



Hydrate Inhibitors: Alternatives to Straight Methanol Injection

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ABSTRACT

Since the early 1900s, clathrate hydrate formation in oil and gas pipelines has led to issues with safety and properly sustained production. To combat these issues, methanol has become the preferred method of chemical treatment to inhibit hydrate formation. However, the use of methanol, while effective at controlling hydrate growth when properly applied, has numerous drawbacks. These drawbacks can include salt and scale precipitation, increased corrosion risk due to dissolved oxygen, and an increased risk of hydrate formation if an insufficient volume of methanol is used.

Low dose hydrate inhibitors (LDHIs), such as kinetic hydrate inhibitors and anti-agglomerants, can be added to associated methanol injection or applied neat to reduce many of the drawbacks resulting from the use of methanol, while maintaining many of the benefits. This paper will outline methods of hydrate control mainly through chemical means. The chemical methods covered will include thermodynamic hydrate inhibitors, kinetic hydrate inhibitors, and anti-agglomerants. Application benefits and drawbacks of each will be outlined. Finally, case histories will be used to support and explain the application of LDHIs to both reduce methanol injection volume and enhance overall treatment.

Keywords: Hydrate Inhibitor, Kinetic, Anti-Agglomerant, Methanol, Glycol

INTRODUCTION

Hydrate formation has been a constant thorn in the side of petroleum producers for generations. It wasn't until the 1930s that investigations began after E.G. Hammerschmidt¹ determined that the material plugging pipelines was a gas hydrate. Since that time, a considerable amount of work and interest has been devoted to discovering what a hydrate is and how to prevent its formation.

To understand how to prevent hydrate formation, one must first understand what a hydrate is. Calling the material a hydrate is actually a simplified version of the phenomena's true name, clathrate hydrate. The word clathrate is derived from the latin word *clathri*, which means lattice. In science a clathrate is a lattice structure compound formed by the inclusion of a guest molecule². Hydrate is defined as "a compound formed by the union of water with some other substance."³ So in effect, a clathrate hydrate is a crystallized water lattice, or cage, containing a guest molecule. In the petroleum industry, the guest molecule for the lattice structure is typically found to be methane, ethane, propane, iso-butane, H₂S, CO₂, and N₂. There are a large number of other gas molecules and guest molecules that can form a hydrate-like cage⁴ structure, many of which exist in natural gas found in conventional petroleum production. The cage is formed not by a chemical reaction, but by a weaker intermolecular bond. This bonding is also known as Van der Waals forces.

Hydrates can form wherever water will come in contact with the aforementioned guest molecules under a specific temperature and pressure to stabilize the Van der Waal forces. In natural gas and oil production, water and the guest molecules will come in contact with each other nearly everywhere. It is the presence of the guest molecules, along with the temperature and pressure of the system that will commonly dictate whether a cage will form. Providing the conditions are met, a hydrate will form.

Hydrate formation in gas and oil systems typically result in a plug, which can restrict and block production flow. Restriction in production may greatly alter the economical viability of producing a well. Whether it be a pipeline that is the main trunk line of a gas-gathering system, a single well or sub-sea umbilical, if production is not being sent through the pipe, money is not being made.

HYDRATE CONTROL METHODS

In order to maintain regular production and prevent hydrate plugging, methods were developed that attempted to mitigate their formation. Hydrate formation is typically controlled by injecting inhibitors, heating, dehydration or lowering the overall system pressure^{4,5,6}. The economics and viability of each of the hydrate control methods depend entirely on the systems

they are meant to control. Therefore, a thorough understanding of the system is essential to applying the correct hydrate control method.

It is good practice, when confronted with a hydrate control scenario, to understand the production conditions associated with the system and to determine the hydrate equilibrium curve for the system. The hydrate equilibrium curve can then be used to determine the subcooling, and from there develop a treatment program to prevent or control hydrate blockages. Subcooling is the difference in temperature between the actual working conditions of a system to the hydrate formation point⁵. Figure 1 displays the relationship of the treatment program to production. The gas species found in the system can have a major impact on subcooling and, therefore, the hydrate treatment program required. In the example in Figure 1, the production conditions display a markedly different hydrate formation depending on the gas composition. Based on the model, if the system contained straight methane, hydrates would not be expected to form at the labeled production conditions. If the system was a “typical” sweet gas that contained a low level of carbon dioxide and a small amount of heavier gases, such as ethane and propane, the system would display a subcooling of 3°C. If the system were to contain a high volume of hydrogen sulfide, H₂S, those same system conditions would lead to a subcooling of 12°C. The treatment styles would likely be different from the sweet system to the sour. The sweet system would most likely have a chemical inhibitor injection program, while the sour system may have a combination of chemical inhibition and line heaters.

Figure 1 is a chart of hydrate curves developed with the assistance of CSMHYD, which is a hydrate equilibrium point modeling program that was developed by the Colorado School of Mines Hydrate Research Group⁷. CSMHYD is one of many programs, such as HYSYS[®], Multiflash[®] and Hydrate Plus[®], that can calculate an equilibrium point for the gas phase and associated production parameters. An equilibrium curve can easily be generated and production conditions can then be plotted and used to understand the degree of hydrate concern. Knowing the system conditions will, in part, dictate how hydrates are controlled.

A majority of the methods of hydrate prevention attempt to alter or affect one or more of three things: system temperature, system pressure or the water itself.

