years. The results also indicated that sub-oceanic hydrates would remain stable within the next 1,000 years.

It is believed that decomposition of sub-oceanic and continental hydrates could have triggered an RGE and thus contributed to the rapid warming at the end of the last glaciation 13,500 years ago [Nisbet, 1992]. Moreover, there is evidence that the temperature in the deep ocean increased by about 6 °C 55.5 millions of years ago [Zachos et al., 1993; Dickens et al., 1997; Simpson, 2000]. This phenomenon is known as *latest Paleocene thermal maximum* [Kerr, 1997]. Characterization of carbonate and organic matter deposited during the *latest Paleocene thermal maximum* revealed that a large influx of ¹²C occurred that resulted in 0.25% drop in the ¹³C values. The relative compositional imbalance is known as a *carbon isotope excursion* and lasted approximately 2 × 10⁵ years [Suess et al., 1999; Dickens et al., 1997]. It was suggested that submarine seismicity, volcanism or simple gravitational slumping induced catastrophic slope failure on continental margins containing methane hydrate reservoirs [Bains et al., 1999]. Based on mass balance calculations it was hypothesized that the source of the lighter carbon was methane hydrate that decomposed [Dickens et al., 1995]. Katz et al. [1999] suggested that the Blake Nose east of the Florida coast is the site where most of the methane release took place.

GAS HYDRATES AND THE SOLUTION OF THE CO₂ EMISSIONS PROBLEM

There are a variety of technologies for CO₂ capture and the largest portion of the cost of a capture and storage sequestration scheme is due to CO₂ separation and compression [Herzog et al., 1997; McKee, 2002; Chakravarti et al., 2001]. The fact that most power plants use air instead of oxygen results in flue gases with relatively small amount of CO₂ (15-19 mol%) and significant amount of N₂. This makes it difficult and expensive to capture CO₂ as a concentrated stream, which is required in most storage, conversion and reuse applications [Klara and Shrivastava, 2002]. Gas hydrate formation is the basis for CO₂ separation from flue gases and for CO₂/H₂ separation. It is noted that gas hydrates are also a basis for removing chlorinated hydrocarbons from aqueous solutions [Seo and Lee, 2001b], removing H₂S from gas mixtures [Yamamoto et al., 2003] and for concentrating aqueous effluents [Gaarder and Englezos, 1995; Ngan and Englezos, 1996].

1. CO₂ Separation from Flue Gases

Kang and Lee [2000] proposed a hydrate-based crystallization process that can recover 99 mol% of CO₂ from the flue gas. The flue gas from a power plant is fed to a commercial desulphurization plant for removal of SO_x. The pretreated flue gas is passed through the first hydrator in which carbon dioxide is separated from nitrogen. The hydrate slurry is then decomposed in a dissociator. The gas from the dissociator is compressed and sent to second hydrator and dissociator and then finally through the third hydrator and dissociator. Kang et al. [2001a] reported equilibrium hydrate formation data for a mixture of carbon dioxide and nitrogen with varying ratios of each. Such data are useful for the design of the separation process. Kang et al. [2001b] reported the *enthalpy of dissociation* for carbon dioxide and nitrogen hydrates. They used a calorimetric tech-

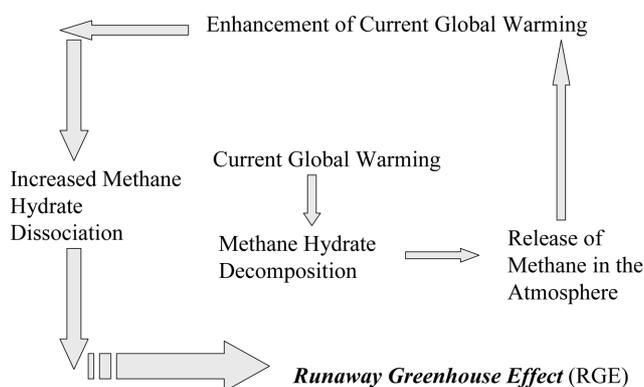


Fig. 7. Schematic of a runaway greenhouse effect.

