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Investigation of the History of Formation of Gas Hydrates

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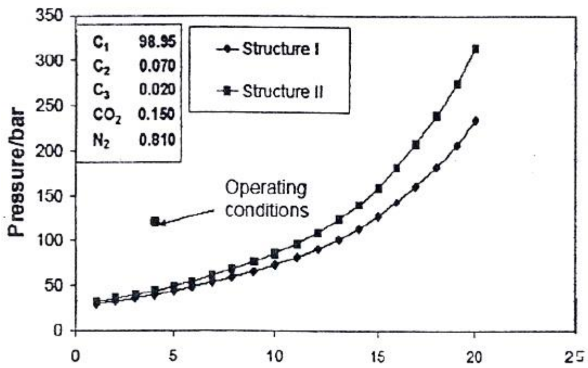
ABSTRACT

In gas transmission lines, there are usually "four main factors that are necessary to create hydration. As it is always necessary to design the pipeline to transfer at high pressure (high density), also pipelines are exposed to ambient temperature and usually" with they face low temperatures. On the other hand, in the presence of water vapor (almost all-natural gases carry some amount of water vapor with them) and, more importantly, the presence of hydrocarbons, hydrate crystals are formed in addition to partial or complete blockage of gas transmission lines. Causes fouling of distillation tower trays, nozzles, valves and heat exchangers, wear on turbochargers, etc. After the discovery of gas hydrates as the cause of blockage of gas transmission pipelines by Hammer Schmidt in 1934. The collection of thermodynamic information increased the formation of hydrates, with more carbon dioxide being produced and released into the atmosphere by burning fossil fuels in homes and cars and burning waste gases in refineries and petrochemical industries, as well as in thermal power plants. It is one of the most important pollutants in the greenhouse effect, which causes global warming and gradual increase in temperature. Isolation and storage of greenhouse gases is one of the most fundamental environmental issues today.

GRAPHICAL ABSTRACT



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INTRODUCTION

Gas hydrate is defined in different ways as follows

Gas hydrates are non-stoichiometric crystalline materials that are formed by the contact of water with suitable gas molecules, under certain temperature and pressure conditions [1-3].

Natural gas including methane, ethane, propane, isobutane, CO_2, H_2S, gases (Ar, Xe, Ne, 0_2, Kr N_2) and hydrocarbons including silco-propane in cage-like structures formed by the hydrogen bonding of water molecules, they are trapped and form hydrates. Hydrates Crystalline materials consist of an icy network with a guest molecule enclosed between water molecules in which water molecules are joined together by hydrogen bonds and a gas molecule is placed in the empty space between them. This gas can be CO_2), C_3H_3, C_2H_6, CH_4, (H_2S), other hydrocarbons with higher molecular weight [4-7].

Hydrates are crystalline structures formed by water that are stabilized by the presence of a guest molecule within the lattice. When guest molecules are preferably light hydrocarbon gases, hydrates are of particular importance in the oil and gas industry [8-11]. Gas hydrates are usually solids composed of crystalline materials from hydrogen bonds of water that place gas molecules with a lower molecular weight in the network. They are formed at low temperatures and high pressures. Gaseous hydrates are geologically formed in two areas:

(1) In cold underground areas

(2) In sub-oceanic sediments bordering continents

Gas hydrates are solid crystals formed by trapping molecules (usually gas) in cages caused by hydrogen bonding of water molecules. These crystals are the result of the physical combination of gas and water molecules. Unlike inorganic hydrates (such as $5H_2$ $CuSO_4$ O) the ratio between water and gas is not constant [11-14].

Gas hydrates are crystalline materials that are formed from the combination of water molecules and other molecules in the appropriate size and conditions of temperature and pressure. Water molecules by hydrogen bonds can form crystals with unstable cage-like structures [15-19]. Appropriately sized molecules are trapped in these cage-like structures, stabilizing the structure and forming gaseous hydrates. Types of hydrates in terms of constituent gas:

Simple gas hydrates

If gas hydrates consist of only one type of gas, it is called simple gas hydrate. Methane, ethane and CO2 gases form simple S-I type hydrates. Propane, I-C4, benzene and cyclohexane give type S-II gas hydrates. Very small molecules, such as O2N2, form S-II hydrates at very low temperatures [20-23]. Recent research has shown that some of these molecules, such as N2, form S-I hydrates at temperatures as high as 0 °C. To date, no material has been identified that can form a simple S-H hydrate and has only one large cage per building unit [24-27].