Line heaters are a common way to maintain control of the production temperature. Drawbacks to line heater use can be the relatively high fuel gas consumption, possibility of increasing the corrosion risk, and increasing the chances of plugging due to scale build up. Thermal insulation can be used to reduce heat loss to the surroundings. A drawback to adding insulation is that it can contribute a great deal of capital expenditure (CAPEX) cost⁶.

Lowering the overall pressure of a gas-gathering system can also reduce or remove the requirement for additional control methods. This can result in lowered overall production rates⁶, and therefore provide a lower return on investment.

Dehydration is another method to control hydrates⁸. Removing the water from gas production can greatly reduce the volume of the chemical treatment needed to control hydrate formation. Dehydration is rarely a process that can achieve complete water removal for economic and/or operative reasons⁵. Therefore, in many cases, some form of additional hydrate control will need to be in place.

One of the most common methods of hydrate-formation control is the addition of chemical inhibitors⁹. There are three types of chemical hydrate inhibitors: thermodynamic, kinetic and anti-agglomerant.

THERMODYNAMIC HYDRATE INHIBITORS

Thermodynamic inhibitors prevent hydrate formation by shifting the freezing / hydrate-formation point of water. If enough of a thermodynamic inhibitor is in place, typically hydrate formation should not be a problem. Common thermodynamic inhibitors are methanol and ethylene glycol. For the purposes of this paper, ethylene glycol will not be discussed. Treatment rates for thermodynamic inhibitors are almost always higher than for other methods of chemical inhibition. For most cases, injection rates of methanol require sufficient volumes to make a 10 to 60 wt. percent solution in the water available within the system^{5,6,10}. High methanol-injection rates or high methanol content in the water phase, while very effective at preventing hydrate formation when a proper percentage is in place, can introduce a number of issues to a system.

- The dissolved oxygen content in methanol can be as high as 40mg/L at 25°C. Dissolved oxygen present in methanol is well known to increase the corrosion rate in both sweet and sour systems¹¹.
- Oxygen presence in sour systems can alter the formed iron sulfide layer leading to a less protective iron sulfide film¹¹.
- Methanol has been found to reduce the effectiveness of some corrosion inhibitors¹².
- Scaling tendencies for barite, calcite and halite can be significantly affected by “high” methanol concentrations in produced fluids. The scale nucleation rate of barite, in particular, can be increased enough to introduce a situation where scale inhibitor performance can be significantly hindered¹³.
- Methanol losses to the gas and hydrocarbon phases can be significant^{14,15}. Methanol injection volumes may need to be increased to sufficiently saturate the gas and hydrocarbon phases to assure correct methanol content in the water phase to adequately inhibit the system.

LOW DOSE HYDRATE INHIBITORS

Because thermodynamic inhibitors exhibit these aforementioned drawbacks, alternate chemical control methods were investigated. These investigations resulted in the commercial availability of low dose hydrate inhibitors (LDHIs) by the mid 1990s. Since then, and especially in the last five years, LDHI's have made an impact in the industry as a viable, and in some cases, required treatment methodology for hydrate control. LDHI's consist of two different classes of compounds, kinetic inhibitors and anti-agglomerants⁵. The term "LDHI" was coined because these products can be used at comparatively low concentration levels (0.25 – 0.50 % by volume in produced water)⁶ compared to the higher required concentrations of more traditional thermodynamic inhibitors such as methanol. A further difference between LDHI's and thermodynamic inhibitors is the inhibition mechanism. Neither of these two methods alters the hydrate equilibrium point of a system as thermodynamic inhibitors do. Kinetic inhibitors will alter the reaction rate while anti-agglomerants will allow hydrate formation but not agglomeration.

Kinetic Hydrate Inhibitors

Kinetic hydrate inhibitors (KHI) work by delaying hydrate crystal nucleation and/or growth until the fluids in question are brought to a zone where hydrates are unstable. Kinetic inhibitors are chemicals that have the ability to increase the induction time for a hydrate crystal to begin growing. The goal of applying such chemistries is to take advantage of the delayed crystallization time to allow produced fluids to be removed from hydrate-forming conditions. The length of time a kinetic inhibitor can delay the onset of hydrate formation can be anywhere from hours to days⁵. KHI's are typically most effective in low-to-moderate hydrate formation conditions. Most KHI's can protect systems with subcoolings up to 12°C, on the newer generation of products^{6,16}.

KHI blends are usually applied in one of two different methods. One method is to apply the blend neat without a supplementary methanol injection. Another method is to apply it, along with methanol, either through separate injection points or mixed into methanol and applied as a single injection. KHI's used as an additive to methanol injection provide both an increase to the subcooling tolerance of the treatment while routinely reducing the overall injection rate by 40 – 60% to that of methanol alone, or more, depending on the system treated. The selection of injection method is based primarily upon cost-to-treat and the required effectiveness of the program.

Anti-Agglomerant Hydrate Inhibitors

Anti-agglomerants (AA) allow hydrate crystals to form but prevent them from agglomerating and adhering to pipe walls¹⁷. AA's are not known to have subcooling limitations and have been found to be effective in low to extreme hydrate stable regions, even during extended shut in periods. The design of the AA molecule is analogous to foaming surfactants used for gas well deliquification. A foaming surfactant has a hydrophilic (water-attracting) head and a hydrophobic (water-repelling) tail. The AA molecule has a "head," which is attracted to the hydrate and will become part of the hydrate crystal. The "tail" portion is dispersible in hydrocarbon liquids and provides crystal dispersion into a hydrocarbon phase. The dispersion has been found to limit the formation of larger crystals,¹⁶ which would then be less likely to cause plugs. A benefit to this characteristic is that since a hydrate crystal is formed and dispersed, there have been no subcooling or residence time limitations as yet discovered. A side effect of the dispersion requirement is that AA's require a liquid hydrocarbon phase to be present for inhibition to be effective. Typically, the water cut must be below 25 – 50% for an AA to be most effective. AA's also display a gas-to-oil ratio (GOR) limitation. A sufficient liquid hydrocarbon phase needs to be present in the production stream to disperse the hydrate crystals effectively. A rule of thumb described in literature states that a GOR of $< 17.8 \text{ e}^3\text{m}^3/\text{m}^3$ (100,000 scf/stb)¹⁶ for AA's is required to be effective. AA's are considered a methanol replacement, and the reduction in injection rate from using methanol to using an AA can be substantial, as supported by the case histories.

