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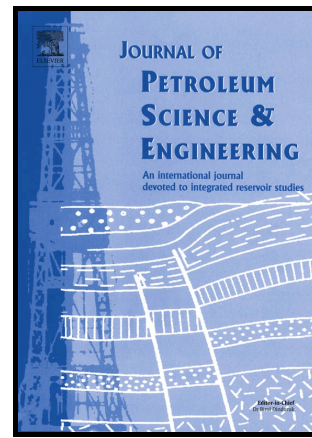
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KINETIC HYDRATE INHIBITOR REMOVAL FROM PRODUCED WATERS BY SOLVENT EXTRACTION

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Abstract

Kinetic hydrate inhibitors (KHIs) offer an attractive option for the prevention of gas hydrate problems in hydrocarbon production operations, and are seeing increasing use within the industry as an alternative to traditional inhibition methods. However, there are several challenges emerging in the handling/treatment and disposal of produced waters containing KHIs. KHIs typically contain polymers as the active component and these can precipitate as solid/semi-solid deposits at higher temperatures and/or in the presence of saline fluids, potentially causing fouling problems. This can occur during produced water handling, for example where KHI containing waters may mix with higher temperature / higher salinity waters prior to re-injection, fouling storage / pumping facilities. Furthermore, precipitation may occur in response to high temperatures experienced during re-injection into formations, where fouling can potentially result in reduced injection efficiency. In addition, there is increasing interest in reducing levels of thermodynamic inhibitor used for hydrate prevention – particularly in the case of MEG – by combining these with KHIs. In this instance, KHI drop-out could result in fouling of MEG regeneration units, interfering with production operations. Here we report the results of preliminary investigations into a technique for KHI removal from produced waters based on solvent extraction. The method uses small fractions of largely water immiscible solvents with a high affinity for KHI polymers. Contact between the solvent and aqueous KHI results in strong partitioning of the KHI polymer into the solvent. The solvent containing the polymer can then be separated by standard physical methods used to separate water and hydrocarbons (e.g. gravity settling, centrifugal separation, coalescing separation). Results show that it is possible to remove up to 100% (within detection limits) of some common KHI polymers (e.g. poly-n-vinylcaprolactam / PVCap), potentially providing a simple means to eliminate or mitigate fouling problems associated with KHI containing produced water handling/treatment.

Keywords: KHI, PVCap, hydrate inhibition, polymer removal, produced waters

Nomenclature

CGI	Crystal growth inhibition
CI	Corrosion inhibitor
EGBE	Ethylene glycol butyl ether
HSZ	Hydrate stability zone
KHI	Kinetic hydrate inhibitor
MEG	Mono-ethylene glycol
MeOH	Methanol
PLONOR	Poses little or no risk to the natural environment
PVCap	Poly-n-vinylcaprolactam
TC	Treatment chemical solvent
SI	Scale inhibitor
TI	Thermodynamic inhibitor
t_i	Hydrate induction / hold time
ΔT	Subcooling [$^{\circ}\text{C}$]

1. INTRODUCTION

1.1. KHI BACKGROUND

Low dosage kinetic hydrate inhibitors (KHIs) have seen increasing use as a cost-effective technology for gas hydrate prevention in the oil and gas industry, offering significant capital / operational expenditure (CAPEX / OPEX) advantages over traditional thermodynamic inhibitors such as methanol, and MEG [Kelland, 2006; Klomp, 2008; Sloan and Koh, 2008]. The widespread understanding within the industry and academia is that KHI polymers (e.g. PVCap) delay / slow down / interfere with the process of hydrate nucleation [Freer and Sloan, 2000; Makogon and Sloan, 2002; Anderson BJ et al., 2005; Kvamme et al., 2005], forcing in an increased 'induction' or 'hold' time, t_i ; the time that passes at a specific subcooling (ΔT from the hydrate phase boundary at pressure, P) within the hydrate stability zone (HSZ) before hydrate nucleation to proceeds to growth. In theory, if the KHI-induced induction time, t_i , at $\Delta T, P$ is longer than the pipeline fluid residence time at that condition, then the KHI should be able to prevent hydrate nucleation / growth, whereby avoiding problematic plugging.

