



## TWELVE YEARS OF LABORATORY AND FIELD EXPERIENCE FOR POLYETHER POLYAMINE GAS HYDRATE INHIBITORS

**Marek Pakulski\* and Steve Szymczak**  
**BJ Chemical Services**  
**11211 FM 2920 W, Tomball, Texas, 77375**  
**USA**

### ABSTRACT

The chemical structure of polyether amines (PEA), mainly electron donating multiple oxygen and nitrogen atoms as well as active hydrogen atoms, make such compounds actively participating in the formation of hydrogen bonds with surrounding molecules. Hydrophobic polypropylene glycol functionality gives PEA's properties of multi-headed surfactants having hydrophilic amine groups. These groups have a strong affinity for water molecules, ice and hydrate crystals. Such PEA compounds have been known for several years. However, the hydrate inhibition properties of PEA's were only discovered about twelve years ago. The first discovery stimulated more research in laboratories and led to practical applications for hydrate inhibition in gas fields. An interesting property of PEAs is their synergistic effect on hydrate inhibition when applied concurrently with polymeric kinetic hydrate inhibitors (KHI) or thermodynamic inhibitors (THI). The combination inhibitors are better inhibitors than a single component one. Quaternized polyether diamines are efficient antiagglomerant (AA) hydrate inhibitors while different derivatization can produce dual functionality compounds, i.e. corrosion inhibitors/gas hydrate inhibitors (CI/GHI). With all of this versatility, PEAs found application for hydrate inhibition in oil and gas fields onshore and offshore in production, flowlines and completion. The PEAs have an excellent record in protecting gas-producing wells from plugging with hydrates.

*Keywords:* gas hydrates, kinetic inhibitors, polyether amine, hybrid hydrate inhibitor

### NOMENCLATURE

AA	Antiagglomerant
BHA	Bottom Hole Assembly
CI	Corrosion Inhibitor
GHI	Gas Hydrate Inhibitor
HHI	Hybrid Hydrate Inhibitor
J-T	Joule-Thomson cooling effect upon gas expansion
KHI, KI	Kinetic Hydrate Inhibitor
LDHI	Low Dosage Hydrate Inhibitor
MPa	Megapascal Pressure Unit
PEA	Polyether Amine
p/T	Pressure and Temperature conditions
S(I)	Small Cage Hydrates, C1, C2
S(II)	Small and Larger Hydrates C1-C5
THF	Tetrahydrofuran

THI	Thermodynamic Hydrate Inhibitor
$\Delta T$	Hydrate Subcooling Temperature

### INTRODUCTION

Gas hydrates form when water molecules crystallize around guests molecules. The water/guest crystallization process has been recognized since its discovery by Sir Humphrey Davy in 1810, is well characterized and occurs with sufficient combination of pressure and temperature [1]. Light hydrocarbons, methane-to-heptanes, nitrogen, carbon dioxide and hydrogen sulfide are the guest molecules of interest to the natural gas industry. Depending on the pressure and gas composition, gas hydrates may build up at

\* Corresponding author: Phone: 281-357-2708 Fax 281-357-2701 E-mail: mpakulski@bjservices.com

any place where water coexists with natural gas at temperatures as high as 30°C (~85°F).

Hydrates formation in oil and gas operations is a growing problem as producers drill in arctic regions and deeper, cooler waters offshore. Hydrates can form in the wellbore as the fluids go through pressure and temperature change resulting in J-T cooling. They also form in the flow lines between wellheads and separation facility.

Hydrates create physical barriers to production and must be inhibited or if formed, dissolved, in order for gas production to occur. The operator must maintain the well and a production line free of hydrates all of the time. Formation of gas hydrates can be eliminated or hindered by several methods. Thermodynamic prevention methods control or eliminate elements necessary for hydrate formation: the presence of hydrate forming guest molecules, the presence of water, high pressure and low temperature. The elimination of any one of these four factors from a system would preclude the formation of hydrates. Unfortunately, elimination of these hydrate elements is often impractical or even impossible. Transmission lines heating and insulating is a common mechanical solution to hydrate problems encountered in long subsea pipelines. Hydrates will never form if the gas/water system is kept above the hydrate formation temperature. Gas dehydration is another method of removing a hydrate component. However, in a practical field operation, water can be economically removed to a certain vapor pressure only and residual water vapors are always present in a dry gas. Hydrate plugs in "dry" gas lines have been reported [2].

