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SELECTION AND OPTIMIZATION OF LOW-DOSAGE INHIBITORS AS APPLIED IN GAS HYDRATE CONTROL

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Abstract: Natural gas hydrate formation is a costly and challenging problem for the oil and gas industry. In recent years, two new families of chemical additives have been commercially developed to prevent hydrate plugging problems in production lines. This approach is commonly known as low-dose inhibition, and the two families are kinetic inhibitors and anti-agglomerants. Evolution of these new products is proceeding at a rapid pace, in order to meet goals of covering a greater range of operating conditions and finding an economically and environmentally attractive alternative to thermodynamic inhibition.Successful deployment of low-dose inhibitors depends on an appropriate selection of inhibitors and a complete understanding of the system. Based on a synthesis of available literature on application of low-dose inhibitors to hydrocarbon processing equipment and handling facilities, this paper describes a methodology for designing a deployment strategy. This guide provides a systematic approach to aid production engineers in deploying low-dose inhibitors in existing facilities and new developments. An easy-to-follow flow chart is given. The information provided in this article was compiled from published data, and experience provided by several companies in the oil and gas industry.

Keywords: Hydrates, Kinetic Inhibitors, Anti-agglomerants

INTRODUCTION

Natural gas hydrate formation is a costly and challenging problem for the oil and gas industry and tends to be most critical for offshore facilities. Since the time when hydrates were first identified [Hammershcmidth, 1934], the oil and gas industry has injected a constant flow of resources into the search for an economic and environmentally friendly solution to the problem of hydrate prevention.

Thermodynamic inhibition has been the conventional approach to natural gas hydrate inhibition. System composition or operating conditions are altered so that over the range of operating temperatures and pressures, the hydrocarbon system falls outside the pressure-temperature region in which hydrate formation can occur. (See Figure 1) [Paez, *et al.*, 2001].

Keeping operating pressures and temperatures out of the hydrate formation region can be achieved by making system adjustments such as applying heat, using insulated pipelines, or adding chemical compounds (thermodynamic inhibitors) that change the behavior of the new mixture.

Over the last ten years, a new family of chemicals termed “low-dose inhibitors” has been developed. These form the basis of a technique that does not operate by changing the thermodynamic conditions of the system. Low-dose inhibitors act at the early stages of hydrate formation by modifying the rheological properties of the system. Low-dose inhibitors (LDIs) are generally discussed in the literature under the sub-classifications kinetic inhibitors (KIs) and anti-agglomerants (AAs). KIs delay the nucleation and growth of hydrate crystals. AAs do not interfere with crystal formation, but impede their agglomeration for a period of time. The advantage of this technique when compared to the use of thermodynamic inhibitors (TDIs) is that low dose inhibitors work at low concentrations (<=1 % wt), reduce environmental concerns and do not require regeneration units, implying capital costs reduction. Although LDIs are more expensive (pound per pound), the fact that very low concentrations are required makes them an economically attractive solution.

Even though LDIs appear to be a good solution for natural gas hydrate prevention, development of these products over the necessary range of operating conditions is still a matter of research. LDIs are not currently effective at extreme conditions, where the concurrent use of some thermodynamic inhibition is still necessary. However, they can reduce the amount of thermodynamic inhibitor needed and in locations where oil and gas processing conditions fall under the current effective range of LDIs, their deployment has met with success.

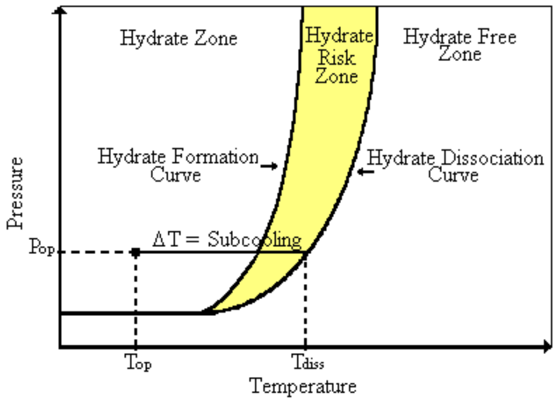

Fig. 1 Schematic pressure vs. temperature diagram for a given gas composition. A graphical definition of subcooling is given.

