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Multiple Recovery and Re-use of Commercial Kinetic Hydrate Inhibitors from Produced Water and Rich Glycol

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Abstract

Kinetic hydrate inhibitors (KHIs) offer an alternative to traditional thermodynamic hydrate inhibitors (THIs) for the prevention of gas hydrates. KHIs have several advantages over THIs, such as lower required volumes, easier logistics and reduced CAPEX. However, KHIs are once through chemicals leading to increased OPEX, are mostly non-biodegradable and therefore cannot be discharged to sea or disposal wells in fear of aquifer pollution. KHIs can also lead to fouling of process equipment, especially at elevated temperatures.

To resolve these issues, a new KHI polymer removal method using a solvent extraction-based technique has been developed. In this approach, an immiscible extraction fluid is mixed into the KHI containing aqueous phase where the KHI polymer partitions into the extraction fluid, which can then be separated from the aqueous phase. In some cases, the KHI separated this way can be re-used. This process has the potential to solve problems with KHI produced water treatment/disposal, including where KHI is used in combination with MEG, reducing the costs and process fouling and protecting the environment.

A new joint industry project (JIP) is underway with the aim of developing the concept into a commercial process for removal and possible re-use of KHIs upstream of PW treatment or MEG Regeneration systems. The first phase of this project is lab scale evaluation of the solvent extraction method for simulated removal and re-use of two commercial KHI formulations for a real gas-condensate field case. Both the removal efficiency and hydrate inhibition performance of 4 cycles of re-injected/re-used KHI has been successfully demonstrated. Removal of KHI from a real MEG system case was also successfully demonstrated. In the second phase of the JIP, lab scale tests were used to screen extraction and separation equipment and identify optimum process conditions. The upcoming third phase of this JIP is dedicated to demonstrating the selected process concept(s) on pilot scale in a flow loop.

In this proceeding we will give highlights of the early laboratory test results from a produced water case where two field qualified KHIs are removed from PW and reused 4 times, still showing adequate hydrate inhibition performance. Successful pilot tests will confirm the operability of this process in the field.

Keywords: Kinetic hydrate inhibitors, extraction fluid, KHI removal & re-use process, crystal growth inhibition

Introduction

Use of thermodynamic hydrate inhibitors (THIs) such as Methanol (MeOH), mono-ethylene-glycol (MEG) and ethanol (EtOH) are very popular for hydrate inhibition in hydrocarbon production operations. However, when applied continuously, large amounts of THIs are often necessary (20-60wt% relative to water production) which requires large storage, regeneration, and injection facilities. Kinetic Hydrate Inhibitors (KHIs) are currently once through chemicals but offer an attractive low dosage option (0.5-2.5wt%) for the prevention of gas hydrates. KHIs can also be used in conjunction with MEG to reduce the MEG requirement. However, there are several challenges emerging in the handling/treatment and disposal of produced waters or MEG containing KHIs.

Active elements of KHIs are generally polymers that are susceptible to precipitation as solid/semi-solid deposits in the presence of some brines and at higher temperatures. This can lead to fouling problems in process equipment, separation, and storage facilities. Also, the environmental impact of KHIs is a concern, preventing widespread use of KHIs.

To overcome these problems, Hydrafact Ltd. had previously developed a patented solvent extraction-based technique in which an immiscible extraction fluid is mixed into the KHI containing aqueous phase. Contact between the solvent and aqueous KHI results in strong partitioning of the KHI polymer into the extraction fluid which can then be separated from the aqueous phase. In some cases, this formulation can be re-used as is. Figure 1 below shows the principles of the method.