There are several approaches to hydrates prevention, dissolution and inhibition. For example Hale, *et al* [3] patented a method of preventing hydrates formation in gas wells with the addition of polycyclicpolyether polyols. The addition of chemicals to the gas/water streams is the most common method of preventing hydrate formation. Large amounts of alcohols, glycols or salts are being utilized. These additives thermodynamically destabilize hydrates and effectively lower the temperature of hydrate formation. However, hydrate prevention with methanol or glycol can be quite expensive due to the high effective dosages required, 20% to 50% of the water phase. Ethylene glycol is usually recovered downstream and recycled while methanol is not usually recovered and poses an environmental problem. Large concentrations of

solvents aggravate potential scale problems by lowering the solubility of scaling salts in water and precipitating most known scale inhibitors [4]. Replacing some of the high methanol volume required for treatment with non-thermodynamic inhibitors offers a significant cost reduction to gas companies and pipeline operators.

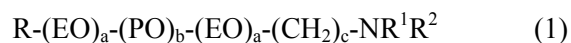
Work on new KHI and AA has progressed in many research laboratories to the point of successful field tests and onshore and offshore commercial applications [5-8].

## LABORATORY EXPERIMENTS

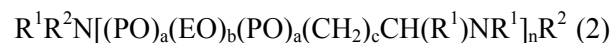
### Early Discovery.

Polyether amines have been known for several years and are commercially available from a few manufacturers. They exist as both, specialty and commodity chemicals. One can distinguish the basic structures of polyether amines as follows:

Alkyl terminated polyether monoamines.



Linear amine terminated polyether diamines and polyamines.



Branched polyether triamines:



where:

$$a+b = 1 \text{ to } >100, c = 1-6$$

R = methyl to octadecyl group,

$R^1, R^2 = H, CH_3, CH_2-CH_2-OH$   
or  $CH(CH_3)-CH_2-OH$

PO and EO are inserted propylene oxide or/and ethylene oxide moieties

A = trimethylolpropane or glycerin.

A common property of all these compounds is their ability to form multiple hydrogen bonds through oxygen, nitrogen and active hydrogen atoms. Thus, they can associate with several molecules of water to attach themselves to ice and hydrate crystals. This feature gained attention in the early discovery process.

Initial work on PEA hydrate inhibition properties started in the early 1990's. The testing equipment available at that time was limited to an ambient pressure, slow flowing 0.3 cm (1/8 inch) diameter, 6 m (20 ft.) long stainless steel loop (Figure 1).

A solution of 20% Tetrahydrofuran (THF) in 3.5% NaCl/water with and without additives was circulated through the simulated pipeline at preset temperatures of -7 to -12°C. The THF/salt water solution simulates gas/water systems without the necessity of running tests at high pressures with highly flammable gas [9]. Typical concentrations of the tested additives were 0.05% to 0.5% active. The volume of fluid inside the loop was 60 ml and allowed a 20-hr fluid residence time inside the loop at a pumping speed of 0.05 ml/min. Test temperatures were selected so that uninhibited fluid would freeze within minutes and inhibited fluid in hours. Build up of a backpressure in the simulated gas pipeline was measured and recorded with time. A 15-micron filter located at the loop intake assured that pressure buildup did not occur from plugging the line with impurities, and that backpressure was caused only by blockage with hydrate crystals being formed in the simulated gas line cooled inside the cold bath. After completion of each test, the loop was warmed up to 60°C (140°F), washed with water and the next test fluid.

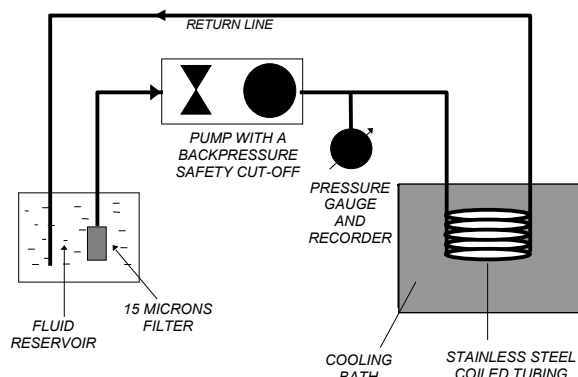


Figure 1. Schematic drawing of simulated gas hydrate testing loop.

The simple test equipment proved to be an efficient tool for pre-screening several PEA compounds along with known kinetic polymeric inhibitors (KHI) and glycols. A library of promising PEAs was developed and used for high pressure testing with natural gas.

