Selection of Hydrate Suppression Methods for Gas Streams

KIMBERLY C. COVINGTON, JOHN T. COLLIE III,
Bryan Research & Engineering,
Bryan, Texas

STEVEN D. BEHRENS,
Mitchell Gas Services, Inc.,
The Woodlands, Texas

ABSTRACT

This paper will discuss and compare the methods used to suppress hydrate formation in natural gas streams. Included in the comparison will be regenerated systems using ethylene glycol and non-regenerated systems using methanol. A comparison will be made between the quantities of methanol and ethylene glycol required to achieve a given suppression. A discussion of BTEX emissions resulting from the ethylene glycol regenerator along with the effect of process variables on these emissions is also given.

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INTRODUCTION

The formation of hydrates in processing facilities and pipelines has been a nuisance to the natural gas industry for over five decades. Whether the problem occurs in transportation or processing, hydrate formation can cause shutdowns and even destruction of valuable equipment. Because of these devastating and often costly consequences of hydrate formation, methods of slowing hydrate solids development in gas streams have been of interest for a number of years.

Gas hydrates are crystalline, "ice-like" compounds composed of water and natural gas. The conditions that tend to promote hydrate formation include the following: low temperature, high pressure, and a gas at or below its water dew point with "free" water present. Two structures of gas hydrates are known to form in light gases: Type I and Type II (GPSA, 1994). Type I forms with smaller molecules such as methane, ethane, and hydrogen sulfide. Larger molecules like propane and butane combine with water to form the diamond lattice structure of Type II. The two hydrate structures are equally damaging; however, an advantage in treating hydrate problems is that all suppression methods are effective on both Type I and Type II structures.

Recently, the existence of a third hydrate structure, Type H, was reported. The importance of the new structure to the hydrocarbon industry is significant. To fully understand its role in the industry, further phase equilibrium data and structural investigations are needed (Englezos, 1993).

METHODS USED TO SUPPRESS HYDRATE FORMATION

The formation of hydrates can be prevented by using any of the following methods.

1. Adjusting the temperature and pressure until hydrate formation is not favored
2. Dehydrating a gas stream to prevent a free water phase
3. Inhibiting hydrate formation in the free water phase

To implement these methods, a number of practices are used throughout the gas industry.

Process Conditions

Process conditions may often be manipulated to prevent or retard the formation of hydrates in process equipment or a pipeline. For example, the addition of a line heater may serve to maintain operating temperatures above hydrate formation temperatures. Also, a reduction in pressure may impede the hydrate formation process. If it is not feasible to adjust the temperature or pressure of a gas stream, an alternative suppression method must be used.

Solid Desiccant Dehydration

Several solid desiccants have the physical characteristics to adsorb water from natural gas. Adsorbents in common commercial use include the following (Kohl, 1985):

1. Silica gel
2. Silica-based beads
3. Activated alumina
4. Alumina-gel balls
5. Activated bauxite
6. Molecular sieves

The equipment and process-flow arrangements for each of the adsorbents are essentially the same with the possible exception of molecular sieves which normally require higher regeneration temperatures. A typical plant for water vapor removal by adsorption will consist of two vessels filled with granular desiccant along with auxiliary equipment for desiccant regeneration.

The areas of application for dry desiccant processes include cases where essentially complete water removal is desired, and installations in which the operating simplicity of the granular desiccant system makes it attractive (Kohl, 1985). Solid desiccant dehydration is generally specified if dew point depressions consistently greater than 80°F are required. For large volumes of high pressure gas, liquid dehydrating systems (diethylene glycol and triethylene glycol) are typically more economical if dew-point depressions of 40° to 50°F are required.

Solid desiccant plants offer the following advantages in comparison to liquid dehydration systems:

1. Simplicity of design and operation of units
2. Insensitivity to moderate changes in gas temperature, pressure, flow rate, etc.
3. Ability to provide extremely low dew points
4. Generally free from corrosion and foaming problems
5. Ability to dehydrate very small quantities of gas at a low cost

Solid desiccant dehydration also has disadvantages. These include high initial cost, higher pressure drop, relatively high heat requirement for regeneration, and susceptibility to breakup or poisoning (Kohl, 1985).