For conditions in which LDIs can be deployed, their application brings several benefits not only from the economic point of view but for health and safety as well. Once these products are deployed, the storage of methanol is substantially reduced which implies a reduction of the amount of hazardous materials on site [Argo, *et al.*, 1997]. Such a strategy is a standard part of current safety practice in the oil and gas industry.

Taking into consideration the use of LDIs during the design stage of a new project [Talley and Mithcell, 2000] can greatly reduce capital costs. Equipment including dehydrators, tanks and chemical pumps can be eliminated from the system. Also, pipelines which would otherwise require insulation can be designed to operate with LDIs instead. The instrumentation needed for low-dose applications is simpler than that for TDIs, and regeneration units are not required. By applying LDIs, the amount of TDIs needed during shut down and start up operations can be reduced. In this paper, published data was reviewed in order to develop a comprehensive guide for LDI deployment.

DEPLOYMENT OF LOW-DOSAGE INHIBITORS

Commercial deployment of LDIs is still incipient. Even where their advantages are known, the transition from TDIs to LDIs has been very slow. There are a few documented cases of commercial deployment of LDIs and most of them are related to the deployment of KIs [Bloys, *et al.*, 1995; Corringan, *et al.*, 1995; Leporcher, *et al.*, 1998; and Notz, *et al.* 1996]. AAs are commercially available but information about their performance has not yet been made public. Successful deployment of LDIs has been reported in the southern sector of North Sea (BP and ARCO), as well as in the South West of France (ELF), in the Gulf of Mexico (Exxon) and in southwestern Wyoming, and Texas, USA (Texaco Group Inc.). (See Table 1).

No information was found about chemicals having kinetic inhibition and anti-agglomerant properties. Several researchers have suggested that chemical design focus on the development of these blends [Kellan, *et al.*, 1995] since they could cover a bigger range of operating conditions, as described in the next section.

Deployment of LDIs is a complex operation that must be carefully prepared in order to prevent any side effects that could compromise normal production operations or the efficacy of additional chemical treatments. Figure 2 gives an outline of a comprehensive guide for the deployment of LDIs.

ANTI-AGGLOMERANTS OR KINETIC INHIBITORS?

This question of whether KIs or AAs will better meet system needs should be answered based on the system conditions and knowledge of the characteristics of these chemicals [Kelland, *et al.*, 1995b]. The process of answering this question corresponds to Step 3 of Figure 2. Table 2 shows a comparison between these LDIs.

KIs are commonly water-soluble polymers that work well when the operating temperature is not more than about 10 °C below the lowest hydrate-free zone temperature (i.e., subcooling is about 10 °C). Because KIs are water-soluble, their efficacy is independent of the watercut. However, subcooling values in the field are greater than 10 °C in some cases. On the other hand, AAs work well under more severe conditions of temperature and pressure, but since they are usually surfactants, they are miscible in both the hydrocarbon (they act only in the presence of a liquid hydrocarbon phase) and in water. High watercuts and water salinity diminish AAs surface activating performance.

KIs often need a carrier chemical, which can be either methanol or water. Special considerations must be taken in order to select the placement of KI injection since in hot spots where carrier liquids are vapourized, there is no solvent to carry a KI, and they can be left behind. In addition, excessive heat may degrade the KI, reducing or eliminating its effectiveness. . On the other hand, AAs should be injected in places with high turbulence since they act by creating an emulsion that keeps hydrates dispersed.