#### Development of Hybrid Hydrate Inhibitor.

In typical field applications of PEA we were facing an existing alcohol storage and pumping facility designed for high volume throughput. Using the existing equipment made more sense from the economical point of view than replacing it with smaller pumps and tanks. Instead of replacing

pumps with smaller ones capable to deliver precisely 1% of former methanol or ethylene glycol rate, PEA was put in solvent to use the same pumps at 20-40% output [10]. After analyzing the field work results, it was noticed that some PEA solutions performed better than expected. This observation warranted further look at the THI/KHI synergy phenomenon.

Further experiments were performed in a custom-built 500 ml volume, 25 MPa pressure rated testing cell. Gas pressure, temperature, stirrer speed and torque are controlled and continuously recorded. The equipment was designed to test all types of hydrate inhibitors, THI, KHI and AA. The fluid was stirred at 250 rpm. The high pressure testing was a two step process. First, the cell was loaded with the fluid and gas, and fast cooled to the desired p/T conditions. Sometimes, a minor pressure adjustment was necessary at the end of this step. Second, the fluid was kept at constant temperature to the point of 10% gas to hydrate conversion. The fluid was continuously stirred during both steps or the stirrer could be stopped for a period of time to simulate gas flow stop and restart. After the completion of each test the cell was warmed up to 30°C (86°F) for 5 hours, the old solution was drained and the cell was flushed with a hot ~50°C (~120°F) solution of the next system to be tested, which was also drained. Finally, the fresh test solution was added to the cell, which was pressurized with a test gas and the cooling was activated. This cell loading procedure sufficiently protects the experiments integrity by removing any hydrate residues from the previous test; thus, eliminating a water "memory" effect that causes accelerated hydrate formation in water/gas systems going through hydrates/warm up cycles [11].

Based on testing experience, 5% gas to hydrate conversion was established as an inhibitor failing point. While this sounds somehow arbitrary, it came from observations of several hundreds of experiments showing no increase in torque requirement of the mechanical stirrer to maintain a constant speed up to 5% gas intake. A small amount of hydrates is dispersed within the fluid and causes no viscosity increase or flow obstructions.

Each test was performed using 200 ml of hydrate inhibitor water solution and 20 ml of condensate. A well established laboratory benchmark, "Green Canyon" gas mixture was used for testing (SII hydrate). Gas and condensate compositions are

provided in Table 1. Schematic drawing of the equipment is depicted in Figure 2.

Component	Green Canyon	Component	Condensate
Helium	-	C-5	8.15
Nitrogen	0.4	C-6	16.8
Methane	87.2	C-7	30.77
Ethane	7.6	C-8	17.11
Propane	3.1	C-9	10.09
i-Butane	0.5	C-10	5.68
n-Butane	0.8	C-11	4.08
i-Pentane	0.2	C-12	3.18
n-Pentane	0.2	C-13	2.22
		C-14	1.25
		C-15	0.70
		C-16	0.20
		C-17+	0.49

Table 1. Green Canyon gas and condensate mole % composition.

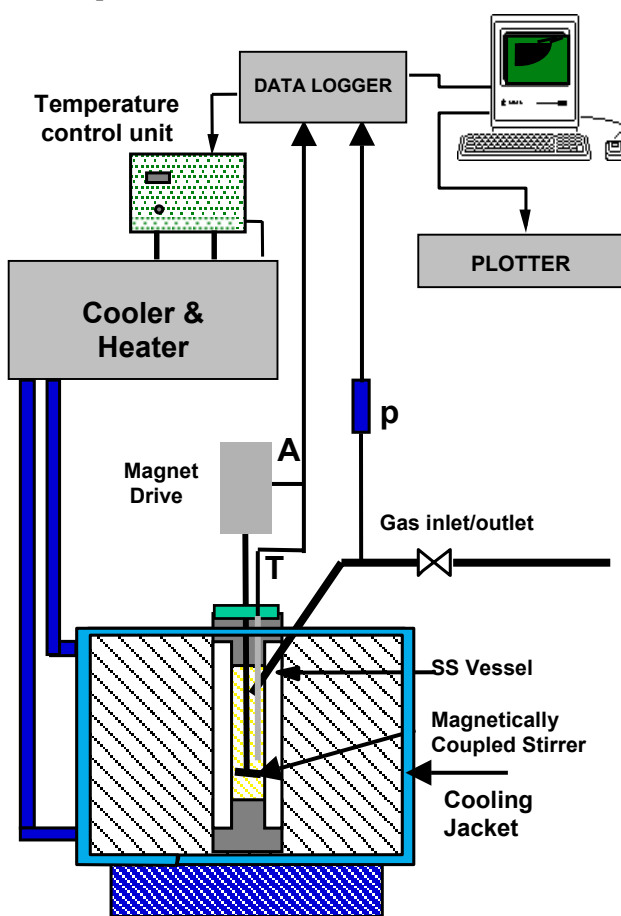


Figure 2. Schematic drawing of the pressure vessel for hydrates testing. A - stirrer speed regulator and current sensor, T - temperature sensor, p - pressure sensor