In addition to nucleation inhibition, KHIs are also powerful crystal growth inhibitors, with this behavior providing both a secondary layer of protection against hydrate problems in addition to having recently yielded new methods to robustly evaluate KHIs for field use. Work in this area first originated from efforts by TOTAL to overcome the problem of poor reproducibility of induction time based KHI testing; nucleation being probability driven thus commonly stochastic. They developed – and used for a number of years – a specific procedure in their semi-industrial hydrate flow loops which was termed the “second germination” (SG) method [Peytavy et al., 2008] and involved using the phenomenon of ‘hydrate history’ to improve repeatability of results. The procedure was subsequently applied in 2006 to autoclave cells with respect to tackling the ongoing problem of stochasticity in laboratory KHI data [Duchateau et al. 2008]. In Duchateau et al. (2009, 2010) (University of Pau in conjunction with TOTAL) this new SG test protocol was reported; with results supporting significant improvements over traditional approaches in terms of repeatability and transferability of KHI test results.

The second germination method was subsequently advanced further by this laboratory which developed a new hydrate Crystal Growth Inhibition (CGI) method for the evaluation of KHIs [Anderson R et al., 2011]. In the CGI method, KHIs are tested with a small fraction of viable hydrate crystals already present in the system, i.e. the very worst case scenario. This work demonstrated that, beginning at low aqueous concentrations, KHI polymers induce a number of highly repeatable, well-defined hydrate crystal growth inhibition regions as a function of subcooling. Discernible by step changes in relative growth rates – commonly by an order of magnitude – CGI regions range from complete inhibition (even hydrate dissociation), through severely to moderately reduced growth rates, ultimately to final rapid/catastrophic growth as subcooling increases. Closely related to induction time data and complementary to this, CGI regions are readily measureable using conventional hydrate laboratory equipment, with subcooling extents – which it is speculated are polymer surface absorption related phenomena – providing a means to assess KHIs more rapidly and robustly, while giving increased confidence in performance under worst case scenario (hydrate present) field conditions. This CGI method is now being increasingly used for field evaluation studies by major operators [Glénat et al., 2011; Glénat et al., 2013; Luna-Ortiz et al., 2014] and can aid in developing new inhibition strategies such as KHI-MEG combinations [Mozaffar et al., 2016].

1.2. KHI FOULING PROBLEMS

Due to the low dosages required (typically >3 % aqueous), KHIs have traditionally been envisaged as a ‘once through’ inhibitor with no attempts made to remove and/or reclaim KHI components. Furthermore, the low dosages used have also likely in part contributed to a not uncommon lack of consideration as to the final destination of formulation components; while doses are low, the potential for accumulation at some point during produced water processing of course still exists. Such accumulation could lead to fouling issues [Hussain et al., 2012].

The most problematic component of KHIs in this respect is the active polymeric component which may comprise up to 20% of a KHI formulation as used in production operations; the remainder being common carrier solvents / synergists such as MEG and EGBE (ethylene glycol butyl ether). Polymer miscibility with water is commonly quite tenuous and sensitive in particular to increases in temperature and/or salinity which may cause it to precipitate, resulting in fouling.

Now that KHIs are seeing widespread use in the field, this issue of fouling an increasingly pertinent one, with various associated problems/concerns emerging, namely:

- KHI polymer precipitation and fouling of water handling facilities such as storage tanks
- Polymer precipitation when produced waters are re-injected into warm/hot reservoir formations, blocking perforations / pore space and so reducing injection efficiency
- Polymer precipitation in MEG reclamation units, causing fouling, a reduction in efficiency, the need for shut down, clean out and disposal of waste
- Concerns over poor polymer biodegradability / regulations with respect to produced water disposal in the natural environment

In light of this, there has been increasing interest in the removal of KHI polymers from produced waters prior to common treatments or disposal. Various methods have been examined, with polymer oxidation (breakdown) showing some promise, with up to 70% removal [Hussain et al., 2012].

