

Invited review

Review of exploration and production technology of natural gas hydrate

Yudong Cui¹, Cheng Lu^{1,2}, Mingtao Wu¹, Yue Peng¹, Yanbin Yao¹, Wanjing Luo^{1*}

¹School of Energy Resources, China University of Geosciences, Beijing 100083, P. R. China

²The Key Laboratory of Unconventional Petroleum Geology, China Geological Survey, Beijing 100029, P. R. China

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Corresponding author:

*E-mail: luowanjing@cugb.edu.cn

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Abstract:

Natural gas hydrate is an ice-like substance which is sometimes called “combustible ice” since it can literally be lighted on fire and burned as fuel. Natural gas hydrate is characterized by widespread distribution, large reserves and little pollution. This paper introduced the distributions of hydrate, hydrate reserves and properties of hydrate. The main exploration methods, such as geophysical exploration and geochemical exploration have been presented. In addition, the main production techniques of natural gas hydrate including depressurization, thermal stimulation and chemical injection have been summed up. Finally, the challenges and outlooks of natural gas hydrate production have been proposed.

1. Introduction

The mixture of water molecules and light natural gases in a crystalline ice-like structure forms gas-hydrate. In this solid structure, the gaseous components are surrounded by the water molecules (Makogon, 1997; Sloan and Koh, 2007). In a hydrate, 80% of the volume is occupied by water and 20% by gas (Makogon, 2007). Methane is the main contributing component in natural gas hydrates (NGH), which are a potentially important energy resource for future demand (Demirbas, 2010; Moridis et al., 2011). Decomposition of one volume of methane gas-hydrate releases approximately 150-180 volumes of methane at standard conditions (Krason and Finley, 1992; Carroll, 2009). The substantial size of the natural hydrate resource is a motivating factor in its development (Moridis et al., 2007, 2011; Demirbas, 2010).

Hydrates find application in energy for flow assurance (Hammerschmidt, 1934) and in resource assessment (Max et al., 2005), as well as in climate change (Kennett et al., 2003), seafloor stability (Ginsburg et al., 1998) and gas transportation and storage (Sanden et al., 2005). There are numerous gas hydrate reserves all over the world, especially in permafrost regions and ocean environments (Trehu et al., 2006). Fig. 1

is the map of discovered gas-hydrate deposits (Wang et al., 2017).

Currently, oil and natural gas are the primary fuels. The abundance of gas hydrate reserves is expected to be more than twice of the combined carbon of coal, conventional gas and petroleum reserves (Aregba et al., 2017). Fig. 2 shows the comparison between hydrate deposits and other sources of fuel, using a unit of 10^{15} g of carbon.

As Fig. 3 shows, clathrate hydrates consist of guest gas molecules inside hydrogen-bonded water lattices (Lee et al., 2011). NGH can be stable over a wide range of pressures and temperatures. Three main structures of gas hydrates-cubic structure I (sI), cubic structure II (sII) and the hexagonal structure (sH) have been identified (Davidson et al., 1973; Englezos et al., 1993; Sloan et al., 2008; Veluswamy et al., 2014). The properties of ice, structures I and II gas hydrates is showed in Table 1 (Aregba et al., 2017).

Temperature and pressure of NGH are not static parameters. They are affected by tectonic activity, sedimentation, changes in sea level, and changes in ocean temperature (Bohrmann et al., 2006).

Fig. 4 demonstrates how uplift or changes in sea level will



Table 1. Properties of Ice, structures I and II gas hydrates (After Areba, 2017).

S/N	Properties (Unit Cell)	Ice	Structure I (sI)	Structure II (sII)
1	Water molecules number	4	46	136
2	Lattice parameters at 273 K, nm	a = 0.452, c = 0.736	1.2	1.73
3	Dielectric constant at 273 K	94	~ 58	58
4	Water diffusion correlation time (μsec)	220	240	25
5	Water diffusion activation energy (kJ/m)	58.1	50	50
6	Shear Velocity (V_s), m/s	1949	1963.6	2001.1
7	Compressional Velocity (V_p), m/s	3870.1	3778	3821.8
8	Refractive index, 638 nm, -3°C	1.3082	1.346	1.35
9	Density, kg/m^3	916	912	940
10	Poissons Ratio	0.33	~ 0.33	~ 0.33
11	Bulk Modulus (272 K)	8.8	5.6	-
12	Shear Modulus (272 K)	3.9	2.4	-
13	Velocity Ratio (comp./shear)	1.99	1.92	1.91
14	Linear thermal expn., K^{-1} (200 K)	56×10^{-6}	77×10^{-6}	52×10^{-6}
15	Heat capacity, $\text{J}/(\text{kg}^*\text{K})$	3800	3300	3600
16	Thermal conductivity, $\text{W}/(\text{m}^*\text{K})$ (263 K)	2.23	0.49 ± 0.02	0.51 ± 0.02

