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Gas Hydrate Applications and Problems in Oil and Gas Industry

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Abstract— This paper presents a brief account of different applications and problems of gas hydrate in oil and gas industry. Broadly, gas hydrate is clathrate physical compounds, in which the molecules of gas are trapped in crystalline cells, formed from hydrogen bonds of water molecules. Gas hydrates can be formed from all the gases in the presence of water under different conditions of high pressures and low temperatures. The oil and gas industry for many years take a strict measures to prevent gas from forming hydrates because of their annoying tendency to plug pipelines. However, natural gas hydrates exist on earth in colder regions, such as permafrost, or sea bottom areas, are an unconventional energy resource available for mankind. The other positive applications are carbon dioxide sequestration, gas separation, and natural gas storage and transportation. Finally, the use of hydrate dissociation energy can be applied in refrigeration processes and cool storage.

Index Terms— Gas hydrate, Clathrate, pipeline plugging, carbon dioxide capture, petroleum industry problems, natural gas storage, transportation .

1 Introduction

NATURAL hydrates are crystalline solids (like ice) composed of water and gas. The gas molecules (guests) are trapped in water cavities (host) that are composed of hydrogen-bonded water molecules as shown in Figure (1) [1-3]. Three structures of the gas hydrates that have been found are Structure I (SI), Structure II (SII) and Structure H (SH) of the isometric (cubic) lattice [3]. In the structure I, the cages are arranged in a body-centre packing and they are large enough to include methane, ethane, and other gases of similar molecular diameters such as carbon dioxide and hydrogen sulfide. In structure II, packing is like a diamond, which resulting in some cages being large enough to include not only methane and ethane but also gas molecules as large as propane and isobutene. Structure H requires both a small molecule such as methane and larger molecules typical of a gas condensate or an oil fraction. Out of these three, structure I is the most common one. Figure 2 shows the three common structures of gas hydrate [4].

Gas hydrates are clathrates that are formed under certain conditions (low temperature and high pressure) and can exist at temperatures greater than the freezing point of water at high pressures. The conditions promoting hydrate formation are high pressure (typically > 30 bar) and low temperature (typically < 20°C) [5]. Precise conditions in terms of pressure and temperature depend on the composition of the fluids. These conditions could exist offshore in shallow depths below the ocean floor and onshore beneath the permafrost.

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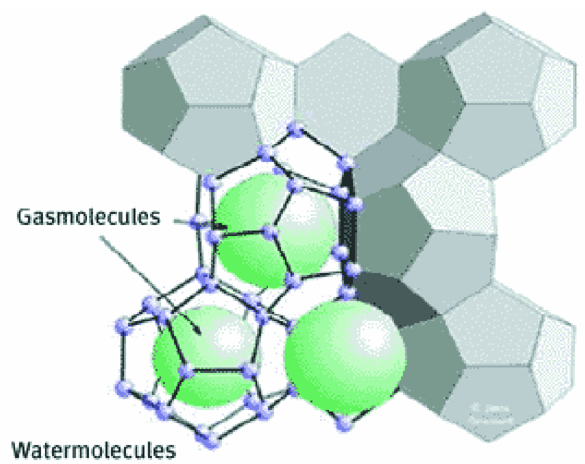

Fig. 1. Host molecules (water) and guests (gas) [2].

The physical properties of gas hydrates that they are non-flowing crystalline solids which are denser than typical fluid hydrocarbons and the gas molecules they contain are efficaciously compressed, these properties give rise to numerous applications in the broad areas of energy and climate effects, such as separation technologies, due to high gas concentration [4]. Gas hydrates can also be used successfully for either carbon dioxide sequestration or storage and transportation of natural gas. Moreover, natural gas hydrates naturally occurring in deep seas and permafrost have high gas concentrations; therefore, turn out to be a possible source of energy, providing less environmental impact. Finally, clathrate hydrates provide high latent heats of dissociation that can be utilized for refrigeration applications, like cold storage or air conditioning [6]. The opposite of these applications it was pointed out that gas hydrate were responsible for plugging natural gas pipelines [7]. Also, the formation of gas hydrate during deepwater well drilling can have several adverse effects on well control and safe operations [8].

The objective of the present review paper is to distinguish various areas of interest related to gas hydrates advantages or hydrate problems in oil and gas industry.

