LOW DOSAGE HYDRATE INHIBITORS

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Abstract

Evidence suggests that oil and gas industry has always been one of the fundamental business sectors in Russian and World's economy. These days a huge oil and gas complex has been built throughout the globe. To achieve that there have been developed a large number of technologies for such processes as drilling, engineering, exploitation of oil and gas production facilities, water, oil and gas fluids processing and transportation. One of the aims of this article is to explain by giving an example of gas hydrate formation, which is the major object of attention of this paper, that even in such advanced infrastructure any petty problem can cause calamitous consequences.

One of the obvious reasons why this article is topical today could be the fact that combination of many additives of natural gas with water leads to gas hydrate formation. What this normally results in is local outbreaks and major accidents. Therefore, the issue of prevention of hydrate precipitation at minimum operating costs is of paramount importance today. In order to overcome this difficulty, various approaches have been developed.

Observing the most significant methods of the crystallization and agglomeration of hydrate particles prevention, our research group emphasized decompression, gas heating in places of hydrate deposition and injection of hydrate inhibitors. It is fair to claim that these methods have a few negative aspects and companies should take into account a spectrum of shortcomings to choose ways to tackle them. The technology of pressure suppression is workable on condition that hydrate plug is eliminated. High explosibility of natural gas is dangerous for heating. The injection of hydrate inhibitors is not always payable due to cost of reagents and toxicity of inhibitors themselves [1].

Another matter which causes unease is search for the most effective method of gas hydration control. It is regrettable that all used methods are based on energy ratio of gas-hydrate former and water. According to statistics, inhibitors, the most popular of which is methanol, are widely-spread in Russia. Unquestionably, methanol is a violent poison that causes serious poisoning and even death. Thus, the amount of methanol used in the industry is sure to be reduced. Our research team firmly believe we could go about this in a number of ways, but it was concluded that the most successful one would be to use Low Dosage Hydrate Inhibitors.

Introduction

The formation of hydrates in processing facilities and pipelines has been a nuisance to the natural gas industry for over five decades (Figure 1).

Figure 1. Gas hydrates in pipeline

Many articles have been published on the problem of gas hydrates which 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 [2].

Gas hydrates are crystalline, «ice-like» compounds composed of water and natural gas (Figure 2).

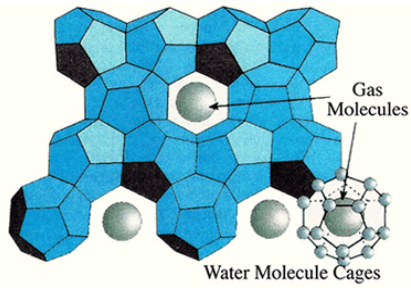

Figure 2. Gas hydrate structure

Two structures of gas hydrates are known to form in light gases: Type I and Type II. 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. The formation of hydrates can be prevented by using any of the following methods.

- Adjusting the temperature and pressure until hydrate formation is not favored
- Inhibiting hydrate formation in the free water phase

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

Hydrate prevention

Prevention of hydrate formation is better than extraction of existing hydrate from an economical view and safety concerns. To accomplish this, the hydrate formation process can be influenced by different ways, which our research team has studied:

- Controlling of pressure and temperature during extraction and transport;
- Injection of hydrate inhibitors;

Pressure and temperature control

If the conditions can be controlled outside of the hydrate formation restriction, wet gas can be transported. However, it is to be taken into account that local pressure and temperature changes can happen. The required technique for temperature control of the whole pipeline or larger sections is expensive, reduced pressure leads directly to lower feed rates [3].

Thermodynamic hydrate inhibitors

With thermodynamic inhibitors the chemical potential between the water molecules is changed. The pressure and temperature level, at which hydrate formation is possible, changes to higher pressure and to lower temperature. Such inhibitors as salts, especially alkali halogenides, alcohols, like methanol and glycols are really widespread.

The advantages of these hydrate inhibitors are proven application, recycling possibilities and flexibility in working with any type of hydrocarbon.

Disadvantages are the necessary high volume amounts of thermodynamic inhibitor. This aspect leads to an extensive logistic support for the transport of inhibitor to the well, the feed rate decreases due to the added inhibitor volume and the recycling of thermodynamic hydrate inhibitor is costly. Also lead the chemical properties of the inhibitor to a higher corrosion rate and to higher safety requirements. Too small percentages of thermodynamic inhibitor can support the hydrate formation instead of preventing it.

Hydrate inhibition with methanol

Relative to hydrate suppression, methanol has several properties which make it especially well suited for the application when compared to other solvents. Methanol exhibits a lower viscosity and surface tension as a function of temperature. The most noted drawbacks of methanol are its toxicity and high vapor pressure

which is significantly higher than that of the traditional glycols resulting in potentially high losses at certain conditions.