Dual gas hydrates

If two or more types of gas molecules participate in the formation of hydrates, the resulting hydrate is called dual hydrate. Mixtures of two or more components containing CO2, C1, C2, and smaller molecules usually form S-I hydrates. But mixtures of two or more components containing small molecules such as C1N2, C2, CO2, medium-sized molecules such as C-C6, C3, I-C4, n-C4, C-C5, and gasoline usually give S-II hydrates. S-I hydrate is stable when the concentration of medium-sized molecules is very low [28-32].

Very large molecules such as C7 H14, AdamantIne along with small molecules such as C1 N2, C2, CO2 may form S-II hydrates [33]. In the S-H building, large cages are mostly filled with very large molecules, while small molecules fill small and medium-sized cages.

If the molecules C5, I-C4, C-C3) and benzene are present in the fluid, the structure of the S-II hydrate is much more stable than that of S-H, unless the concentration of large, heavy molecules is very high [34-37]. S-II to S-H have been tested for several systems, with critical concentrations varying from system to system and much higher than in natural systems. Recent studies have shown that in stable systems the content of C1 and large molecules and heavy (system I - C5 C1,), it is possible to change SH hydrate to S-I by increasing the pressure and temperature of the system [38].

Interesting properties of gaseous hydrates

Hydrates have the following properties

Trapping a large amount of gas (maximum 15% molar percentage):

Hydrates store a lot of gas and can hold up to 15% mol in their building, which is a lot. In fact, one volume of hydrate is capable of storing 175 volumes of gas under standard conditions. A number of researchers are considering storing and transporting oil and gas in the form of hydrates. This idea potentially changes the economic balance of many marginal oil and gas fields. So many technology challenges need to be addressed [39-42].

Separation of light components from oil and gas

Hydrates can separate the light components in oil and gas. Hydrates are made up of small molecules (AdamantIne, N2 C02, C1-C4). Hydrates must be formed in a calculated way as it will increase the viscosity of the remaining oil [43-47].

A number of researchers have suggested that hydrate formation should be used as an opportunity to separate oil and gas and reduce the size of conventional separators as much as possible.

Gas hydrates are formed at temperatures close to zero degrees Celsius. They are usually lighter than water. The presence of gas molecules in the empty spaces of the building hydrate crystal contributes to the stability of the building. Spherical molecules, about the size of empty space, are usually the best molecules for forming gaseous hydrates, as they have strong van der Waals bonds with adjacent water oxygen atoms. The potential for hydrate formation at high freezing point temperatures has both positive and negative effects, which will be explained later [48].

There is more than 85% of water in the building

There are more than 85% moles of water in gaseous hydrates. The number of water molecules in each building unit of various gaseous hydrates is constant. In different molar ratios of water, the ratio of empty spaces to total spaces will be different [49-52].

Contains salt and other impurities

Gaseous hydrates remove all impurities from their building. And are composed only of water and gas molecules. This means that if gas hydrate is formed in saline water, the concentration of residual saline water will be higher, and if it decomposes, the concentration of the resulting solution will be lower [53-55]. This property has been tested for the design of desalination plants based on hydrate formation. However, due to the fact that a small amount of salt water and salt are trapped between the hydrate crystals, it is impossible to extract very pure water [56]. The phenomenon of hydrate formation is used in wastewater treatment in the fiber industry and to measure the amount of gaseous hydrate in submarine sediments by changing the concentration of chloride ions [57-59].

Different ways to prevent the formation of hydrates

There are several ways to prevent the formation of hydrates, including:

- Dehydration
- Underwater separation
- Injection of thermodynamic inhibitors
- Injection of kinetic inhibitors
- Use of anti-fouling inner coatings AntI-deposItIonal
- Electric heating or bundle tube heaters (with boiling water)
- Use of anti-fermentation inhibitors

The effect of water-soluble impurities

In general, water-soluble impurities prevent the formation of hydrates. Substances such as salts, glycols, ethanol, etc. prevent the formation of hydrates. Substances such as THF and dioxin accelerate the formation of hydrates. Concentrations of some substances in low concentrations accelerate the formation of hydrates and in high concentrations prevent the formation of hydrates.