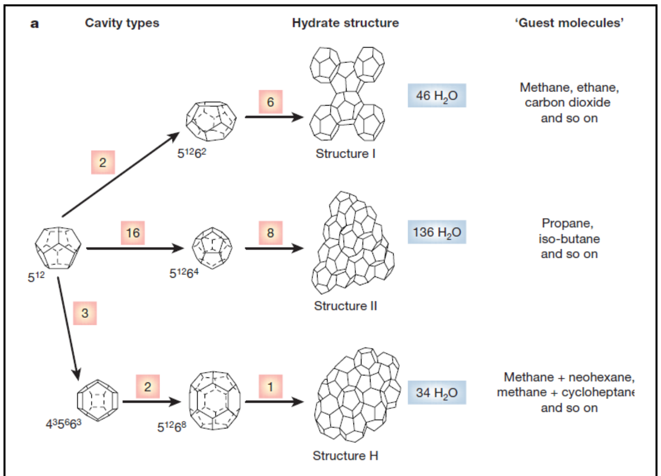

Fig. 2. The three common hydrate unit crystal structures [4].

2 Gas Hydrate: Problems In Oil And Gas Industry

2.1 Gas Hydrate Occurrence during Drilling in Offshore Regions

Increasingly complex challenges will be faced in offshore oil and gas drilling with increasing water depths. One of these challenges is the formation of gas hydrates. If shallow sediments that contain natural gas are encountered during deep-water drilling, this gas will enter into the drilling fluid leading to gas hydrate formation under low temperature and high pressure [9]. Also, if the drilling fluid used was not hydrate inhibited, gas hydrate could easily formed when mud circulation was stopped and gas entered into the drilling fluid, Resulting in an unexpected gas kick during drilling operation, which will block the pipe, annular clearance or blowout preventer (BOP) [10]. This may be catastrophic in several situations. Solid Hydrate can plug choke and well kill-lines and cause well control problems.

Hydrate can form in riser and in the annulus between the casing and drill string, which may stop the circulation of drilling fluid and prevent the movement of drill string and seriously affect drilling operations as shown in Figure (3) [11]. Therefore, since the 1990s, strict measures have been taken to prevent gas from forming hydrates in deep-water drilling. The main preventive measure is to add certain chemical compounds that cause drilling fluid to inhibit formation of gas hydrates like thermodynamic inhibitors and low-dosage hydrate inhibitors (LDHI). During deep-water oil and hydrate drilling, thermodynamic inhibitors normally are added to the drilling fluid, whereas kinetic hydrate inhibitors (KHI) are still under investigation.

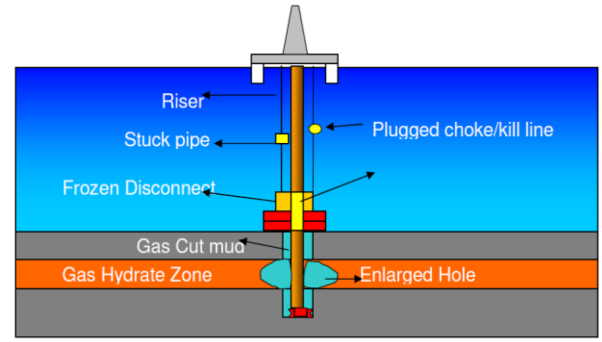

Fig. 3. Pictorial representation of some notable problems encountered while drilling through gas hydrate formation [11].

2.2 Flow Assurance Issues

Transportation of oil and gas in the pipeline is a common way of transporting oil and gas from wellhead to production site. If the temperature and pressure of pipe line falls within hydrate zone in phase diagram, gas hydrate particles start to form. These particles could eventually plug the pipeline as shown in Figure 4 [2].

Hydrates form and plug transmission pipelines, making uneconomical operation, production stoppages, sometimes for as long as months, in large extended pipelines. Hydrate propagation tends to gradually form a plug that separates the pipe into two pressure sections: a high pressure section between the well or the high pressure gas source and the plug, and a second section at low pressure between the plug and the gas recovery division. In the high pressure section, a pipe blast can occur due to pressure growth. The plug can destroy the pipe when the pressure difference between the upstream and downstream sections increases. Both problems can endanger personnel safety and damage production equipment [12].

