# PREVENTION OF GAS HYDRATES FORMATION IN NATURAL GAS PIPELINES-REVIEW

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*Abstract :*  Gas hydrates poses serious problems in oil and gas industry. It can be formed from gas and water molecules at low temperature and high pressure. Solid hydrates are ionic solids in which the ions are surrounded by water molecules and form crystalline solid. In the natural gas industry, hydrates are crystalline solid compounds formed from water and smaller molecules. They are considered to be subset of compounds known as clathrates or inclusion compounds. Various methods are used for determining the conditions of pressure and temperature at which hydrates would form for natural gas mixtures. Another ways of combating hydrate formation is to avoid the regions of pressure and temperature where hydrates would form.

*IndexTerms - Hydrates, Clatharates, Oil and gas industry.*

## I. INTRODUCTION

Even though all terrestrial gases (e.g., air, volcanic emissions, and swamp gas) are natural, the term natural gas is customarily reserved for the mineral gases found in subsurface rock reservoirs. These gases are often associated with crude oil. Natural gas is a mixture of hydrocarbons such as methane, ethane, propane (1, 2) and a few nonhydrocarbons (hydrogen sulfide, carbon dioxide, nitrogen, etc., and water). The hydrocarbons have value as fuels and as feedstocks for petrochemical plants. As fuels, they are used for heating and cooking in private homes, to generate electricity, and increasingly as fuel for motor vehicles. In chemical plants, they are converted to a host of consumer products everything from industrial chemicals, such as methanol, to plastics, such as polyethylene. The nonhydrocarbons are less valuable; however, depending on the market situation, hydrogen sulfide has some value as a precursor to sulfur. Sulfur in turn has several applications, the most important of which is probably the production of chemical fertilizer. Carbon dioxide and nitrogen are used to pressurize the well system.

In its most general sense, a hydrate is a compound containing water molecule. There is a type of inorganic compounds called solid hydrates. These are ionic solids in which the ions are surrounded by water molecules and form crystalline solid. In the natural gas industry, hydrates are crystalline solid compounds formed from water and smaller molecules. They are considered to be subset of compounds known as clathrates or inclusion compounds. A clathrate is a compound in which a molecule of one substance is enclosed in a structure built up from molecules of another Substance. Clathrates of water are also called hydrates. Although hydrates were studied earlier, credit for their discovery is usually given to the famous English chemist, Sir Humphrey Davy. He reported the discovery of the hydrate of chlorine in the early nineteenth century which is followed by Michael Faraday, also studied the hydrate of chlorine. Throughout the nineteenth century, hydrates remained basically an intellectual curiosity to be found out. Early studies focused on finding which compounds formed hydrates and under what conditions they would form. Many of the important hydrate formers were discovered in twentieth century for the industrial importance of gas hydrates(3).

In combination with water molecules, many of the components commonly found in natural gas form hydrates. One of the problems found in the production, processing, and transportation of natural gas and liquids derived from natural gas is the formation of hydrates; however, the importance of natural gas hydrates was not apparent in the early era of the gas business, when gas was produced and delivered at relatively low pressure, thus hydrates were never encountered. In the twentieth century, with the expansion of the natural gas industry, the production, processing, and distribution of gas became high-pressure operations. Under pressure, it was discovered that pipelines and processing equipment were becoming plugged with what appeared to be ice, except the conditions were too warm for ice to form. In the 1930s, Hammer Schmidt (1934) demonstrated that the "ice" was actually gas hydrates(4). In the petroleum industry, the term hydrate is reserved for substances that are usually gaseous at room temperature. These include methane, ethane, carbon dioxide, and hydrogen sulfide. This leads to the formation of gas hydrates and to one of the popular misconceptions regarding these compounds. It is commonly believed that hydrates will not be formed from non-aqueous liquids, however, liquids may also form hydrates. An example of a compound that is liquid at room conditions, yet forms a hydrate, is dichlorodifluoromethane (Freon 12).