KHI removal could encourage more widespread KHI use as an alternative to thermodynamic inhibitors (TI) or to reduce TI quantities required through combined KHI-TI inhibition strategies; something which is currently being hindered in part by increasing operator concerns about KHI handling/disposal post-use.

On the other hand, high concentrations of TI in produced waters can result in a requirement for large MEG regeneration units (high CAPEX and OPEX), particularly at late reservoir life when the water-cut is high. This could adversely affect the economics of field development and/or reduce the ultimate recovery factor. In such scenarios, the combination of TI + KHI could be a very attractive option which can reduce the amount of TI by 20-40 wt% based on case studies conducted by Hydrafact and experimental work at Heriot-Watt University [Mozaffar et al., 2016].

With respect to the above, in the course of developing a method for measuring low concentrations of aqueous polymers in water, research at Hydrafact (a Heriot-Watt Hydrate Group spin-out company), a technique for polymer extraction from aqueous solutions has been found to show potential as a method for polymer removal from produced waters [Anderson R et al., 2013].

2. BACKGROUND

2.1. KHI REMOVAL STUDIES

As noted, the removal method originated in work to develop a technique for the determination of polymer content of produced waters, particularly for low polymer concentrations where accurate measurements are challenging using typical laboratory approaches (e.g. HPLC, FT-IR). The concept was to find a largely water-immiscible solvent which caused significant displacement of polymer from the aqueous phase, concentrating it in the solvent 'treatment chemical' (TC). With the polymer enriched in the TC, measurement of the polymer content of the TC could be carried out accurately. With known mass of TC, produced water, and calibration for polymer partitioning to the TC as a function of aqueous concentration, then the polymer content of the original solution could in theory be determined from measurement of the polymer content of the TC following contact with and separation from the produced water phase.

Various treatment chemicals were examined. During this process, one family was found which apparently displaced all or nearly all (depending on the sample used) PVCap from the aqueous phase, i.e. when calibrations were undertaken it was found that, in addition to being an accurate means to determine aqueous polymer concentration (± 0.006 wt% polymer was readily achieved), up to 100% of the polymer had been

displaced into the TC for some KHIs. Subsequent drying of separated aqueous phases confirmed these findings and lead to the realization that TC extraction could offer a potential solution to the problem of polymer removal from produced waters.

Since initial discovery, work within the context of an industry-funded project at Heriot-Watt University and also internal investigations at Hydrafact Ltd. has focused on confirming the ability of the TC family to displace KHI polymers from aqueous solution at different concentrations, and in the presence of common pipeline fluid components/chemicals such as salts, MEG, methanol, liquid hydrocarbons, scale and corrosion inhibitors.

Studies have primarily focused on PVCap due to it being one of the most effective, widely used and studied KHI polymers. Initial tests on other KHI polymers/formulations have shown some success, however so far it has been found to be most effective with PVCap-type chemistry. Given that MEG and PVCap show excellent synergism with respect to kinetic hydrate inhibition, with small fractions of PVCap (0.5 to 1.0 wt%) offering the equivalent inhibition of 10's of wt% MEG [Anderson R et al., 2011; Mozaffar et al., 2016], the method opens up particular opportunities in this area.

2.2. TREATMENT CHEMICAL PROPERTIES

The first group of treatment chemicals discovered are the fatty alcohols [Anderson R et al, 2013], with the main focus of work being on linear chain normal hexanol, heptanol and octanol. The fatty alcohols are naturally-occurring chemicals which are produced in large volumes synthetically for a variety of industrial purposes. They are generally of low toxicity (typically classed as 'irritants'), low volatility, have high boiling points (Table 1) and are safe to handle, in addition to having good biodegradability. A number of them potentially qualify for PLONOR (Poses Little or No Risk to the natural environment) classification.

Table 1 Boiling point (BP), density and aqueous miscibility of n-fatty alcohols as a function of carbon number (C_n).