Table 1. Facilities Deploying Low-dose Inhibitors *Threshold Hydrate Inhibitor

Location	Subcooling	Type of LDI and dosage used
Southern sector of North Sea	8°C [3] 8 – 9°C [5,7]	KI (< 0.5 wt. %) KI (0.5 wt. %) THI* (5000ppm)
Gulf of Mexico	6°F	KI (0.1 wt. %)
Southwest of France	8 °C	KI (0.5 wt. %)
Texas and Southwestern Wyoming, US	5 – 10°F	KI (< 0.1wt. %)

Table 2. Comparison Between AAs and Kis

Kinetic Inhibitors	Anti-Agglomerants
Not affected by watercut	Affected when watercut > 40%
Work at subcoolings up to $10^{o}C$	Work under more severe conditions
Water soluble	Water and oil soluble
Slow crystal growth	Impede hydrate agglomeration
Injection at cold points	Injection at turbulent regions

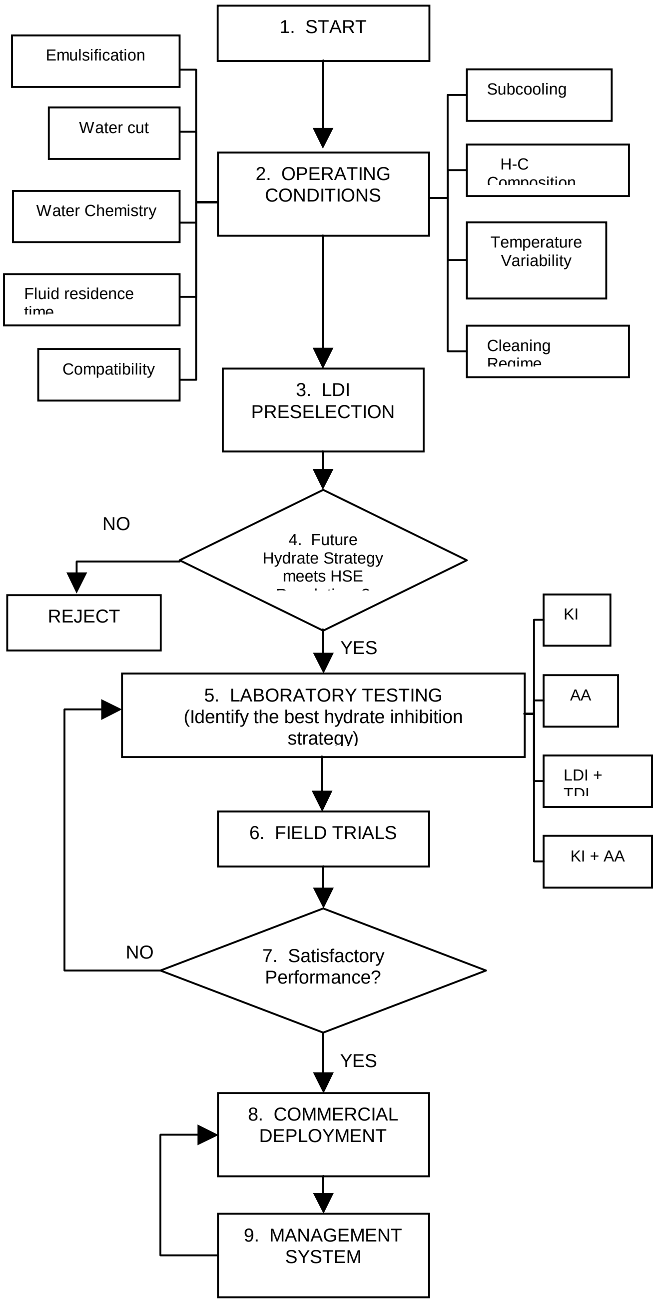

Fig. 2 Steps that should be followed in order to successfully deploy a Low-dose Inhibitor.