Figure 3 presents examples of hydrate formation rates in various mixtures of PEA and methanol in water. The mixtures were prepared starting with 5% MeOH and 0% PEA, and subsequently replacing each percent of MeOH with 0.135% of PEA, i.e. 3.5% MeOH, 0.2% PEA or 1.25% MeOH, 0.5% PEA...etc. The PEA:MeOH ratio was in the 0 to 30 range. The rationality behind such mixture formulations was to produce equal cost products. The cost of methanol is about 14% of PEA price. The system undertreated with methanol will not produce any hydrates for some number of hours but converts gas to hydrates very rapidly at a certain time. With larger proportions of PEA in the mixture, the slope of curves representing gas to hydrate conversion with time decrease.

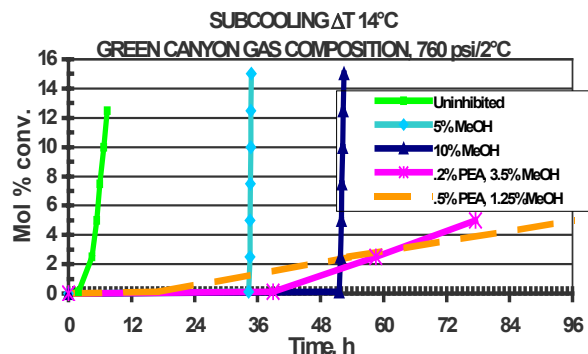


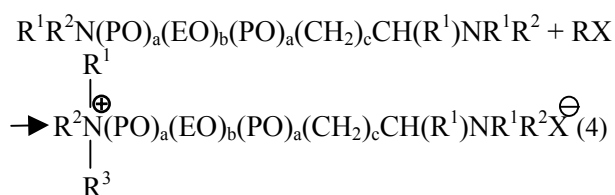
Figure 3. Hydrate formation rates with various inhibitors

The hydrate forming process sometimes starts earlier; however, it is very slow. The results illustrated in Figure 3 where, in the laboratory test, the combination of 0.2% PEA and 3.5% MeOH started producing hydrate after 39 hours at hydrate conditions. The formula containing 0.5% PEA and 1.25% MeOH or 5% MeOH with no PEA showed first signs of hydrate at 17 hours and 34 hours respectively. Notice, that if one uses 5% gas to hydrate conversion as inhibitor end of life, both PEA/MeOH combinations are superior to 10% MeOH. The addition of 5% or 10% methanol significantly shifts the hydrate equilibrium curve toward lower temperatures. The solvent addition lowers  $\Delta T$  value by 2°C (3.6°F) for 5% and 5°C (9°F) for 10%; however, at given p/T conditions the system remains at hydrate conditions. Consequently, both solutions made hydrates and in both cases once the process started, its progress was catastrophic. The conversion curves are almost vertical for MeOH being the only additive

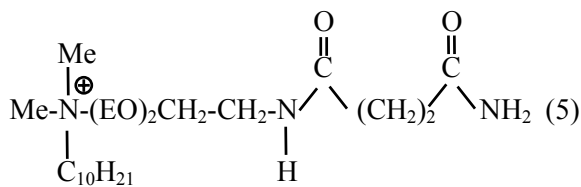
while hydrate forms slowly in the presence of the PEA/MeOH mixtures. Practical consequences of such "slow to fail" behavior is that in the field application, operators have more time to react if hydrates form slowly versus an instant plugging wells and lines if the hydrate forming process is fast. Complete data indicate there is a performance peak at a certain PEA/MeOH ratio range and a commercial Hybrid Hydrate Inhibitor (HHI) was formulated to maximize benefits of the best THI/KHI combination. The inhibitor is being applied worldwide to treat S(II) hydrates. Its effectiveness is particularly visible in gas producing wells and flowlines subject to temperatures below freezing in cold environment or due to J-T cooling effect.