C_n	Boiling point (°C)	Density (g/cm ³)	Aq. Misc. (Mass%)
5	138	0.811	2.15
6	157	0.814	0.59
7	176	0.819	0.17
8	195	0.824	0.05
9	214	0.827	0.01
10	233	0.829	< 0.01

The main desirable feature is that they have very low water solubility (Table 1) with very little required to displace PVCap from solution, in addition to being excellent solvents for KHI polymers. So far, tests on a number of members of the fatty alcohol family have shown good polymer displacement properties, giving scope for formulating different mixtures with respect to displacement effectiveness, density, viscosity etc. Densities are typically lower than water (Table 1), but some variants (in terms of the hydrocarbon chain structure) have higher densities. Recently an additional family of treatment chemicals have been found which show equal or greater potential for polymer removal and these are the subject of a further patent application.

3. EXPERIMENTAL

3.1. TREATMENT METHODS

The basic method for the removal technique is as follows (see Figure 1):

- The treatment chemical (TC) is injected into the produced water phase under moderately turbulent / mixed conditions. The injection of the TC causes immediate clouding of the aqueous phase as the polymer is displaced from solution

- Displaced from the aqueous phase, the polymer enters the treatment chemical phase in which it is highly miscible (e.g. complete mutual miscibility for pure n-fatty alcohols and PVCap)
- If mixing is stopped, the aqueous and TC + polymer phases separate due to immiscibility and differing densities; the TC + polymer phase is typically of lower density so gravity settles upwards
- Where some micro-droplets of the TC + polymer phase remain suspended in the water phase, full physical separation can be achieved using standard methods such as centrifugation or coalescing separation

Typically, the dose of TC would be at least ~2 parts (mass or volume) per ~1 part polymer or ~2 parts TC per ~5 parts KHI formulation (polymer typically is at most 20% of a KHI formulation as used in the field) to yield an immiscible TC liquid phase capable of extracting the polymer whilst remaining fluid.

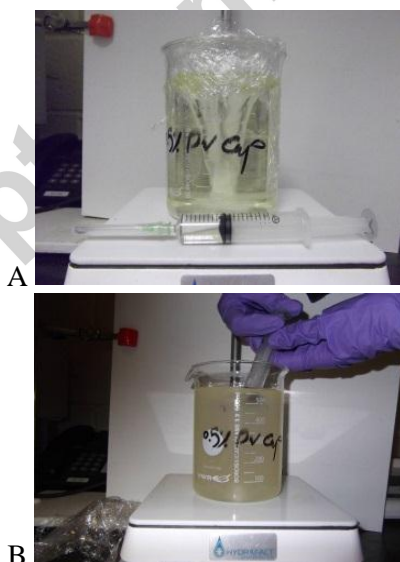
For some TC variants (in terms of the structure of the hydrocarbon chain), dosing in excess of water saturation is not required and KHI polymer can be displaced directly. The disadvantage here is that the displaced polymer precipitates directly as a solid/semi-solid making handling more difficult in terms of processing.

As noted, typically the TC + polymer phase is of lower density than the produced water, causing it to settle upwards. There is however potential for gravity settling downwards using TCs with a higher density than water and/or those where dosing in excess of water saturation is not required.

3.2. EXPERIMENTAL METHODS

Polymer removal levels reported here were ultimately determined by a gravimetric method. However, a UV-Vis technique was also developed and used, primarily as rapid means for measuring removal levels, e.g. for TC 'screening'. Both approaches are based on measuring remnant polymer in the aqueous phase solution after treatment and TC + polymer physical separation.

In both cases, KHI solutions to be tested are prepared gravimetrically at a known mass% aqueous. The treatment chemical (TC) is then added under mixed conditions (Figure 1 B).