Dehydration

Reducing water concentration is a very effective way to prevent problems with hydrate formation. Where one of the important reactants (water) of the system is greatly reduced. In this case, water will act as a limiting reactant, the removal and reduction of which will reduce the formation of hydrates. This practice is currently used in several ways, including:

- Reducing the dew point of the system to a temperature below the minimum pipe temperature, which is a cost-effective method.
- Removing and reducing water from the system (by content separators (DecIcont).
- It is necessary to reduce the amount of water and use the degree of SubcoolIng.

- I wish the amount of water in the system could be combined with inhibitory injection methods (thermodynamic, kinetic and anti-cumulative) and finally with an economic process to reduce or eliminate the hydrate formation reaction [60-63].

Insulation and heating of the pipeline

The temperature of the fluid inside the tube strongly depends on its external temperature. By insulating the pipe, hydrate formation can be prevented, but if hydrate is formed, the insulation will prevent it from decomposing. So far, pipe heating has been used by some companies, such as Konoco in the North Sea, to keep the temperature of the fluid constant to prevent the formation of hydrates or waxes [64-66].

Heating some high-pressure points is also used to accelerate the breakdown of hydrates.

* In the fourth point (GTU FED) studied in this project, insulation operation and the use of steam heaters (steam coils) around the relevant pipes and fittings were performed, which was somewhat effective but was not completely eliminated [67].

The effect of salt water

Saline water is usually a solution of water and salt with a high concentration of salts. Electrolyte aqueous solution prevents the formation of hydrates. In hydrocarbon reservoirs, areas with very low salinity are areas where hydrate is rarely found. Many thermodynamic models are able to calculate the inhibitory capacity of saline water. Although the salt of some of them must be converted to Nacl [68-70].

Saline Formation water along with organic inhibitors

If the inhibitory effect of (saline) water is not sufficient, an increase in mineral inhibitor can be used. However, increasing the organic inhibitor causes mineral salts to leak out of the water, resulting in the production of scale or corrosion. Only a few thermodynamic models are able to predict the combined effect of salts with organic inhibitors on the hydrate-free zone of the hydrocarbon reservoir [71].

The concentration of the inhibitor in the water-enriched phase is important; increasing the organic inhibitor is not economical for water-enriched systems.

The effect of interior coatings

Interior coatings are commonly used to reduce friction and pressure drop in the pipeline. This reduction in pressure reduces the formation of hydrates in the pipeline. Recent studies have shown that the use of internal coatings (such as quartz microbalance crystals) reduces the deposition of solid particles in the pipeline and its blockage [72-75].

Hydrate inhibitors

Methanol, Ethanol, Monoethylene Glycol (MEG), Diethylene Glycol (DEG), Triethylene Glycol (TEG) Low Injection Inhibitors (LDHI), Anti-Cumulative (AA), Synthetic) (KI)

Pahlavanzadeh and colleagues investigated the thermodynamic conditions for the formation of tetra-an-butyl ammonium chloride-like hydrate and carbon dioxide and water. As a result of this study, equilibrium data at a pressure of 10 bar to 30 bar show that at high concentrations of TBAC (40% by weight), the initial pressure has very little effect on the equilibrium points. Also, the use of high weight percentage of TBAC brings the temperature of carbon dioxide hydrate formation closer to ambient temperature, which is significant in industrial processes and in the results showed that the initial temperature of the reactor has no effect on equilibrium points [76].

Fan *et al.* The effect of TBAB and TBAF as thermodynamic enhancers on the rate of CO2 hydrate formation as well as the efficiency of CO2 separation from the gas mixture using clathrite-like hydrate formation at 7.1 and 4.5 °C and 31 MPa pressure injection range/7-19/2 examined. For this purpose, TBAB and TBAF with a concentration of 0.293 mol% were used. They showed that the rate of hydrate formation increases with increasing feed pressure and the rate of constant rate of hydrate formation in the presence of TBAF is higher than TBAB. They also stated that in the feed pressure range, the maximum CO_2 release factor in the presence of TBAF is about four times higher than in the presence of TBAB.