2.  FACTORS FOR HYDRATE FORMATION WITH WATER:

2.1.  WATER MOLECULE:

Many of the usual properties of water (and water does have some unusual properties) can be explained by the structure of the water molecule and the consequences of this structure. Of particular interest to us is the fact that the structure of the water molecule leads to the possibility of hydrate formation.

• Normal boiling point of water.
• Enthalpy of Vaporization.
• Expansion upon freezing.
•   Shape of the water molecule and hydrogen bond.

2.1.1. NORMAL BOILING POINT OF WATER:

As an example of the unusual properties of water, consider the boiling Point, boiling point of water is unusually high. The periodic table of elements is not just a nice way to display the elements. The original design of the table comes from alignment of elements with similar properties. Thus elements in the rows of the table have similar properties or at least properties that vary in a periodic, predictable manner. The 6A column in the table consists of oxygen, sulfur, selenium, and tellurium. We would expect these elements and their compounds to have similar properties, or at least to behave in a predictable pattern.
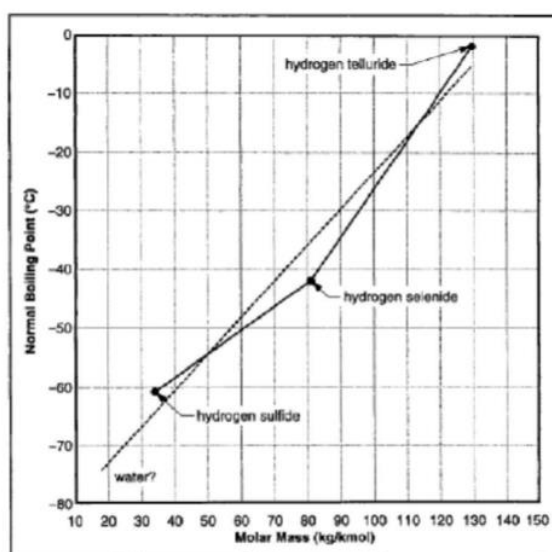


Fig.1.Normal Boiling Point of Hydrogen Compounds

The hydrogen compounds of the column 6A elements are water, hydrogen sulfide, hydrogen selenide, and hydrogen telluride. All have the chemical formula $H_2X$, where X represents the group 6A element. If we look at the normal boiling points of $H_2S$, $H_2Se$, and $H_2Te$, we should be able to predict the boiling point of water by plotting the normal boiling points for these compounds Vs Molar mass of the compounds. As the size of the molecule increases the normal boiling point also increases. As the graph is not exactly linear, we can use a linear approximation to estimate the boiling point of water.
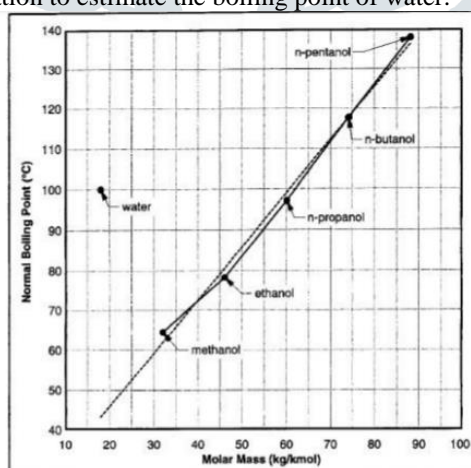


Fig.2. Normal boiling point of alcohols

2.1.2. EXPANSION UPON FREEZING:

Another unusual property of water is that it expands upon freezing. In common terms, this means that ice floats on water. In engineering terms, the density of ice ($917kg/m^3$ or $57.21b/ft^3$) is less than that of liquid water ($1,000 kg/m^3$ or $62.4 lb/ft^3$) at the freezing point. The reason for this expansion is that the water atoms arrange themselves in an ordered fashion, and the molecules

in the crystal occupy more space than those in the liquid water. This behaviour is also caused by the shape of the water molecule and something called the hydrogen bond. The molecules in solid water form a hexagonal crystal. This is most obvious in snow.