### PEAs derivatization.

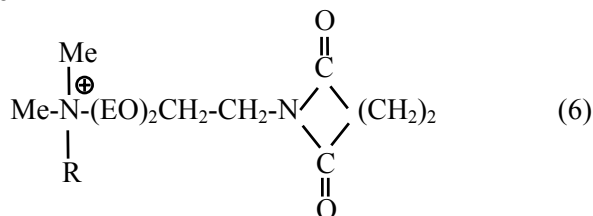
It has been documented and described in literature that by reacting PEA with alkyl halides one creates hydrate antiagglomerant (AA) [12] *i.e.* structure (2) n=1 reacts to form a quaternary compound (4).



Dahlmann *et al.* [13] patented several structures of derivatized PEA being water soluble corrosion and gas hydrate inhibitors:



or



R = C<sub>1</sub> - C<sub>22</sub>

Structures (5) and (6) are examples of derivatized triethylene glycol diamine. Inventors claim these products are more biodegradable than classic quaternary corrosion and hydrate inhibitors.

### Additional PEA properties making them more attractive hydrate inhibitors.

Tubular and equipment iron corrosion is a well recognized problem in oilfield operations. Corrosion inhibitors (CI) are usually continuously injected to every part of upstream or downstream flow lines and corrosion mitigation costs make significant part of production chemical expenses. Chemical structure of PEAs indicates they must scavenge oxygen and be capable to adhere to metal surfaces. A systematic work on PEAs anticorrosion properties was published a few years ago. Hope *et al.* [14] reported results showing that underivatized PEAs are superior CI in sour systems. They also counteract the corrosiveness of methanol (Table 2). The economy of a producing field can be improved if PEA can be LDHI/CI in one molecule and replace some or all of the commercial CI.

Exp. Number	Composition	Corrosion mm/year	Pitting mm/year
1	DI Water only	0.442	0
2	66% MeOH	0.324	11.7
3	66% MeOH, 0.25% CI-C*	0.091	2
4	40% MeOH, + PEA	0.193	0
5	40% MeOH, 0.25% CI-C* + PEA	0.208	0
6	10% MeOH, + PEA	0.21	0
7	10% MeOH, 0.25% CI-C* + PEA	0.191	0

Table 2. Corrosion rates of steel in sour solutions at various conditions. \*CI-C – commercial CI

More enhancing properties are listed below:

- Being low freezing liquids they never build solid residues in pipes and equipment in potential hot spots and don't require solvent carrier.
- Soluble in water or organic solvents including aliphatic hydrocarbons. Can be delivered in anhydrous solvent and then they partition into water phase. Solutions in glycols or heavier hydrocarbon solvents are safety qualified non-flammable.
- Unlike polymeric KHI, PEAs dissolve hydrates.
- Low toxicity, biodegradable

## **FIELD EXPERIENCE**

As mentioned above gas hydrates in the production and transmission of oil and gas represent a significant operational issue for the producing and transporting companies. In order to properly address and solve the problems related to hydrate formation the operator must know the cause in terms of the field conditions and find a cost-effective solution. Although it is possible to successfully address hydrate issues through mechanical and thermal means, it is typically not a cost-effective measure. For that reason the industry has moved towards addressing hydrate problems through two approaches, mechanical and chemical.

### **Mechanical Means to Control Hydrates.**

The first approach is design. In the gas production scenario the design element will focus on water elimination and temperature retention. On their own merits these design considerations typically will not take care of the problem alone. An example of a design approach might be pipe-in-pipe sub-sea flow lines whereby a transmission line is placed inside of an insulating line. The annular space between the pipes can be filled with an insulating material in order to retard the loss of heat to the cooler external environment. Another design approach is to fill the annular space in a producing well with an insulating fluid [15]. In both of these approaches the intent is to provide an insulating barrier between the produced fluid and the external environment.

Water removal in the gas production process is more problematic. In all normal cases the produced water has to be produced up the well with the hydrocarbon. Water removal is practical in the production surface equipment prior to the pipeline. Surface equipment specifically designed to separate and remove water is commonly employed in the process. For land production this separation facility would be placed in a central location where all well production commingled. In an offshore environment the separation equipment is placed on the hub platform. Bear in mind that dehydrated gas, i.e. gas from which the free water has been removed, still has water. Thus it is not uncommon to see hydrates form down stream of the water separation plant. This is commonly caused by a localized J-T effect.

Once the design measures are in place it is typically necessary to supplement the hydrate inhibition process through the addition of hydrate

inhibitors. As discussed above these range from the THI to the KHI and AA. The experiences with selecting and administering the proper PEA inhibition chemistry will be the focus of the remainder of this discussion on field experience.