CASE HISTORIES

KHI #1

A large sweet gas field was operated by a producer in northern British Columbia that had winter access-only roads for the majority of the field. During the warmer months, when the winter roads could not be used, methanol was required to be flown in to replenish tanks. The cost to fly in methanol during the summer months was high; therefore, alternatives to straight methanol injection were sought.

A system assessment was performed and a hydrate equilibrium curve was generated. Refer to Table 2 for the gas composition and Figure 2 for the hydrate equilibrium curve. Subcoolings for the field were found to be between 3 to 5°C during summer months. Methanol injection rates were originally between 50 to 100 L/day for the majority of the field. A KHI mixture with methanol was selected as the most economic means of treatment. A KHI blend was mixed into the methanol tanks to make a 5% solution and was applied initially to selected well sites as a test of viability. It was discovered that the test wells were able to lower the overall treating rates by 60% and not result in hydrate formation. Over time, the program was expanded to encompass the majority of the field with little to no issues.

The hydrate inhibitor program was considered a success as the methanol injection rates were lowered sufficiently to allow onsite tankage to be sufficient to control hydrate formation throughout the summer months. In many cases, fly-in methanol / KHI tank fills were not required until winter access was resumed.

KHI #2

A producer in central Alberta operated a 5 km long sales line requiring on average 600 L/day of methanol to prevent hydrate formation. Production through the flow line was 400 e³m³/day of sweet gas along with 10 m³/day of condensate. Water production through the line was estimated by the producer to be approximately 1m³/day, although this was not accurately metered. The line was mostly downhill with few liquid hold ups. Pigging was conducted monthly or as required, whichever came first, and no hydrates were ever discovered. Hydrate formation was not a typical issue for the line, but was generally avoided at all cost through high methanol injection rates.

The production parameters were reviewed and it was decided that a KHI would be a good option to trial to reduce the daily methanol injection volume. Refer to Table 3 and Figure 3 for data pertaining to the case. A KHI blend was added to methanol to make a 10 percent solution. Initial optimizations were able to reduce the methanol rate to approximately 250 L/day with no hydrate formation issues. Optimizations are ongoing and lower injection rates are expected to be reached. The program was considered a success as the methanol injection rate was dropped considerably and hydrate formation was not observed.

KHI #3

A producer in central Alberta operates a sales line that typically carries 100 e³m³/day of gas production containing 2000 ppm H₂S, along with approximately 50 L/day each of condensate and water. Prior to entering the line, production is separated to remove hydrocarbon liquids and water. . Saturated gas entered the flow line at 27°C and exited the line at 8°C. The line temperature was determined to be stable throughout winter and summer. Line pressure was again fairly stable at 4350 kPa. Subcooling for the system was determined to be 8°C. The calculated methanol volume required to inhibit hydrate formation was approximately 64 L/day. Historically hydrates were found during the pigging operation. The flow line was periodically pigged, but was not on a regular schedule Refer to Table 4 and Figure 4 for gas composition data and hydrate equilibrium curve.

Upon calculating the methanol partition volumes for the production, a KHI blend was applied neat without methanol injection. Initial injection rate was set at 10 L/day. Optimizations brought the neat KHI injection down to 6 L/day. The neat KHI hydrate inhibitor

program has been considered a success as hydrates were no longer observed during pigging operations.

AA #1

A producer drilled a number of new oil wells in northern Alberta. As they began to bring them online, it was discovered that they were prone to both extreme paraffin and hydrate issues. The wellhead temperature was found to be below the cloud point of the oil, causing the production of a paraffin stabilized emulsion. One such well produced on average 9 m³/day of 19,000 ppm TDS brine, 36 m³/day oil, and 4 e³m³/day of sour gas into a flow line over 9 km long. If the well was allowed to flow, it would produce, on average, one hour before the flow line would plug with hydrates and then production would cease. Additionally, no convenient location for methanol injection was available for injecting methanol to dissolve the hydrate blockage. To remove hydrate plugs, the lines required depressurizing on both sides of the plug to portable pressure vessels and flare stacks. The hydrates were then allowed to disassociate naturally under controlled, depressurized conditions. This proved to be a slow process, requiring long production down times and significant operator time.

The production parameters were investigated and a hydrate equilibrium curve was generated. It was discovered that the system subcooling was approximately 16°C for the produced gas. Calculations showed that the system required a minimum of approximately 4800 L/day of methanol to inhibit hydrate formation effectively. Refer to Table 5 and Figure 5 for a representative gas composition and resulting hydrate equilibrium curve.

The following is a timeline of events for the hydrate inhibitor trials:

1. Methanol injected at steadily increasing rates until 6000 L/day reached, hydrate plugs formed.
2. It was determined that wax may be inhibiting ability of methanol to reach water phase. Attempts made to mitigate wax formation unsuccessful.
3. AA blend injected at 200 L/day, no hydrate formation noted.
4. 25% KHI blend in methanol solution injected up to 6000 L/day, hydrate plugs formed.
5. AA blend injection re-instituted, again, no hydrate formation resulted.