Four main processes were investigated in order to combat hydrate plugs and ensure regular flow: chemical additives, hydraulic, thermal and mechanical processes [6]. Chemical method can be divided into thermodynamic inhibitors (THI) and low dosage hydrate inhibitors (LDHI). Thermodynamic inhibitors reduce water activity, shifting the hydrate phase boundary to lower temperature and higher pressure, which can effectively prevent gas hydrate formation. However, it is not unusual that high concentrations of up to 60 mass % methanol and glycol may be required for certain field cases. The need of a large volume of methanol and glycol leads to high cost and raises environmental and logistical concerns. In contrast, low dosage hydrate inhibitors are relatively new category of chemical additives that can be active and effective at only a few mass % for typical applications. Low dosage hydrate inhibitors are subdivided into two types, i.e., kinetic hydrate inhibitors (KHI) and anti-agglomerants (AA). Anti-agglomerants do not hinder hydrate formation, but prevent gas hydrates from agglomerating into non-transportable lumps. Kinetic inhibitors are polymer-based chemicals. It is believed that kinetic inhibitors do not prevent but delay hydrate formation. A typical concentration of around one mass % is sufficient to control the hydrate formation process until the gas or oil is transported to the destination or the processing facility where it is outside the thermodynamic conditions of hydrate formation [13]. The hydraulic removal method is based on the dissociation of the hydrate plug by depressurization process. This method appears promising, given the porous structure of the gas pipeline plugs. However, it is not suitable for liquid hydrocarbons since depressurization causes its vaporization. The thermal method consists in-situ delivering a heat flow towards the plug through the pipe wall in order to raise the system temperature above the hydrate formation condition. This method is possible for external pipelines but unsuitable for subsea equipment [6]. Also, the mechanically pigging can be used to clean the pipeline for deposit. The method involves moving a large disc or a spherical or cylindrical device made of a flexible material e.g. neoprene rubber and having an outside diameter nearly equal to the inside diameter of the pipeline to be cleaned, but it is expensive to shut the production down to perform this method [14].

Fig. 4. Hydrate formation in natural gas transmission pipeline [2]..

3 Clathrate Hydrates: Potential Applications

3.1 Natural Gas Hydrates as a Possible Source of Energy

Large amounts of methane gas hydrate occur in the form of solid in sediment and sedimentary rock within 2000 m of the earth's crust in permafrost and deep-water regions [15]. The amounts of gas hydrates in the earth's crust might be considered as a new source of unconventional resource of energy. It was pointed out that under the same pressure conditions and at standard temperature, one volume of methane hydrate can hold 164 times more methane than one volume of gaseous methane [6]. Potential reserves of gas in hydrate that distributed in offshore and on land are more than 1.5×10^{16} m^3 [16].

Gas hydrate plays an important role to satisfy worldwide energy needs, therefore the exploitation, development and production of gas from gas hydrate is dedicated to being a distant prospect for the twenty first century [17].

Gas recovery is generally produced by either thermal, depressurization, and/or chemical inhibition. In order to release gas from a gas hydrate deposit by thermal stimulation one has to warm the formation through the injection of heated fluid or potentially direct heating of the formation. Depressurization is more preferable and economical than the thermal stimulation method, because it does not require large energy expenditure and can be used to drive dissociation of a significant volume of gas hydrate relatively rapidly [18]. But it requires high porosity hydrate deposits and in the transport stage the extracted gas and water may re-crystallize into gas hydrates inside the transporting lines and then provoke pipe plugging [6]. Chemical inhibition like certain organic (e.g., methanol and glycol) or ionic salts compounds, is used to change the gas hydrate stability condition [19]. Seawater salt or other chemical inhibitors might be required during some stages of production of gas from methane hydrate deposits but would not be the primary means of dissociating gas hydrate nor used for a long period or on a large scale.

3.2 The Capture and Sequestration of Carbon Dioxide

The effect of the industrial emission of CO_2 and its impact on the environment leading to global warming has gained importance in the recent years [20]. The main source of carbon dioxide emissions in the atmosphere are thermal power generation, cement manufacturing, iron and steel making, oil and natural gas refining, and petrochemical industries [21] The carbon dioxide capture and sequestration (CCS) has become an important area of research in industrialized countries to overcome worldwide concerns over the threat of global warming [22]. Moreover, the basis of CO_2 capture is to look at CO_2 not only as polluting greenhouse gas, but also as an important raw material [21]. Currently available techniques for carbon dioxide capture and separation are chemical solvents, absorption, adsorption, chemisorptions, and chemical bonding through mineralization. Certain factors such as the amount of chemicals used in these processes, the energy legislations, and the costs associated with these processes make these processes less attractive for large-scale carbon capture [22]. Therefore, the development of new less energy intensive process is the major research interest. The gas hydrate crystallization techniques have certain advantages, the main chemical required for carbon dioxide hydrate formation is water, which provides the process with abundant (cheap) and green chemical. In addition, reduction of energy requirements for hydrate formation can be obtained by including certain organic chemicals in low concentrations, known as a hydrate promoter in the hydrate forming system [23]. After separation, the captured carbon dioxide must be definitely: sequestered. The main steps of CCS processes: capture, transportation, storage are shown in Figure (5). Many methods under study for CO_2 sequestration, such as storage in depleted oil reserves, salt formations, terrestrial ecosystems, and geological formations or direct injection into the deep ocean [24]. Methods of carbon dioxide sequestration into the sea have been investigated for many years and a wide range of ideas has been considered. In bulk, gaseous carbon dioxide and sea water are compressed and transported as a solution in pipelines or in pressurized and chilled vessels and then pumped to the same pressure. The solution is then pumped downward to the depth in which the pressure and temperature is suitable for carbon dioxide hydrates formation. These hydrates sink towards the deep sea bottom where they stabilize in long term due to their densities

