Original Article: An Overview of Methane Gas Hydrate Formation

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ABSTRACT

This article reviews the formation of methane gas hydrate. Gaseous hydrates are solid and crystalline grids of water molecules that are hydrogen bonded together and trap low molecular weight gas molecules in their cavities. The type of these gases depends on the gaseous composition of the environment. Methane of thermogenic and biogenic origin is the most common gas stored in gas hydrates that accounts for about 99% of the gases that make up gas hydrates. Gaseous hydrates are very different from ice and, unlike ice under high pressure conditions, also form at temperatures above zero degrees Celsius. Understanding the conditions under which gaseous hydrates are formed and remain stable to determine the extent is important. This source of energy is essential. Gaseous hydrates are very sensitive to environmental conditions and changes in pressure, temperature, water salinity, type and amount of saturated gas forming hydrate inside the pores of the sediment, and cause the growth and stable conditions of gas hydrates. Gaseous hydrates are formed in systems that include water and gas, a network of water molecules (host molecules), paraffins such as methane, ethane, propane, isobutene, carbon dioxide, etc. (guest molecules). High pressures are trapped in their cavities. Gaseous hydrates are non-stoichiometric solids that are similar to ice (or snow) in appearance but completely different in structure.

Introduction

In general, the following conditions are necessary for the formation and stability of hydrates in sediments:

1. Suitable thermodynamic conditions that include low temperature and high pressure.

2- Existence of sufficient amount of hydrocarbon gases of thermogenic or biogenic or non-hydrocarbon origin, which must be provided by subsurface sediments or bacteria [1-5].

3. The gas produced below the hydrate stable zone must be able to migrate to the hydrate region.

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4- The presence of water is an essential factor for the formation of a solid ice network.

Due to the special thermodynamic conditions required for the formation and stability of gaseous hydrates, these compounds are found in two geological regions:

1- Areas with high latitude and depth of less than one to two kilometers where the temperature is low and also more than zero degrees Celsius.

2- In the depths of seas and deep lakes and in the sediments of continental slopes and deeper parts of the oceans which have low temperatures and high pressures [6-9].

At present, gas hydrates have been considered by researchers and scientific societies due to their numerous potentials. The importance of gas hydrates can be summarized as follows:

1- Gas hydrates as the world's fuel supplier in the coming years [10-12].
2. Blocking gas transmission lines and wells.
3. Drilling hazards.
4- Instability of the seabed [13].
5- Greenhouse effect of gas in the structure of hydrate and increase of global temperature.

Soheila Jokar *et al.* [14] investigated the conditions for the formation of gaseous hydrates of pure methane and ethane systems in the presence of acetone using Plato van der Waals theory. Acetone may not necessarily have accelerating or inhibitory properties in different systems. In this work to calculate the fugacity of acetone from 5 different cubic state equations including Peng Robinson (PR), Sva Redlish Wang (SRK), Patel Teja (PT), Schmidt Wenzel (SW), and Nasrifar Boland (NB) and also to calculate acetone activity coefficient, we used three activity models NRTL, UNIQUAC and UNIFAC. For the methane-acetone system, the NRTL activity model predicted the temperature well, and at most concentrations of acetone, the Peng-Robinson and Patel-Taj equations were more accurate than the other equations. The UNIFAC activity model also calculated the ethane-acetone hydrate

formation temperature more accurately [15-19].

Mach et al. [20] investigated the effect of NaCl and methanol and ethylene glycol on the equilibrium phase of methane hydrate in aqueous solution of tetrahydrofuran (THF) with a concentration of 0.005 to 0.01 and tetra n-butyl ammonium bromide (TBAB) with a concentration of Weighed 0.1 to 0.2 and used the above inhibitors with a concentration of 0.03 to 0.1 in THF and TBAB aqueous solution. The results of this study showed that NaCl inhibitor in the combination of $CH_4 + H_2O +$ THF had the greatest inhibitory effect and Methanol inhibitor had the greatest effect on $CH_4 + H_2O + $ TBAB.