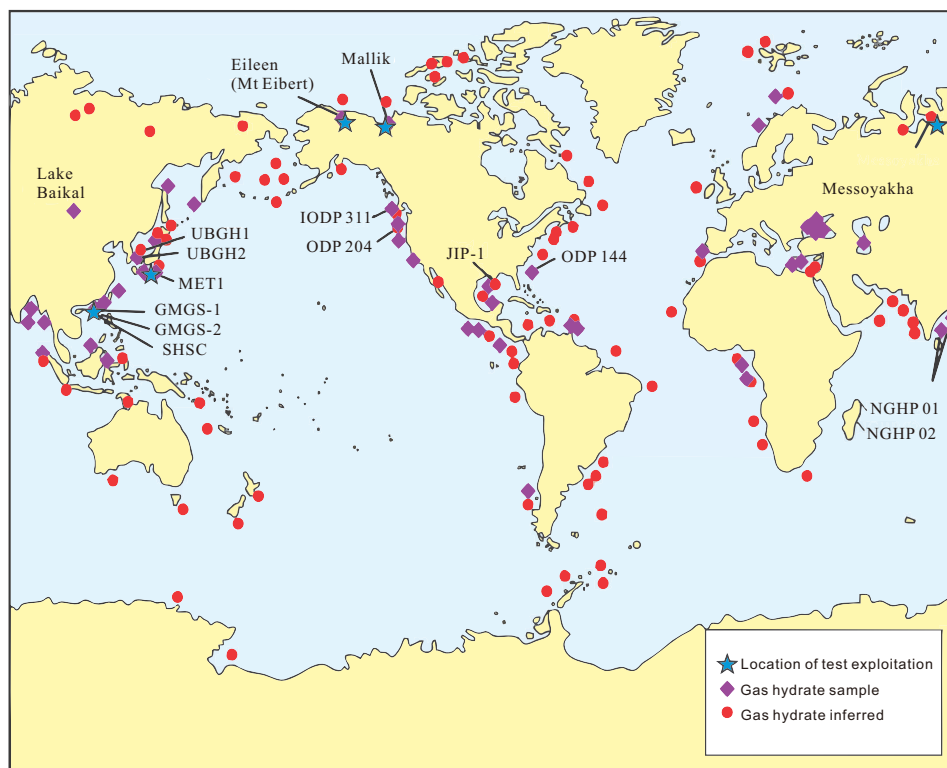


Fig. 1. Location of test exploitation, sampled and inferred gas hydrate occurrences in oceanic sediments of outer continental margins and permafrost regions (SHSC-Shenhu Test Exploitation; IODP-Integrated Ocean Drilling Program; UBGH-Ulleung Basin Gas Hydrate Expedition; ODP-Ocean Drilling Program; JIP-Joint Industry Project; METI-Ministry of Economy, Trade, and Industry; GMGS-Guangzhou Marine Geological Survey; NGHP-India National Gas Hydrate Program. After Wang et al., 2017).

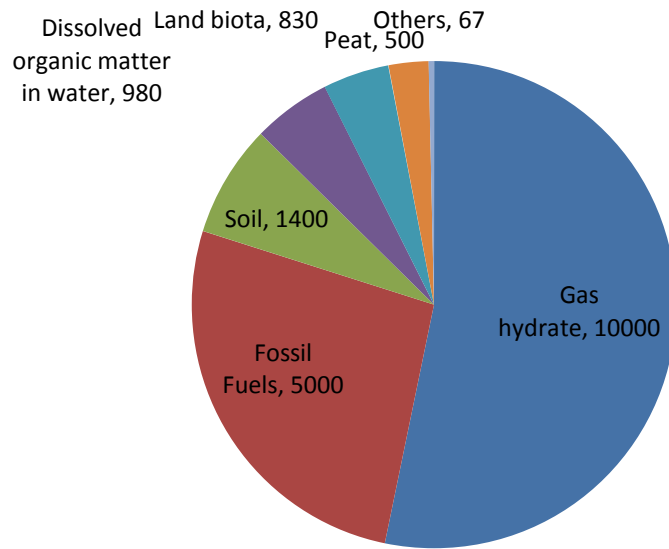


Fig. 2. Gas hydrates deposits compared with other fuel resources, units=10¹⁵ g of carbon (After Tohidi, 2014).