### **Selection and Application of PEA Inhibitors.**

Further in this discussion the topics will split into cold weather environments, e.g. Canada, and offshore environments, e.g. Gulf of Mexico. In this section the discussion will focus on the selection and application criteria that are in common with both production areas.

In all applications it is necessary to gain an understanding of the water, gas, temperature and pressure conditions for a particular system. Bear in mind that in all of the discussed applications the operator was using a THI (usually methanol) or an LDHI (KHI or AA). There were no cases where the initial application used the PEA. In the majority of cases the operator was using methanol. There are software programs available that will predict the methanol requirement for inhibition based on the various inputs. In most cases the starting feed rate of the PEA product was applied based on the methanol rate. Various PEA products were used. Some were a blend of THI and PEA and some were only PEA. As discussed above significant lab testing was also carried out to predict the sub-cooling of the PEA products versus the standard (usually methanol). This testing was necessary to confirm the range of PEA sub-cooling. However, in all cases the actual application had a precedent of inhibitor treatment. Once the system is understood and the modeling confirms the applicability of the PEA product it is time to initiate the field trial. The field trial is the most visible step in the process by which the PEA chemistry replaces the incumbent product. That visibility is based on the reality that a failure in the field has significant financial and operational consequences.

### **The Field Trial.**

The field trial has several distinct steps. It is necessary to conduct the trial in a planned and deliberative manner. The goal of the field trial is the successful application of the product with the desired result of inhibiting hydrate formation. Because the record of the field trial will serve as the primary product record it is imperative to make changes one at a time. More valuable application information has been lost due to simultaneous,

multi-variable changes than to any other reason. Following are the prescribed steps for conducting a meaningful field trial:

1. Establish the current system by collecting relevant data prior to the introduction of the new product. The operator and the chemical field personnel will determine the time necessary to establish the benchmark and the relevant data.
2. Introduce the new chemical at a sufficiently high feed rate so as to not starve the system for inhibitor. During the transition from original chemical to the new chemical it is best to err in favor of high dosage.
3. Calculate the time necessary to displace the original product from the system. This time includes displacement of the fill line and dilution of the product from the separation equipment. A common rule of thumb is to use twice the calculated time. For example, if it takes one day to displace the original chemical from the fill line then run the new chemical for two days to insure that the performance data reflects the new product only.
4. Start to reduce the feed rate in definite increments in order to reach the desired feed rate. This must be done in a fashion similar to the original product turnover process. If the feed rate reductions are made too quickly then it is impossible to determine the critical rate. If it took two days to see the results of the new product, then it would not be unreasonable to take one day to see the results of a feed rate reduction.
5. Upon seeing a negative response to a feed rate change it is necessary to increase the rate above the last performing rate. This is done because a low rate will starve the system and jeopardize the operation. Hence, once the lowest rate has been determined it is necessary to raise the rate higher, gain control of the system and then begin to lower the rates again.
6. Once the system stabilizes begin returning to the lowest rate at which the system ran smoothly.
7. Observe the system at this new rate. If it maintains performance then this is the new rate for the PEA. Compare the empirical data with the theoretical data in order to create a best fit curve for that particular application.

It is obvious from the steps of the field trial why single variable changes are important. Often is the

case where an operational problem coincided with a series of simultaneous independent changes. In this case it is impossible to point to the cause and the process must return to a prior condition for which the system was stable.

#### **Case Histories - Canada.**

Following are relevant case histories on the application of the PEA chemistry in a cold region. These break down in to four types of applications. These are downhole, well head, pipeline and underground gas storage.

*Downhole.* Hydrates that form in the production tubing must be attacked below the point of formation. In order to do that the chemical must be applied in the well bore. This is problematic and costly for wells that were not completed with the appropriate chemical delivery system in place. An economical approach to delivering hydrate inhibitor below the point of hydrate formation is the use of capillary tubing. This tubing, typically 0.25 or 0.375 inch OD is inserted through the top of the well and hung off above the perforations and below the hydrate formation point as a permanent installation. The chemical is fed through the line and is controlled by a Bottom Hole Assembly (BHA) that includes a one way check valve.

*Wellhead.* Commonly hydrates will form at the wellhead as a result of a pressure change and the resulting Joule-Thomson cooling. To remedy this problem the PEA inhibitor is fed upstream of the pressure drop in order to have the inhibitor in contact with the fluids before the drop.