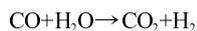
nique to measure the enthalpy of dissociation of hydrates. The enthalpies of dissociation reported were for CO₂ (65.2±1.0 kJ/mol of CO₂ hydrate) and for N₂ (65.8±1.0 kJ/mol of N₂ hydrate) at 273.7 K and 0.1 MPa.

Seo and Lee [2004] studied the structure and guest distribution of mixed (CO₂+N₂) hydrates of carbon dioxide and nitrogen using X-ray diffraction and C NMR spectroscopy. X-ray diffraction results showed that for mixed (CO₂+N₂) hydrates with 3-20 mol% CO₂, the unit cell parameter was ~11.8 Å and the structure formed is structure I. For 1 mol% CO₂, the unit cell parameter was found to be 17.26 Å and the structure formed was identified as Structure II. They also found that the NMR spectra results revealed that carbon dioxide molecules mainly occupied the large 5¹²6² cages of structure one when the mixed hydrate (CO₂+N₂) was formed at a vapor phase composition range of 10-20 mol% CO₂. They also reported that with a small increase of carbon dioxide in the vapor phase the amount of carbon dioxide in the mixed (CO₂+N₂) hydrates increased greatly. Finally, Seo and Lee reported that CO₂ molecules may occupy both large and small cavities of structure I when the CO₂ content in the gas phase exceeds 33%.

Recently, Seo et al. [2005] studied CO₂-N₂ hydrate formation in porous silica gels and presented phase diagrams illustrating phase compositions. It was concluded that kinetic studies with H NMR micro imaging showed that the dispersed water in the silica gel pore system reacts readily with the gas. It is also noted that C cross-polarization NMR spectral analysis and direct measurement of CO₂ content in the hydrate phase suggested that the mixed hydrate formed of more than 10 mol% of CO₂ gas is structure I and the CO₂ molecules occupied mainly the more abundant 5¹²6² cages.

2. CO₂/H₂ Separation

Integrated gasification-combined cycle (IGCC) power plants gasify the coal producing pressurized synthesis gas (mainly CO and H₂). Next, synthesis gas is either used in a gas turbine followed by capture of the highly concentrated CO₂ or reacted with steam in a shift reactor to produce CO₂ and H₂.



H₂ is separated from CO₂ and is used to produce carbon-free energy or ammonia (NH₃), whereas the CO₂ is available for use or storage. IGCC power plants have long been advocated for their relatively high efficiency and low levels of conventional pollutants. Theoretically, the technology is feasible and it is required to economically separate CO₂ from the CO₂+H₂ mixture. A novel CO₂/H₂ separation process that is being considered by the US Department of Energy to be incorporated in these power plants is based on CO₂ hydrate [McKee, 2002; Klara and Srivastava, 2002]. The 40% CO₂-60% H₂ mixture is mixed with water to form gas hydrate crystals. The hydrate slurry is then separated from the product gas and is decomposed into CO₂ gas and water by lowering the pressure. The CO₂ is compressed and may be sent for sequestration.

3. Disposal of CO₂

The ocean has a capacity of storing 10,000 Gigatons of carbon (GtC) compared to a 900 GtC capacity of depleted oil and gas reservoirs and 20 GtC of unminable coal seams. While these estimates vary, the deep ocean has by far the largest storage potential. The concentration of CO₂ in the deep ocean is approximately 0.1 kg/m³ which are 2-3 orders of magnitude below its in situ solubil-