In the industry of hydrate formation in natural gas transmission pipelines, it causes a decrease in flow pressure, blockage of the path and sometimes explosion of the flow transmission pipeline. Since Iran is one of the countries with rich natural gas reserves, the need for study and research on this issue will be inevitable. Heat exchangers are prone to hydrate formation due to the sharp drop in gas temperature and hence are one of the most important and practical equipment in the oil and gas industry, especially gas and liquefied gas facilities, faced with the phenomenon of gas hydrates. Clogging of the converters due to the formation of hydrates reduces the production of light gas due to the reduction of the gas propulsion force and even if the pressure difference is increased, it may cause the production to stop [21-25].

Accordingly, in order to prevent the formation of gas hydrates, thermodynamics will be very effective. Water molecules in the hydrate structure, like the ice structure, form hydrogen bonds together, creating hollow (cage-like) cavities and instability. At specific temperatures and pressures, and in the presence of gas molecules commensurate with the size of the cages, hydrates are formed [26-29].

There is no chemical interaction between the guest molecules and the structure formed by the water molecules, and only by physical interactions (van der Waals

forces) between the trapped gases and the host molecules of the hydrate, the structure is stabilized, hence the hydrates. Clathrites are composed of a combination of a number of host molecules and one or more guest molecules, the stability of which depends on the presence of both

components. The general formula of gaseous hydrates is MnH_2O, where M represents guest molecules [30-33]. Figure (1) shows the entrapment of guest gas molecules in the hydrate cage structure.
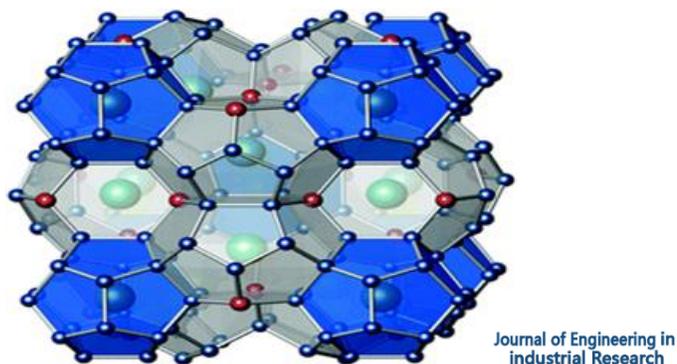

Figure 1. Bonding of trapped guest molecules [23]

History of gas hydrates

Chemists discovered the composition of gaseous hydrates in the early nineteenth century [34-38]. The importance of finding gas hydrates in the oil industry dates back to the 1930s, when the formation of gas hydrates blocked natural gas transmission lines in the polar regions and created problems for the industry [39]. In the 1960s, gaseous hydrate compounds were found in the Mesoyakha gas field in the Siberian Arctic. Gaseous hydrates were first discovered by Joseph Priestley, who left the window open as he left the laboratory one winter evening, when Returning to the lab, he found that SO2 vapor saturated the water and froze it, which was not the case for HCL and SiF4.

In 1811, Humphrey Davey noticed the formation of crystals similar to what Priestley had observed while cooling a chlorine-saturated aqueous solution at minus 40 degrees Fahrenheit, and Davey chose the name "hydrate" for his discovery. Thus, although Priestley discovered it 30 years before Dewey discovered hydrate, because Priestley's experiment was not validated, Dewey's discovery of hydrate is considered to be the first observation of hydrate [40-45].

From 1810 to 1934, studies on hydration were generally conducted on the following two axes:

1. Identifying all the compounds that can form hydrates.

2- Quantitative description of compounds in terms of percentage composition and physical properties.

Since the discovery of the hydrate, there have been approximately 40 reports published during this period, over 400 in 2000 alone, indicating the importance of this issue in the present world [46].

From 1934 onwards, research on hydrates has led to ways to prevent this phenomenon from occurring in gas transmission lines. Therefore, due to the existence of pristine hydrate mineral reserves in regions of Alaska, Siberia and Canada, this issue was given serious attention. In 1950, the structure of the hydrated crystal lattice was examined by X-ray. This led to the development of statistical thermodynamic thinking and the conditions for the formation of these crystals were interpreted [47].