[25].

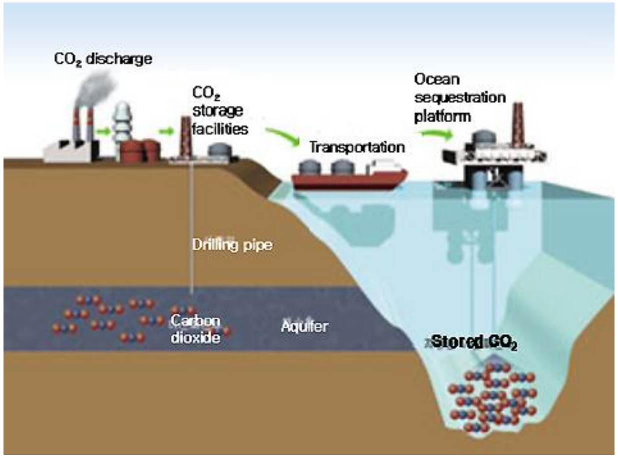

Fig. 5. The main steps of CCS processes: capture, transportation, storage

3.3 Natural Gas Storage and Transportation

Gas hydrate is implemented for storage and transportation of natural gases, due to the ability of hydrates to provide a high gas concentration [23]. Several studies show that the gas hydrate structures have a potential as storage media for various gases. Natural gas hydrate (NGH) is regarded an important technique among many possible technologies of transporting gas from production fields to the place of use, which includes pipelined natural gas (PNG), liquefied natural gas (LNG), compressed natural gas (CNG), gas to liquids (GTL), gas to commodity (GTC), and gas to wire (GTW), i.e. electricity. Storage and transportation of natural gas in the form of gas hydrates have the economic advantage mainly because of lower investment in infrastructure and equipment [26]. The key of NGH storage and transportation is to overcome longer induction time and accelerate the hydrate formation. A great deal of research has been done in order to increase the hydrate formation rate, including adding surfactants, stirring, bubbling to the solution. However, the economic aspect remains is the separation factor in determining the optimal process efficiency.

3.4 Cool Storage Application

The increasing demand to electric power for residential air-conditioning and the depletion of the ozone layer by chlorofluorocarbons (CFCs) emphasis on using alternative cool storage systems which shifts this demand to off-peak period and eliminate the need of using conventional refrigerants such as CFCs (chlorofluorocarbons) and HFCs (hydrofluorocarbons) [27]. CO_2 hydrate is one alternative way used in the refrigeration process in the form of clathrate hydrate slurries as a two-phase (solid-liquid) refrigerant. These two-phase refrigerants, because of high latent heat of fusion (sometimes also known as phase change materials), are more energy efficient than single-phase refrigerants. CO_2 hydrate slurries are promising systems in the field of cold distribution and storage as phase-change materials due to the fact that the melting temperatures of some clathrate hydrates are consistent with the temperature needed in applications, such as, air conditioning. Instead of using mechanical methods, the heat of dissociation of CO_2 hydrates can be generated by direct gas injection into an aqueous solution as in the case of ice slurries. The heat of dissociation of these slurries has been found to be suitable for its application in refrigeration [27].

4 Conclusions

Gas hydrate is a regard of important process which can happen naturally or artificially. Gas hydrate can be used in many applications like source of energy, storage and transportation, gas separation from the flue gas mixture, and cool storage application. At the same time it is regarded as a problem in the oil and gas industry due to the formation of gas hydrates during gas and oil drilling in offshore, and in gas and oil transporting pipe lines, which causes many problems in spirits and finances. This paper gave various areas of interest related to gas hydrate advantages or hydrates problems in oil and gas industry and thus removes the confusion accompanying with gas hydrate.

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