2.1.3. SHAPE OF THE WATER MOLECULE AND THE HYDROGEN BOND:

The water molecule consists of a single atom of oxygen bonded to two hydrogen atoms. In the water molecule, the bond that exists between the oxygen and hydrogen atoms is a covalent bond. A covalent bond is essentially a shared pair of electrons. The angle between the two hydrogen atoms in the water molecule is about 105 degrees. There are two pairs of unbounded electrons on the "back" of the oxygen molecule. These electrons induce a negative charge on the oxygen molecule and a small positive charge on the hydrogen atoms. Thus the water molecules will tend to align, with a hydrogen molecule lining up with an oxygen molecule.

This aligning of the hydrogen and oxygen atoms is called a hydrogen bond. The hydrogen bond is essentially an electrostatic attraction between the molecules. The hydrogen bond is only 1/10th or 1/20th as strong as a covalent bond, but this is still strong enough to explain the properties.

The hydrogen bonds are particularly strong in water, although they are present in other substances, such as the alcohols discussed earlier. Therefore, the normal boiling points of the alcohols are significantly larger than their paraffin analogues. When the water molecules line up, they form a hexagonal pattern. From elementary geometry, it is well known that the angle between the sides of a regular hexagon is 120 degrees, which is greater than the 105-degree angle in the water molecule. This seeming paradox is overcome because the hexagonal pattern of the water molecule is not planar. The hexagonal pattern of the water molecule is Ice crystal.

3.  HYDRATE TYPES AND FORMERS:

Hydrates are generally classified by the arrangement of the water molecules in the crystal, and hence the crystal structure. There are two types of hydrates commonly encountered in the petroleum industry. These are termed as Type I and Type II, sometimes referred to as Structure I and II. A third type of hydrate that may also be encountered is Type H (Structure H), but it is less common.

3.1 TYPE I HYDRATES:

The simplest of the hydrate structures is the Type I. It is made from two types of cages:
 (1)     Dodecahedron, a 12-sided polyhedron where each face appears to be a regular Pentagon.
 (2)     Tetrakaidecahedron, a 14-sided polyhedron which includes 12 pentagonal Faces and two hexagonal faces.

The Dodecahedral cages are considerably smaller than the Tetrakaidecahedral cages, thus the dodecahedra cages are often referred to as small cages, whereas the Tetrakaidecahedra cages are referred to as large cages. Type I hydrates consists of 46 water molecules. If a guest molecule occupies each of the cages, then the theoretical formula for the hydrate becomes: X. 5x3/4 H20, where 'x' is the hydrate former.

3.2 TYPE I FORMERS:

Some of the most common Type I hydrate formers include methane, ethane, carbon dioxide, and hydrogen sulfide. In the hydrates of CH4, CO2, and H2S, the guest molecules occupies both the small and large cages. Whereas in the ethane molecule occupies only the large cages.

TYPE II HYDRATES:

The structure of the Type II hydrates is significantly more complicated than that of the Type I hydrate. The Type II hydrates are constructed from two types of cage structures. The unit structure of a Type II hydrates are,

1. Dodecahedron is a 12-sided polyhedron where each face is a regular pentagon.

2. Hexakaidecahedron is a 16-sided polyhedron with 12 pentagonal faces and four hexagonal faces. The dodecahedral cages are smaller than the Hexakaidecahedron cage structure.

The Type II hydrate mainly consists of 136 molecules of water. If a guest molecule occupies all of the cage structures, then the theoretical composition is: $X.5*2/3 \, H_2O$, where X is the hydrate former. Or, as is more commonly the case, if the guest molecules occupies only the large cages, then the theoretical composition is $X.17H_2O$. As with Type I,Type II hydrates are not stoichiometric, so the compositions of the actual hydrates differ from the theoretical values.

3.3.TYPE II FORMERS:

Among the most common Type II formers in natural gas are nitrogen, propane, and isobutane. It is interesting to note that nitrogen occupies both the large and small cages of the Type II hydrate. On the other hand, propane and isobutane occupies only the large cages.

