

Hydrate Risk Management at High Watercuts with Anti-agglomerant Hydrate Inhibitors

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Gas hydrate blockages pose an outstanding flow assurance challenge for hydrocarbon production with high watercuts because hydrate inhibition with thermodynamic inhibitors, such as methanol, often becomes economically and logistically unpractical. Some production wells can be prematurely terminated as a result of risks of hydrate blockages because subcooling in deepwater production is generally too high for kinetic hydrate inhibitors (KHIs) to be effective and it is commonly believed that anti-agglomerant hydrate inhibitors (AAs) are not designed to work at watercuts higher than 50%. To demonstrate the feasibility and principles for managing gas hydrate risks at high watercuts with AAs, systematic hydrate laboratory testing at various watercuts was conducted on a rocking cell apparatus. Results showed that the ability of an AA to prevent hydrate blockages at high watercuts strongly depends upon the brine salinity. Even though a small increase in the salinity does not shift the hydrate phase diagram by much, it can cause a step change in the performance of an AA at high watercuts. Hydrate problems in higher salinity systems are generally drastically easier to manage than in lower salinity systems even if they have the same subcoolings. It was also revealed that, when a thermodynamic hydrate inhibitor, such as methanol, is mandatory, a small dosage of AA in combination with methanol can significantly reduce the amount of methanol required.

1. Introduction

Gas hydrates,¹ also known as clathrate hydrates, are non-stoichiometric ice-like crystalline compounds composed of water clathrate cage structures that enclose guest molecules with appropriate diameters. The light alkanes (methane, ethane, propane, etc.) commonly encountered during oil/gas exploration can form gas hydrates with the produced water in production flowlines under appropriate temperature and pressure conditions.² The hydrate particles can agglomerate into hydrate plugs that restrict or completely block the flow of produced fluids and result in lost production.^{3,4} They can also damage the integrity of a production facility and create potential safety hazards for operational personnel if not handled properly during remediation processes.²

Besides managing gas hydrate risks through engineering means, such as, thermal and pressure controls, gas dehydration, subsea separation, etc., operators commonly employ hydrate-inhibitor chemicals to prevent system upsets caused by hydrate blockages.⁵ Three types of hydrate inhibitors⁶ are currently available to the energy industry for controlling gas hydrates: thermodynamic hydrate inhibitor (THI), kinetic hydrate inhibitor (KHI), and anti-agglomerant hydrate inhibitor (AA). They differ by the purported mechanisms by which they address hydrate

problems. A THI, such as methanol and monoethylene glycol, prevents hydrate formation by shifting the hydrate equilibrium curve toward higher pressures and lower temperatures, so that the operating conditions are outside the hydrate stability region. THI has been in application for over half a century, and well-established thermodynamic models are available for predicting the amount of THI required for hydrate prevention. However, it normally takes a large amount of THI to be effective, as much as 100% based on the volume of the produced water, and a significant portion of it can be lost to the hydrocarbon phase.⁷ In addition, high concentrations of THI in the produced water can induce salt precipitation, and crude oils that contain excessive methanol are less desirable to refineries. KHI is a particular class of water-soluble polymers with functional groups that can be accommodated into clathrate hydrate cages. Unlike thermodynamic inhibitors, they do not change the hydrate equilibrium curve but significantly delay the hydrate nucleation and/or growth, so that the induction time is longer than the residence time of the fluids in the flowlines. In field applications, a small dose rate of KHI has been shown to significantly reduce the methanol consumption. However, the major limitation of KHI lies in that it ceases to function when the subcooling is over about 20 °F.⁵ It is also commonly known in the industry that KHIs have difficulty in preventing structure I hydrate, and their performance can be significantly compromised in the presence of some other production chemicals, especially corrosion inhibitors.⁸

AAs are molecules that generally have a hydrophilic head and a hydrophobic tail. They allow gas hydrates to form but keep the hydrate crystals small and dispersed in the hydrocarbon

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(1) Sloan, D.; Koh, C. *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press: Boca Raton, FL, 2007.

(2) Sloan, D. *Hydrate Engineering*; Society of Petroleum Engineers: Richardson, TX, 2000.

(3) Gao, S.; House, W.; Chapman, W. G. *J. Phys. Chem. B* **2006**, *110*, 6549–6552.

