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Natural gas hydrates

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1. Introduction

Natural gas hydrates are ice-like materials formed under low temperature and high pressure conditions. Natural gas hydrates consist of water molecules interconnected through hydrogen bonds which create an open structural lattice that has the ability to encage smaller hydrocarbons from natural gas or liquid hydrocarbons as guest molecules. Interest in natural gas hydrates as a potential energy resource has grown significantly in recent years as awareness of the volumes of recoverable gas becomes more focused (Sloan & Koh, 2008). The size of this resource has significant implications for worldwide energy supplies should it become technically and economically viable to produce. Although great efforts are being made, there are several unresolved challenges related to all parts in the process towards full scale hydrate reservoir exploitation. Some important issues are: 1) Localize, characterize, and evaluate resources, 2) technology for safe and economic production 3) safety and seafloor stability issues related to drilling and production. This chapter gives a brief introduction to natural gas hydrate and its physical properties. Some important characteristics of hydrate accumulations in nature are also discussed. Experimental results presented in this chapter emphasis recent work performed by the authors and others where we investigate the possibilities for producing natural gas from gas hydrate by CO₂ replacement. By exposing the hydrate structure to a thermodynamically preferred hydrate former, CO₂, it is shown that a spontaneous conversion from methane hydrate to CO₂ hydrate occurred. Several experiments have shown this conversion in which the large cavities of hydrates prefer occupation by CO₂ (Lee et al., 2003; Jadhawar et al. 2005; Ota et al., 2005; Graue et al., 2008). This is also supported by simulations (Phale et al., 2006; Kvamme et al., 2007). Other production schemes proposed in the open literature are also reviewed in this chapter.

2. Structures and Properties

There are three known structures of gas hydrates: Structure I (sI), structure II (sII) and structure H (sH). These are distinguished by the size of the cavities and the ratio between large and small cavities. SI and sII contain both a smaller and a larger type of cavity, but the large type cavity of sII is slightly larger than the sI one. The maximum size of guest molecules in sII is butane. SH forms with three types of cavities, two relatively small ones and one quite large. The symmetry of the cavities leaves an almost spherical accessible

volume for the guest molecules. The size and shape of the guest molecule determines which structure is formed due to volumetric packing considerations. Additional characteristics are guest dipole and/or quadropole moments, such as for instance for H₂S and CO₂. The average partial charges related to these moments may either increase the stability of the hydrate (H₂S) or be a decreasing factor in thermodynamic stability (CO₂). SI forms with for instance propane and iso-butane and sH with significantly larger molecules, as for instance cyclo-hexane, neo-hexane. Both methane and carbon dioxide form sI hydrate. SI hydrates forms with guest molecules less than 6 Å in diameter. The cages and the number of each cage per unit cell are shown in Figure 1. SI cages are shown at the top of the figure. The unit cell of sI hydrate contains 46 water molecules and consists of 2 small and six large cages. The unit cell is the smallest symmetric unit of sI. The two smaller cavities are built by 12 pentagonal faces (5¹²) and the larger of 12 pentagonal faces and two hexagon faces (5¹²6²). The growth of hydrate adds unit cells to a crystal.

Fig. 1. Hydrate structures, from top: cages of sI, sII, and sH (Husebø, 2008)

3. Hydrates in the Earth

Natural gas occurrences in nature were first recognised in the late 1960s and early 1970s in sub-permafrost in Siberia and the North Slope of Alaska during drilling in established provinces of conventional oil and gas (Makogon et al., 1971). Evidence of natural occurrences of sub-marine gas hydrate accumulation was first found one or two decades later as more deep sea expeditions encountered hydrate bearing sediments. In recent years, a growing number of expeditions have been dedicated to assessing marine gas hydrate accumulations; their nature and their geological settings. Rather comprehensive mapping of hydrate has been devoted to many of the world’s continental margins in recent years, as for example in India, Japan and Taiwan. There is no exact information of world wide quantities of gas hydrates. Estimates are based on both indirect (seismic surveys) and direct evidence

(drilling) which is very incomplete. Figure 2 shows the world's occurrences of gas hydrate both in permafrost regions and in marine sediments. Estimates of in situ hydrates range from $3053 \times 10^{15} \text{ m}^3 \text{ STP}$ (Trofimuk et al., 1973), to $0.2 \times 10^{15} \text{ m}^3 \text{ STP}$ (Soloviev et al., 2002). Estimates have generally decreased with time; however, even the most conservative exceed the estimates of conventional gas (Sloan & Koh, 2008). A widely cited estimate is of $20 \times 10^{15} \text{ m}^3$, (Kvenvolden, 1988), which exceed the energy in conventional fossil fuels combined.