3.4. TYPE H HYDRATES:

Type H hydrates are much less common than either Type I or II. In order to form, this type of hydrate requires a small molecule, such as methane, and a Type H former. The Type H hydrates are constructed from three types of cages: 1. A dodecahedron, a 12-sided polyhedron where each face is a regular pentagon. 2. An irregular dodecahedron with three square faces, six pentagonal faces, and three hexagonal faces, 3. An irregular icosahedron, a 20-sided polyhedron, with 12 pentagonal faces and eight hexagonal faces. The unit crystal is made up of three dodecahedral cages (small), two irregular dodecahedral cages (medium), and one icosahedral cage (large). It consists of 34 water molecules. Because two formers are required to form a Type H hydrate, it is a little difficult to give the theoretical formula; however, if we assume that the small molecule, X, enters only the two smaller cages, and we know that the large molecule, Y, enters only the large cages, then the theoretical formula is $Y*5X*34$ $H_2O$.

3.5. TYPE H FORMERS:

Type I and II hydrates can be formed in the presence of a single hydrate former, but Type H requires two formers to be present: A small molecule such as methane. 2. A larger Type H-forming molecule.
Type H formers include the following hydrocarbon species:
- 2-methylbutane
- 2, 2-dimethylbutane
- 2, 3-dimethylbutane
- 2, 2, 3-trimethylbutane
- 2, 2-dimethylpentane
- 3, 3-dimethylpentane
- Methylcyclopentane
- Ethylcyclopentane
- Methylcyclohexane,
- Cycloheptane, and Cyclooctane.

These compounds are not commonly found in natural gas. In fact, most analyses do not test for these compounds.

3.6.OTHER HYDRATE FORMERS:
- Halogens
- Noble gases
- Air
- Sulfur dioxide

4.INHIBITING HYDRATE FORMATION WITH CHEMICALS:

This outlines some design information for battling hydrates using chemicals. People who live in colder climates are well aware of methods for combating ice. Polar solvents, such as alcohol , glycol and ionic salts, such as common table salt, are known to inhibit the formation of gas hydrates. It is important to note that they do not prevent hydrate formation, they also inhibit it. That is, they decrease the temperature or increase the pressure at which a hydrate will form. The small presence of an inhibitor does not mean that a hydrate will not form. The inhibitor must be present in minimum concentration to avoid hydrate formation. In the natural gas industry, alcohols (mainly methanol) and glycols (Ethylene glycol or Triethylene glycol) are commonly used to inhibit hydrate formation. These chemicals exhibit degree of hydrogen bonding, and thus interface with hydrogen bond of water. Dosing the alkanolamines, for treatment of sweetening natural gas, and also inhibit the hydrate formation. Due to the addition of inhibitor, changes the properties of the hydrate such as freezing point depression etc.

5. DETERMINATION OF THE EFFECT OF HYDRATE INHIBITOR:

There are some methods to predict the effect of hydrate inhibition such as,
- Hammerschmidt Equation.
- Nielson-Bucklin Equation.
- Brine solution method.

5.1. HAMMERSCHMIDT EQUATION METHOD:

A relatively simple and widely used method to approximate the effect of chemicals on the hydrate-forming temperature is the Hammer-Schmidt equation:

$$\Delta T = K_H W / M (100-W) \qquad (1)$$

Where, $\Delta T$ – Temperature depression in°C, M – Molar mass of the inhibitor in g/mol. W- Concentration of the inhibitor in weight percent in the aqueous phase, and $K_H$ – is a constant with a value of 1,297.
For calculating the concentration of the inhibitor required for desired temperature depression is,

$$W=100M\Delta T/K_H+M\Delta T \qquad (2)$$

To use the Hammerschmidt equation, you must first estimate the hydrate conditions without an inhibitor present. The Hammerschmidt equation only predicts the deviation from the temperature without an inhibitor present, not the hydrate-forming conditions themselves. Originally the $K_H$ in Equations (1) and (2) was a constant, but over the years some have proposed making $K_H$ a function of the inhibitor in order to improve the predictive capabilities of the equation.