Glycol Dehydration

Glycol dehydration, most commonly with diethylene glycol (DEG) or triethylene glycol (TEG), is the most widely used method of removing water from natural gas. The process works on the basis of glycol's high affinity for water. Glycol units, such as the one shown in Fig. 1, are designed for bulk removal of water and can do it cost effectively with few operating problems. They can be easily automated for unattended operation; for example, dehydration at a remote production well. However, dehydration alone may not have the ability to remove enough water for subsequent low temperature processing. This situation usually leads to an additional step in the process. Typically, a molecular sieve unit or an injection unit may follow a glycol system to ensure sufficient dehydration ahead of cryogenic processing.

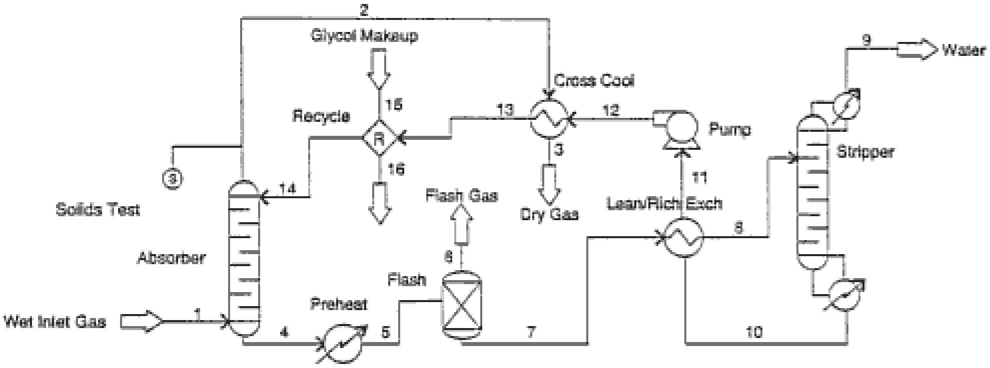


Figure 1. Typical dehydration unit.

Hydrate Inhibition

Hydrate inhibition is typically employed when it is not cost effective to install a full dehydration unit, or when an operating dehydration unit cannot obtain the desired dew point depressions. Inhibition utilizes the injection of a known hydrate inhibitor into the process upstream of the location where solids formation is predicted to occur. The inhibitor provides some dehydration, but its primary function in this type of operation is to act as an "antifreeze" agent in suppressing the formation of solid hydrates (Kohl, 1985).

The most common inhibitors are methanol, ethylene glycol (EG), and TEG. Since glycol’s viscosity makes effective separation difficult at cryogenic conditions, methanol is usually preferred under these circumstances. For continuous injection in non-cryogenic conditions, one of the glycols generally offers an economic advantage (GPSA, 1994). Typically, methanol is used in a non-regenerable system while EG and TEG are used in regenerable processes. The regenerable process purifies the glycol in a regenerator and recycles it to the injection site.

The choice between inhibitor alternatives must be based on physical limitations as well as economics. Operating conditions may limit the number of choices available.

CALCULATION METHODS

There are numerous methods available for calculating hydrate formation conditions and the performance of the various practices to avoid hydrates. The most common methods are discussed below. A detailed discussion of these and other methods may be found in the GPA Research Report RR-134 (Daubert, 1992) and the Engineering Data Book (GPSA, 1994).

K-Chart Method

The K-chart method is used to predict the temperature or pressure at which hydrates form in a gas. An example of the method is shown in the GPSA Engineering Data Book (1994) on page 20-11. The method is valid up to pressures of approximately 1100-1500 psia, depending on the composition of the gas. Computer solutions are generally more accurate and have applicability up to 4000 psia (GPSA, 1994). The K-Chart method is limited to prediction of the temperature or pressure when hydrates may form and does not accommodate inhibition or dehydration methods.

Hammerschmidt's Equation

Hammerschmidt's equation may be used to calculate the minimum inhibitor concentration that is required to prevent significant hydrate formation in the free water phase (Sloan, 1990). For a given inhibitor concentration in the free water phase, the equation calculates the resulting temperature depression for hydrate formation. The equation was found to be valid for typical natural gases with methanol concentrations less than 0.2 mol% and glycol concentrations less than 0.4 mol% (Sloan, 1990). The Hammerschmidt equation may be used in conjunction with other hand methods such as the K-chart method to predict inhibitor feed rates. The equation is shown below (GPSA, 1994).

$$d = \frac{K_H(I)}{100MW_I - (MW_I)(I)} \tag{1}$$

where:

K_H = 4000 for glycols
K_H = 2335 for methanol
d = hydrate temperature
I = Weight percent inhibitor in the liquid phase
MW_I = Molecular weight of the inhibitor

Equation (1) does not consider dehydration methods or the capability to predict formation temperatures in the absence of inhibitors.