Optimizations were performed and it was found that the AA injection rate was able to be dropped by 55% (optimized injection rate 90 L/day) without hydrate plug formation being noted. The AA blend was brought in to use at more wells displaying similar production issues to the initial well and all responded to the treatment like the first well. The AA application was considered a great success. Wells were able to produce continuously without hydrate plug formation using a relatively low injection rate in an application where even high volumes of methanol, and a KHI and methanol mixture, were proven unsuccessful.

AA #2

A producer operated a number of wells in central Alberta that were found to be prone to severe hydrate blockages during the winter when flow line temperatures dropped. It was not economical for the wells to be flowed from November through May due to the hydrate issues. With relatively high methanol injection rates, weekly hydrate blockages would still result. Therefore, from November through May, the wells would be shut-in and the flow issues avoided. Typical daily production on one such well in operation was 2 m³ of water, 3.5 m³ of oil, and 0.5 e³m³ of gas. Line pressure for the gathering system was low at 1000kPa although the flowing temperature was expected to be highly variable.

Production data was used to develop a hydrate equilibrium curve. Refer to Figure 6 and Table 6 for the hydrate equilibrium curve and gas composition data. After reviewing the data and the curve it was decided that the wells would be a good candidate for a trial using an AA blend. An AA was selected for this treatment due to the low water rate and the unknown day-to-day flow line temperature. For one such well, an AA blend was initially trialled at 15 L/day to make a blend concentration of 7500 ppm in the produced water. The AA was applied with no supplementary methanol injection. No hydrate blockages were noted and the chemical was optimized down at regular intervals. The end result was that the minimum pump rate of 3.5 L/day was realized with no hydrate blockages noted during the entire winter. This injection rate resulted in a blend concentration of 1750 ppm in the produced water.

The AA application was considered a success because wells that would typically be shut in for winter were able to be flowed with a low injection rate of neat hydrate inhibitor.

CONCLUSIONS

As shown by several case histories, hydrate inhibitors can be excellent alternatives to the use of straight methanol. With proper implementation and optimization, significant reductions to methanol volumes can be introduced to a hydrate inhibition program. In some cases the use of neat methanol can be completely replaced by low injection rates of the correct hydrate inhibitor.

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APPENDIX

Table 1

Data used to calculate hydrate equilibrium curves for Figure 1

Component	Straight C1 (mol %)	“Typical“ Sweet (mol %)	High H ₂ S (mol %)
N ₂	0	2.0	2.1
H ₂ S	0	0	38.5
CO ₂	0	0	10.0
C1	100	89.8	49.2
C2	0	4.7	0.2
C3	0	2.0	0
i-C4	0	0.5	0
n-C4	0	0.5	0
i-C5	0	0.2	0
n-C5	0	0.1	0
C6	0	0.1	0
C7+	0	0.1	0

