

Problem Is The Result of Industry's Move To Use Higher Pressures

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H hydrate formation is one of the problems that challenge the industry's move to high-pressure natural gas production, processing, and transportation.

Hydrates are solid, crystalline compounds formed from water and small molecules. They are very much like common ice in both their appearance and their properties — with at least one important exception. Hydrates form at temperatures greater than 32°F, which is the freezing point of water. In addition it takes at least two compounds to make a hydrate. Those compounds are water and a hydrate former.

In the early era of the natural gas business, 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. It was not until the 1930s that Hammerschmidt (1934) demonstrated that the "ice" was actually gas hydrates.

What Are Gas Hydrates?

In a hydrate, the water molecules form a three-dimensional cage-like structure. The other molecule is trapped within the cage. Examples of gases that form hydrates include methane, ethane, propane, butane, carbon dioxide, and hydrogen sulfide. These are all common components of natural gas. Only small molecules form hydrates. Typically, gases larger than butane do not form hydrates.

The water molecules are referred to as the "host" molecules and the other compounds, which stabilize the crystal, are called the "guest" molecules. The guest molecules are more often referred to as "formers". The hydrate crystals have complex, three-dimensional structures where the water molecules form a cage and the guest molecules are entrapped in the cages.

Another interesting thing about gas hydrates is that there is no bonding between the guest and host molecules. The guest molecules are free to rotate inside the cages built up from the host molecules. Therefore these compounds are best described as a solid solution.

Three Conditions

The formation of a hydrate requires the following three conditions:

1. The right combination of temperature and pressure. Hydrate formation is favored by low temperature and high pressure.

2. A hydrate former must be present.

3. A sufficient amount of water—not too much, not too little. Free water is not required.

The exact temperature and pressure depends upon the composition of the gas. Fig. 1 shows the temperature and pressure at which hydrates form for several substances. Methods for predicting hydrate formation in natural gas mixtures are discussed in the literature (Carroll, 2003). Other phenomena that enhance — but are not necessary for — hydrate formation include the following:

1. **Turbulence** (high velocity, agitation),

- a. **High Velocity.** Hydrate formation is favored in regions where the fluid velocity is high. This makes choke valves particularly susceptible to hydrate formation. First, there is usually a significant temperature drop when natural gas is choked through a valve due to the Joule-Thomson effect. Second, the velocity is high through the narrowing in the valve.

- b. **Agitation.** Mixing in a pipeline, process vessel or heat exchanger enhances hydrate formation.

2. **Nucleation Sites.** In lay terms, a nucleation site is a point where a phase transition is favored, and in this case the formation of a solid from a fluid phase. Nucleation sites for hydrate formation include an imperfection in the pipeline, a weld spot, a pipeline fitting (elbow, tee, valve). Silt, scale, dirt, and sand all make good nucleation sites as well.

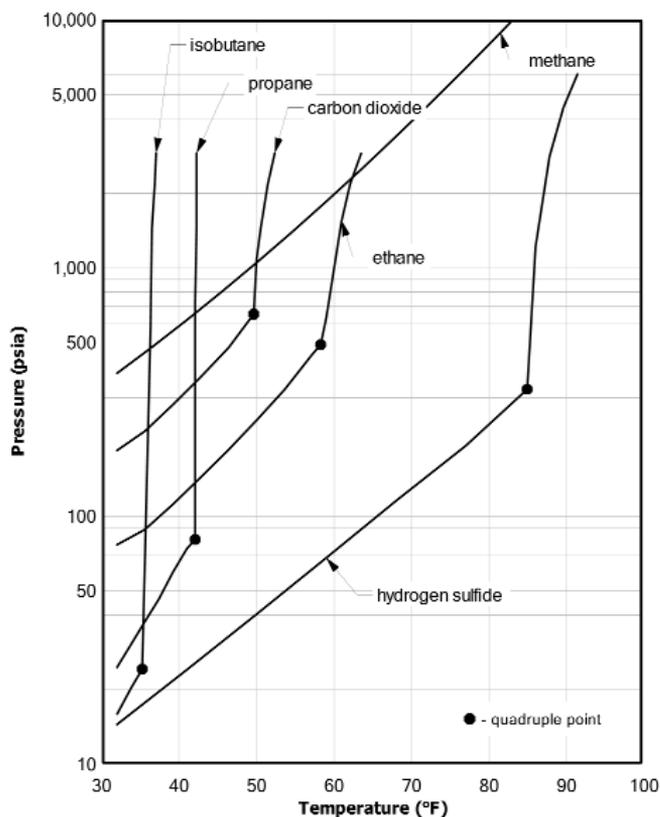


Figure 1: The hydrate loci for several components found in natural gas.

3. **Free-Water.** No, this is not a contradiction to earlier statements. Free-water is not necessary for hydrate formation, but the presence of free-water certainly enhances hydrate formation. In addition, the water-gas interface is a good nucleation site for hydrate formation.

The items listed above enhance the formation of a hydrate, but are not necessary. Only the three conditions given earlier are necessary for hydrate formation.

Another important aspect of hydrate formation is the accumulation of the solid. The hydrate does not necessarily agglomerate in the same location as it is formed. In a pipeline the hydrate can flow with the fluid phase, especially the liquid. It would tend to accumulate in the same location as the liquid does. Usually it is the hydrate accumulations that cause the problems. In a multiphase pipeline, it is the accumulations that block the line and plug and damage equipment.