CSMHYD Hydrate Prediction Program

The CSMHYD Hydrate Program accompanies the textbook, *Clathrate Hydrates of Natural Gases* (Sloan, 1990). This program may be used to predict hydrate formation temperatures and pressures as well as hydrate depression temperatures for methanol inhibition. The program does not handle dehydration processes or downstream effects of inhibition, nor inhibition with glycols. The results of the CSMHYD program are compared for two gases in Table 1 and Table 2.

Computer Simulation

PROSIM is an advanced process simulation program developed by Bryan Research and Engineering (BR&E) to design and optimize processes in the oil, gas, chemical and refining industries. With this program, the user may construct the process flowsheet on the computer screen and enter the process operating parameters on pop-up forms. After this step has been completed, complete material and energy balances for steady state operating conditions may be performed. PROSIM's solids test block may be attached to any process stream in the flowsheet. The test block calculates and exhibits results which include the following:

1. CO_2 freeze out temperature
2. Water dew point temperature
3. Water ice point temperature
4. Formation temperatures for Type I and Type II hydrates

The calculations for the test block are based on the pressure and composition of the process stream to which it is attached.

Since PROSIM is a full process simulator, various possibilities for hydrate inhibition with methanol, EG, DEG, or TEG may be studied. For example, the flow rate of an inhibitor may affect downstream operations within the process system. PROSIM is capable of predicting these effects. PROSIM may also be used to model glycol dehydration processes. Existing dehydration units may be optimized to eliminate solids formation problems or, as an alternative, the addition of a dehydration unit to the process may be studied. In addition, PROSIM is capable of predicting VOC and BTEX emissions from glycol dehydration units.

Results from PROSIM have been extensively compared to the GPA Hydrate Databank from Research Report 134 (Daubert, 1992). The results from two typical cases are included in Tables 1 and 2. In these tables, the gas used is initially presented on a dry basis. Various amounts of water and/or methanol are added to the dry composition and, at various pressures, the experimental solids formation temperatures are compared to calculated values from PROSIM. Table 1 compares the results for a gas containing only water, methane, and propane while Table 2 adds various amounts of water and methanol to a natural gas. As can be seen from the tables, PROSIM predicts the hydrate formation temperatures quite accurately for cases with and without methanol.

Table 1. Comparison of experimental and calculated hydrate formation temperatures.

Gas Composition (Dry)				
Component		**Mole Fraction**		
Water		0.0000		
Methane		0.9469		
Propane		0.0531		
		Hydrate Formation Temperature		
Water Added mol frac x 10^4	Pressure psia	Data* °F	PROSIM °F	CSMHYD °F
1.620	300	20.0	20.5	20.1
0.852	300	8.4	8.1	7.8
0.242	300	-16.5	-14.2	-14.5
0.3578	1000	14.0	11.8	10.3
0.2542	1000	8.4	5.1	3.7
0.0703	1000	-16.5	-18.5	-20.2

*Experimental data from GPA Research Report RR-134 (Daubert, 1992)

Table 2. Comparison of experimental and calculated hydrate formation temperatures.

Gas Composition (Dry)				
Component		**Mole Fraction**		
Water		0.0000		
Nitrogen		0.0591		
Methane		0.7106		
Ethane		0.0469		
Propane		0.0193		
n-Butane		0.0078		
n-Pentane		0.0078		
Carbon Dioxide		0.1485		
		Hydrate Formation Temperature		
MEOH in aq. phase mol fraction	Pressure psia	Data* °F	PROSIM °F	CSMHYD °F
0.0583	2424	60.2	58.3	60.9
0.1208	306	24.9	31.0	28.5
0.1199	2434	49.0	52.4	50.4

*Experimental data from GPA Research Report RR-134 (Daubert, 1992)

COMPARISON OF SELECTED HYDRATE SUPPRESSION METHODS

One of the most common means of controlling hydrate formation is by injecting an inhibitor, such as methanol or glycol, to decrease hydrate stability conditions in a gas stream (Sloan, 1991). Regenerated systems using ethylene glycol and non-regenerated systems using methanol are perhaps the two most popular methods of inhibition.