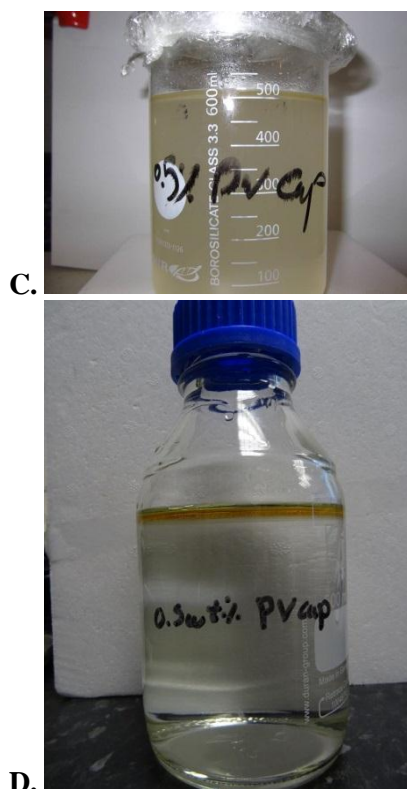


Figure 1 Images of the TC method demonstrated in the laboratory. (A) 0.5 mass% PVCap aqueous solution and TC in a syringe. (B) Injection of the TC into the PVCap solution under mixed conditions, which induces polymer drop-out and partitioning into the TC phase. (C) After mixing is stopped, the bulk of the TC + polymer phase gravity settles and depending on the system (TC, water composition, presence of other chemicals), micro-droplets may be left in suspension, in which case physical separation can be encouraged by e.g. centrifugation; (D) showing post-centrifugation.

Following a short period of mixing – which induces polymer displacement to the TC phase – the sample is left at static to settle (Figure 1 C). If gravity settling is not sufficient to clarify the water phase, then the sample is centrifuged or passed through a coalescing medium to achieve this (Figure 1 D).

Following this, in the case of the gravimetric method, the ‘treated’ water is drained, weighed, and then oven dried. Once the water has been evaporated, the sample is weighed again to determine the mass of polymer remaining post-treatment.

The alternative UV-Vis method utilizes the strong absorbance of UV by double bonds (and relative transparency of water) common to polymers such as PVCap. A *Hitachi U-3010* dual beam UV-Vis spectrometer was used for the work reported here.

Figure 2 shows UV-Vis spectra for different solutions of aqueous PVCap (water baseline) with the region where calibration for aqueous concentration is possible highlighted. As can be seen, PVCap at levels of just 0.03125 mass% or less can be readily and repeatedly detected from absorbance in the range 300-400 nm wavelength.

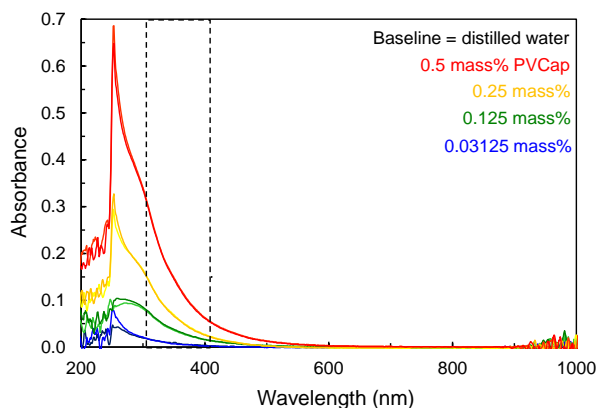


Figure 2 UV-Vis spectra for different solutions of PVCap showing the region where calibration for aqueous concentration is possible. Similar color pairs are repeats of the same sample.

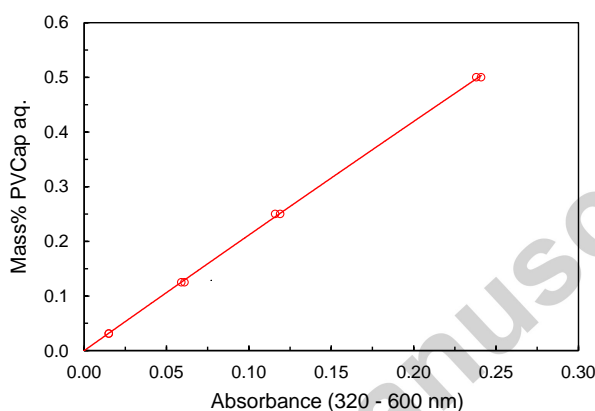


Figure 3 UV-Vis spectra calibration (absorbance at 320 nm compared to baseline at 600 nm wavelength) derived for PVCap-water solutions.