Research on the storage and transport of natural gas by gas hydrates has also been proposed by Bonesh since 1942. This issue

was suggested by scientists such as Miller and Strong (1946), Parent (1948) and Zhidenko (1979). In Iran, one of the most obvious cases is the formation of hydrates and its problems in offshore facilities. In South Pars phases, 10 to 12 wells are drilled for each phase and the output of these wells containing sour gas, gas condensate and water is transported by 32-inch pipes as far as a distance of 110 km [48].

Therefore, in order to prevent the formation of hydrates, a solution had to be considered. For this purpose, currently in phase one of South Pars, the method of removing water by drying the gas at the beginning of the transfer pipeline to land is applied and in the next phases of MEG inhibitor at the inlet gas to the pipeline is used to prevent the formation of hydrates and their consequences. Hemingsen et al., (2019) examined methyl ethylene glycol in the presence of methane and propane at different concentrations, and found a drop in hydrate formation temperature at concentrations above 60% by weight. No thermodynamic model can justify all this experimental information. Using a combination of 88.13% mol methane and 11.87 mol% propane, they simulated and compared it with experimental data [49].

The reason for using this special combination was that at a pressure above 60 bar, the condition of not forming a temperature hydrate is higher than 20 ° C. And at temperatures higher than the freezing point of water, this trend can be observed in the presence of at least 50% by weight of methyl ethylene glycol. Experimental accuracy on hydrate equilibrium conditions is critical [50].

Hydrate structures

The major structure of hydrate is water. For this reason, many of its mechanical properties are similar to ice, so it is best to first explain a little about the water molecule and its structure.

A molecule of water in a gaseous state consists of one oxygen atom and two hydrogen atoms. The oxygen atom has four electrons in the final circuit that share two electrons with two hydrogen atoms. These three atoms are in a pyramid-shaped building [51].

The molecule of water in the liquid state of this pair of free electrons provides oxygen to other hydrogens relative to other water molecules and forms a hydrogen bond. By forming this bond, a polymer network is formed in water as a liquid phase. Hydrogen bonding is shown as hatched rods [52]. By studying the structure of water molecules in the liquid state, researchers have found that rings formed from water molecules due to hydrogen bonding are much more stable than open chains. Further, Plummer and Chen (2019) have shown that if these rings contain five molecules of water, twelve of these rings form a regular dodecahedron, which is shown as 512.

This building is only a stable state. The water molecule is a liquid at a temperature above 230 Kelvin. The structural properties of the hydrate crystal lattice were first studied in the late 1940s and early 1950s by Stockelberg et al. using X-ray (2018) diffraction and proposed two structures for hydrates by that time. Both were cubic structures and were named as Structures I and II [11]. They can produce type H hydrate crystals. Previously, researchers thought that molecules larger than normal butane, due to their large size, could not fill the space created in the hydrate crystal lattice and form hydrate crystals [53].

Cavities of the hydrate structure network unit

All hydrate structures are composed of a repetitive combination of asymmetric and spherical crystal lattices of hydrogen bonds of water molecules known as cages. For each hydrate structure network unit, there are three types of cages: type S cage (small cage), type M cage (medium cage), type L cage (large cage). The S-type cage, which is the base cage for all three hydrate structures, consists of the twelve or five facets that make up water molecules. This cage has six holes for trapping paraffins. The M-type cage is found only in the H structure. It is polygonal, which is a combination of 3 hexagons, 6 pentagons and 3

quadrilaterals and has two holes in its network.

Type L cage, which consists of a sum of a number of polyhedra, exists in all three structures, but the number of cavities it creates in each structure is different. Each of these cavities can only host molecules with the appropriate molecular diameter and geometry (smaller than the diameter of the cavities) [54].