Fig. 2. Map of more than 90 documented hydrate occurrences (Hester and Brewer, 2009). Indirect hydrate markers, as seismic reflectors and pore-water freshening in core samples were used to identify the inferred hydrate deposits. Areas where hydrate samples have been taken are marked as known hydrate deposits. Hydrate deposits are distributed in marine environments and regions of permafrost.

4. Classification of Hydrate Deposits

Boswell and Collett, 2006, proposed a resource pyramid to display the relative size and feasibility for production of the different categories of gas hydrate occurrences in nature (Figure 3). The top resources of the gas hydrates resource pyramid are the ones closest to potential commercialization. According to Boswell and Collett, these are occurrences that exist at high saturations within quality reservoirs rocks under existing Arctic infrastructure. This superior resource type is estimated by US geological survey (USGS) to be in the range of 33 trillion cubic feet of gas-in-place under Alaska's North Slope. Prospects by British Petroleum and the US DOE anticipate that 12 trillion cubic feet of this resource is recoverable. Even more high-quality reservoirs are found nearby, but some distance away from existing infrastructure (level 2 from top of pyramid). The current USGS estimate for total North Slope resources is approximately 590 Tcf gas-in-places. The third least challenging group of resources is in high-quality sandstone reservoirs in marine environments, as those found in the Gulf of Mexico, in the vicinity of existing infrastructure.

Fig. 3. Hierarchy of production feasibility for gas hydrate resources (left) and conventional gas (right) (Boswell and Collett, 2006)

There is a huge variation in naturally occurring hydrate reservoirs, both in terms of thermodynamic conditions, hosting geological structures and trapping configurations (sealing characteristics and sealing geometry). Hydrates in unconsolidated sand are considered as the main target for production. For the sake of convenience, these types of hydrate occurrences have been further divided into four main classes, as shown in Figure 4 (Moridis and Collett, 2003). Class 1 deposits are characterized with a hydrate layer above a zone with free gas and water. The hydrate layer is composed with either hydrate and water (Class 1W) or gas and hydrate (Class 1G). For both, the hydrate stability zone ends at the bottom of the hydrate interval. Class 2 deposits exist where the hydrate bearing layer, overlies a mobile water zone. Class 3 accumulations are characterized by a single zone of hydrate and the absence of an underlying zone of mobile fluids. The fourth class of hydrate deposits is widespread, low saturation accumulations that are not bounded by confining strata that may appear as nodules over large areas. The latter class is generally not regarded as a target for exploitation.

Fig. 4. Schematic over types of hydrate deposits

5. Proposed Production Schemes

The three main methods for hydrate dissociation discussed in the literature are (1) depressurization, where the hydrate pressure is lowered below the hydration pressure P_H at the prevailing temperature; (2) thermal stimulation, where the temperature is raised above the hydration temperature T_H at the prevailing pressure; and (3) through the use of inhibitors such as salts and alcohols, which causes a shift in the P_H - T_H equilibrium due to competition with the hydrate for guest and host molecules. The result of hydrate dissociation is production of water and gas and reduction in the saturation of the solid hydrate phase (Figure 5).

Fig. 5. Gas hydrate production options (after Makogon, 1997)

5.1 Numerical studies

Moridis et al. (2008) report rather comprehensive numerical studies that assess the hydrate production potential for the three classes of hydrate deposits with the three production options. They found that Class 1 deposits appear to be the most promising target due to the thermodynamic proximity to the hydrate stability zone. That is, the boundary between the free gas zone and the hydrate layer forms the equilibrium line, and hence, only small changes in temperature or pressures will induce dissociation of hydrate. In addition, the free gas zone will secure gas production regardless of the hydrate gas contribution. They found Class 1G to be a more desirable target within Class 1 due to less water production and more evenly distributed pressure fields. Class 2 may attain high rates but are burdened with long lead times with little initial gas production. Class 3 may supply gas earlier, but with lower rates. Moridis et al. (2008), concluded that depressurisation is the favourable production option for all three classes, meaning that the deposit is not a desirable target if depressurisation appears to be ineffective. It is, however, very important to stress that numerical simulations of hydrate exploitation scenarios are still in an early stage, with corresponding challenges at the fundamental level as well as in the parameterisation.