Troba *et al.* investigated the kinetics of the formation of tetran-tetra-butyl ammonium fluoride-like hydrate-like hydrate with hydrogen (H2) and carbon dioxide (CO2) to determine the storage potential of H2 and CO2 in the hydrate. Nucleation was determined by growth and gas uptake in hydrate [77-79]. Their results showed that the kinetics of H2-TBAF-like hydrate-like hydrate formation is more desirable at high pressures and concentrations of TBAF, while high concentrations of TBAF do not show much effect on the hydrogen-forming kinetics of CO2-TBAF-like hydrates [80].

Zhang *et al.* investigated the effect of driving force (high pressure) on the separation of CO2 by hydrate formation from a mixture of chile gas in the presence and absence of THF [81].

Their results showed that high driving force reduces the ultimate gas uptake as well as significantly reduces the CO2 separation and reduction coefficient [82-85]. Yang et al. Had the effect of a mixture of additives (THF / SDS) on the formation and decomposition of carbon dioxide hydrate in the porous medium has been studied [86-88]. The results showed that SDS with 1000 mg.lit-1 concentration is the best concentration due to shorter induction time and more saturated hydrate than other concentrations. Also, the presence of 3% molar THF in addition to significantly reducing the equilibrium pressure of hydrate formation, increases the driving force is also the formation of hydrates.

In similar studies, Yang *et al.* Investigated the effect of mixture (THF/SDS) and its mechanism of action on the thermodynamic and kinetic properties of CO2 hydrate formation in a porous medium by maintaining a constant temperature and using a constant volume method, Tang *et al.* SDS and THF were investigated for the separation of CO2 + N2 and CO2 + CH4 mixtures, and Torre et al. Reported the effectiveness of the mixture (THF / SDS) at high pressure on the kinetics of CO_2 hydrate formation [89-91].

The village and his colleagues investigated the effect of SDS and THF and stirrer on the kinetics of CO_2 hydrate formation. The results of their experiments showed that in three concentrations of 300, 500 and 1000 (in terms of ppm) of sodium dodecyl sulfate has no effect on increasing the rate of hydrate formation. Addition of THF to 2 mol% significantly reduces the hydrate formation pressure and also increases the rate of hydration significantly by increasing the stirrer speed from 400 to 800 rpm.

Mohammadi *et al.* investigated the effect of silver nanoparticles and SDS on CO_2 hydrate formation rate and storage capacity and showed that silver nanoparticles and SDS did not have a significant effect on reducing induction time or increasing CO2 storage capacity, if mixed. SDS and silver nanoparticles have a significant effect on CO2 storage capacity [92-95].

Mr. Ganji *et al.* investigated the effect of non-ionic surfactants Tween-20 and Tween-80 on the rate of methane hydrate formation and its storage capacity. Concentrations of 100 and 500 ppm were used and the results were compared with hydrates formed in pure water and aqueous solution at a concentration of 500 ppm from SDS. Different concentrations of nonionic surfactants had different effects on the rate of hydrate formation and its storage capacity. It was concluded from this study that 2000 ppm of Tween-20 increases the rate of hydrate formation and its storage capacity. However, when 1000 ppm was used, it effectively prevented the formation of hydrates. Tween-80 reduced the rate of hydrate formation at both concentrations and the highest storage capacity was Tween-20 with a concentration of 2000 ppm (125 V/V).

Mr. Varaminian *et al.* Investigated the effect of surfactants of polyoxyethylene sorbitan monopalmitate (Tween-40), sodium dodecyl sulfate (SDS) and dodecyl tri-methylammonium bromide (DTAB) on the kinetics of ethane hydrate formation and their results show that SDS compared to two Surface activators Tween-40 and DTAB have a greater effect on the rate of hydrate formation. Tween-40 also has a higher rate of ethane hydrate formation than DTAB [96-98].