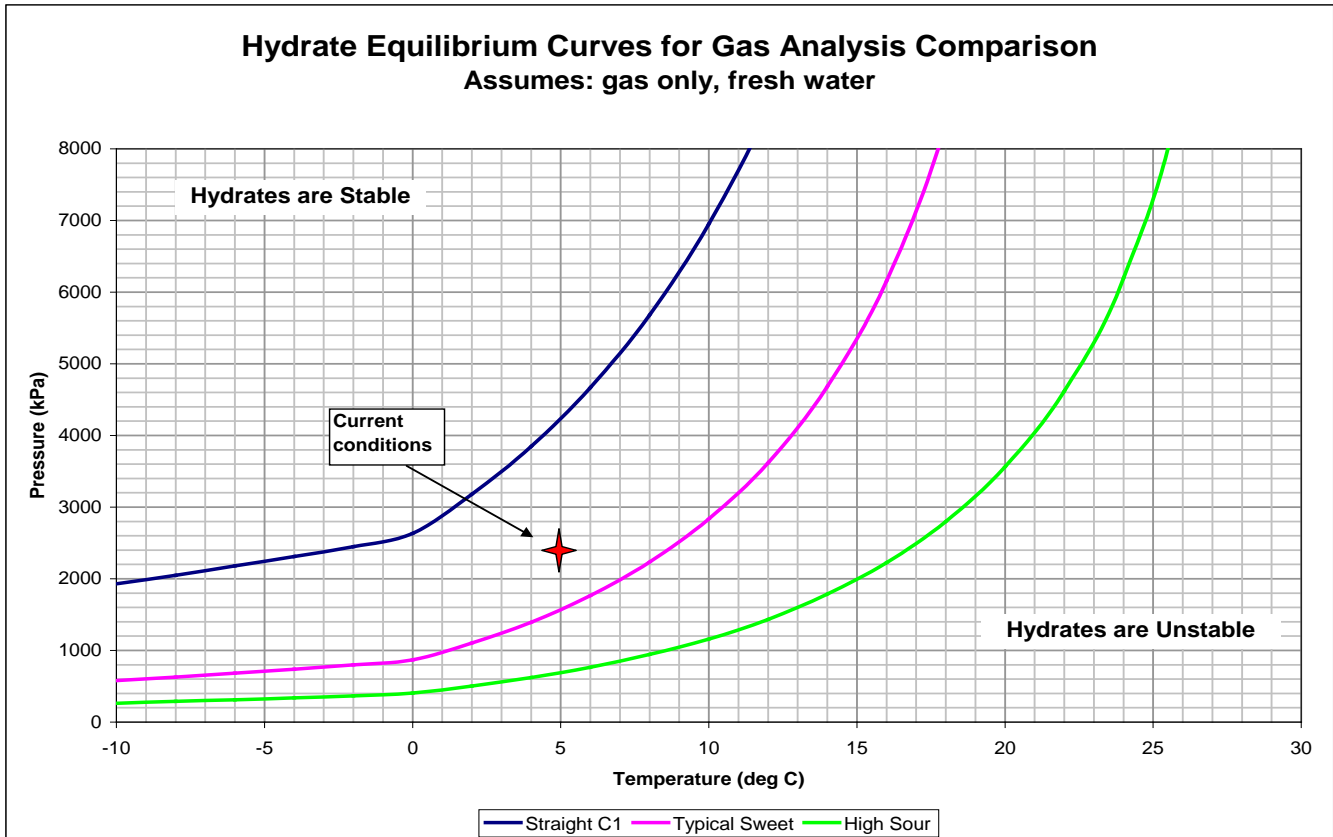


Figure 1: Production condition subcooling comparison using different gas analyses.

Table 2

Case History - KHI #1 typical gas composition

Component	KHI # 2 Gas Composition (mol %)
N ₂	0.3
CO ₂	0.6
H ₂ S	0
C1	96.5
C2	1.4
C3	0.5
C4s	0.3
C5s	0.2
C6+	0.1

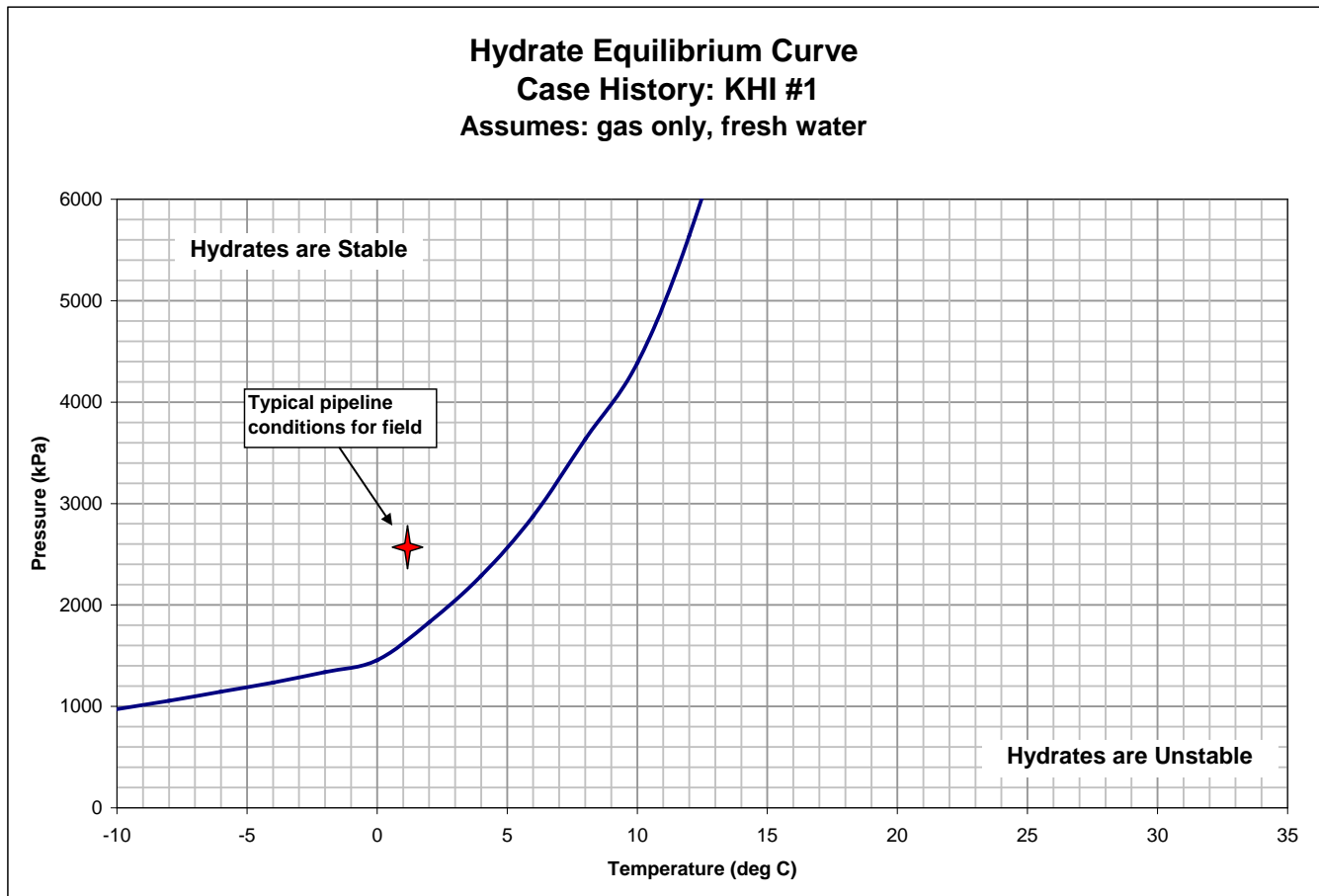


Figure 2: Case History - KHI #1, typical hydrate equilibrium curve

Table 3

Case History - KHI #2 gas composition data

Component	KHI # 2 Gas Composition (mol %)
He	0.1
N ₂	1.6
H ₂ S	0
CO ₂	0
C1	87.8
C2	5.8
C3	2.6
i-C4	0.6
n-C4	0.7
i-C5	0.3
n-C5	0.2
C6	0.2
C7+	0.1