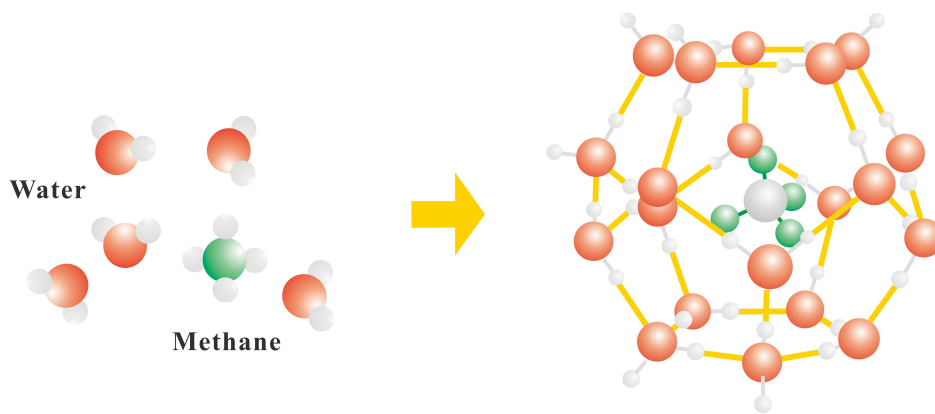


Fig. 3. Schematic Diagram of Natural Gas Hydrate Formation in Molecular Scale (Tetrahedral molecule is methane and dipole molecules are water, after Lee, 2011).

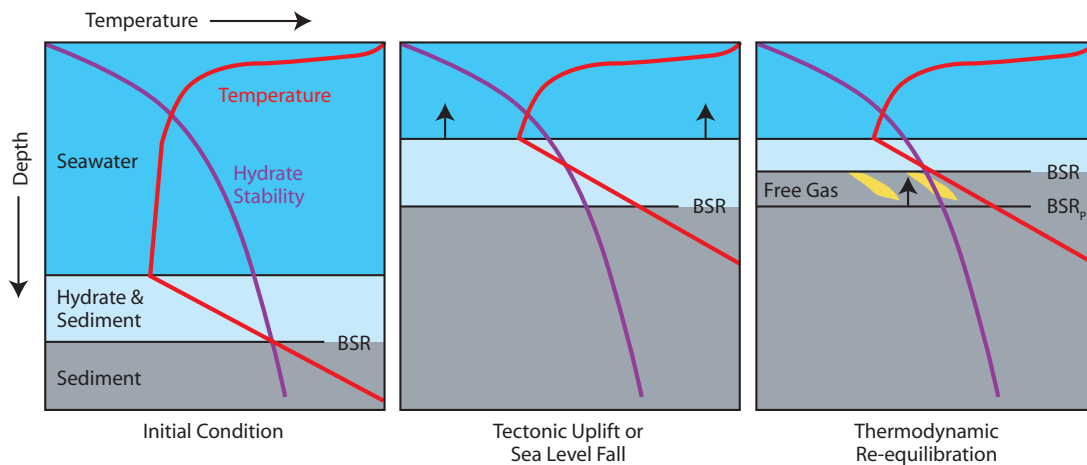


Fig. 4. Effect on gas hydrate stability of tectonic uplift or sea level fall (After Trehu, 2006).

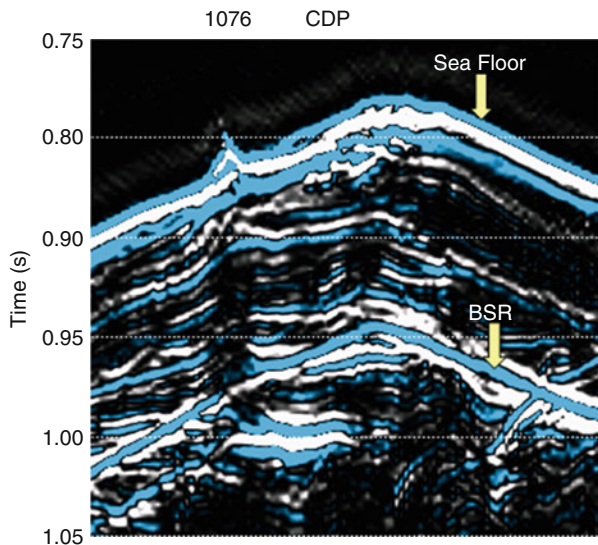


Fig. 5. A classic example of identified BSR (After Thakur, 2010).

affect the gas hydrate stability zone (Pecher et al., 1998, 2001). Similarly, an increase in the temperature will thin the gas hydrate stability zone, although such temperature changes require thousands of years to propagate into sediments. Short-term changes in bottom water temperature and pressure can also affect gas hydrate deposits (Ruppel, 2000; MacDonald et al., 2005).

China's marine geological science and technology personnel first drilled high-purity gas hydrate samples in the eastern waters of the Pearl River Estuary in Guangdong Province and obtained considerable control reserves through drilling. May 10, 2017, the China Geological Survey mined out natural gas from the South China Sea. July 9, 2017, accumulated natural gas production exceeded 300, 000 m³ in a continuous test for 60 days, and the well has been officially shut down. Acquired 6.47 million scientific experiment data set has laid a solid foundation for further work.