(4) Mehta, A. P.; Walsh, J.; Lorimer, S. *Ann. N.Y. Acad. Sci.* **2000**, *912*, 366–373.

(5) Mehta, A. P.; Hebert, P. B.; Cadena, E. R.; Weatherman, J. P. *SPE Prod. Facil.* **2003**, *Feb*, 73–79.

(6) Kellan, M. A. *Energy Fuels* **2006**, *20* (3), 825–847.

(7) Bruinsma, D. F. M.; Notz, P. K.; Desens, J. T. SPE Annual Technical Conference and Exhibition, Denver, CO, 2003.

(8) Clark, L. W.; Anderson, J. International Petroleum Technology Conference, Dubai, United Arab Emirates, 2007.

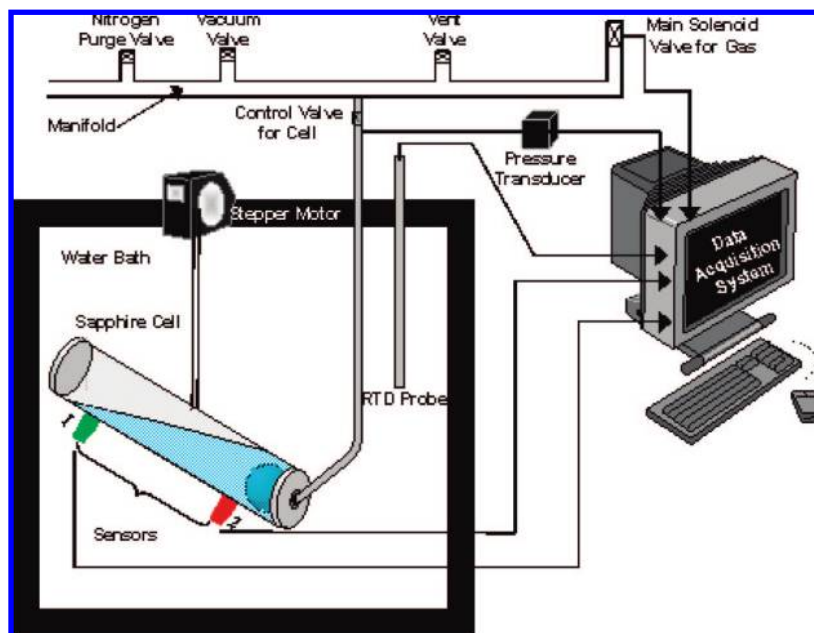


Figure 1. Champion Technologies hydrate rocking cell apparatus.

phase, so that they do not agglomerate into hydrate plugs. The hydrate crystals are then transported as slurry in the production stream. The amount of AA required for hydrate blockage prevention is normally only a fraction of the THI dosage, and therefore, AA does not noticeably shift the hydrate thermodynamic equilibrium curve of a system. Because of the mechanisms by which AA works, its successful application demands the presence of a hydrocarbon phase. It was commonly claimed^{9,10} that AA ceases to be effective when the water volume percentage of the total liquid production stream (commonly referred to as watercut) becomes higher than 50% without referencing to important system-specific parameters (such as brine salinity, temperature, and pressure) or the performance difference between different AA chemistries. Conservatively following this coarse rule of thumb can be costly because it can result in premature termination of a production well when neither THI nor KHI is an economically or technically feasible option to mitigate the hydrate risks. Although there have been field examples¹⁰ where AAs were successfully applied to 50+% watercuts, hydrate formation and blockage prevention are not well-understood at such high watercuts.

To understand the crucial parameters that dictate the hydrate management strategies at high watercuts, hydrate testing using a rocking cell apparatus was systematically conducted at various watercuts with a proprietary Champion Technologies AA in this work. It was discovered that a small change in salinity can cause a step change in the AA performance at high watercuts. With appropriate sets of conditions, AA can be an excellent hydrate blockage prevention tool at 80% watercut. If a thermodynamic hydrate inhibitor, such as methanol, becomes necessary to successfully prevent hydrate problems, a small dosage of AA in combination with methanol can significantly reduce the amount of methanol required. The effect of subcooling was also investigated, and results established that the hydrate problem

Table 1. Green Canyon Gas Composition

component	mol %
nitrogen	0.4
carbon dioxide	0.0
methane	87.2
ethane	7.6
propane	3.1
iso-butane	0.5
<i>n</i> -butane	0.8
iso-pentane	0.2
<i>n</i> -pentane	0.2

in a higher salinity system is much easier to treat if two systems have the same subcooling but different salinities.