Figure 3 shows an example calibration for PVCap in distilled water using absorbance at 320 nm. Calibration data show the maximum absolute deviation on test samples to be ± 0.004 mass% PVCap.

4. RESULTS AND DISCUSSIONS

4.1. POLYMER REMOVAL EFFECTIVENESS

The method has primarily been focused on PVCap removal as noted. For this, it has been found – at standard temperature and pressure (STP) conditions – to be effective in removing up to 100% PVCap (within measurement limits) from the aqueous phase depending on the nature of the sample (particularly average molecular weight). It has also shown varying effectiveness for other commercial KHI polymers, although it seems particularly suited to PVCap-type chemistry.

Figure 4 shows mass% PVCap polymer removed from aqueous solution by the TC method as a function of n-fatty alcohol carbon number. Also shown is aqueous solubility data for the n-fatty alcohols (see Table 1). As can be seen, at carbon numbers of >6 , the n-fatty alcohols become largely immiscible in water. For this PVCap sample, removal effectiveness peaked at 95 mass% or greater removed with n-hexanol to n-octanol.

Where a small fraction of some remnant dissolved aqueous solids have been detected post treatment (i.e. $< 100\%$ apparent removal), it is suspected these are lower molecular weight polymer strands which have a much higher water miscibility or ‘contaminants’ in polymer samples, e.g. un-polymerized monomers. Treating the water at a higher temperature aids removal of the former; all tests reported here being conducted at ambient laboratory temperature.

While work has focused on PVCap, studies have also been carried out on other different commercial polymers and KHI formulations (polymer with solvents /synergists) with varying degrees of success (Figure 5), suggesting the potential method is not confined to PVCap-type chemistries alone.

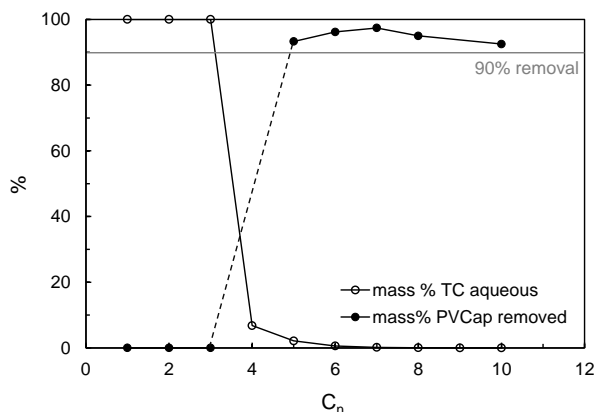


Figure 4 Mass% PVCap polymer removed from aqueous solution by the TC method as a function of n-fatty alcohol carbon number. Also shown is aqueous solubility data for the n-fatty alcohols.

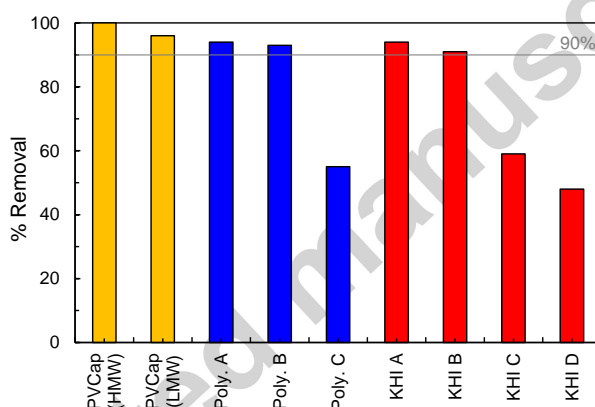


Figure 5 Example data for mass% polymer removed from aqueous solution for PVCap, three commercial base polymers (Poly. A, B and C), and 4 commercial KHI formulations (KHIs A-D).