2. NGH Exploration Methods

2.1 Geophysical Exploration

As an important future energy, NGH's exploration is of great significance (Moridis et al., 2008; Lee et al., 2011). Gas hydrate deposits are identified principally on the basis of their acoustic expression. The phase boundary between methane hydrate and methane plus water gives rise to a prominent negative-polarity event known as a BSR. Besides, the addition of hydrate to pore fluids has been interpreted to cause acoustic blanking, a suppression of sediment reflectivity. Fig. 5 is a classic example of identified BSR.

Previous studies suggest that most of the BSR amplitude is due to the velocity reduction of the underlying free gas (Singh et al., 1993; MacKay et al., 1994; Hyndman et al., 2001; Pecher et al., 2001). The presence of a free-gas zone (FGZ) is an important part of the gas hydrate system, and is particularly important if the presence of gas hydrate is to be

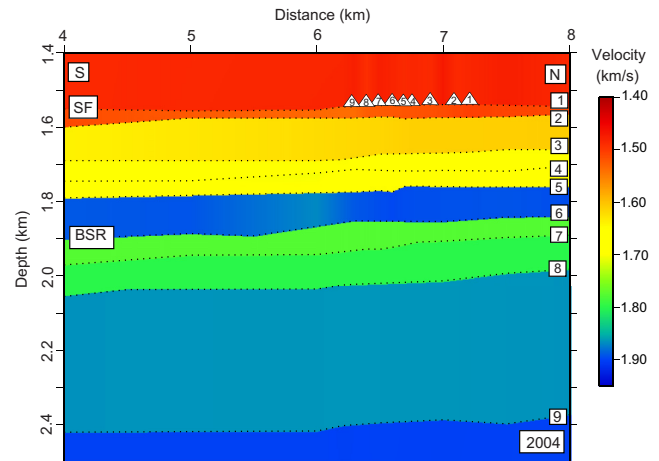


Fig. 6. Reduced velocity of BSR (After Schlesinger, 2012).

inferred by observation of a BSR (Haacke et al., 2007).

Fig. 6 shows that the BSR marks the transition to a layer of reduced velocity below a high-velocity zone (Schlesinger et al., 2012). The saturation of the free-gas is less sensitive to the seismic amplitude, but the amplitude of natural gas hydrate with different saturation is quite different (Boswell et al., 2016).

Both methane hydrate and free gas exist even where a clear BSR is absent (Holbrook et al., 1996). The low reflectance, or blanking, above the BSR is caused by lithologic homogeneity of the sediments rather than by hydrate cementation. The average methane hydrate saturation above the BSR is relatively low (5 to 7 percent of porosity).

2.2 Geochemical Exploration

Geochemical exploration is performed by analyzing actual core samples. However, geochemical exploration serves an important role in gas hydrate exploration combined with geophysical exploration. Geochemical indicators of hydrate include dissolved gas distribution, gas and organic compound composition in sediments, chlorinity, salinity, alkalinity of pore fluid, and the isotope compositions of water. These indicators inform us about the origins of natural gases and gas hydrate formation mechanisms.

During gas hydrate formation process dissolved ions such as Na⁺ and Cl⁻ are excluded from the hydrate structure and only water molecules crystallize into cubic lattice structure (Hesse and Harrison, 1981). Surrounding pore waters initially become more saline during the process of hydrate formation. During hydrate crystallization the exclusion of salinity (chlorine) and intake of $\delta^{18}\text{O}$ is due to the solidfluid isotope fractionation that causes preferential uptake of the heavy isotope $\delta^{18}\text{O}$ in the solid phase and depletion in the fluid (Hesse, 2003). During the dissociation of hydrates the release of pure water in the host sediments reduces the chlorinity. During the dissociation of hydrates release of heavy isotope water and its mixing up with lower order isotopic water component results in enrichment of $\delta^{18}\text{O}$ in the host sediments

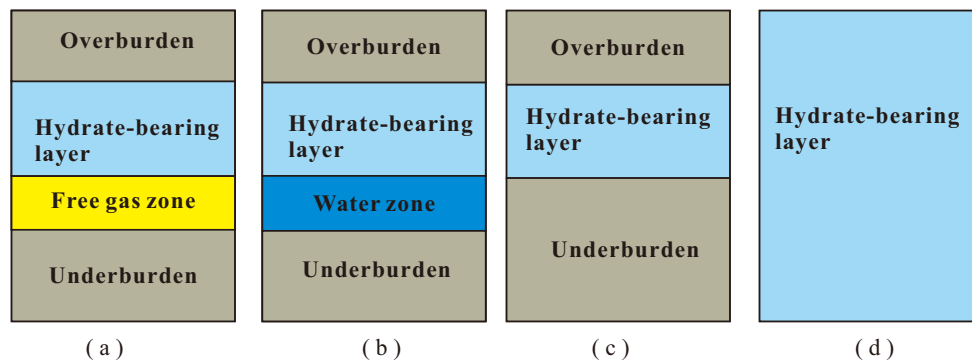


Fig. 7. Classes of Hydrate Reservoir (a) Class 1, (b) Class 2, (c) Class 3, (d) Class 4.