ity limit [Herzog and Edmond, 1994]. The top 200 m of the ocean is a well mixed region and saturated with CO₂ with respect to atmospheric CO₂. CO₂ can be released in the ocean as gas, solid or liquid. However, there are serious concerns regarding ocean disposal of liquid CO₂. Any consideration of CO₂ sequestration into the ocean has to take into account the CO₂-seawater phase diagram. CO₂ changes from gas to liquid at depths below about 450 m and it forms a hydrate (solid) at depths below 600 m [Chun and Lee, 1996; Uchida, 1997; Brewer et al., 1999; Lee et al., 2002; Seo et al., 2002; Seo and Lee, 2003a]. The latter two studies provided hydrate formation data for methane and carbon dioxide in porous media and in the presence of NaCl. Disposal of CO₂ in the ocean in the form of CO₂ hydrate is considered an alternative to liquid or dry ice CO₂ disposal [Yamasaki, 2000; West et al., 2003]. Takahashi et al. [2000] proposed the use of deep ocean aquifers as storage sites. This may be classified as geological sequestration. Because of the serious concern about ocean disposal as a mitigation option geological storage in depleted oil and gas reservoirs, deep saline aquifers and deep unminable coal seams is considered [McKee, 2002; Cale, 2002; Thambimuthu et al., 2002]. It is noted that CO₂ from gas fields is stored in an undersea aquifer in the North Sea [Herzog et al., 1997; McKee, 2002].

4. Natural Gas Storage and Transport (Gas to Solids Technology)

Gudmundsson et al. [2002] presented a capacity-distance diagram for the transport of stranded gas that shows how natural gas hydrate-based technology or gas to solids technology (GTS) is appropriate for medium to low volumes (0.1 to 1 billion cubic meters) and medium to short distances (100 to 5,000 km). The current gas to liquid technology (GTL) by liquefying the natural gas (LNG) is costly due to handling the system under cryogenic temperature. Thomas and Dawe [2003] reviewed ways to transport natural gas and suggested that hydrate is a promising method. Methane hydrate can be self-preserved for several weeks at -10 to -20 °C under atmospheric pressure even though the equilibrium temperature is -80 °C. The presence of ice layer inhibits further hydrate decomposition. Recently, Mitsui Engineering & Shipbuilding Co., Ltd. in Japan has built a pilot plant natural gas hydrate production facility. Hydrate pellets, which can be stored around -15 °C under ambient pressure, are produced [Takaoki et al., 2002; Nakajima et al., 2002]. Safety measures of natural gas hydrate carriers have also been discussed based on a conceptual design [Ota et al., 2002].

According to Khokar et al. [1998], structure H hydrate has the maximum storage capacity and energy density among hydrate structures. This is because the medium size cavity of sH hydrate can be filled with methane molecule. It is also known that structure H hydrate forms under a lower pressure those of structure I or II at the same temperature. The gas storage capacity in the hydrate state can be calculated if the lattice parameters of a unit cell and the hydration number are known. These parameters are usually obtained by x-ray diffraction. The lattice parameters are required to calculate the volume of unit cell, which is used to calculate the density or molar density of hydrate. The unit cell formula is required to calculate the molecular weight of hydrate and/or the mole of gas in the hydrate. The methane storage capacity of hydrates was calculated according to methods provided by Makogon [1997] and Ripmeester [2004]. The calculated maximum gas storage in the hydrate

Table 2. Gas storage capacity of all three-hydrate structures per m³ of hydrate at STP

| Structure | Maximum CH ₄ gas storage (m ³) | Volume of CH ₄ gas in small cavities (m ³) | Energy density (kcal/m ³) ^b |
|---------------|---|---|--|
| sI | 172.18 ^a | 43.04 ^a | 56.02 ^b |
| sII | 172.41 ^a | 114.94 ^a | 154.08 ^b |
| sH | 168.67 ^a | 140.55 ^a | 200.93 ^b |
| LNG @ -160 °C | 600.00 ^b | - | - |

Note: Superscript 'a' refer to the calculation method of Ripmeester [2004] or Makogon [1997]

Superscript 'b' refer to data reported by Khokhar et al. [1998]

if all cavities or only the small cavities are filled are shown in Table 2 along with values reported by Khokhar et al. [1998].