2. Experimental Section

The experiments were performed on a state-of-the-art Champion Technologies hydrate rocking cell (CTHRC) apparatus.^{11,12} It contains pressure cells made of sapphire tubes, each containing a stainless-steel ball. For each hydrate test, the cells are charged with appropriate sample liquids prior to being placed on a rack. The rack is then immersed in a water/glycol temperature bath. Once the cells are immersed in the temperature bath, they can be charged with a test gas to the desired pressure. The rack is then rocked up and down, so that the ball in the cell moves back and forth to induce mixing between different phases. Figure 1 shows a schematic of the rocking cell device.

A 40° API crude oil (its gas chromatography analysis is available in the Supporting Information), Green Canyon gas blend (Table 1), and synthetic brines with 4, 7, and 11 wt % NaCl were used during this study (hydrate phase diagrams for these salinities are illustrated in Figure 2). Nominal watercuts tested (on the basis of dead oil volume) were 30, 60, and 80%. The total added liquids in each test cell occupied 50% of the total internal volume. A proprietary Champion Technologies AA product and methanol were the chosen hydrate inhibitors for blockage prevention in this work. Each experiment was conducted in duplicate to confirm reproducibility.

The following procedure was followed for all of the hydrate rocking cell tests: (1) equilibrate the system at the desired pressure (kept constant throughout the test) and 75 °F for 2 h or until no further gas consumption is observed, (2) cool from 75 to 34 °F in

(9) Mokhtab, S.; Wilkens, R. J.; Leontaritis, K. J. *Energy Sources Part A* **2007**, 20, 39–45.

(10) Harun, A. F.; Fung, G.; Erdogmus, M. *SPE Prod. Oper.* **2008**, 23, 100–107.

(11) Gao, S. *Energy Fuels* **2008**, 22, 3150–3153.

(12) Gao, S.; Chapman, W. G.; House, W. *Ind. Eng. Chem. Res.* **2005**, 44, 7373–7379.

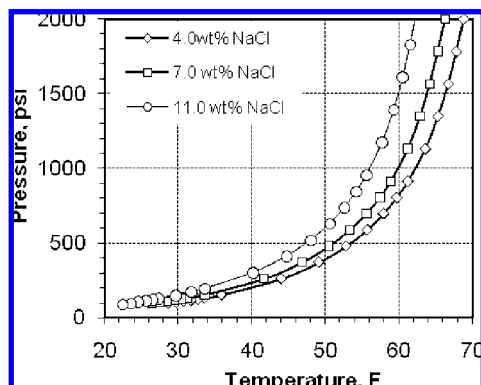


Figure 2. Hydrate phase diagrams for different salinities.

5 h while rocking, (3) continue rocking at 34 °F for 10 h to allow more hydrates to form, (4) stop rocking and simulate production shut-in for 24 h at 34 °F, and (5) resume rocking for another 3–5 h to simulate cold start-up.

Untreated samples were evaluated for all of the systems of interest to confirm their hydrate formation potentials without any hydrate inhibitors. AA minimum effective dosages (MEDs) were first screened for 4.0 wt % NaCl brine at 30, 60, and 80% watercuts and 1000 psi to evaluate the impact of watercut on AA dosage. The amount of methanol usage to drive the system out of the hydrate region was also experimentally investigated, followed by hydrate testing with a combination of methanol and AA at 80% watercut. Using the same set of experimental parameters, AA MEDs were screened with both 7.0 and 11.0 wt % brines at 80% watercut to gauge the impact of salinity on hydrate management at high watercut.