Mr. Varaminian *et al.* Investigated the effect of two anionic surfactants (SDS) and (SDBS) and two non-ionic surfactants Triton and Tween 40 on the rate of propane hydrate formation and the results show that SDS has an effect on the concentrations tested. It does not speed up the formation of hydrates, but even at higher concentrations, it reduces the formation of hydrates. SDBS has a great effect on reducing the formation time of propane hydrate, so that at a concentration of 100 ppm and a stirrer speed of 500 rpm, it reduced the formation time of propane hydrate by 74%. Triton, like SDS, had no effect on hydrate formation rate at the concentrations tested. Tween 40 also has a great effect on reducing the formation time of propane hydrate, and considering that it initially reduces the initial rate of formation of propane hydrate, but ultimately reduces the formation time of propane hydrate. Moradi et al. Investigated the effect of two ionic liquids, 1- butyl 3-methylimidazolium tetrafluoroborate [Bmim] [BF4] and 1-butyl 3-methylimidazolium methyl sulfate [Bmim] [MS], on the formation kinetics of carbon dioxide. The results of their studies showed that increasing these two ionic liquids with a mass concentration of 0.6% at an initial pressure of 35 bar, by reducing the induction and nucleation time, accelerates the process of carbon dioxide hydrate formation and acts as a kinetic enhancer. So that they have a recovery coefficient of 68% and 52%, respectively [99].

Makala et al. investigated the kinetics of CO2 hydrate formation in seawater and pure water in the presence of silica particles. The observations indicated that with decreasing the size of silica particles, CO2 consumption in the structure of the hydrate increases, also the average rate of hydrate formation at a pressure of 6.0 MP, a temperature of 276.15 K and in the presence of 0.46 mm silica particles is the highest.

Babu et al. Investigated the performance of a new porous medium, polyurethane foam (PU), for the separation of CO2 from a gas mixture in a fixed bed reactor using a hydrate-based separation process. It was observed that in the presence of PU foam, gas consumption and water to hydrate conversion increase significantly. Also, in the presence of this additive as a porous medium, water to hydrate conversion increases sharply in the early hours and the induction time of hydrate formation decreases.

Babo *et al.* investigated the effect of temperature and pressure on the formation of TBAB-like hydrated clathrate hydrate with a molar percentage of 0.3 and CO_2. Induction time according to Figure (2-20 a-), increase of total gas consumption according to Figure (2-20 b-) and increase of hydrate formation rate according to Figure (2-20 c-). In another step, by increasing the pressure from 6 to 4.5 MPa, it increases the induction time according to the figure (2-20a-), decreases the total gas consumption according to the figure (2-20a-) and decreases the rate of hydrate formation according to the figure (2-20a-).) Becomes. According to Figure (2-20d-) CO2 consumption has decreased in both stages of temperature and pressure reduction, which may reduce the solubility of CO2 due to these conditions [100].

Li and Zhang investigated the kinetics of the formation of carbon dioxide hydrate in a non-stirred batch reactor in the presence of silco-pentane (CP) as a thermodynamic enhancer at 274 K and a pressure of 1.9-4.4 KPa. Their experiments were performed in two volumes of 100 and 200 cubic centimeters of water. The results showed that the growth rate of hydrate, in addition to being strongly dependent on the volume of water, also depends on the pressure, so that at the end of the hydrate formation process, CO2 hydrate and CO2 + CP double hydrate are present together and the molar ratio of CO2 trapped in structure I Hydrate to CO2 in dual hydrates per 100 cm3 of water is greater than 200 cm3 of water. Also, increasing the pressure to 3.06 MPa increases the growth rate of hydrates, but with increasing the pressure of this amount, the growth rate decreases [101-103].

Due to the lack of information about the kinetic parameters of hydrate formation of clathrite-like, in this study, the effect of adding Tween and TBAB on the kinetic parameters of hydrate formation of carbon dioxide has been investigated [104-107].

In kinetic studies on the formation of gaseous hydrates, the aim is to investigate parameters such as induction time and storage capacity. In general, kinetic studies in this field with and without improvers are very limited, unlike thermodynamic studies in this field. For this reason, many kinetic data on the formation of gaseous hydrates and quaternary gaseous hydrates are incomplete. Therefore, the kinetic study of the formation of hydrates, especially pseudo-clathrites, can be the first priority of research in this field [108].

Disadvantages and limitations

(1) They have a short residence time.

(2) Low temperatures have low efficiency.

(3) A special type should be designed for the fluid and production conditions of the tank.

(4) They are used in low pressures.

Many existing kinetic inhibitors are non-reversible and harmful to the environment.