## 5.2. NIELSON-BUCKLIN EQUATION METHOD:

 Nielsen and Bucklin (1983) used first principles to develop another equation for estimating hydrate inhibition of methanol solutions. The equation is,
$\Delta T = -72 \text{In} (1-x_M)$ -------------------------------------→ (3)
Where,
$\Delta T$ – Temperature difference in °C.
$x_M$ - The mole fraction of methanol. They claim that this equation is accurate up to mole fraction of 0.8(about 88wt %).
This equation can be rearranged to estimate the methanol concentration given the temperature depression:
$X_M = 1-\exp [-\Delta T/72]$ -----------------------------→ (4)
 -Then to calculate the weight percent from this mole fraction, the following equation is used,

$X_M = x_M M_M/18.015+x_M (M_M-18.015)$------------------------------→  (5)

Where, $X_M$ – Weight fraction of Methanol. $M_M$ – Molar Mass of Methanol.
 The Nielsen-Bucklin equation was developed for use with methanol, however, the equation is actually independent of the choice of inhibitor. The equation involves only the properties of water and the concentration of the inhibitor. Therefore, theoretically, it can be used for any non-ionic inhibitor.

## 5.3. BRINE SOLUTION METHOD:

 Ionic solids also inhibit the formation of hydrate, in much the same way they inhibit the formation of ice. McCain provides the following correlation for estimating the effect of brine on the hydrate formation temperature:
$\Delta T = AS + BS^2 + CS^3$
The above equation is limited to salt concentrations of 20 wt% and for gas gravities in the range $0.55 < \gamma < 0.68$.
Where, $\Delta T$ – the temperature depression in °F
 S – Salinity in wt%, the coefficients A, B, and C are functions of the gas gravity, $\gamma$, which is defined in the equation given below,
 $A = 2.20919 - 15057463\gamma + 12.160172\gamma^2$
$B = -0.106056 + 0.722692\gamma - 0.85093\gamma^2$
$C = 0.00347221 – 0.01655647\gamma + 0.049764\gamma^2$

## 6. COMBATING HYDRATES USING HEAT AND PRESSURE:

These methods are used for determining the conditions of pressure and temperature at which hydrates would form for natural gas mixtures. Another ways of combating hydrate formation is to avoid the regions of pressure and temperature where hydrates would form.

## 6.1 USE OF HEAT:

In order to prevent the formation of hydrates, the fluid has to be kept warmer than the hydrate-forming conditions (with the inclusion of a suitable margin for safety). It may be possible alternatively to operate at a pressure less than the hydrate formation pressure. With a buffed pipeline, which loses heat to the surroundings as the fluid flows through the pipeline, the temperature must be such that no point in the pipeline is in the region where hydrate will form. This heating is usually accomplished by two means, either by using line heaters or by using heat tracing unit.
A heater is used to warm the fluid. Since this is a single-point injection of energy, the amount of energy must be such that the fluid remains above the hydrate point until the next point where added heat is reached. This means that the temperature of the fluid entering the pipeline must be well above the hydrate temperature. Another method used to add heat to a system is to use heat tracing. In this method, heat is injected along a line continuously.
Thus the fluid temperature does not need to be very high at any single point, but with the continuous injection of energy, the temperature of the fluid needs to be only above the hydrate temperature and not warmer.
Heat tracing can be electrical or a fluid medium (for example hot oil or glycol). In either case, the heat trace is placed adjacent to the line that is to be heated. Heat tracing is especially useful on valves. Valves are notorious for freezing because of cooling due to the Joule-Thomson effect.
Another important tool in the fight against hydrate formation is insulation method. An insulated pipeline will loses heat at a slower rate than an uninsulated one. This translates into a lower temperature requirement for the outlet of the heater and

ultimately a lower heater duty, which translates into lower operating costs. As a matter of fact, the proper use of insulation may, in some cases, make ineffective the requirement for a heater altogether.