The structure of the hydrate consists of five types of cavities, as shown in Figure 2. Jeffrey *et al.* (1948) showed that the number of edges of type i is one face and m is the number of faces of type i. For example, a type S hole is shown with 512, which represents the 12 sides of a pentagon.
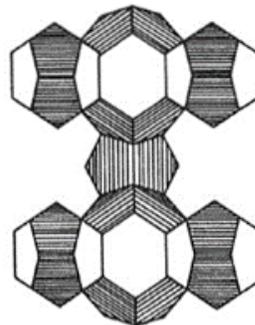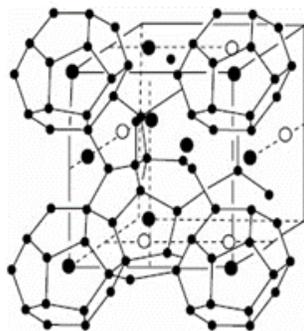
Figure 2. Type I hydrate structure [11]
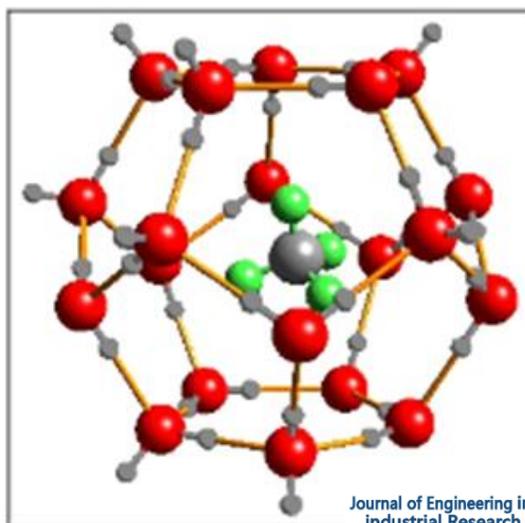
Figure 3. Crystal structure of methane hydrate [12]

Structure I

Structure **I** is usually formed with smaller molecules such as methane, carbon dioxide, ethane, etc. In this structure, two holes 512 (small hole) and six holes 51262 (large hole) form the network of this space by sharing the sides due to repetition in space.

Therefore, each cell unit of this structure contains 46 water molecules and has eight holes for gas molecules, of which two are small holes and six are large, and the structure is cubic. Therefore, in this structure, there are 46 molecules of water per eight molecules of gas. Structure **I** is deviated by 4% from the spherical state [5].

Structure II

Molecules with diameters between 5 and 6.7 angstroms that cannot be in structure I can only occupy structure II.

Therefore, this structure is formed by larger molecules such as propane and isobutane. This structure is composed of sixteen holes 512 (small hole) and eight holes 51264 (large hole) by sharing surfaces. Therefore, each cell unit of this structure contains 136 water molecules

and has 24 cavities for gas molecules, of which eight are small cavities and sixteen are large cavities.

Therefore, in this structure, there are 136 molecules of water per 24 molecules of gas. Structure II deviates by ten percent from the spherical state. Therefore, it has the most spherical structure among hydrate structures. This structure is suitable for water desalination (Figure 3 to 6) [6].
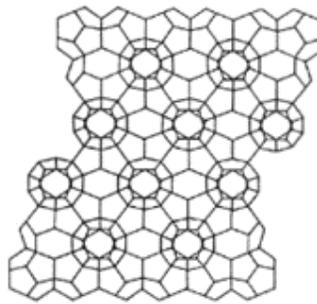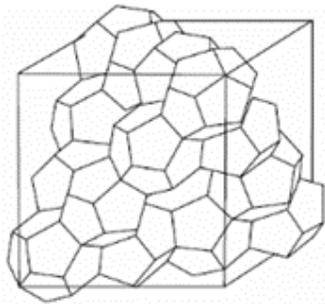
Figure 4. Hydrate structure of type II [11, 13]

Type H structure

This structure was unknown until 1987 and is still not as well-known as the other two structures. This structure consists of a combination of three cavities 512 (cast iron cavity), two cavities 435663 (medium cavity) and one cavity 51268 (large cavity). Therefore, each cell unit of this structure contains 34 molecules of water and has six cavities for gas molecules, of which three are small cavities, two medium cavities, and one large cavity.