Curve of the effect of increasing kinetic inhibitor on the hydrate formation curve

Applications of gaseous hydrates include

(1) For oil and gas separation

(2) Gas storage and transfer

(3) De-salting (De salIvatIon)

(4) Waste water treatment

(5) Gas treatment

Gas transmission

At present, ships (liquefied petroleum gas) are used to transport gas in short distances through pipelines, which are very expensive and dangerous in long distances. But today, the use of gas hydrates is a method of gas transfer. Because if natural gas is transferred as hydrate instead of liquid, it will reduce costs and risks, and to use, having enough information about the breakdown of hydrates is key [109-110].

Energy source

One of the potential sources of natural gas is gaseous hydrates, which are found in subsurface sediments off the continents. Natural gas hydrates found in submarine sediments or deep-sea sediments are considered a huge source of energy for the future. The US Geological Survey has declared US hydrate sources to be 320,000 Tcf.

Existing estimates the amount of gas in the hydrates under the seas varies between 1015 and 1018 * 7.6 cubic meters.

There are large amounts of gaseous hydrates in sediments under the oceans and deep seas and frozen underground layers (Permafrost). They can stick sediments together, reduce porosity and permeability, change the degree of fluid saturation and mechanical properties of rocks, contain large amounts of methane hydrates, and act as a gas storage cap.

There are huge sources of methane gas hydrates in the continental slopes of the continent. If they are economically recycled, they have huge energy potential.

The first gas to be considered as a source of energy storage is methane gas. The volume of methane in a hydrate unit may be equivalent to 164 volumes of methane gas at standard temperature and pressure

Kenvolden estimated in 1993 that the amount of methane stored as hydrate on the continents and ocean floor was about 10 grams. If such an estimate is correct, the amount of methane in methane hydrates is twice the amount of carbon in fossil fuel deposits around the world.

-DIcken estimated in 1997 that the methane stored in the South Carolina continental shelf (Blake Ridge) hydrates would be enough to power the United States for 105 years, with an annual natural gas consumption of 1996. 99% of the gases in gaseous hydrates are methane gas. Other gases such as CO2, ethane and propane have been observed in the Gulf of Mexico and the Caspian Sea (containing 9 to 79% of gases other than methane).

Due to the uncertain geological and geographical conditions in which hydrates are formed, no specific technology has yet been developed to extract methane from hydrates.

Hindu Japan and other nations have begun research programs to extract methane from hydrates.

Safety and environment

A new way to reduce greenhouse gases, such as CO2, would be to bury these gases as hydrates in the deep oceans, which would require detailed information on the decomposition kinetics of hydrates to determine a stable region with suitable conditions.

CO2 hydrates can be used as an important fire extinguishing agent.

Because the two strong extinguishing agents combine (solidity, which causes it to spread over the fire, and CO2 from the top of the fuel, which causes suffocation) and there is no chance of damaging it. Gaseous hydrates, with the exception of monohydrate hydrates, are molecules with higher molecular masses such as CO2, Xe, etc. are lighter than water. The gaseous hydrates that form in many reservoir fluids are lighter than water and facilitate their separation and transport. Due to the fact that hydrates containing CO2 are heavier than water, this property can be used to bury CO2 gas in deep oceans.

The main gas in gas hydrates is methane gas. Methane is a greenhouse gas that is 21 times stronger than CO2, and the decomposition of hydrates will release large amounts of methane into the atmosphere. It is believed that during glacial periods (ice age) and over time due to the transfer of water as ice to the hearts and as a result of reducing the sea level by about 100 meters, underwater hydrates will decompose and according to the effect Neutral will reduce the increase in the concentration of greenhouse gases during the glacial period.

Gas hydrates can be used in refrigeration cycles due to their high latent heat.

Gas hydrates can be used for agricultural products due to not leaving much soot.

In pipelines, process facilities, drilling operations on the continental shelf, submarine sediments and areas of frozen subsoil and porous rocks can be formed.

Scientists believe that hydrates have had an insignificant effect during geological periods, but have been effective in moving submarine layers and large ocean waves. Hydrates provide an opportunity to collect CO2.

Although hydrates may be considered as a potential source of hydrocarbons on the one hand and a means of transporting and storing natural gas on the other hand, their existence has so far been considered as an operational and safety problem.