Subcooling is a term frequently relied on to describe the driving force of a system to form gas hydrate, and it is a function of many parameters, including pressure, temperature, salinity, and the composition of the hydrate-forming mixture. The higher the subcooling, the more likely it is for gas hydrate to form and the more THI is needed to prevent hydrate formation. It was indicated in the literature¹³ that subcooling is not the right driving force for comparing the effectiveness of KHIs, and the author's own experience with KHI testing concurs with that observation. Unlike a KHI, an AA allows hydrate particles to form while keeping them dispersed. This hydrate formation process causes salts to become concentrated in the remaining liquid phase.^{14,15} Therefore, for the same subcooling, the difference in salinity can potentially be an important factor to AA performance. To evaluate the effect of salinity on hydrate management with AA when the subcooling is identical, in this work, hydrate testing was conducted on two systems with the same subcooling but different salinities (4.0 wt % NaCl and 1000 psi and 11.0 wt % NaCl and 2000 psi). The results would also elucidate whether subcooling is a reliable indicator to gauge the severity of the hydrate problem if treated with the AA technology. Other factors, such as temperature, gas composition, and oil characteristics, may also impact the performance of AA for systems with the same subcooling, but they are outside the discussion of this work.

3. Results and Discussion

Untreated samples were first evaluated to determine the hydrate formation potential for the system with 4.0 wt % brine and 1000 psi pressure at 30, 60, and 80% watercuts. Massive chunks of gas hydrates were observed in the cells, and the ball was completely immobilized (Table 2). The AA was then added into each system for dosage screening. AA dosages were based

Table 2. Hydrate Testing Results with 4 wt % NaCl Brine

30% Watercut, Untreated, Fail
30% Watercut, 1.0% AA, Fail
30% Watercut, 1.5% AA, Pass
60% Watercut, Untreated, Fail
60% Watercut, 0.5% AA, Fail
60% Watercut, 1.0% AA, Pass
80% Watercut, Untreated, Fail
80% Watercut, 3.0% AA, Fail

on the volume of the water phase. The results were classified as “pass” or “fail” based on whether hydrate blockages were detected. As shown in Table 1, the minimum effective dosages of this AA were found to be 1.5% at 30% watercut and 1.0% at 60% watercut. The AA was not able to prevent hydrate blockage at 80% even at 3.0% dosage (All of the pictures were taken near the end of the tests after the cold restarts. The positions of the cells were tilted at certain angles when their pictures were taken. The pictures were rotated to a horizontal position in this paper just for illustrative purposes. The liquid surfaces in the cells that passed the hydrate tests are the actual horizontal lines).

Because AA alone was unable to prevent hydrate blockage at 80% watercut, hydrate testing was conducted to determine the amount of methanol required to prevent hydrate formation. After establishing that 40 vol % methanol (on the basis of the volume of the water phase) was needed to eliminate the hydrate risk based on hydrate rocking cell tests, the option of hydrate prevention with an optimal combination of methanol and AA was then systematically explored. Results showed that 0.5% AA in combination with 15% methanol was able to successfully prevent hydrate agglomeration (Table 3). This demonstrated that a small amount of AA can significantly reduce the methanol usage, from 40 to 15% in this case. There were free water phases remaining in the samples because salt and thermodynamic hydrate inhibitors are mostly excluded from the formed hydrate particles,^{14,15} and they become concentrated in the remaining

(13) Arjmandi, M.; Tohidi, B.; Danesh, A.; Todd, A. C. *Chem. Eng. Sci.* **2005**, *60*, 1313–1321.

(14) Ussler, W., III.; Paull, C. K. *Geo-Mar. Lett.* **1995**, *15*, 37–44.

(15) Hesse, R. *Earth Sci. Rev.* **2003**, *61*, 149–179.

(16) Austvik, T.; Li, X.; Gjertsen, L. H. *Ann. N.Y. Acad. Sci.* **2000**, *912*, 294–303.

Table 3. Methanol in Combination with AA Hydrate Testing Results with 4 wt % NaCl Brine



80% Watercut, 15% methanol, Fail

80% Watercut, 0.5% AA + 15% methanol, Pass


Table 4. Hydrate Testing Results with 7 wt % NaCl Brine


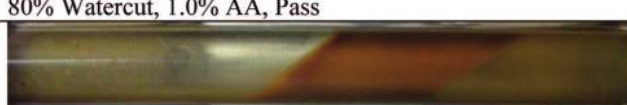
80% Watercut, Untreated, Fail

80% Watercut, 1.0% AA, Pass


Table 5. Hydrate Testing Results with 11 wt % NaCl Brine

80% Watercut, Untreated, Fail

80% Watercut, 0.5% AA, Pass


water phase. This increased concentration can inhibit further hydrate formation. In the samples that formed bulk hydrate plugs, the free water phases were not visible probably because the remaining liquid was incorporated into the pores and crevices within the plugs.¹⁶