5.2 Field example: the Mackenzie River Delta

The Mackenzie River Delta of Canada was explored mainly for conventional petroleum reserves, but a total of 25 drilled wells have identified possible gas hydrate sites. The gas hydrate research well (JAPEx/JNOC/GSC Mallik 2L-38) drilled in 1998 was designed to investigate the nature of *in situ* hydrates in the Mallik area to explore the presence of sub-permafrost gas hydrate. A major objective was to investigate the gas hydrate zones obtained by well logs in 1972 in a nearby well which was believed to have encountered at least ten significant gas-hydrate stratigraphic units. Drilling and coring gave 37 meters of recovered core in the hydrate interval from depths 878 to 944 meters. Visible gas hydrates were identified in a variety of sediment types, i.e. interbedded sandstone and siltstone. No hydrate was found in the siltstone dominated units, indicating a strong lithological control on gas hydrate occurrence. Well logs suggested the presence of gas hydrates sands from 890-1100 meters depth, with up to 90% gas hydrate saturation. The presence of gas hydrate contributes substantively to the strength of the sediment matrix (Grace et al., 2008). Two production tests were initiated at the Mallik site. The 2007 test was performed without sand controls in order to assess the strength of the sediments. A substantial amount of sand was produced and constrained the test to 24 hours. In March 2008 the test was repeated, this time with sand screen to choke the inflow of sediments. The last Mallik test suggests that a significant gas rate can be achieved by depressurising a sand dominated gas hydrate reservoir (Grace et al., 2008).

6. Environmental Aspects of Gas Hydrates

6.1 Climate change

The natural gas produced from hydrates will generate CO₂ upon combustion, but much less than conventional fuel as oil and coal per energy unit generated. The global awareness of climate change will most likely make it more attractive in relation to oil and coal if fossil fuels, as anticipated, continue to be a major fuel for world economies the next several decades. However, increased global temperatures have the potential of bringing both

permafrost hydrates and subsea hydrates out of equilibrium. As a consequence, huge amounts of methane may be released to the atmosphere and accelerate the greenhouse effect due to feedback. In general hydrate is not stable towards typical sandstone and will fill pore volume rather than stick to the mineral walls. This implies that if there are imperfections and leakage paths in the sealing mechanisms the hydrate reservoir will leak. There are numerous small and large leaking hydrate reservoirs which results in methane fluxes into the ocean. Some of these fluxes will be reduced through consumption in biological ecosystems or chemical ecosystems. The net flux of methane reaching the atmosphere per year is still uncertain. Methane is by far a more powerful greenhouse gas than CO_2 (~20 times). Kenneth et al., 2003, hypothesized that major release from methane hydrate caused immense global warming 15 000 years ago. This theory, referred to as “clathrate gun” hypothesis is still regarded as controversial (Sloan & Koh, 2008), but is supported in a very recent paper by Kennedy et al. (2008). The role of gas hydrate in global climate change is not adequately understood. For hydrate methane to work as a greenhouse gas, it must travel from the subsurface hydrate to the atmosphere. Rates of dissociation and reactions/destruction of the methane gas on its way through sediment layers, water and air are uncharted.

6.2 Geomechanical Stability

Gas hydrates will affect the seafloor stability differently for the different types of hydrate occurrences. All of these hydrate configurations may take part of the skeleton framework that supports overlying sediments, which in turn is the fundament for pipelines and installations needed for production. These concerns have already been established for oil and gas exploitation where oil and gas reservoirs that lie below or nearby hydrate bearing sediments. However, geohazards would potentially be far more severe if gas hydrate is to be produced from marine hydrate deposits. During melting, the dissociated hydrate zone may lose strength due to under-consolidated sediments and possible over-pressuring due to the newly released gas (Schmuck and Paull, 1993). If the shear strength is lowered, failure may be triggered by gravitational loading or seismic disturbance that can result in submarine landslides (McIver, 1977). Several possible oceanic landslides related to hydrate dissociation are reported in the literature. Among these are large submarine slides on the Norwegian shelf in the North Sea (Bugge et al., 1988) and massive bedding-plane slides and slumps on the Alaskan Beaufort Sea continental margin (Kayen and Lee, 1993).

7. Production of CH_4 from hydrates by CO_2 exposure

Thermodynamic prediction suggests that replacement of CH_4 by CO_2 is a favourable process. This section reviews some basic thermodynamics and earlier experimental studies of this CH_4 - CO_2 reformation process to introduce a scientific fundament for the experimental work presented later in this chapter.

7.1 Thermodynamics of CO_2 and CH_4 Hydrate

CO_2 and CH_4 form both sl hydrates. CH_4 molecules can occupy both large and small cages, while CO_2 molecules will prefer the large $5^{12}6^2$ cage. Under sufficiently high pressures or low temperatures both CO_2 and CH_4 will be stable, but thermodynamic studies suggest that

CH₄ hydrates have a higher equilibrium pressure than that of CO₂ hydrates for a range of temperatures. A summary of these experiments is presented in Sloan & Koh, 2008. Figure 6 shows the equilibrium conditions for CO₂ and CH₄ hydrate in a P-T diagram. This plot is produced using the CSMGem software (Sloan & Koh, 2008), which supplies the most recent thermodynamic predictions.