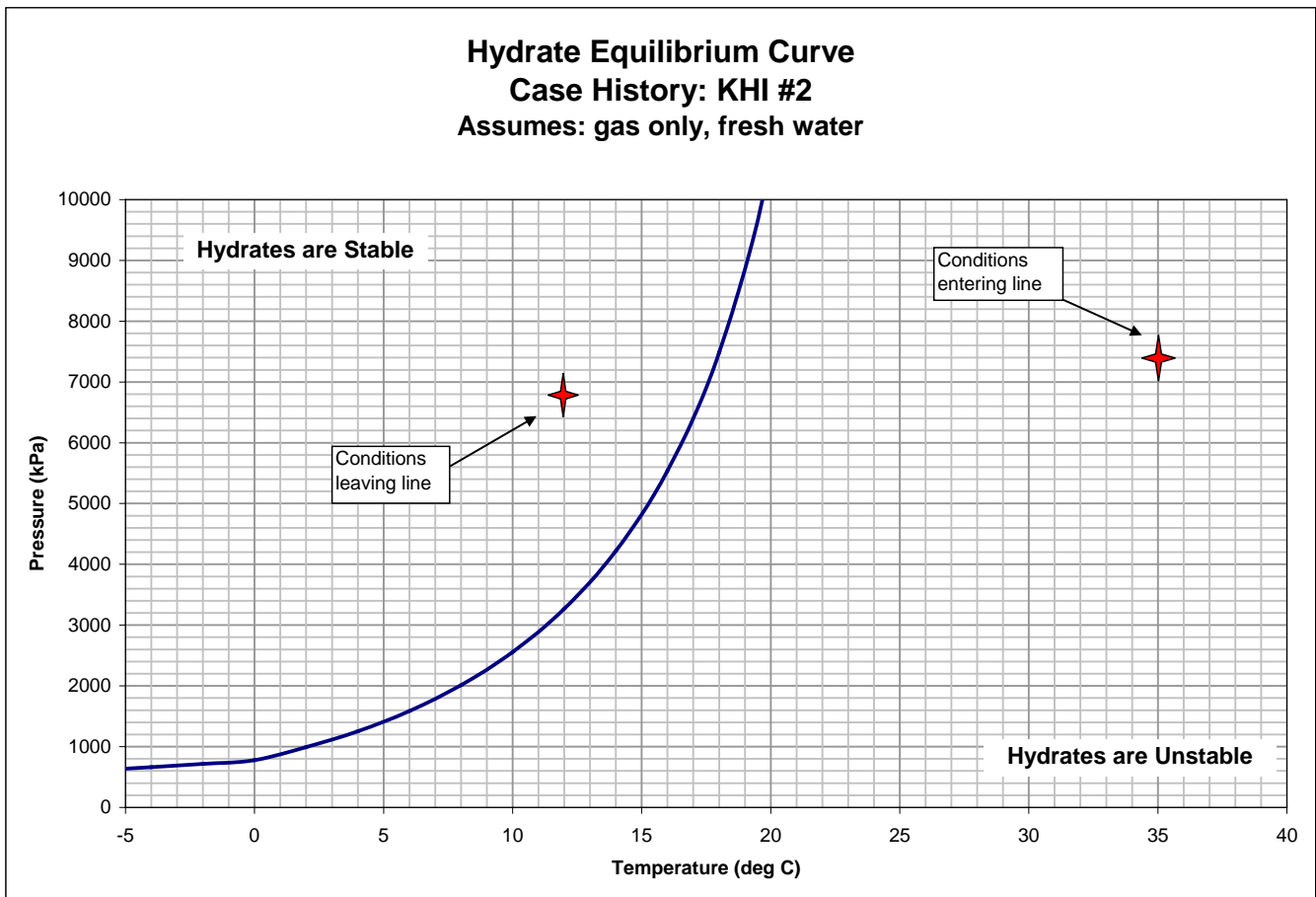


Figure 3: Case History - KHI #2 hydrate equilibrium curve

Table 4

Case History - KHI #3 gas composition data

Component	KHI # 2 Gas Composition (mol %)
N ₂	0.6
CO ₂	2.5
H ₂ S	0.2
C1	76.8
C2	10.4
C3	5.5
C4s	2.8
C5s	0.9
C6+	0.3