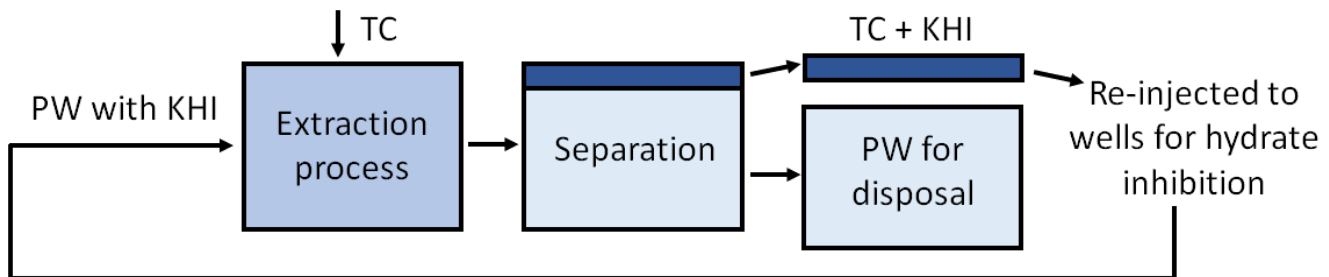


Figure.1 Schematic overview of extraction, separation, and re-injection of KHI in field. TC = Treatment Chemical; PW = Produced Water

A joint industry project (JIP) lead by NOV in cooperation with Hydrafact, TotalEnergies and Chevron is ongoing with the aim of demonstrating the concept for KHI removal upstream of produced water (PW) or MEG regeneration systems and potential re-use of the KHIs.

The proof of concept is to be demonstrated first in lab scale tests followed by pilot scale tests. The aim for the lab scale investigations is to demonstrate multiple recovery/removal and re-injection/re-use of KHIs. The second phase of the JIP is to experimentally screen extraction and separation equipment that can be applied to a commercial process. The upcoming third phase is intended to demonstrate the selected process concepts on Pilot tests in a flow loop at NOV's test facilities at Flotta, Orkney Islands. Successful testing would confirm the operability of an up-scaled process and qualify the optimum KHI extraction and separation equipment from a cost/benefit perspective.

This proceeding will mainly concentrate on achievements in the early lab scale tests, with focus on KHI achieved removal efficiency, mass balance and hydrate inhibition properties after multiple stages of recovery and reuse.

Extraction and Reuse of KHI

Two field specific cases, namely KHI in produced water and KHI in rich MEG, were selected for KHI removal investigations using three different extraction fluids/ treatment chemicals (TCs) named TC1, TC2 and TC3. Several commercial KHIs were initially screened for extractability, out of which five KHIs were picked for further investigations. Two were used in produced water only and three were designed to be used in combination with MEG. In this proceeding the former two KHIs are named as KHI A and KHI B and the latter three KHIs are named as KHI C, KHI D and KHI E.

A gravimetric drying method was used to measure the extraction efficiency of the KHI polymers. The results of removal tests for each tested KHI using different extraction fluids are presented in Table 1. The data shows that TC1 and TC2 only manage to remove around 30% of the initial polymer, whilst the TC3 extraction fluid showed a better performance; with more than 90% removal of the initial polymer in some cases. As TC3 had given the best polymer removal efficiency at the 1st stage, it was selected as the extraction fluid for the tests going forward.

Table 1 Percentage of polymer removed from five tested KHIs in DiW using three different extraction fluids (TC1, TC2, TC3)

KHI	KHI Removal Percentage Using each Extraction Fluid/ Treatment Chemical (wt%)		
	TC1	TC2	TC3
KHI A in PW	~30	~30	~50-60
KHI B in PW	~30	~30	~100
KHI C in rich MEG	~30	~30	~80-90
KHI D in rich MEG	~20	~10	~75-80
KHI E in rich MEG	~20	~20-30	>90

The above findings indicate that KHI removal can be successfully achieved in both water and rich MEG systems using a suitable extraction fluid. Following the success of KHI removal in both systems, the possibility to re-use the extracted polymer and recovering it multiple extraction cycles was investigated. The efficiency of this process in terms of polymer loss and transfer/collection at each stage was also studied. Due to specific project requirements, KHI A and KHI B were selected for multiple extraction and re-use of the extracted (TC+KHI). The tests were performed in presence of a hydrocarbon fluid, here represented by heptane (C7) to investigate potential losses of KHI into a condensate phase when reinjected.