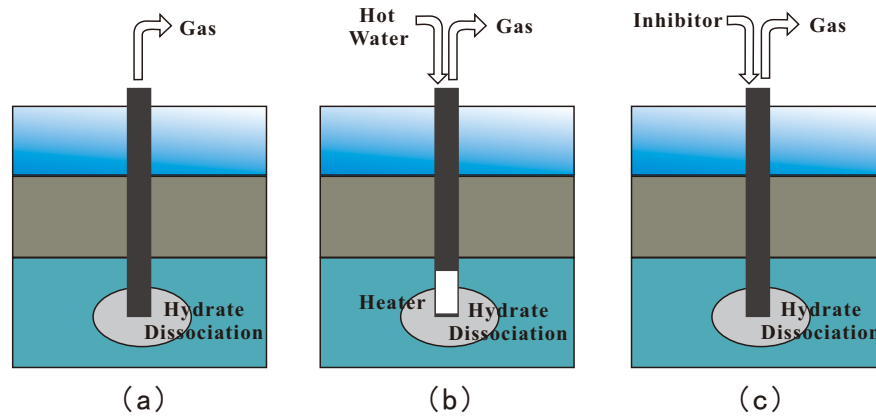


Fig. 8. NGH Production Methods (a) Depressurization, (b) Thermal Stimulation, (c) Inhibitor Injection (After Lee et al., 2011).

pore waters. The $\delta^{18}\text{O}$ values increase with increasing depth and appreciable higher values recorded in the hydrate bearing sediments. The observed combined anomalies of chlorinity and $\delta^{18}\text{O}$ in the pore water chemistry of the host sediments provides a reliable measure for identification of gas hydrates. Lower values of chlorine concentration in the hydrate stability zone may suggest the occurrence of hydrates even when the prominent geophysical signature (BSR) is found missing (Holbrook et al., 1996).

3. Production Methods

3.1 Classification of Gas Hydrate Reservoirs

Gas hydrate reservoirs have been classified according to the geologic setting of the reservoir for the purpose of developing optimal production strategies for each geologic condition (Moridis and Sloan, 2007; Moridis and Collett, 2013). The four classes are depicted in Fig. 7.

Class 1-3 has overburden and underburden layers in the geologic setting. Class 1 reservoir consists of a hydrate-bearing layer with underlying free gas zone, class 2 reservoir consists of a hydrate-bearing layer with underlying water zone, and class 3 reservoir consists of one hydrate-bearing layer without underlying free-fluid phase zones. Class 4 reservoir consists of single hydrate-bearing layer.

3.2 Techniques of gas production

Release and production of methane from hydrate-bearing formations are associated with hydrate dissociation. Different methods have been proposed to enhance gas production (Pooladi-Darvish, 2004; Sloan and Koh, 2007; Demirbas, 2010). The most prominent methods are (i) lowering the reservoir pressure below the hydrate equilibrium pressure at the prevailing temperature, known as depressurization; (ii) raising the temperature above the hydrate equilibrium temperature at the existing pressure, normally known as thermal stimulation; and, (iii) shifting the thermodynamic equilibrium curve of hydrate by means of injection of inhibitors, such as methanol or brine, to decompose the hydrate. Combinations of these methods can also be used. In general, where conditions are suitable, it is believed that the depressurization technique would be the most economical and practical method in the production from gas-hydrate deposits (Grace et al., 2008).

3.2.1 Depressurization

The depressurization method is currently regarded as the most promising method among others. However, it still exists several inevitable issues, such as subsidence during the depressurization and hydrate reformation due to endothermic depressurization event. All the problems should be solved in

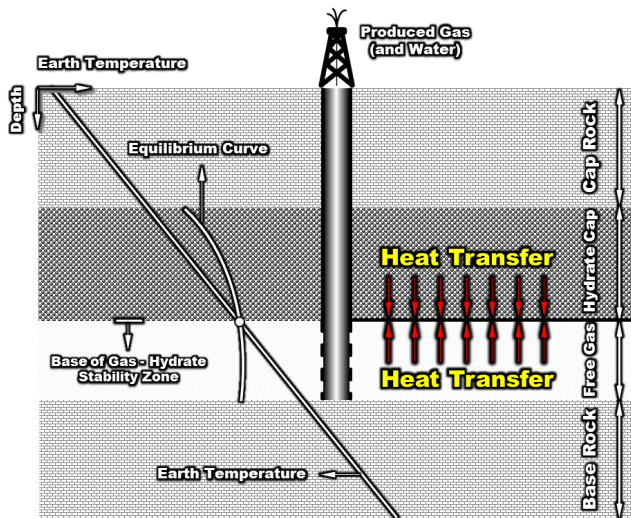


Fig. 9. Conceptual model for methane recovery from hydrates using depressurization (After Tabatabaie, 2014).