## 6.2. HEAT TRACING:

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## 6.3. LINE HEATERS:

A heater is used to warm the fluid. Since this is a single-point injection of energy, the amount of energy reached must be such that the fluid remains above the hydrate point until the next point where heat is added. It means that the fluid entering the pipeline must be well above the hydrate temperature. Heat is a logical solution to freezing problems. It is also a costly approach to the hydrate problem for several reasons. If the gas is never allowed to reach freezing temperature, ice cannot form and will not be present. The water will likely not be removed, which remains an issue for operations and contracts, but the freezing is eliminated.
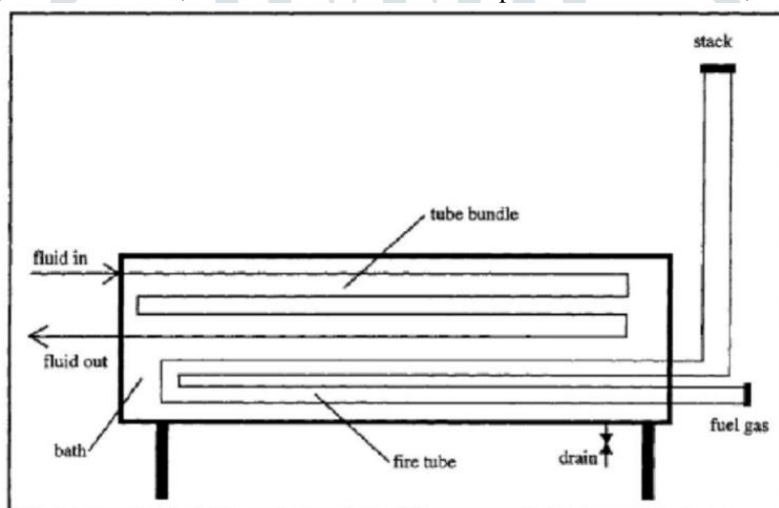


Fig.3. Schematic Diagram of a Line Heater

## 6.4. DEPRESSURIZATION:

Another method that is used to remove the hydrates once they have formed is to reduce the pressure. When the pressure is reduced, the hydrate is no longer the stable phase. This is different from ice. Depressurizing would have little effect on the freezing point of ice. Theoretically, this technique will work, but the process is not instantaneous; it takes some time to melt the hydrate. There are many horror stories about people who depressurized a line and then uncoupled a connection only to have a hydrate projectile shot at them. A potentially dangerous scenario for the melting of a hydrate plug using pressure reduction is presented in Figure 7. As shown, an attempt is made to melt the hydrate blockage by bleeding the pressure off the line. In this case, however, the pressure is only bled off one side of the hydrate. The plug can loosen and is projected along the line at high velocity. The hydrate can accelerate along the line like a bullet in a rifle barrel. The speed of the plug can often be enhanced by a fine film of water that acts as a lubricant. In this situation, it is better if the pressure is bled off both sides of the blockage. If possible, an attempt should be made to keep the pressure nearly equal on both sides of the plug. Maintaining equal pressure on both sides will prevent significant movement of the plug. If it is not possible to bleed off both sides of the line, then the pressure should be bled off one side of the plug in a step-like manner. First, release some pressure and allow the plug to melt, which will increase the pressure. Then more pressure is released. Continue to step down in pressure until the plug melts. The problem with this method is that sufficient pressure must be bled off that will result in hydrate melting but not in the plug becoming a projectile. If the pressure in the line is well above the hydrate formation pressure, then bleeding off some pressure will not melt the hydrate. If the line pressure is high, even bleeding of 1,400 to 2,000 kPa (200 to 300psia), which is sufficient to create a dangerous projectile, may not be enough to melt the blockage.

Therefore, it is important to know the hydrate formation pressure in order to know how much pressure to bleed. Standard procedures are in place in most jurisdictions that are designed to prevent accidents during the maintenance of oil field equipment. Operating companies often have even more stringent procedures for contractors working in their employ. It is wise to follow such procedures carefully.

7. CONCLUSION:

In every natural gas industry, the formation of gas hydrates is a problem during Transportation and Processing, now a day there are many methods for inhibiting the natural gas hydrates. But combating with heat is a cost effective method. In this method having, Initial cost and very low operating cost. So we must implement this method to combat the natural gas hydrate. By using this method we may reduce the processing cost of natural gas by avoiding the methanol dosing which begins in the 1st stage separator inlet. But the minimum amount of methanol must be present in the natural gas for the safety margin when transportation to consumer line.

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