Hydrates can be formed at higher pressures and lower temperatures than equilibrium pressures and temperatures in oil and natural gas pipelines, which block pathways. For example, when the gas flow passes through a narrow path (pressure control valve) is formed due to a sudden drop in hydrate temperature. In addition to potential problems caused by solid deposits (such as waxes, asphaltene, etc.), hydrate formation is also a problem. Serious for the technology of exploration and extraction and transfer of oil and gas at sea.

Hydrates can also form in drilling equipment or pipelines in deep water and cause blockage and rupture of pipelines and explosion of drilling equipment, etc., ultimately harming humans.

A number of researchers believe that if there are slight changes in sea level or sea water temperature, gaseous hydrates will decompose and release large volumes of gas, which in turn will have adverse effects on the marine environment. Methane hydrates cause sea floor instability. The presence of gaseous hydrates in ocean sediments alters the physical and geological properties of the seabed, including porosity, permeability, sonic velocity, fluid composition, and fluid velocity.

Hydrates fill in the gaps and give the deposits extra mechanical strength by sticking the grains together.

Due to the high sensitivity of hydrates to temperature and pressure changes, the slightest change in pressure and temperature due to the movement of layers causes the hydrates to decompose and release gas.

Gas hydrates may increase the concentration of greenhouse gases such as methane, which is environmentally friendly for nature.

Gas hydrates in the oil industry

Hydrates can be formed in oil and gas pipelines. Water may also come from condensate or water production. For the transfer, a pressure difference is required and the low temperature is caused by atmospheric or environmental conditions (submarine) or sudden expansion. In process facilities, heavy hydrocarbon separators, hydrates can be formed after control valves, gas temperature reducing heat exchangers or submarine sediments. In submarine sediments, due to high hydrostatic pressure with low water temperature, the conditions for hydrate formation from the released gases resulting from biogenic and thermogenic activity are provided.

Gas hydrates in pipelines

As mentioned earlier, gas hydrates can form in pipelines and cause operational and safety problems. Hydrates can be formed in many common operations, such as the following:

Expansion process

For many fluids, sudden expansion is accompanied by a decrease in temperature (Joule-Thomson effect). This phenomenon occurs after the control valve, samovar valves and some other places and causes the formation of hydrates. Also, during the vertical movement of fluids, where the pressure decreases, the gas separates from the mixture and removes its evaporating heat from the system, reducing the system temperature. Hydrate decomposition is possible by transferring the system conditions from the stable hydrate region to outside it. For example, in the figure below, the system is stable at point A in the hydrate range. With a temperature-constant pressure reduction process (T=0) we reach point B. If pressure drop occurs at a short distance such as control valves and samovar valves (H=0) to point D which in the system is transmitted in a stable hydrate state. For a reversible adiabatic process the pipeline conditions are expressed by point f. From a practical point of view, in real systems, temperature-constant expansion usually occurs very slowly and perhaps impossibly. Thus, in order to prevent the formation of gaseous hydrates due to the processes of pressure reduction and expansion of the fluid, the system must operate at a higher temperature. Or the pressure must be reduced in a few steps and considered with a unique distance to transfer heat, and finally we use an inhibitor to inject upstream and transfer the stabilization zone of the hydrate and prevent the formation of hydrates.

Sleep and start

In underwater pipelines, the water temperature is usually lower than the reservoir fluid temperature. At the beginning of the operation, the pipe temperature is lower than the fluid temperature. Therefore, after the fluid flow, gaseous hydrates are formed in the pipelines. During soaking, after reducing the flow and stopping it, the temperature of the fluid will drop and hydrate will form.

For the following reasons, the formation of hydrates in the commissioning and laying of continental shelf pipelines is very likely:

- In submarine pipelines, the temperature of the pipeline drops to about 4 degrees Celsius, which is the ambient temperature.
- There is a possibility of hydration formation during sleep due to pressure drop and at startup due to pressure.

To prevent such problems during commissioning and laying of pipelines, you should

(1) Fuzzy boundary and fuzzy behavior of the system should be analyzed under normal conditions and dormant operations. Prevention techniques and laboratory measurements are used for this purpose.

(2) Considering the lowest possible sea water temperature and the highest operating pressure, the inhibitor should be injected into the part of the pipeline that is taken out of service. The amount of injectable inhibitor depends on the amount of water in the gas, and the injection of thermodynamic inhibitor changes the hydrate fuzzy boundary to the left. (3) In case of starting the part that has been taken out of service without a plan, a stopper should be injected into it before the fluid flows in the pipeline. The type of inhibitor is selected depending on the condition of the pipeline (usually methanol due to its high vapor pressure).