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 term “gas hydrates” and also leads to one of the popular misconceptions regarding these compounds. It is commonly believed that non-aqueous liquids do not form hydrates. However, liquids may also form hydrates, provided the three criteria listed above are met.

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Gas Industry Practice

In the natural gas business hydrates are highly problematic. They are notorious for plugging wells and transmission lines and damaging process equipment. There are four approaches that are usually used in the business to combat hydrates:

1. Dehydration. The first of these is to remove the water from the gas, which is called dehydration. No water, no hydrates — it’s that simple. Several processes have been developed to remove water from natural gas. However, the purpose of dehydration is not to remove all of the water. The water level is reduced to the point where hydrates are no longer a problem. Typically, a water content of less than about 10 lb/MMcf (165 mg/m³[std]) is usually sufficient to prevent hydrate formation. However, depending upon the temperature and the mixture, the minimum water content to prevent hydrate formation may be different from this value.

2. Heat. The second method that is commonly used is to heat the gas. If the gas is sufficiently warm then hydrates will not form. Or hydrates that have already formed will melt.

For pipelines it is common to use a line heater to warm the fluid before it enters the pipeline. The fluid should be sufficiently warm that by the time it exits the pipe it has not cooled below the hydrate temperature. It may require a series of line heaters if the pipeline is long.

The other method is to use heat tracing. Here the heat is added locally using electrical resistance or a heated fluid.

3. Pressure. Alternatively, the pressure can be reduced. If the pressure is

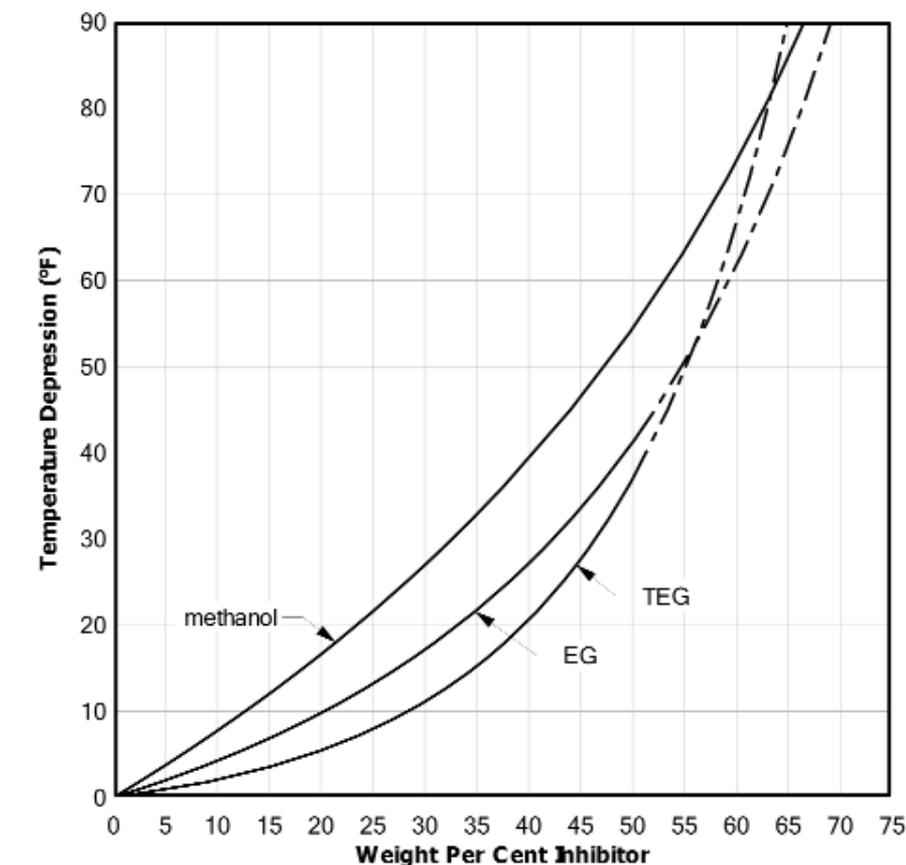


Figure 2.: The inhibiting effect of methanol, ethylene glycol (EG), and triethylene glycol (TEG).

sufficiently low than hydrates will not form or hydrates that have formed will melt. This is not often an option in the gas industry. The pressure is dictated by other concerns (the reservoir or processing conditions for example). Usually depressurization is only used as a remedial method to melt hydrates that have formed. However some consideration should be given to the pressure in the design stage.

4. Inhibitors. The final method is using chemicals to inhibit hydrate formation. In cold and moderate climates it is common to use salt to melt ice that forms on roads and sidewalks. On occasionally airplanes must be de-iced. This is achieved by spraying them with glycol. The same principle is used to inhibit the formation of hydrates. In the natural gas business the most common substance used for this purpose is methanol.

Fig. 2 is useful for approximating the temperature depression for a given weight percent of inhibitor. Note this is the weight percent in the aqueous phase only. Also, the temperature depression is given in Fahrenheit degrees. To convert to Celsius multiply by 5/9. This is a temperature difference and the conversion is not the same as converting temperature. From the graph you can see that a 50 wt% solution of methanol would result in a 55°F degree

decrease in the hydrate temperature. This is equivalent to 30.6°C degree decrease. **P&GJ**

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- Hammerschmidt, E.G., “Formation of Gas Hydrates in Natural Gas Transmission Lines”, Ind. Eng. Chem., 26, 851-855, (1934).



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