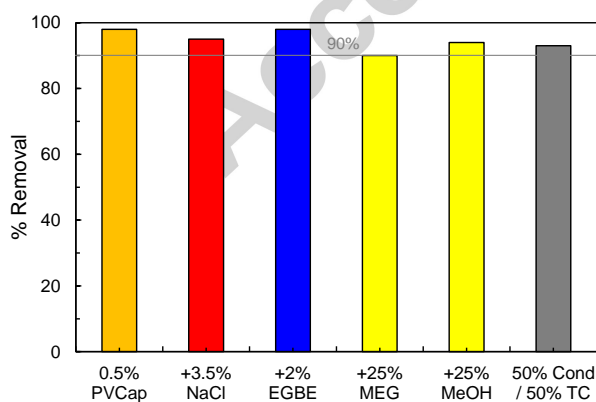


Figure 6 Example data for mass% PVCap polymer removed from aqueous solution in the presence of salt, common KHI solvent/synergist ethylene glycol butyl ether (EGBE), MEG and methanol (MeOH) and condensate (50% dilution of treatment chemical).

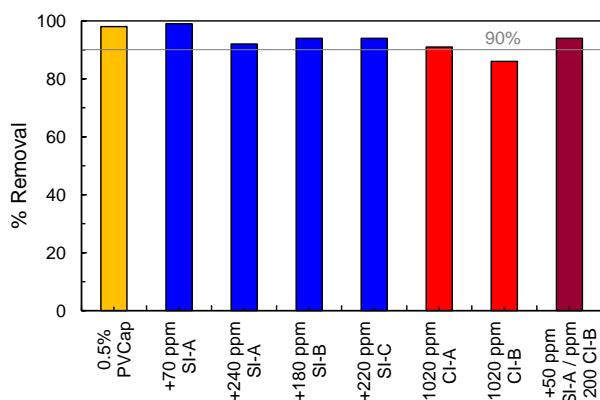


Figure 7 Example data for %PVCap polymer removed from aqueous solution in the presence of various commercial corrosion (CI) and scale inhibitors (SI) at varying doses.

4.1.1. Effect of Salts, MEG, Methanol and Liquid Hydrocarbons

Produced water salinity, whilst commonly enhancing KHI performance, can encourage polymer drop-out if salt levels are high. This property means salinity does not affect the TC method (e.g. Figure 6) and can even promote higher removal levels. With respect to thermodynamic inhibitors, TC removal effectiveness remains largely unaffected to quite high concentrations of methanol and MEG (Figure 6) at STP. Treatment at higher temperatures, such as those associated with MEG regeneration, could improve removal levels in such systems.

It is envisaged treatment process would be carried out after separation of the bulk of liquid hydrocarbons (e.g. condensate) from produced water. However, at this stage there still may be modest quantities of liquid hydrocarbon present in the water phase either in solution or as suspended droplets carried over. As TCs are miscible with liquid hydrocarbons, this could affect removal efficiency potentially. As seen in Figure 6, dilution of the TC by 50% condensate does not significantly impact removal effectiveness.

4.1.2. Effect of Scale and Corrosion Inhibitors

Various studies have been undertaken to assess what effect common pipeline chemicals such as scale and corrosion inhibitors might have on polymer removal effectiveness.

Figure 7 shows example results for mass% PVCap polymer removed by the TC method for one TC member for different commercial scale inhibitors (SI), corrosion inhibitors (CI) and combinations at various dosages. As can be seen, the majority of the tested SI's and CI's do not show a significant impact on TC performance, only at higher, less typical dosages of corrosion inhibitor, does removal efficiency apparently reduce somewhat.

4.2. EFFECT OF TREATMENT ON POLYMER CLOUD POINT AND FOULING

As noted, when KHI solutions are exposed to high temperatures, clouding and polymer drop-out can occur, leading to coagulation of the precipitated polymer and fouling. For example, untreated aqueous PVCap solutions typically show cloud points of ~35-40 °C, beyond which further polymer precipitates and coagulates with increasing temperature. Moderate levels of MEG do not impact this behavior greatly; only when systems become MEG-dominated do cloud points rise significantly.