Unknown capabilities of natural gas hydrates

The discovery of large amounts of gas hydrates on the northern slopes of Alaska and down the southeastern Gulf of the United States reinforces the idea that gas hydrates are a very important source of energy in the future. However, very important technical issues must first be addressed in order to introduce gas hydrates as an important source of energy in the world. Gas hydrates are naturally in the form of crystalline materials composed of water and gas. In hydrates, a solid network of water holds gas molecules in a cage-like structure. Gas hydrates are mostly found in frozen and polar regions and under the sea in sedimentary layers. While methane, propane, and other gases can be trapped in cage-like structures, methane hydrates are much more likely to form. The amount of methane trapped in gas hydrates is very high and the estimated amount is more conjectural and hypothetical and its range is from 100,000 to 270,000,000 trillion cubic feet. The primary goal of research on gas hydrates is to study the geological parameters that control the formation of gas hydrates. Another goal is to assess the volume of natural gas stored within the global storage of gas hydrates.

Gas production from gas hydrates

Proposed methods of recovering gas from hydrates usually involve separating or melting gas hydrates in the following ways: 1) heating the tank to the temperature of hydrate formation 2) reducing the tank pressure below the hydrate balance 3) injecting an inhibitor such as methanol or glycol into the tank to reduce hydrate stabilization conditions. At present, however, the recycling of gas from hydrates is delayed because the hydrates are usually spread in the harsh Polar Regions and deep-sea areas. Recently, a series of simple thermal excitation models have been used to evaluate the production of gas hydrates from hot water and steam streams, which shows that enough gas can be produced from hydrates so that gas hydrates become a technically recyclable source. However, the high cost of these advanced gas recycling techniques prevents recycling. The use of gas hydrate inhibitors to produce gas from hydrates is physically possible, although the use of large volumes of chemicals such as methanol has high economic and environmental costs.

Among the various techniques for producing natural gas from hydrates, the most economical and cost-effective method is the decompression scheme. The Messoyakha gas field in the northern part of the western Siberian basin is often used as an example of gas production from hydrocarbon deposits. All geological information has been used to confirm the presence of gas hydrates in the upper part of this area. The history of gas production from hydrates in this field shows that gas hydrates are an immediate source of natural gas production and production can be started and maintained by conventional methods.

Long-term production of the gas hydrate section of the Messoyakha Basin is accessible with a simple decompression program. Production began in 1999 from the lower part of the free gas field. In 1971, however, the tank pressure deviated from the expected value. This deviation is attributed to the release of free gas from separated gas hydrates. About 30 percent (about 183 billion cubic feet) of gas has been extracted so far. Although some researchers believe that the gas was not produced from hydrates, the results show that the technology uses hydrates to store and transport the use of hydrates to collect and trap gas in offshore rigs, especially when the tank is small and scattered, is used (NGH) [120].

Conclusion

Different methods are used to separate the various components of a gas mixture, the most important of which are the adsorption of gas by the liquid, the adsorption of gas on the solid, and the use of membranes. The process of hydrate formation is known as one of the newest methods of separation of gaseous mixtures. In this method, CO2 emissions from factory chimneys, which is the largest volume of exhaust gases from industrial chimneys, are separated using hydrates and stored on the ocean floor, due to the high storage capacity and long-term ability of hydrates to remain in Offshore This method is recognized by the US Department of Energy as the most promising technology for CO2 capture. On the other hand, there are three other important solutions to control greenhouse gas emissions into the Earth's atmosphere, which are: the use of non-carbon fuels, increasing energy efficiency and underground storage of carbon in various ways. There are different methods for storing CO2 and methane in underground formations. Including their injection into drained oil and gas reservoirs, injection into salt water formations, etc. Among these existing methods, injecting CO2 into natural sources of gas hydrate is a very suitable option. This method maintains a large volume of CO2 safely and long-term in natural gas hydrate sources, and the extracted CH4 is a good source of energy, which adds to the importance of hydrate as a nature-friendly process.

Conflict of Interest

The authors declared that they have no conflicts of interest in this work.

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