*Pipeline.* In cold weather regions hydrate formation in surface transmission pipelines is a common occurrence. The traditional approach has been to feed methanol to provide thermodynamic inhibition. As reported by Budd, *et al.* [10] the blended THI/PEA product provided superior performance when compared to methanol. In a current application in Canada the operator was faced with a situation whereby a thermodynamic quantity of methanol could not be delivered to the pipeline due to volume restrictions. In this case the operator constantly fought freezing problems and had to install line heaters at critical locations to complement the methanol. The THI/PEA product was applied and the hydrate problems dissipated. After monitoring the system for a

period of time the operator turned off the line heaters. Here is a case where the methanol was not acting in the thermodynamic range and was therefore ineffective. The THI/PEA product required less volume than the methanol and could be applied in a quantity sufficient to provide inhibition.

*Gas Storage.* Gas usage is cyclical, but gas production is constant. In order to store gas in the low usage periods, i.e. warmer months, operators pump natural gas into storage caverns. During the cold months the gas is produced and sold to the market. During storage it is common for the water content of the gas to increase. During subsequent withdrawal of the gas from the caverns the increased water leads to hydrate formation problems. An application of the PEA chemistry upstream of the initial pressure drop mitigates hydrate formation.

#### **Case Histories – Gulf of Mexico.**

Following are relevant case histories on the application of the PEA chemistry in an offshore environment. These break down in to four types of applications. These are downhole, well head, flow line and pipeline.

*Downhole.* The difference between a downhole treatment offshore and one on land has to do with the type of well completion. Whereas a land well can receive a capillary line that runs internal to the production tubing an offshore well has a surface controlled sub-surface safety valve that precludes any insertion of a capillary line. Thus operators install capillary lines in the annular space between the tubing and the casing and run the line below the hydrate zone and then enter the production tubing through a specialty entry port. In the event that the well was not constructed with a chemical line below the hydrate zone or if that line is damaged the operator must consider a workover. In a recent application on a deep water facility in the Gulf of Mexico the operator produced from a well that had a chemical supply line placed below the hydrate producing zone in the well. The operator fed methanol into the well to control hydrates. Because of the high volume of methanol, the increasing cost of methanol and the logistical cost of transporting methanol to the platform the operator looked for a cost-effective alternative.

A THI/PEA hydrate inhibitor was formulated and fed to this well. Initial results indicated the well performed with the new inhibitor. Subsequent to the establishment of a satisfactory feed rate the well experienced a hydrate upset. The THI/PEA product was replaced with methanol. The methanol could not control the hydrate formation at the previous rate. The operator determined that critical production changes occurred. Currently the operator is preparing to put the THI/PEA product back on the well at a higher rate to see if it can control the hydrates better than the methanol.

*Wellhead.* The most common application of the PEA chemistry in the Gulf of Mexico is for the control of hydrates in fuel gas systems. A portion of the gas that is produced onto a platform is used as a fuel source to run platform equipment, e.g. gas compressors and turbines that generate electricity. This fuel gas goes through a separation process in which hydrates form under Joule-Thomson conditions. The utilization of a PEA hydrate inhibitor for these applications controls hydrate formation and allows smooth operation of the platform.

*Flow lines.* Szymczak, *et al.* [16] reported on the use of a THI/PEA inhibitor in the Gulf of Mexico to control hydrate formation in a subsea flow line. In that case hydrates formed in the flow line between the producing well and the platform. Although this was shelf production (deep water is defined as 1,000 feet of water depth or more) the sea temperature combined with the producing pressure was sufficient to create hydrates. Methanol was the standard treatment. Due to the cost of methanol transport and the intermittent hydrate problems that occurred because the methanol rate was on the edge of thermodynamic inhibition, the operator switched to the THI/PEA product. As a result of the change the flow pressure stabilized and the hydrate problems disappeared.

*Pipeline.* A flow line is different from a pipeline in that the flow line transports gas from the well to the platform. At that stage the gas still belongs to the operator. A transmission pipeline is a trunk line that takes gas from a variety of producing platforms. Pipeline applications of hydrate inhibitor are the most critical application. Gulf of Mexico gas pipelines carry millions standard cubic feet of gas per day. A hydrate plug carries a high



financial consequence. A THI/PEA product is fed into a pipeline. This is a winter time application only.

#### CONCLUSIONS

Polyether amines made slow nevertheless steady advance from the laboratory to single field application to several hundred applications around the world. Applied in combination with solvent they fill a niche between inexpensive high usage volume of alcohols and extremely expensive; however, low usage volume polymeric KHI.

Hydrate inhibition with PEA is a proven technology.