Ethylene Glycol Injection

In a glycol injection system, glycol is injected into a gas stream at a point upstream of hydrate prone areas such as high pressure or low temperature regions. The glycol present in the gas stream prevents hydrate forming conditions by absorbing the free water in the system. The glycol and water mixture may be separated by regeneration, allowing the glycol to be recycled. Ethylene glycol is generally preferred to DEG or TEG for this type of operation due to its low solubility in hydrocarbons. EG also possesses a low viscosity and is more effective on a weight basis for hydrate inhibition (Kohl, 1985).

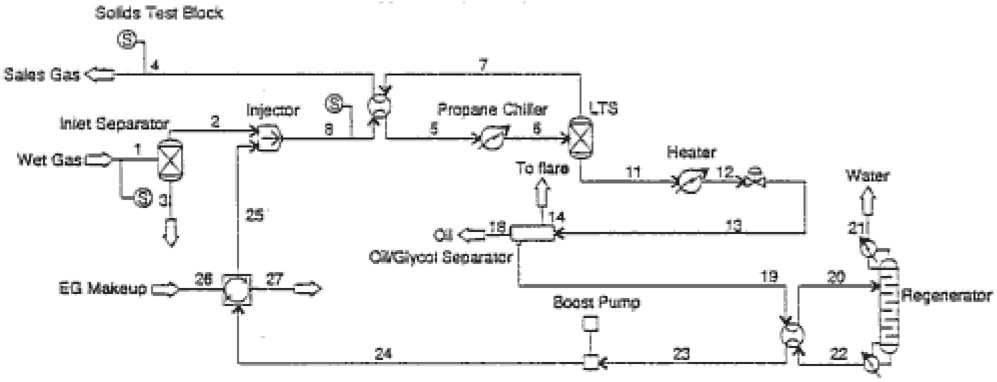


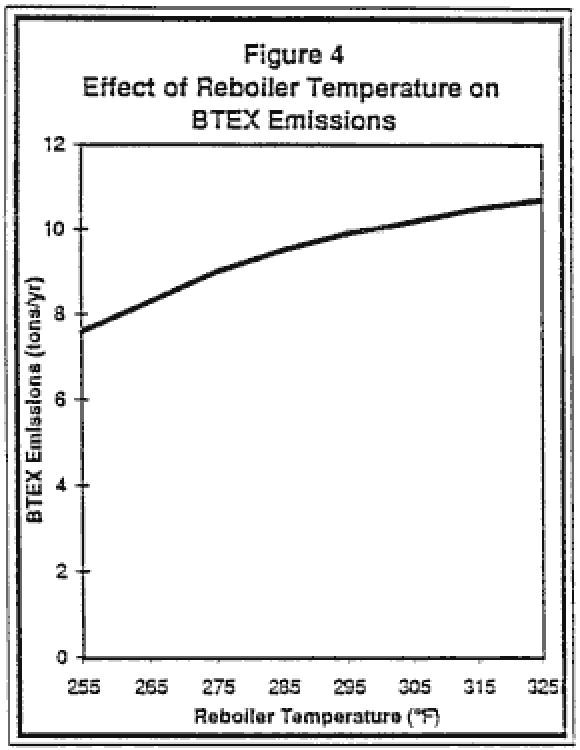
Figure 2. Typical glycol injection unit.

A common environmental concern with operating glycol units is the rate of harmful emissions from the glycol regenerator. In many cases, the inlet feed to the glycol unit contains small quantities of aromatic hydrocarbons that are quite soluble in the glycol. The aromatics are primarily composed of benzene, toluene, ethylbenzene, or xylenes (BTEX). These aromatics travel to the regenerator where the application of heat removes virtually all volatile gases. Since the regenerator is usually vented to the atmosphere, the plant may have a serious environmental impact. Even in small plants, the total aromatic emissions can easily exceed 18 tons per year (Hernandez-Valencia, 1991).

To determine the effect of process variables on the BTEX emissions from the regenerator, the glycol injection unit shown in Fig. 2 was modeled using PROSIM. The inlet gas temperature, pressure, and composition are listed in Table 3. In the first scenario, the reboiler temperature was increased while holding the EG recycle flow rate constant. This results in a composition ranging from 80-96 weight % ethylene glycol. As shown in Fig. 4, the BTEX emissions increased as the reboiler temperature increased. In the second scenario, the EG recycle flow rate was increased while the solids formation temperature was held constant by manipulating the reboiler temperature over a 10^{o} temperature range. As the ethylene glycol recycle flow rate increases, the BTEX emissions also increase. The results of this case are illustrated in Fig. 5.