Results of each removal and recovery stage for KHI A and KHI B are presented in Table 2. KHI B clearly performs better than KHI A in terms of recoverability. Figure 2 summarizes the percentage of KHI B polymer recovered, and percentage transferred to produced water phase at each stage for 4 times recovery and re-use. The overall recovered KHI polymer relative to the initially injected KHI (from 1st stage) is also shown.

Results of each removal stage for KHI B clearly demonstrate that removal of this polymer from water using TC3 is very efficient resulting in almost 100 % polymer recovery at all stages. The main losses seem to be due to KHI lost to condensate phase and partly also due to poor phase separation of the condensate (C7) phase from the produced water phase. However, the overall recoverability improves for each stage, suggesting that the most recoverable KHI polymer strands are enriched over time while the less recoverable polymer strands are lost.

Conclusively, around 66 wt% of the originally KHI B polymer added was still remaining after 4 cycles of recovery and re-use. On average this means that only ~8.5% of the polymer is lost per cycle and thus the need for top-up of fresh KHI chemical can potentially be reduced by more than 90% compared to a once through system.

Table 2 Percentage of extracted polymer at each removal stage relative to the initial amount of polymer added at that stage and percentage of polymer transferred back into the aqueous phase at each re-use stage relative to the amount of polymer added at that stage for both KHI A and KHI B. Extraction fluid used is TC3 and C7 was used as the condensate in each re-use stage.

Test stage	KHI A		KHI B	
	Polymer extraction from the DiW (wt%)	Polymer transferred to DiW from (TC+KHI) mixture for reuse (wt%)	Polymer extraction from the DiW (wt%)	Polymer transferred to DiW from (TC+KHI) mixture for re-use (wt%)
1st	59	100	99	100
2nd	83	74	98	80
3rd	95	91	100	92
4th	90	97	100	93

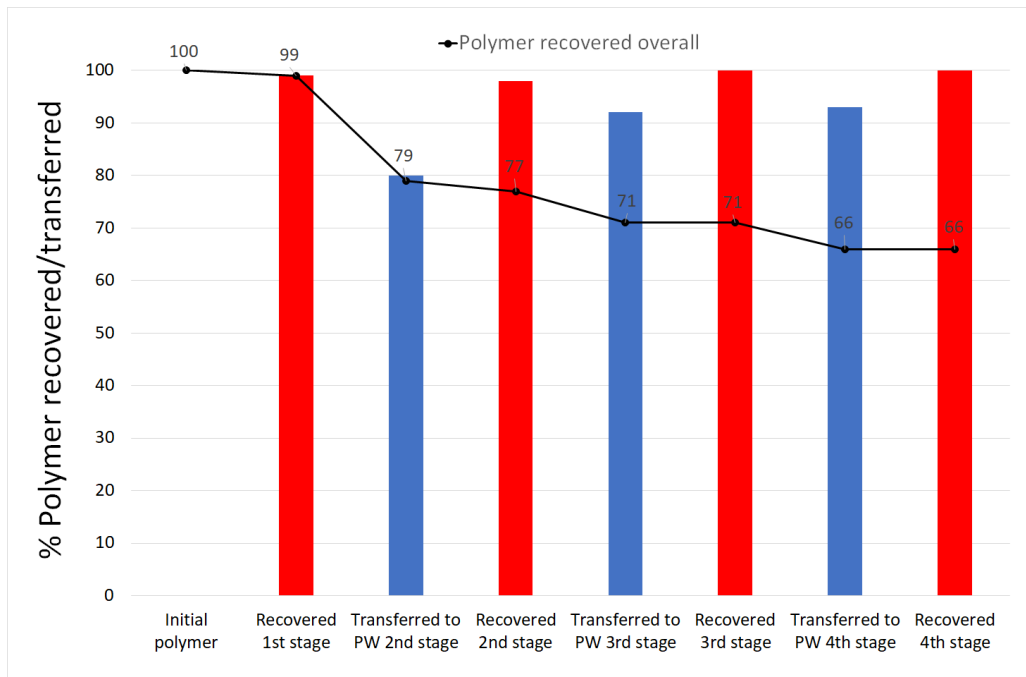


Figure 2 Percentage of the initial (1st stage) added polymer (KHI B) recovered using TC3 (red bars) and percentage transferred to the PW phase (blue bars) in the presence of C7 at each removal/re-use stage. The overall recovered KHI relative to the originally injected KHI is shown as the black line.