As shown in Figures 8 and 9, in contrast, TC method treated fluids typically remain clear up to high temperatures / the boiling point of the aqueous phase. Only where the treatments has not been fully effective (potentially some lower molecular weight strands remaining as noted) is some slight clouding seen at higher temperatures, but with no solids drop-out/surface adherence / coagulation observed.

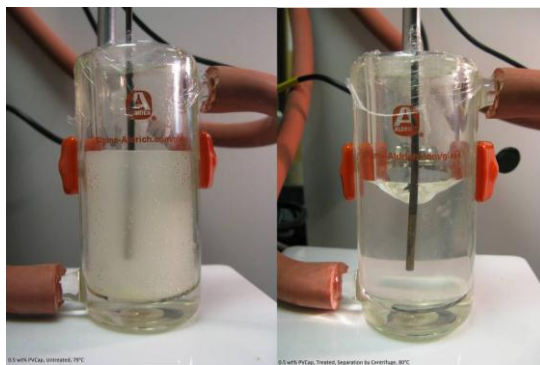


Figure 8 Images of untreated (left) and treated (right) 0.5 mass% PVCap aqueous solutions at 80 °C. In the untreated case, effectively complete polymer drop-out/clouding has occurred with coagulation of settled polymer causing the stirrer to become stuck. In contrast, the treated fluid remains clear.

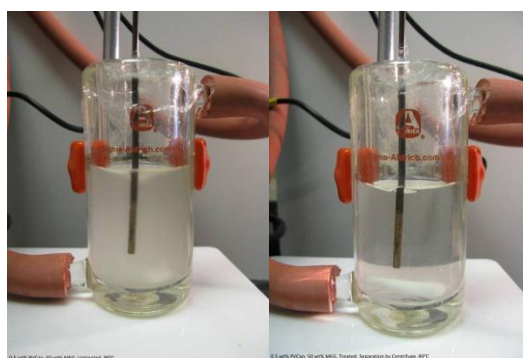


Figure 9 Images of 50 mass% MEG / 0.5 mass% PVCap at ~90 °C (left) and the same solution post polymer-removal treatment also at ~90 °C (right). In the untreated case, polymer drop-out/clouding is observed whereas the treated fluid remains clear.

5. CONCLUSIONS

A technique has been developed for KHI removal from produced waters where small quantities of organic water-immiscible solvents are used to extract KHI polymer from the produced water, leaving it largely or wholly KHI-free and so reducing or eliminating fouling problems during subsequent water processing or disposal. The solvents used in the method are common industrial chemicals used for a variety of industrial purposes and are relatively benign with some having potential for PLONOR status. The physical separation component of the method only requires existing technologies such as gravity settling, centrifugation or coalescing separation.

Polymer removal effectiveness is not significantly affected by the presence of common pipeline chemicals such as salts, modest quantities of liquid hydrocarbons, corrosion and scale inhibitors. The chemistry of the treatment chemical can be adjusted to optimize effectiveness for different polymers and ease of physical separation.

As the method works for KHI removal from rich-MEG systems, it provides an opportunity for combining KHI with MEG; an option which could increase the application of KHIs. Furthermore, considering the fact that 1% KHI could replace 20-40 wt% MEG, the technique could significantly reduce MEG injection rates and/or increase field life, hence recovery factor.

The method also opens up opportunities for potential KHI recovery and novel KHI design to avoid problems associated in water processing and disposal.

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Highlights

- A technique is developed to remove Kinetic Hydrate Inhibitors from produced water.
- Treatment chemicals employed in this method are commonly used industrial chemicals.
- Physical separation component of the method only requires existing technologies.
- The TC chemistry can be adjusted to optimise effectiveness for different polymers.
- The method opens up opportunities for potential KHI recovery and novel KHI designs.