To investigate the effect of salinity on hydrate management at high watercut, 4 wt % NaCl brine was replaced with 7 wt % NaCl brine for AA dosage screening at 80% watercut. The change of subcooling from this salinity increase was only 2–3 °C based on the modeling prediction by the DBR hydrate program. Without any hydrate inhibitor, the sample with 7 wt % NaCl brine formed a complete hydrate blockage in the cell. On the other hand, 1.0% AA by itself was able to completely prevent hydrate blockage (Table 4). This showcased that salinity plays a crucial role in preventing hydrate blockages at high watercuts and a small increment in salinity can result in a step change in AA performance. Hydrate testing with 11 wt % NaCl was also conducted with the same set of *P* and *T* parameters at 80% watercut. Hydrate chunks were observed in the untreated sample, and it required only 0.5% AA to prevent hydrate blockage formation (Table 5).

To investigate the impact of salinity on the hydrate management if two systems have the same subcooling, AA dosage screening was conducted with 11 wt % NaCl brine and 2000 psi pressure at 80% watercut. Its subcooling is identical to that of the 4.0 wt % salinity and 1000 psi system, in which AA alone was not enough for hydrate blockage prevention. As shown in Table 6, the untreated sample for this 11 wt % brine and 2000 psi system had a flow assurance failure as expected. AA dosage screening yielded that 1.5% AA was able to create well-dispersed hydrate slurry and successfully negated the hydrate plugging potential. This is a step change compared to the hydrate prevention requirement of 0.5% AA plus 15% methanol for the 4.0 wt % NaCl brine, 1000 psi, and 80% watercut system. This result suggested that subcooling is not a

Table 6. Hydrate Testing Results with 11 wt % NaCl Brine under 2000 psi, Which Has the Same Subcooling as 4 wt % NaCl and 1000 psi Pressure

80% Watercut, Untreated, Fail

80% Watercut, 1.0% AA, Fail

80% Watercut, 1.5% AA, Pass


precise term to describe the hydrate plugging risk when AA technology is employed. For two systems that have the same subcooling, the higher salinity the brine, the easier the hydrate problem is to manage. As indicated earlier, this phenomenon lies in the fact that salt becomes concentrated in the remaining liquid water phase as hydrate forms. For example, if half of the liquid water volume is converted to hydrate, the salinity could increase to ~22 wt % for the 11 wt % NaCl brine and only to ~8 wt % for the 4.0 wt % NaCl brine. The salinity difference between these two brines would double. As a result, the higher salinity brine may have come out of the hydrate region, while the lower salinity brine still favors continued hydrate formation. Therefore, even with the same subcooling, a lower salinity brine would eventually produce more hydrate than a higher salinity brine and poses a more demanding hydrate problem.

4. Conclusions

Systematic hydrate testing with an anti-agglomerate hydrate inhibitor and methanol was conducted on a rocking cell apparatus to investigate the feasibility and strategy for managing gas hydrates at high watercuts with AA. Results revealed that brine salinity plays a critical role in hydrate management at high watercuts with AA. A small increase in salinity can generate a step change in AA performance. Therefore, although AA has a watercut limit for successful applications, this limitation should be only referred to in the context of system-specific parameters, especially salinity, instead of being treated as a generalized rule of thumb. It was also shown that the addition of a small AA dosage can significantly curtail the amount of methanol required for hydrate blockage prevention, in case AA reaches its watercut limitation. Results also demonstrated that subcooling is not a precise term in describing the difficulty of treating hydrate problems with AA technology. If two systems have the same subcooling, the one with higher salinity poses a much lesser hydrate challenge than the other. Therefore, when evaluating whether an AA is an adequate tool to prevent hydrate blockage and its required dosages for field applications, thermodynamic modeling predication is never enough and laboratory hydrate testing is often mandatory.

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Supporting Information Available: Gas chromatography analysis of the oil sample used in this work. This material is available free of charge via the Internet at <http://pubs.acs.org>.