Table 3. Base inlet conditions used in the BTEX analysis and the process comparison.

Parameter		**Value**
Inlet gas temperature (^{o}F)		110
Inlet gas pressure (psia)		1000
Flow rate (MMSCFD)		25
Inlet gas composition (mol %)	**BTEX Analysis**	**Case 1/Case 2 Comparison**
Water	0.1659	0.1622
Methane	83.73	85.91
Ethane	5.897	6.050
Propane	3.299	3.385
i-Butane	0.817	0.8386
n-Butane	1.323	1.358

n-Pentane	2.238	2.296	 Figure 4 Effect of Reboiler Temperature on BTEX Emissions
Benzene	0.973	0.000	
Toluene	0.487	0.000	
Ethylbenzene	0.487	0.000	
o-Xylene	0.243	0.000	
p-Xylene	0.243	0.000	
m-Xylene	0.097	0.000	

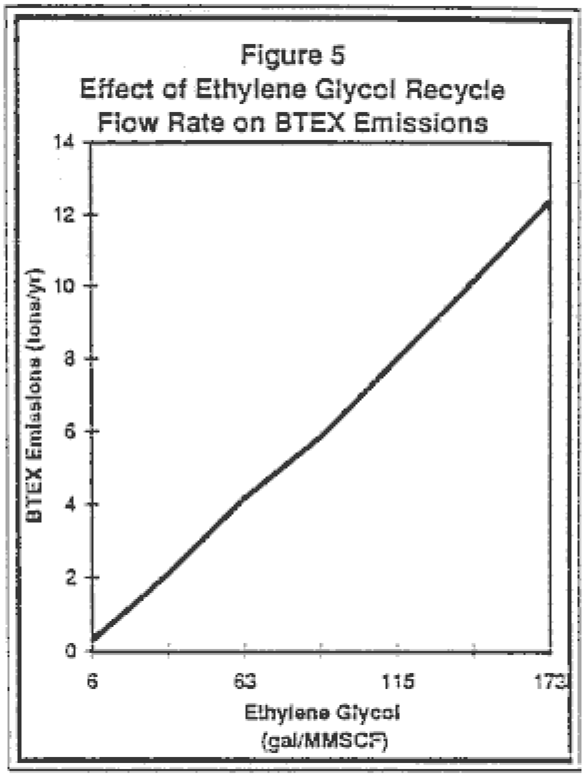


Figure 5
Effect of Ethylene Glycol Recycle Flow Rate on BTEX Emissions

Methanol Injection

Methanol is also used to control hydrate formation. The methanol injection process is sufficiently similar to the glycol injection process previously discussed (Kohl, 1985). Unlike the glycol process, methanol is typically not regenerated in gas processing systems. Therefore, BTEX emissions are not a consideration in the non-regenerated methanol system.

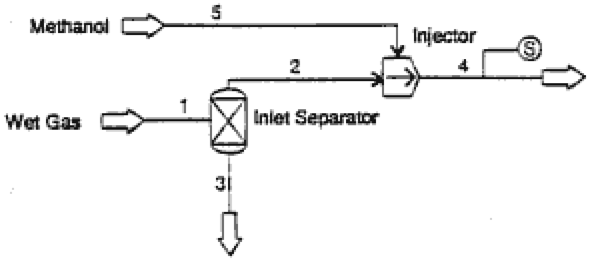


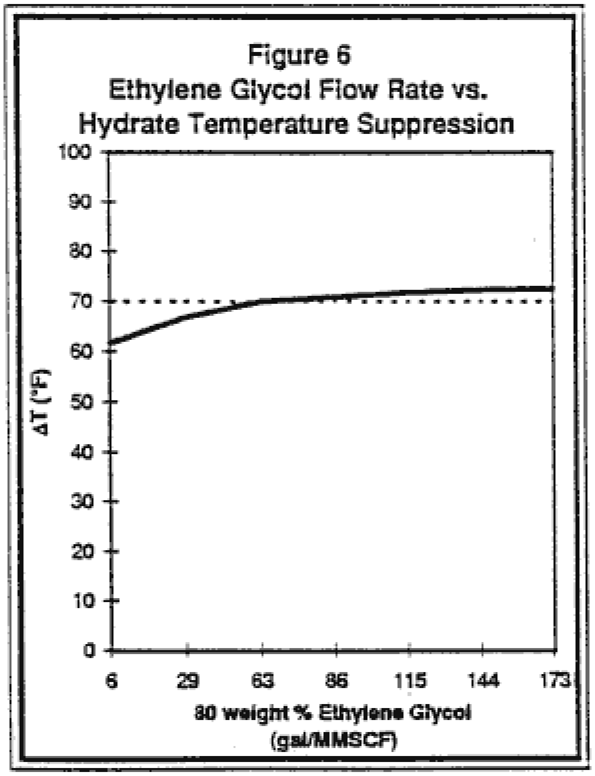
Figure 3. Typical methanol injection unit.