#### ACKNOWLEDGEMENTS

Authors thank the management of BJ Chemical Services for approving the publication of this work and Dr. Mike Brown for helpful review comments.

#### REFERENCES

- [1] Katz D.L., *Prediction of Conditions of Hydrate Formation in Natural Gases*. Trans. AIME, 160:140.
- [2] Kashou S.F., Subramanian S., Matthews P., Subik D., Qualls D., Akey R., Carter J., Thummel L., Fauchaux E., *Gulf of Mexico Export Gas Pipeline - Hydrate Plug Detection and Removal*, OTC 16691, presented at the Offshore Technology Conference in Houston, Texas, May 3 - 6, 2004.
- [3] Hale A.H., Dewan A.K.R., Blytas G.C. *Gas Hydrate Inhibition*, US Patent 5076364.
- [4] a) Kan A.T., Fu G., Tomson M.B., *Effect of methanol on carbonate equilibrium and calcite solubility in a gas/methanol/water/salt mixed system*; Langmuir 2002, 18, 9713-9725; b) Kan A.T., Fu G., Tomson M.B., *Effect of methanol and ethylene glycol on sulfates and halite scale formation*; Ind. Eng. Chem. Res. 2003, 42, 2399-2408; c) Tomson M.B., Kan A.T., Fu, G. *Inhibition of Barite Scale in the Presence of Hydrate Inhibitors*, SPE 87437, Presented at the 6<sup>th</sup> International Symposium on Oilfield Scale, Aberdeen, UK, May 26-27, 2004.
- [5] Argo C.B., Blain R.A., Osborne C.G., Priestley I.D., *Commercial Deployment of Low Dosage Hydrate Inhibitors in a Southern North Sea 69 Kilometer Wet-Gas Subsea Pipeline*, SPE 37255, Presented at the SPE International Symposium on Oilfield Chemistry in Houston, Texas, February 18-21, 1997.
- [6] Fu S.B., Cenegy L.M., Neft C.S., *A Summary of Successful Field Applications of a Kinetic*

*Hydrate Inhibitor*, SPE 65022, Presented at the SPE International Symposium on Oilfield Chemistry in Houston, Texas, February 13-16, 2001.

[7] Frostman L.M., Przybylinski J.L.: *Successful Applications of Anti-agglomerant Hydrate Inhibitors*, SPE 65007, Presented at the SPE International Symposium on Oilfield Chemistry in Houston, Texas, February 13-16, 2001.

[8] Pakulski M., Prukop G., Mitchell C., *Field Testing and Commercial Application of High Efficiency Non-Polymeric Gas Hydrate Inhibitor in Offshore Platforms*, SPE 49210, Presented at SPE Annual Technical Conference in New Orleans, Louisiana, September 27-30, 1998.

[9] Couch S.R., Davidson D.W, Can. J. Chem, 49, 2691, (1971).

[10] Budd D., Hurd D., Pakulski M., Schaffer T.D., *Enhanced Hydrate Inhibition in Alberta Gas Field*, SPE 90422, Presented at the SPE Annual Technical Conference in Houston, Texas, September 26-29, 2004.

[11] Miyazaki K., Yasuoka K., *Molecular Dynamics Simulation of Dissociation and Formation Process for Methane Hydrate*, Presented at the Fourth International Conference on Gas Hydrates, Yokohama, May 19-23, 2002.

[12] Pakulski M., *Quaternized Polyether Amines As Gas Hydrate Inhibitors*, US Patent 6025302.

[13] Dahlmann U., Feustel M., *Additives for Inhibiting Gas Hydrate Formation*, US Patent 7214814, *Corrosion and Gas Hydrate Inhibitors Having Improved Water Solubility and Increased Biodegradability*, US Patents 7253138, 7323609, 7341617.

[14] Hoppe R., Martin R., Pakulski M., Schaffer T., *Corrosion Mitigation with Gas Hydrate Inhibitors*, SPE 100474, Presented at the SPE Gas Technology Symposium in Calgary, Alberta, Canada, May 15-17 2006.

[15] Wang X., Javora P., Qu Q., Percy R., *A New Thermal Insulating Fluid and Its Application in Deepwater Riser Insulation in the Gulf of Mexico*, SPE 84422, SPE Production and Facilities 2005;20(1):35-40.

[16] Szymczak S., Sanders K., Pakulski M., Higgins T., *Chemical Compromise: A Thermodynamic and Low Dose Hydrate Inhibitor Solution for Hydrate Control in the Gulf of Mexico*, SPE 96418, SPE Projects Facilities and Construction 2006;21(6):1-5.