OPERATING CONDITIONS

In order to deploy low-dose inhibitors, operators must have a complete understanding of the system. This exercise corresponds to Step 2 in Figure 2. For the expected range of hydrocarbon compositions that will be seen at a production facility, the hydrate zone and hydrate risk zone (see Figure 1) must be predicted (use of models and available correlations [Sloan, 1998] is common practice), and the placement of the operating conditions in the hydrate risk zone known. Residence time of the fluids in the system plays a very important role for the selection of the hydrate inhibitor. Water chemistry and watercut may influence the selection as well. Other chemical treatments should be considered and the influence of a new chemical on emulsification must be analyzed. Phillips and Grainger proposed a survey [Phillips and Grainger, 1998], which once answered provides a good understanding of the conditions in the system. Operators must identify where hydrates form in the transport and production system.

Operating conditions must always be evaluated. Production strategies usually change during the life of a reservoir, a fact that if ignored, could lead to LDIs inefficiency.

The following are some of the system conditions that should be taken into account in a complete experimental design at the laboratory and field scales. These considerations apply to both existing and new facilities.

Subcooling. Difference between operating temperature and hydrate dissociation temperature at operating pressure (see Figure 1). KIs work up to about $10\ ^{o}C$ subcooling whereas AAs are effective at more extreme subcoolings.

Hydrocarbon composition. Hydrate temperatures and pressures of formation are strongly influenced by composition. Gas, oil and/or condensate compositions must be recreated in laboratory in order to achieve representational hydrate formation conditions.

Seasonal temperature variability. Where seasonal temperature fluctuations exist, they must be taken into account. The hydrate strategy may either be designed for the worst case, or a more responsive regime may be developed as a function of temperature. It is important to keep in mind that LDIs' dosage in winter is greater than in summer in some regions. Optimal seasonal dosages should be identified in order to keep hydrates from forming, and to minimize costs.

Emulsification. Regardless of whether AAs or KIs are being considered, emulsification tests must be carried out to determine the influence of the LDI on this phenomenon. Separation of oil and water in production facilities can be greatly affected if these fluids are trapped in emulsions.

Water chemistry. Even though water salinity works as a hydrate inhibitor, high salinities can diminish the performance of AAs and increase the risk of emulsification when using KIs. Usually laboratory tests are carried out using deionized water, which implies no additional hydrate inhibition so the worst case can be reproduced. However, interactions of hydrate inhibitors with other chemicals present in produced water must be studied. It is important to keep in mind that water chemistry can change over the life of a reservoir, a fact that is likely to affect hydrate formation conditions.

Water cut. The ratio of produced water to produced hydrocarbons is a key factor in the selection of a LDI. As explained before, AAs' performance can be diminished at high water cuts.

Fluid residence time. It is key to know the length of time that produced fluids will be exposed to hydrate formation conditions in the system. Shut-downs and start-ups are special cases under which fluids undergo greater subcoolings and the induction time of hydrate crystal formation may be exceeded. LDI's should be tested in lab and field trials in order to corroborate their performance under these circumstances. The pipeline profile should be studied in order to identify regions with longer residence time. These scenarios should also be considered in laboratory tests.

Cleaning regime. Pigging and sphering are common pipeline cleaning practices. In locations where these procedures are applied, the maximum residence time (no fluid flow) can be taken as the time between pipeline cleanings.

Compatibility. The selected LDI must not affect any other chemical treatment, nor production operations Its efficacy may also be reduced by interactions with other chemicals. Targeted laboratory tests must be carried out in order to identify the compatibility of the new chemical with produced fluids and additional treatments.

Existing Environmental Legislation. Some LDIs are not acceptable under existing environmental legislation of some countries. Before beginning lab testing, it must be clear that the product will be safe and environmentally friendly. For example, in the Canadian North Atlantic, hydrate inhibition chemicals are assessed according to the Offshore Chemical Selection Guidelines. This consideration, corresponding to Step 4 in Figure 2, is assessed on a go/no-go basis.