Therefore, in this structure, 34 molecules of water per six molecules of gas are present. This structure does not form when natural gas components such as propane and isobutene are present. The H structure is known as the dual structure, and a small molecule such as methane and a large molecule such as methyl cyclohexane must be present to form it. One of the most important mechanical properties of H structure is low forming pressure and high storage capacity [7].
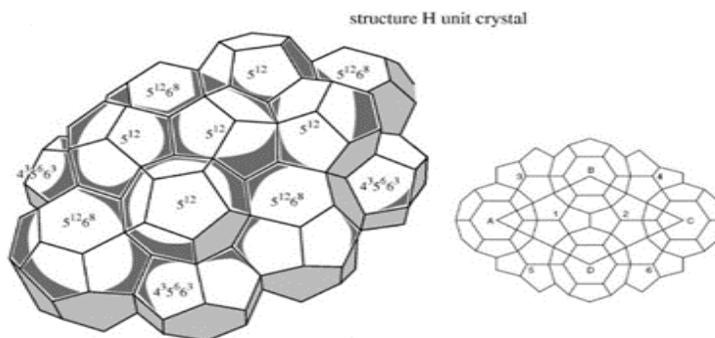
Figure 5. Hydrate structure of type H [12, 13]
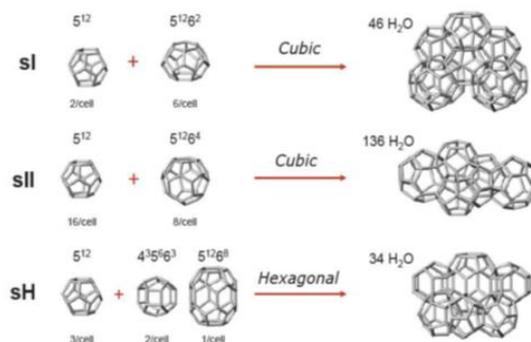
Figure 6. Different structures of gas hydrates [13]

Of the three structures mentioned, only structures I and II occur naturally in the presence of natural gas, and the problems arising from the hydrate phenomenon that exists in the gas transmission industries are of these two structures. In the oil industry, where molecules such as isopentane, neohxane, and methylcyclopentane are present, hydrate crystals are formed with the structure H [1].

General conditions of hydrate formation and properties of guest molecules

In general, hydrate needs the following conditions to form:

- Presence of water in liquid, vapor or solid state (ice crystals)
- Presence of non-polar or slightly polar molecules of suitable size
- Suitable thermodynamic conditions (high pressure and low temperature)

The process of hydrate formation has completely similar steps to the crystallization process and includes two stages of nucleation and growth. Studies have shown that if the necessary conditions are created, hydrate crystals do not form quickly but it takes some time for the necessary makeup to form. As a result, cages are formed, which is called induction time [2].

In addition to classifying hydrates based on their constituent structures, there is a second type of hydrate classification in which hydrate is evaluated according to guest molecules. This classification is a function of two parameters: a) The chemical nature of the guest molecules, b) the size and shape of the guest molecules [3].

Mc Mulan (1967) divided guest molecules into four groups: 1. Hydrophobic compounds, 2. Water-soluble acidic gases, 3. Water-soluble polar compounds, and 4. Three-component or four-component water-soluble alkyl ammonium salts [1].

In order to classify hydrates based on the chemical nature of the guest molecule, Jeffrey (2019) stated that guest molecules must not have a group of strong hydrogen bonds or a number of weak hydrogen bonds in order to be able to form hydrates.

Molecules in natural gas do not have a hydrogen bond, so they can form hydrates. On the other hand, most natural gas components are hydrophobic and have the ability to form hydrates, with the exception of two notable exceptions, carbon dioxide and hydrogen sulfide, which can form hydrates because they are a family of water-soluble acidic gases [4].