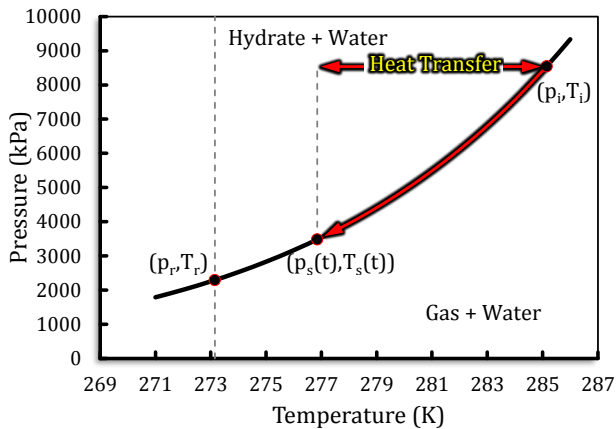


Fig. 10. Methane hydrate equilibrium curve (After Tabatabaie, 2014).

the future. The problems could be relieved by using combined methods. Such as the combination of the depressurization and the gas swapping for mitigating the subsidence, and the combination of the depressurization and the thermal stimulation for mitigating hydrate reformation.

Class 1 reservoir is considered as the most promising reserve since the underlying free gas zone guarantees gas production and the T/P condition is close to the hydrate equilibrium condition (Moridis et al., 2007). In most cases, the depressurization method is the most promising method because it is the most simple and cost effective (Moridis et al., 2007). Class 2 is less effective in propagating depressurization front since the underlying free water zone continuously supply a large body of water (Moridis and Kowalsky, 2007). Class 3 reservoir would exhibit even slower propagation of depressurization front due to the absence of free gas or water zone that is more permeable than hydrate-bearing layers and can serve as a conduit for depressurization front (Moridis et al., 2007). Class 4 reservoir has been reported as the least effe-

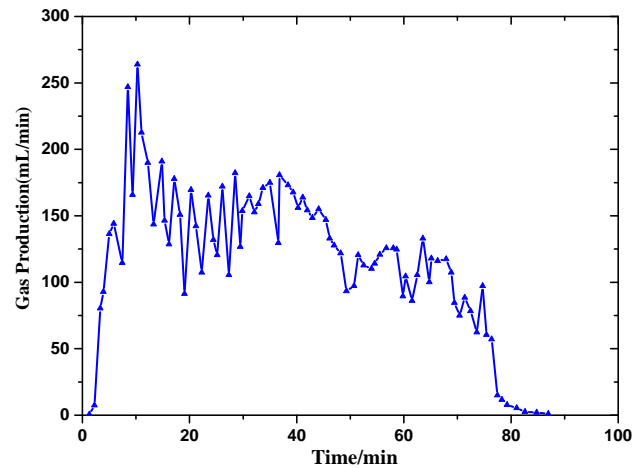


Fig. 11. Production rate curve of depressurization method (After Hao, 2016).

ctive in depressurization, producing very large amount of water and small amount of gas (Moridis and Sloan, 2007).

Fig. 9 shows a schematic representation of the depressurization method of gas production from Class 1 hydrate reservoirs. A well is completed in the free-gas zone. The depth of the hydrate layer can be found by superimposing the gas-hydrate equilibrium curve and the geothermal gradient (Demirbas, 2010). The base of the hydrate zone is at thermodynamic equilibrium pressure and temperature.

As the gas is removed, the pressure in the free-gas zone is reduced to some pressure below the equilibrium pressure corresponding to initial temperature, causing the hydrate to decompose (Hong and Pooladi-Darvish, 2005; Moridis et al., 2007). Fig. 10 shows a gas-hydrate phase diagram illustrating the dissociation mechanism. As the picture depicts, hydrate exists only in a high pressure and low temperature environment. Once the pressure is lower than critical pressure (i.e. equilibrium pressure) or temperature is beyond critical temperature (i.e. equilibrium temperature), solid hydrate will decompose and produce natural gas and water. Hydrate decomposition needs to absorb heat from the surrounding environment. The temperature of the hydrate bearing layers will be reduced if there is a single depressurization.

The NGH dissociation by depressurization can be divided into three stages:

(1) Free gas produce in the early stage. With the reduction of system pressure, the associated free gas is rapidly produced and the gas production rate increases rapidly.

(2) Gas release from hydrate dissociation in the second stage. Natural gas hydrate decomposition rate is larger because of the larger fractional surface area.