Instrumentation. Pumps, valves and special instrumentation must be put in place before LDI field trials. In locations where LDIs will replace TDIs, modifications must often be made

LABORATORY TESTING

Laboratory testing is crucial in the successful deployment of low-dose inhibitors. This comprises Step 5 in Figure 2.

Deciding which chemical products should be tested from the many on the market can be a challenge. Chemical suppliers offer LDIs that match a range of operating conditions. A pre-selection can be done according to products suggested by suppliers, once operating conditions are defined. This process corresponds to Step 3 in Figure 2. KIS, AAs, TDIs + LDIS or KIs + AAs can be considered during the pre-selection phase. An efficient approach is to run a fast laboratory-screening test to select two or three products for complete laboratory testing. There are many publications on the subject of fast screening of LDIs. Usually tetrahydrofuran (THF) is used as a hydrate former because this liquid chemical produces hydrates at easy to reach 'low' temperatures (around 5^{o}C at ambient pressure) and is safer than running tests with flammable gases. Using THF, a large number of products can be easily and inexpensively evaluated.

THF evaluation techniques vary from inhibiting single crystals in a plexiglass experimental cell [Larsen, *et al.*, 1998; Taras, *et al.*, 1997], to hydrate crystal induction time experiments including using a testing flow loop (20m long x 1mm in diameter) [Pakulski, 1997], immersing testing tubes that contain stainless steel balls in a temperature-controlled bath [Lederhos, *et al.*, 1996; Long, *et al.*, 1994; Panchalingan and Sloan, 1996] and running viscometric experiments [Kalbus, *et al.*, 1995].

Once the two or three products that showed the best performances with THF are selected, field simulated tests can be carried out. Published studies usually report the testing of up to three LDIs before field trials.

Laboratory tests should be conducted in a way that simulates the real operating conditions under which the product will be working. There are several ways to test LDIs' performance and transferability of results between lab and field has been studied [Lederhos and Sloan, 1996b]. To simulate field conditions, some researchers have studied LDIs in flow loops [Gaillard, *et al.*, 1999], and some others have used high-pressure reactors [Cincigotti *et al.*, 1999]. Every system is unique and LDIs must be matched, accordingly. Laboratory testing helps to determine the future performance of the new LDI, and to understand why an unsuccessful field trial could have been unsatisfactory. A good laboratory test can help to determine conditions under which the efficacy of the LDI may be diminished. This provides a good tool in case something unforeseen happens in the field.

Once operating conditions have been matched with the properties of potentially effective LDIs, the selected AAs, KIs, or combination of an LDI with a TDI are tested in order to find the best hydrate prevention strategy (type and dosage of hydrate inhibitors). After laboratory testing is done, the LDI that showed the best performance is selected for the field trials. The selected LDI is be the one that supports the largest subcooling for the longest period of time with no undue influence on other chemicals' performances, emulsification, or normal production operations. An ideal strategy may include the use of an LDI cocktail, but no such studies currently exist in the published literature.

DEPLOYMENT OF SELECTED LDI

Once it is established whether KIs or AAs, some combination of LDI, or LDIs and TDIs, will be used, field trials can be carried out on the selected LDI. This phase corresponds to Step 6 in Figure 2. It is good to run field trials in alternative pipeline systems, running in parallel to production pipelines wherever possible. This approach would not affect normal production operations.

System recovery in the case of hydrate formation during the field trial must be assured before the application of the new chemical. This helps as an emergency response procedure in case of hydrate formation. To probe the system's capacity to return to normal operating conditions from a hydrate formation situation, the system should be brought to hydrate formation conditions and hydrate formation indicators must be designed, applied, and monitored. Talley and Mitchell (2000) give a good example of hydrate formation indicators. In this paper the ratio of pipeline pressure drop to gas flow rate is constantly monitored. Values greater than 1 psi/MSCFD indicated hydrate formation. Other indications of hydrate formation include reduction in pressure caused by viscosity change, deposition and plugging, increase in temperature profile (exothermic reaction), reduction in produced water flow, and evidence of hydrates in a pig, Then hydrate formation can be allowed and recuperation techniques (i.e. P reduction, adding TDIs, pigging, sphering, etc.) must be applied. This gives confidence that the deployment of the new LDI can be carried out safely. It is recommended to have a TDI available as a backup if hydrate plug recovery trials do not go as smoothly as planned.