Fuzzy behavior of hydrate formation

Gas hydrates consist of two molecules that are not chemically bonded together. Fuzzy equilibrium is very complex in these systems. To investigate the equilibrium conditions of hydrate crystal formation, it is best to introduce the phases in which they are likely to occur.

Gas phase (V): This phase mainly contains gases that can (some may not) form hydrated crystals. Depending on the condition of the system, there may be some water vapor in it.

Liquid phase which is mainly water (LW): Other compounds in the system that are dissolved in water can also be present in this phase.

1- Liquid phase which mainly contains hydrocarbons (L¬H): This phase mainly contains hydrocarbons in which water can be dissolved in small quantities.

2- Solid hydrate phase (H): This phase consists of hydrate crystals which include water molecules and hydrocarbon molecules that can enter the hydrate crystal lattice. Under certain conditions, several types of hydrate crystals may form simultaneously.

3- Ice phase (I): This phase consists of water molecules that have become solid.

It is important to note that depending on the system conditions, some of the phases mentioned above may not be present. This theorem can be understood by modeling and examining the phase stability in terms of Gibbs free energy comparison [5].

Hydrate crystals in separation processes

Separation by formation of gaseous hydrates is a new method. There are two reasons for using hydrates in separation processes:

1. Hydrate crystals are composed only of guest molecules and water.
2. Not every gas molecule as a guest molecule can be included in the structure of hydrate crystals and only certain molecules due to their chemical nature, shape and size can participate in the structure of hydrate [6].

Separation of components of a gas mixture, concentration of solutions and desalination of water are among the separation branches through the formation of gaseous hydrates.

Oxygen enrichment using gaseous hydrate formation

Oxygen can be enriched by the formation of gaseous hydrates. Due to the fact that the solubility of oxygen in water is higher than nitrogen, the rate of conversion to hydrate for oxygen is higher than hydrogen. Therefore, by using gaseous hydrates, oxygen can be enriched from a standard concentration of 21% in air to 28%. In this method, tetrahydrofuran can be used as an additive to reduce the operating pressure required in separation [12].

Concentration by hydrate formation

When the solution to be concentrated is in the vicinity of a gaseous component capable of hydrate formation, under appropriate conditions of temperature and pressure, hydrate is formed and the amount of dissolved water is reduced due to the presence of water in the hydrate structure. The desired solution is concentrated.

Among the applications of this method, the following can be mentioned:

- Concentration of ionic liquids [16].
- Concentration of sodium chloride in aqueous solution [16].
- Concentrated coffee [17].

Gas hydrate and seawater desalination

Seawater desalination is another example of the use of hydrate crystal formation in separation processes. The idea of desalination of seawater using gaseous hydrates is based on the fact that during the formation of hydrates, the salts in saline water are not included in the structure of the formed hydrate phase, so by separating the hydrate phase from the seawater solution, One of the advantages of this method is the very low energy consumption for this work.

So far, several different processes have been developed for semi-industrial desalination of seawater using hydrate formation (especially with propane gas), but all of them have faced the problem of separating the crystal from the saline water and recovering the gases resulting from the decomposition of hydrate. Therefore, they did not have a good economic justification [15].

Hydrate crystals in the environment

Decomposition of hydrate crystals in the earth's crust can have negative effects on the environment. For example, in offshore oil reservoirs, due to the formation of hydrate crystals in the depths of the earth and the separation of light hydrocarbons to participate in the construction of hydrates, heavy oil is no longer extracted quickly and gradually rises in the reservoir layers and causes pollution. It covers a large area of the sea floor and causes serious damage to the marine environment.

On the other hand, due to rising global temperatures, the hydrates in the earth's crust gradually decompose and release trapped methane. The effect of methane in intensifying the greenhouse effect alone is 21 times that of carbon dioxide, and this process is intensified by the continuous decomposition of hydrates. Also, adding inhibitors to natural gas and not effectively recovering them at consumption points is an important source of environmental pollution [18].