As seen in the table, the gas storage capacity in small cavities of hydrate that is calculated using the procedure given by Ripmeester [2004] or Makogon [1997] and the number that was reported by Khokhar et al. [1998] differ significantly. The lattice parameters used in the calculation and reported by Khokhar et al. [1998] are the same. There is probably a mistake in the values reported by Khokhar et al. The above calculations are valid under the assumption that small cages of structure I or II are completely filled with the gas molecule. The assumption for sH hydrate is that the small and medium cage are filled with small molecule and stabilized with large molecule that fills the large cavity. In practice, not all cages are filled so the molar density of the density of hydrate is expected to be lower and hence, the gas storage capacity in hydrate obtained by solid phase characterization should be lower than the number shown in Table 1.

A rapid hydrate formation rate is required so that gas storage in hydrate media can be applicable in industrial operations. Solubility and the contact between hydrate formers and water are very important to speed up the process by reducing the mass transfer resistance. The hydrate formation using water droplet and water spraying is being investigated, mainly in Japan [Ohmura et al., 2002; Fukumoto et al., 2001]. Takahashi et al. [2003] studied the hydrate formation using micro-bubble technology which is an alternative concept. Seo and Lee [2003b] studied the methane-THF and methane-neohexane systems to determine the degree of cavity filling. The use of micellar surfactant solutions can also be used to increase the hydrate formation rate and storage capacity [Sun et al., 2003; Link et al., 2003]. The merits and disadvantages of the two options for hydrate formation (bubble technology and water droplet spraying) have been discussed in detail by Mori [2003]. According to Mori's comprehensive review less effort has been devoted to the hydrate processing, storage and decomposition (or re-gasification) aspects of the overall technology for natural gas storage.

HYDROGEN HYDRATE AND STORAGE

It was a general perception that hydrogen molecules are too small to fit into the hydrate cages, and no stable clathrate hydrate structure can be formed. However, high-pressure optical and x-ray studies of H₂-H₂O mixtures have revealed the formation of the first hydrogen clathrate hydrates [Vos et al., 1993]. More recently hydrogen clathrate of sII structure was synthesized and characterized [Mao et al., 2002; Lokshin et al., 2004]. It was found that the hydrogen clathrate has an unusually high H₂/H₂O ratio (1 : 2). The result was confirmed with a statistical mechanical model in conjunction with

first principle quantum chemistry calculations [Patchkovskii and Tse, 2003]. This unusually high ratio of hydrogen to water ratio (1 : 2) was attributed to the fact that hydrogen can stabilize the relatively bigger cages of H₂O by occupying it in clusters of 2-5 hydrogen molecules. The hydrate forming temperature and pressure reported in the paper is 280 K and 300 MPa, respectively [Mao et al., 2002]. Subsequently, Mao and Mao [2004] synthesized hydrogen clathrate, H₂(H₂O)₂, that holds 50 g/liter of hydrogen by volume or 5.3% percent by weight. Thus, hydrogen clathrate formation can be used as a means for hydrogen storage. However, the need to operate at lower temperatures has initiated a search for additives to achieve this objective. Recently, it was found that clusters of H₂ can be stored at low pressures as structure II binary hydrate with tetrahydrofuran [Florusse et al., 2004; Lee et al., 2005].

CONCLUDING REMARKS

It is estimated that there are about 20,500 trillion cubic meters (TCM) of natural gas in the form of hydrate stored in the earth's crust. This constitutes the largest source of unconventional natural gas. Unlike conventional natural gas (370 TCM reserves) gas hydrates are distributed evenly around the world. Efforts are underway to develop technology so that some portion of this resource becomes a reserve. The recent tests in the Arctic (Mallik project) showed that the commercial production of gas from hydrates may not be that far off. The development analogy with coal bed methane is invoked to estimate that within 20-25 years recovery will begin. On the other hand, dissociation of these naturally occurring methane gas hydrates and release of the methane in the atmosphere has the potential to cause a runaway greenhouse effect. Such a drastic global climate change occurred 55 million years ago as well as 13,500 years ago. Gas hydrate formation is seriously considered as a platform to develop clean technologies. Technologies being investigated are CO₂ separation from flue gases and from CO₂/H₂ mixtures, natural gas transport and storage (gas to solids technology) and hydrogen storages. Finally, the natural gas storage capacity in the form of hydrates was also recalculated since there appears to be an error in the literature values.

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