Critical variables for hydrate formation (temperature, pressure, composition, gas flow rate and watercut) must be constantly monitored and used in hydrate formation calculations or simulations in order to determine whether hydrates are being formed. Expert systems are being developed in order to detect hydrate formation immediately, so that the necessary treatment [Abdulah and Islam, 2001] can be applied. In some deployments, LDI dosage has been controlled by a computer acquisition system [Talley and Mitchell, 2000].

In situations where LDIs are being deployed to replace TDIs, the changeover must be conducted gradually. The normal TDI dosage must be decreased slowly, and hydrate formation indicator checked carefully. In some situations, LDIs are deployed in order to reduce the use of TDIs. Even partial replacement represents improved economics.

The injection port placement for LDI deployment is key in the performance of this product. For example, AAs require good mixing whereas KIs should not be placed in hot spots where their carrier chemicals can evaporate, leaving them out of solution.

Initial dosages of LDIs should be bigger than the ones determined in the laboratory testing. A boosted concentration ensures hydrate protection from the beginning and can help determine any potential adverse effects of this product downstream (increased emulsification, or incompatibility with other additives, for example) as this would be the maximum concentration the system would see. At all times, production fluids exiting the system should be sampled in order to verify the level of LDI and to understand its influence on emulsification, and compatibility with other system fluids.

Once hydrate inhibition protection is guaranteed, reduction in LDI dosage can begin. LDI dosage should be reduced gradually until the optimum concentration for the field conditions is found. Every time the dosage of the LDI is reduced, the system must be kept at the new concentration long enough to make sure that it works well under all operating conditions. During this stage of the trial hydrate plugs or crystals may form, but this procedure is necessary to determine the minimum effective concentration for the system. Reversing plugs is a complicated, time consuming and costly procedure [Baugh *et al.*, 1997; Lang *et al.*, 1999; and Castro *et al.*, 1998].

Shut downs and start-up trials must also be done, and additional procedures to ensure their safe execution must be developed. For example, TDIs might be used for extra protection during these situations when their duration is longer than expected.

Finally, if the performance of the selected LDI is found to be satisfactory and economically viable in trials, commercial deployment can take place, corresponding to Step 8 in Figure 2. In situations where the selected LDI did not perform well, the information collected during the trial must be analyzed to determine the causes of the failure so that the second round of laboratory testing can be more complete, or so that another chemical can be selected. Deployment of LDIs is an expensive undertaking, which can be designed for success when every detail is taken into account from the beginning.

MANAGEMENT SYSTEM

Successful deployment of LDIs can be achieved following the guidelines given above. However this success depends on specific operating conditions present at the time of the deployment. During a lifetime of a reservoir new problems appear daily and production strategies are usually changed in order to keep operations commercially viable. New situations like these may change normal operating conditions and lead to the formation of natural gas hydrates. Keeping track of the variables affecting hydrate formation as well as the performance of the deployed LDI helps to predict hydrate formation in the system. Once a LDI is deployed, a management system should be created to keep track of the performance of the treatment (Figure 2, Step 11.), to help predict situations where hydrates can form and optimize or improve this performance whenever possible.

CONCLUSIONS

1. Easy to follow guidelines are given in this paper in order to help achieve success in the deployment of LDIs.
2. Success of LDIs deployment depends on a full understanding of operating conditions and complete laboratory and field-testing.
3. A management system should be installed to optimize the performance of the selected LDI and identify possible failures before happening.

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