Low Dosage Hydrate Inhibitors (LDHI)

New sorts of chemicals, named Low Dosage Hydrate Inhibitors (LDHI), have been taken into account as the most effective option regarding the replacement of thermodynamic hydrate inhibitors . However, because of their low dosage, LDHI do not change the hydrate stability zone fully, in contrast to the thermodynamic inhibitors; so that the unprocessed effluents are allowed to transit inside the hydrate stability zone. Consequently, the use of LDHI is not as straightforward as that of the thermodynamic inhibitors: based on an associated risk analysis, a proper hydrate management strategy has to be developed for the field in order to define adequate contingency procedures and back-up solutions. There are two types of LDHI: the Kinetic Hydrate Inhibitors (KHI) and the Anti-Agglomerants (AA). The development of LDHIs has been subjected to a lot of research works for the last eighteen years, and to several field testing and deployment for the last twelve. LDHI can be efficiently used at dosages far lower than that of the thermodynamic inhibitors: the required concentration for these additives is currently expected in the range of 0.5-3 wt % in water. However, it is worth mentioning that these dose rates are low compared only to methanol or glycols. Owing to their low dosage, the most interesting economic advantage expected from LDHIs should have been the reduction of operating expenditure. In fact, the main economic incentive of using LDHIs is today the large reduction of capital expenditure via the reduction of the size of the storage, pumping and piping facilities; they also have the benefit that they are far less volatile and flammable, and more environmentally friendly than methanol, resulting in the reduction of HSE risks [4].

Kinetic hydrate inhibitors

A KHI is a chemical product composed of active matters formulated in a solvent. The active matters are water soluble polymers with eventually synergist products, and the solvent is composed of monoethyleneglycol and/or heavy alcohols. They act by delaying hydrate nucleation step and by slowing down the initial crystal growth during a finite period defined as “hold-time”. The hold-time due to KHI is dependent on the subcooling and on the test pressure. Consequently, the applicability of a KHI depends upon two factors: the subcooling to which the produced effluents are exposed, and the residence time of the water inside the hydrate stability zone. For a given pressure, the subcooling can be defined as the difference between the thermodynamic hydrate forming temperature (dissociation temperature) and the ambient temperature (layer temperature for instance). The subcooling is the “driving force” of the hydrate crystallization kinetics; so, the higher the subcooling, the lower the efficiency of the KHI. There is in practice an absolute subcooling limit above which the hydrate formation is quite instantaneous, whatever the dose rate of the KHI. Nowadays, this limit can be evaluated at around 14-15°C for the best KHIs. Subsequently, for a given subcooling, the applicability of a KHI depends on its ability to delay hydrate formation for a time longer than the residence time of the water inside the hydrate areal. Regarding TOTAL Group experience with KHI, two field tests were carried out in France in 1997, and in Argentina in 1999. First actual field experience with KHI is that of South-Pars in Iran. The success of this first application was a strong incentive to use a KHI as the base case for hydrate prevention on Dolphin, a large gas field situated offshore Qatar. The KHI injection has been started to protect the sealines and the onshore slug catcher.

Anti-Agglomerants

AAs are generally surface active products mixed in a solvent. They can be water or oil soluble depending on the technology used. Contrary to KHIs, they do not avoid hydrate formation but they decrease their growth and agglomeration, so that the tiny hydrate crystals can be transported in the oil phase. Besides, in contrast to KHIs they can sustain high subcooling levels, up to 18 20°C. So in the cases where waxes are not an issue, the potential use of AAs could allow to liquidate the insulation, or at least to reduce it, resulting in significant capital expenditure savings. However, their main drawback is that their efficiency is limited to a certain watercut: as soon as the watercut is higher than 30-40 %, the hydrate particles concentration becomes so high that AAs are no longer able to allow the transport of the suspension. Consequently, the potential use of AAs, on a continuous injection basis, is limited to situations where the watercut is rather low (technical limitation) and where the water flow rate is rather low (operating expenditure limitation). Because of their operating expenditure limitation, AAs are mainly used today in transient situations on oil fields, especially to allow reducing the methanol injection and thus to quicken the cold restart of wells up to a certain watercut. In the future, the continuous injection of AAs will be possible to contemplate most probably when the wellhead (or downhole) water separation has become a field proven technique [5].

Economic feasibility of LDHI appliance

Our research group has made a comparison of economic benefit between the use of a single thermodynamic hydrate inhibitor (methanol) and a mix of methanol and LDHI. We decided to choose kinetic hydrate inhibitor "Konkrepol-PVP" as the most suitable and widespread in Russia.

The table below provides information about the estimation of both variants. There are final results:

Table 1. Results of economic estimation

Feature	Unit	Without "Konkrepol-PVP"	With "Konkrepol-PVP"	Difference
Operational expenditure	Thous. RUB	173 659,6	170 248,4	–3 411,2
Net present value (NPV)	Thous. RUB	–97 993	–96 068	1 924,9

These results demonstrate feasible and doubtless argumentum of LDHI efficiency and pecuniary benefit.

Conclusion

As far as gas and oil industry is concerned, safe and environmentally friendly production is said to be an ultimate aim. From our perspective it seems to be achievable if we never stop improving used technologies and making further breakthrough, one of which is Low Dosage Hydrate Inhibitors. To understand all the aspects better, it is necessary to perform a more thorough study of it and explore all avenues experimentally.

References

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