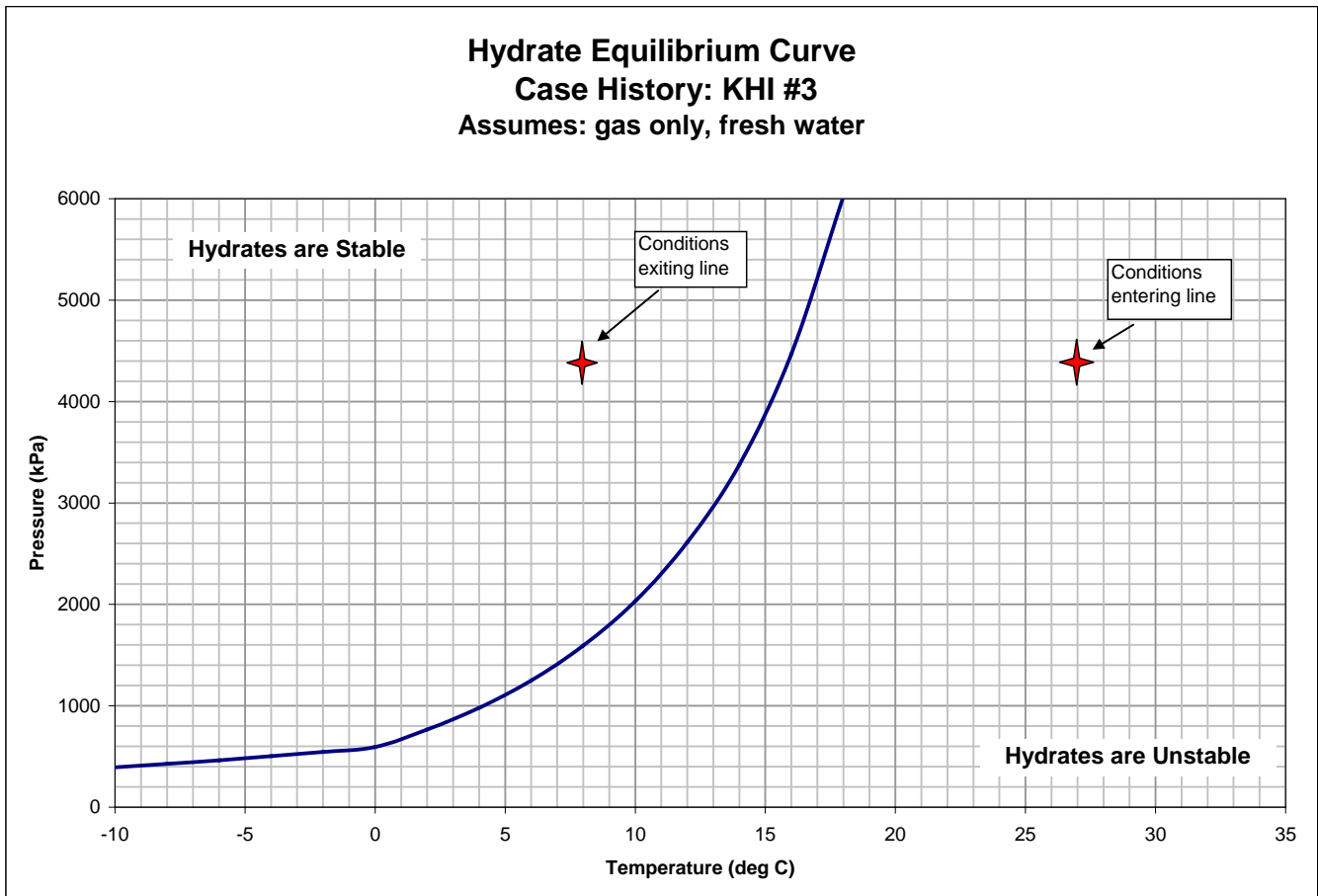


Figure 4: Case History - KHI #3 hydrate equilibrium curve

Table 5
Case History - AA #1 Gas Composition Data

Component	Mole %
N ₂	0.5
CO ₂	2.6
H ₂ S	5.5
C1	72.5
C2	11.4
C3	4.6
C4s	1.9
C5s	0.6
C6+	0.4