(3) Surplus free gas release in the third stage. Decomposition rate gradually decreases with the smaller decomposition of the surface area.

3.2.2 Thermal Stimulation

Simple depressurization appears promising in Class 1 hydrates, but its appeal decreases in Class 2 hydrates. The most promising production strategy in Class 2 hydrates involves co-

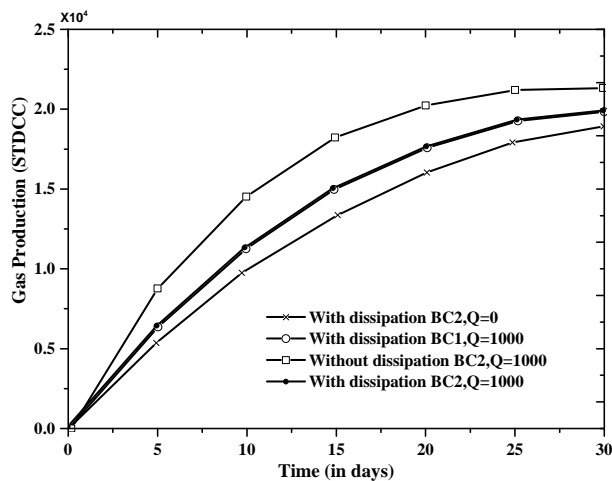


Fig. 12. Cumulative production of methane with time (After Kumar, 2014).

ombinations of depressurization and thermal stimulation. (Moridis et al., 2002).

The concept of thermal stimulation is straightforward. Natural gas hydrates are heated in situ till the local temperature is away from the hydrate stability region. When hydrate decomposes, the entrapped gas is released from water cages and flows through the wellbore to be recovered. External heat is supplied through wellbore or point sources. The thermal stimulation method dissociates hydrates by raising temperature above the hydrate equilibrium temperature. In the thermal stimulation method, the energy that takes in the dissociation and the production should not exceed the energy we can get from produced gases to meet a simple economic principle. The energy needed for the hydrate dissociation is governed by thermal characteristics of the hydrate-bearing region. Fig. 12 shows that the use of heat source increased the production significantly.

The thermal stimulation method has the disadvantage of losing substantial amounts of the introduced energy in the injection path and surroundings. As a result, in this technique, only a small fraction of injected energy is usefully employed to dissociate the hydrate.

3.2.3 Chemical Injection

As compared to depressurization and thermal stimulation, chemical inhibition as a recovery method has been relatively less studied. The chemical injection method injects inhibitors of gas hydrates to dissociate hydrates in the reservoir. Chemical inhibitor injection works by shifting the equilibrium curve towards higher pressures and lower temperatures, thereby destabilizing hydrate at natural conditions. There are two main types of inhibitors, namely thermodynamic inhibitors which alter the hydrate equilibrium conditions and kinetic inhibitors which slow down the rate of hydrate formation.

Thermodynamic inhibitors are of particular interest to the applications for gas production. Two of the most common thermodynamic inhibitors used are methanol and ethylene glycol (Demirbas, 2010). Ethylene glycol (EG) is more commonly studied due to its higher availability in the market,

lower toxicity and better performance in inducing hydrate dissociation owing to its higher density compared to methanol (Dong et al., 2009). Several factors have been identified to control the rate of dissociation, including the concentration and temperature of inhibitor solution, inhibitor injection rate (Fan et al., 2005), pressure, and hydrate-inhibitor interfacial (contact) area (Sira et al., 1990). Apart of EG and methanol, NaCl also possesses inhibitory properties and it is widely found in nature (Qi et al., 2012). A molecular dynamic study has provided an insight into the possible roles of Na^+ and Cl^- on methane hydrate recovery (Yi et al., 2014). The possibility of using brine injection to recover gas from methane hydrate in pure water and Berea sandstone was also explored (Lee, 2009). The salt also inhibits hydrate formation and dissociation kinetically.

3.2.4 CO_2 Injection

The thermodynamic feasibility of CO_2 - CH_4 replacement was fully proven through numerous studies. From the thermodynamic point of view, both pure CO_2 and CH_4 molecules typically form hydrates under corresponding conditions, and the enthalpy of CO_2 hydrate formation (about -57.98 kJ/mol) is lower than that of CH_4 hydrate formation (-54.49 kJ/mol). It means CO_2 hydrate is more stable than CH_4 hydrate under the same condition of temperature and pressure (Li et al., 2016). Yuan (2012) proposed a conceptual mechanism for CO_2 - CH_4 replacement in hydrate-bearing sediments.

The schematic diagram for CO_2 - CH_4 replacement in the hydrate is shown in Fig. 13, which is divided into four steps:

(a) Diffusion of CO_2 molecule to the surface of CH_4 hydrates in porous media, which would disturb the stability of the methane hydrate structure.