Hydrate inhibition with recovered KHI

Following the successful multiple removal and re-use of KHI polymers, investigating whether the ‘multi-pass’ recovered KHI retains its hydrate inhibition performance was of similar importance. For this purpose, non-time/nucleation dependent in-house ‘crystal growth inhibition’ (CGI) evaluation approaches were used to measure original and recovered KHI performances.

As KHI B was found to show better removal and recovery capacity using the TC3, in this proceeding we will present comparison of measured CGI regions for 1.0% (0.1% active) 4th pass recovered KHI B (with TC3 extraction fluid) with data for 1st TC recovered KHI and original formulation (Figure 3). As can be seen in the following figure, as per 1st recovered KHI B, hydrate inhibition performance is also very good following the 4th simulated recovery, with results closely comparable to that of the original KHI in terms of the key CIR (complete inhibition region, 0.00 % hydrate formation/hr) extent of ~7.3-7.7 °C (from s-II ‘gas only’ reference). Multiple recovery does seem however to reduce the extent of the subsequent, but much less important SGR(S) (slow growth region, ≥ 0.05 to < 0.5 % hydrate formation/hr) region, which offers a modest safety margin. This may be e.g. due to ‘refining’ of polymer average molecular weight, during repeat dissolution / extraction cycles.

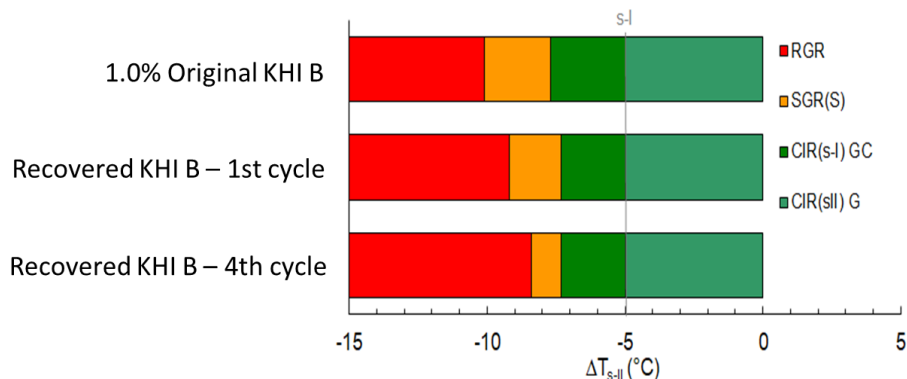


Figure 3 Measured KHI CGI inhibition regions for 1st and 4th pass TC3 recovered KHI B compared to original (Org.) KHI. System: 20% Water + 60% Condensate + 2% C3 / 98% C1 mix, at ~110 bar. CIR (s-I) = Complete inhibition region relative to s-I phase boundary, 0.00 %/hr, CIR (s-II) = Complete inhibition region relative to s-II phase boundary, 0.00 %/hr, SGR (S)= Slow growth region, 0.1 (≥ 0.05 to < 0.5 %/hr), RGR=rapid growth region, 10 (≥ 5 %/hr).