Additives on the formation of hydrates

Add-ons fall into four general categories:

- Inhibitors.
- Additives that stabilize hydrates in one of the structures I, II or H.
- Thermodynamic additives (thermodynamic enhancers).
- Kinetic additives (kinetic enhancer).

Conclusion

Asfouri et al. (2019) [14] used one or more electrolytes or solutions containing electrolytes and polar inhibitors such as MEG, DEG, and TEG with the aim of achieving a new prediction model to predict the formation of gaseous hydrates. In this design, the gamma-fi method (Υ-φ) was used to use the equation of state in the vapor phase and the model of the coefficient of activity in the liquid phase was used, and the equation of state used in this case was Patel-Teja. To model the formation of hydrate in the presence of inhibitors, the NRTL activity coefficient model for the liquid phase

and also the Marguls equation have been used to estimate the activity of water in a solution containing a polar inhibitor. The results of this modeling have been reasonably close to experimental results. For solutions containing only one electrolyte, the results of the existing models are close to the results of this modeling. The average deviation from the hydrate formation pressure for a solution containing a single electrolyte with 144 experimental data is 5.86% and for a solution containing several electrolytes with 190 experimental data is 23.2. This deviation rate was announced as 14.13% for the solution containing electrolyte and MEG, 5.82% for the solution containing electrolyte and DEG and 5.28% for the solution containing electrolyte and TEG.

Hemingsen et al. (2019) examined methyl ethylene glycol in the presence of methane and propane at different concentrations and found a drop in hydrate formation temperature at concentrations above 60% by weight. No thermodynamic model can justify all this experimental information [13]. Using a combination of 88.13% mol methane and 11.87 mol propane, they simulated and compared it with experimental data. This rate of MEG injection is common in North Sea pipelines and it is critical to use accurate empirical information on hydrate equilibrium conditions to prevent hydrate formation. In the face of the problem of hydrate formation in gas transmission pipes using inhibitors, by calculating the reduction of freezing point during the use of thermodynamic inhibitor as ΔT, the hydration formation temperature can also be accessed.

Kinetic

Kinetic Hydrate Inhibitors are chemicals of polymeric origin that have high molecular weight and are effective at concentrations typically 10 to 100 times lower than the concentrations of thermodynamic inhibitors. Another advantage of this type of inhibitor is that it does not prevent the formation of hydrates but delays the initial stage (nucleation) and reduces the tendency for

hydrate crystals to accumulate. Synthetic inhibitors are insensitive to the hydrocarbon phase and are therefore used in a wide range of hydrocarbon systems.

Unlike the anti-accumulation method, this method does not require the presence of a liquid hydrocarbon phase. These types of inhibitors, which have been considered in the last decade, change the formation kinetics instead of changing the thermodynamic conditions of hydrate formation. These compounds both slow down nucleation and the growth rate of crystals. The molecular mechanism of these substances and their effects have not yet been properly proven. But two theories are of interest, both of which have been proposed using molecular dynamics simulations. The first theory states that the adsorption of these compounds onto the crystals causes their active points to disappear or be severely reduced, thus stopping their growth.

The second mechanism suggests that kinetic inhibitory polymer molecules act as a barrier to the penetration of guest molecules and prevent crystal evolution. Kinetic inhibitors are high molecular weight polymers that are injected into the system at very low concentrations (often less than 1%). These types of inhibitors are relatively insensitive to the non-carbon phase and can therefore be used in a wide range of non-carbon systems. Kinetic inhibitors include psi vinyl pyrrolidene, polyvinyl methyl acetamide and vinyl caprolactam. The consumption of this type of inhibitor is very low compared with thermodynamic inhibitors. Ming Wu et al. (2007) focused on natural gas transmission lines of two types of thermodynamic inhibitors and kinetic inhibitors, in which they based their calculations and analysis on the reduction of freezing temperature before and after the addition of inhibitors. The basis was concluded that the addition of 10% thermodynamic inhibitor of methanol and monoethylene glycol can completely prevent the formation of hydrates. They saw better and declared the highest efficiency in the simultaneous use of both inhibitors.

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