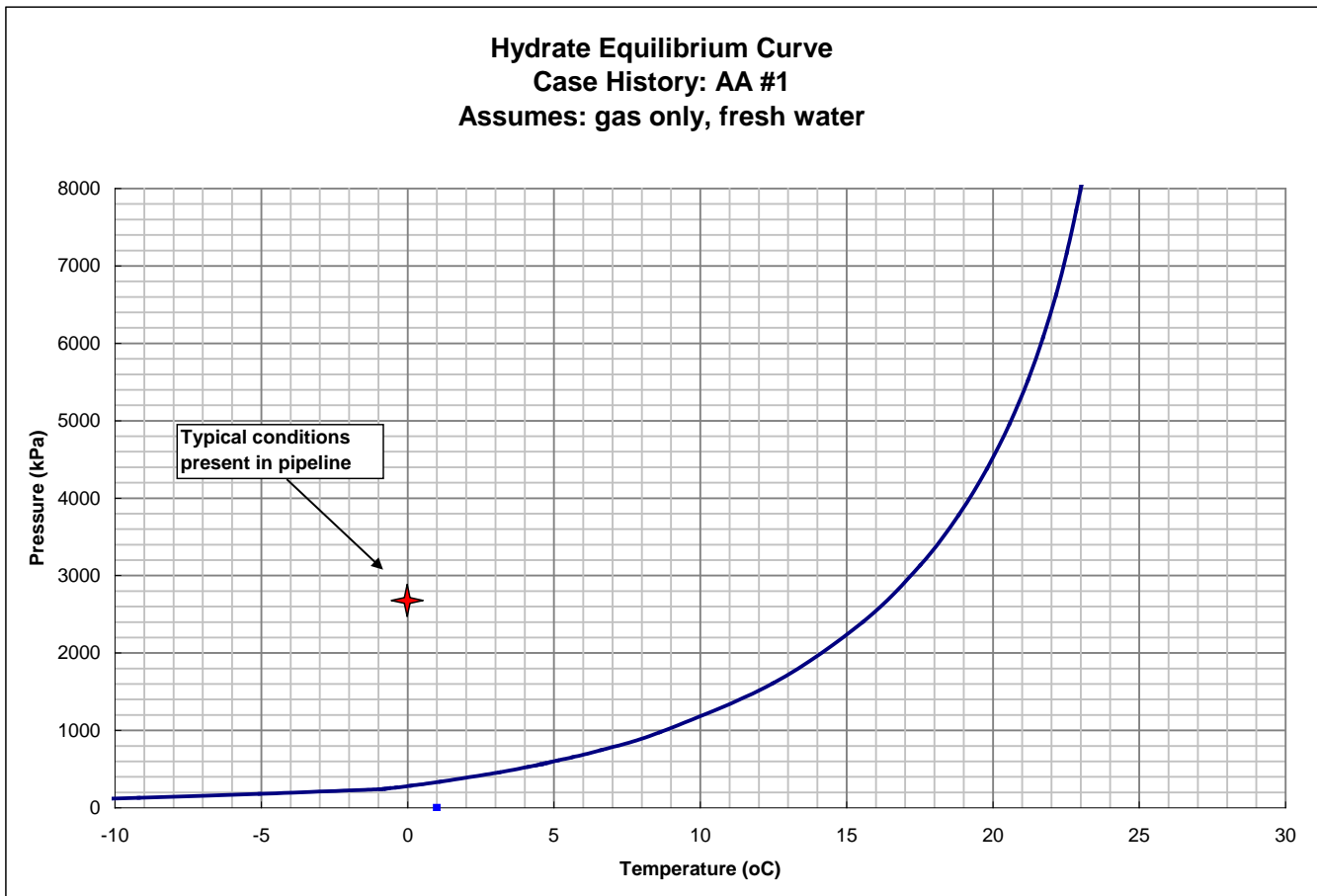


Figure 5: Case History – AA #1 hydrate equilibrium curve

Table 6
Case History - AA #2 Gas Composition Data

Component	Mole %
N ₂	3.4
CO ₂	3.0
H ₂ S	9.3
C1	66.9
C2	11.1
C3	4.4
C4s	1.5
C5s	0.3
C6+	trace

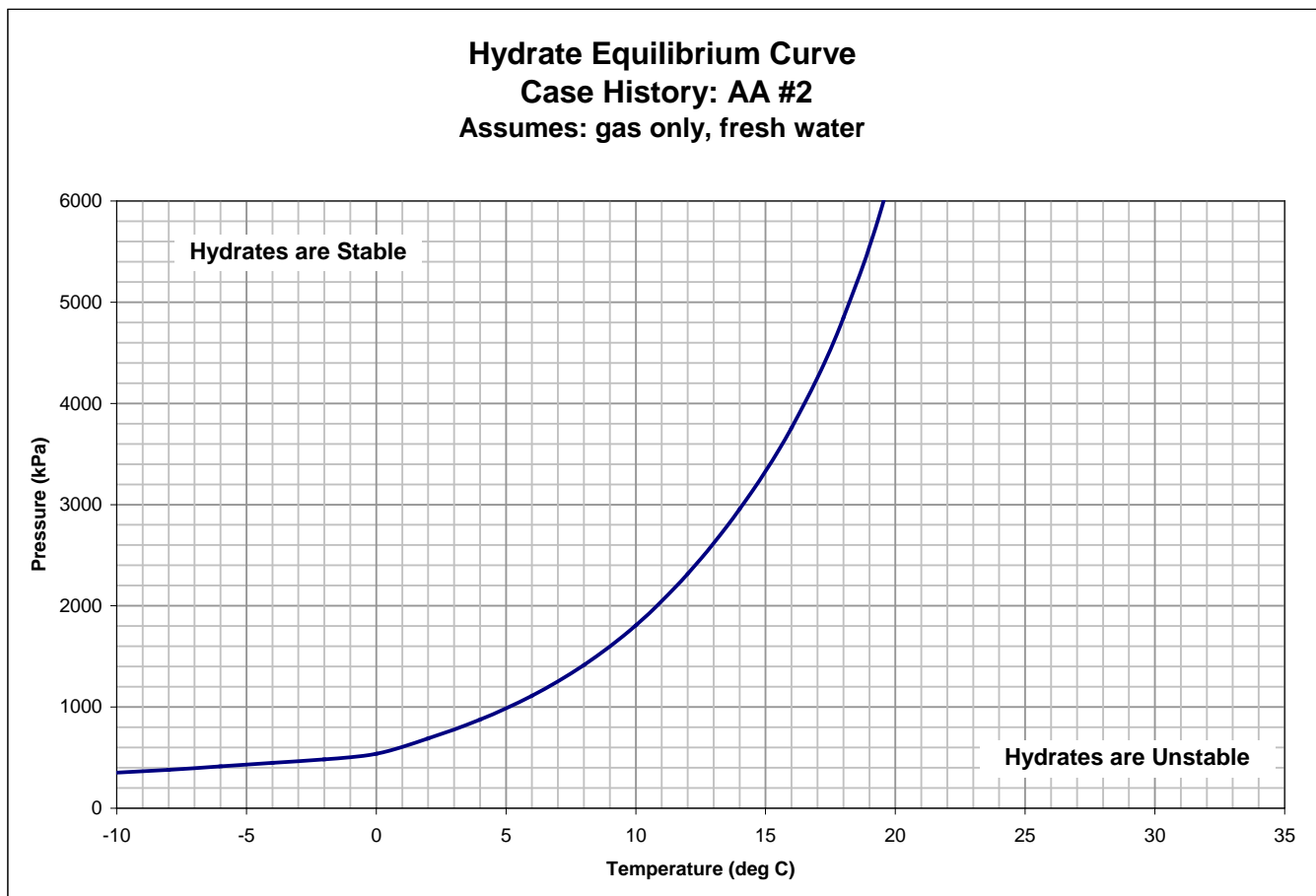


Figure 6: Case History – AA #2 hydrate equilibrium curve

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