Separation and Pilot Trials

During the laboratory tests it was generally observed that the KHI polymer contributed to creating stable emulsions of the TC in the aqueous phase, see Figure 4 below. This occurred at any mixing condition, but the severity of the formed emulsion appeared to be a function of mixing intensity. The emulsification did not develop when KHI was not present, so it was the presence of KHI that caused the emulsions. These observations are key in moving the concept from the laboratory to a real process. Overall, the formation of an emulsion seems inevitable if a high KHI recovery/removal rate is needed. By filtration, it was found that the dispersed TC phase was typically ~2000ppm remaining in the aqueous phase. Trials with demulsifiers have not been successful, hence a polishing step is needed to recover TC that would otherwise be lost into the aqueous phase.

Pilot trials of the entire process in a flow loop are currently underway with the focus on mixing and separation. The purpose is to demonstrate the performance of various equipment on a more realistic scale and ultimately provide input to equipment sizing and costing. Initial trials show positive results for the mixed stage but challenges in the separation stage. Conventional treatments such as applying emulsion breakers combined with gravity separation were found to be insufficient. Trials on other separation technologies methods are ongoing.

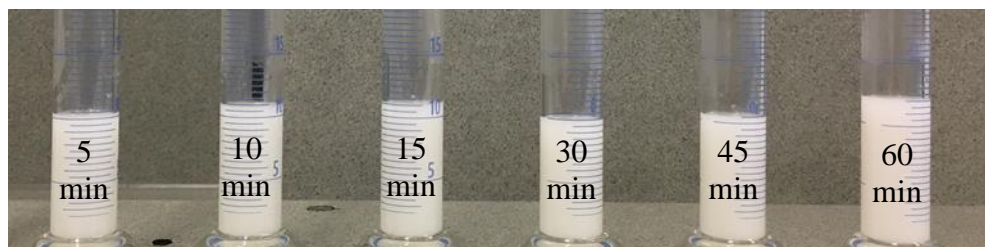


Figure 4: Stable emulsion forms when mixing TC phase into aqueous phase in presence of KHI polymer

Applicability to MEG systems

It is well known that KHIs can be used together with MEG and offer a synergistic effect, whereby the dosage rate required for each chemical can be reduced. This can then offer flexibilities in terms of field development and make it easier for new tie-ins in the situation where existing MEG distribution system is not sized for the extra tie-ins. However, as mentioned earlier, the KHI active polymer do tend to precipitate/cause fouling and thus should ideally be removed upstream the MEG recovery unit to increase uptime.

All test results suggest that the efficiency of KHI removal from MEG containing fluids is comparable to that of produced water systems. However, the solubility of the TC chemical is typically higher with increasing MEG content and the separation efficiency of the TC phase from the aqueous phase is slightly worse which could mean higher OPEX due to more losses of TC. While the KHI removal efficiency seems more than adequate to protect the MEG process from fouling, the impact of carry under of TC on the MEG regeneration and MEG loop must be investigated.

Conclusions

Based on experimental findings it can be concluded that KHIs can be successfully removed from both PW and rich MEG. Two KHIs (KHI A and KHI B) that were qualified for use in a specific gas condensate field can be recovered and directly re-used multiple times for adequate hydrate inhibition using the solvent extraction method. The overall recoverability was much better for KHI B compared to KHI A. Thus, when selecting the KHI for a project, not only the compatibility and hydrate inhibition performance must be evaluated, but also the recoverability. When tested for 4 cycles only ~8.5% of the KHI B polymer was lost on average per cycle and thus the need for top-up of fresh KHI chemical can potentially be reduced by more than 90% compared to a once through system.

The main challenges seem to be related to the separation and polishing step due to formation of stable emulsions of TC in the aqueous phase. Pilot tests are underway to address this issue and aid in selection of process equipment as well as establishing likely performance of the process under close to real conditions. Successful pilot tests will confirm the operability of this process in the field and be the first step in commercialization of this process. The envisaged process will consist of:

1. Extraction step – whereby the KHI partitions into the TC
2. Separation step – whereby the majority of TC containing KHI is separated from the aqueous phase
3. Optional polishing step pending on efficiency of step 2.
4. Re-injection of KHI + TC or separation of KHI from TC to recover the latter

Acknowledgements

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