(b) Dissociation of CH_4 hydrate and CH_4 molecule escapes from the hydrate cage. Both the large and small cages of methane hydrate rupture, and CH_4 molecule escapes from the hydrate cage.

(c) Rearranging of CH_4 and CO_2 in hydrate cage. In the reformed hydrate, CO_2 molecules mainly enter the large cages of the hydrate, and CH_4 molecules can enter both the small cages and the large cages of the hydrate, but mainly enter the small cages.

(d) Diffusion of CH_4 molecule from the hydrate surface to gas phase and CO_2 molecule diffusion into deeper hydrate-bearing sediment layer. CO_2 molecules diffuse into deeper hydrate layer and the replacement reaction continues.

The experimental results show that the method of CH_4 replaced with gaseous CO_2 is not suitable for the reservoir, in which hydrate layer with absence of underlying zones of mobile water. For high water saturation reservoir, gaseous CO_2 will react with free water firstly which results in the inferior effect of replacement. In comparison, for low water saturation reservoir, the replacement effect is perfect and encouraged in CH_4 hydrate exploitation.

The techniques have their individual limitations such as high energy consumption, low gas recovery, low gas production rate and environmental issues. The combination of those techniques is considered as a better technique to enhance the

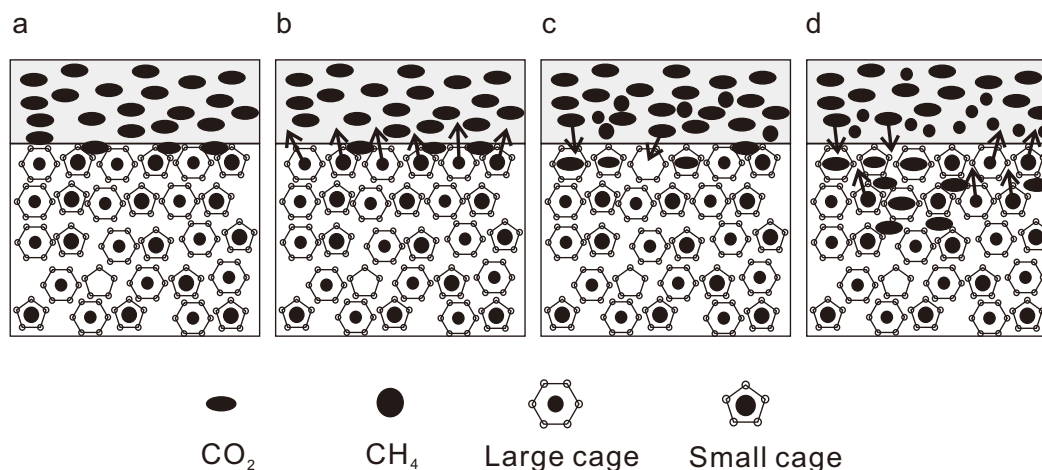


Fig. 13. Schematic diagram for CO₂-CH₄ replacement in hydrate (After Yuan, 2012).

efficiency of gas production, lowering the energy consumption, accelerate the gas production, etc. Compared with thermal stimulation or depressurization, the combination technique is proven to be more efficient in natural gas production from NGH reservoirs (Li et al., 2016).

4. Challenges and Outlook

With the gradual depletion of traditional energy such as oil and coal, natural gas hydrate has a wide range of distribution, huge amount of resources and low pollution characteristics which make it become “future energy”. The abundance of gas hydrate reserves is expected to be more than twice of the combined carbon of coal, conventional gas and petroleum reserves. Natural gas hydrate has changed the pattern of the world’s energy. The challenges and problems for gas hydrate exploration and development are listed as following:

(1) For NGH’s exploration, although a potential for characterizations of hydrate reservoir using seismic indicators has been reported in literatures, characterizing based only on seismic survey results is less reliable.

(2) For NGH’s development, it’s difficult to produce methane from the NGH reservoir and assess hydrate recovery rates. Besides, locating potential resources, quantifying hydrate content, keeping process safe from geomechanical impacts from hydrate dissociation are worth considering.

(3) For the environment and application, Hydrate development should not only consider its economic benefits, but also the ways of transporting the extracted natural gas to the market. Whats more, development of natural gas hydrate may do more harm to environment. Methane gas greenhouse effect is much greater than the carbon dioxide gas.

In the future, the researcher should pay more attention on how to develop nature gas from hydrate, such as do more work on hydrate simulation and hydrate production test. Besides, the properties of hydrates should be studied. The kinetics arena will represent the largest challenge for advancing the information on hydrates. Although we know quite a lot about what hydrates are, the question of how hydrates form is still

very much unanswered. Finding the answers to such questions provides the intrinsic motivation for future research.

Acknowledgments

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