Process Comparison

To compare the two injection processes, an ethylene glycol unit and a methanol unit were modeled using PROSIM. The process flow diagrams of the glycol and methanol systems are shown in Fig. 2 and Fig. 3, respectively. The inlet compositions for each of the two cases are listed in the last column of Table 3.

Case 1. Regenerated Ethylene Glycol Injection System.

In the regenerated ethylene glycol injection system shown in Fig. 2, the solids formation temperature of stream 4 was determined using a solids test block. Ethylene glycol was injected into the system at various flow rates in order to lower the hydrate formation temperature. The composition of the recycled EG was maintained at 80 weight percent. As shown in Fig. 6, a desired temperature depression of 70°F was achieved at an EG flow rate of 1.2 gallons per minute (70 gal/MMSCF). The 70° depression is the difference in the hydrate formation temperature of stream 1 and stream 4.



Case 2. Non-regenerated Methanol Injection System.

A gas stream identical to the inlet stream in the previous case was fed to the methanol injection system shown in

Fig. 3. Methanol (95 weight %) was supplied to the system at various flow rates in order to achieve a given temperature suppression of 70^{o}F. The solids formation temperature was recorded in the solids test block attached to stream 4. As shown in Fig. 7, the desired temperature suppression was achieved at a methanol flow rate of 0.45 gallons per minute (25 gal/MMSCF).

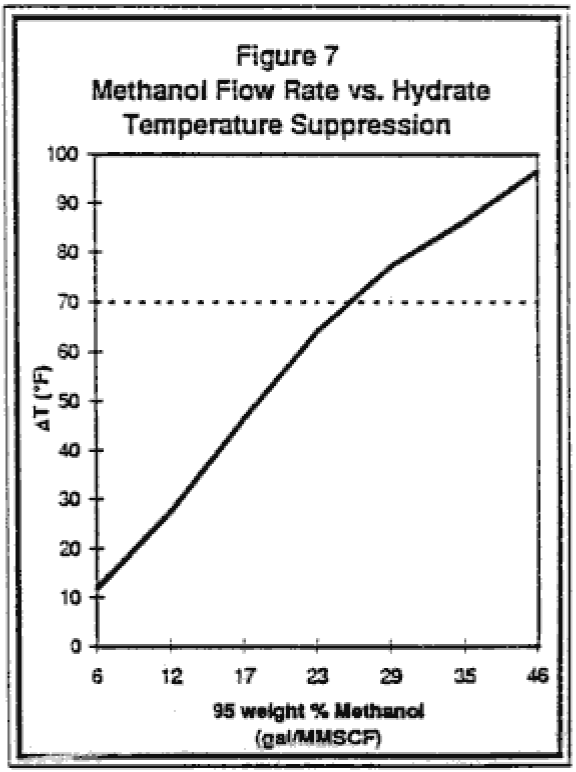


Figure 7
Methanol Flow Rate vs. Hydrate Temperature Suppression

Economic Discussion

To thoroughly compare the two cases previously discussed, the economics of the process must be considered. Although methanol is approximately three times less expensive than EG (Chemical Market Reporter, 1996), one must pay particular attention to the amount of methanol necessary to treat the inlet gas. With increasing gas flow rates, the EG injection process typically becomes a more viable option because the inhibitor is regenerated. The increased cost of utilizing methanol injection to treat larger gas volumes can be directly associated to the raw material make-up cost.

CONCLUSION

When selecting a method to suppress hydrate formation, a number of alternatives should be considered. If a solid desiccant or glycol dehydration unit cannot achieve a desired dew point or is not cost effective, an injection unit is often a more suitable option. Both regenerated and non-regenerated injection systems are common methods of hydrate inhibition. To determine the system that is most appropriate for a required temperature suppression, a thorough investigation of each alternative should be conducted.

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