DEVELOPMENT OF A CRYSTAL GROWTH INHIBITION BASED METHOD FOR THE EVALUATION OF KINETIC HYDRATE INHIBITORS

Ross Anderson¹²*, Houra Mozaffar¹ and Bahman Tohidi¹²
1. Centre for Gas Hydrate Research, Institute of Petroleum Engineering
   Heriot-Watt University, Edinburgh, EH14 4AS
   UNITED KINGDOM
2. Hydrafact Ltd.
   Heriot-Watt University Research Park, Edinburgh, EH14 4AP
   UNITED KINGDOM

ABSTRACT

Over the past decade, low dosage hydrate inhibitors (LDHIs) – which include anti-agglomerants (AAs) and kinetic hydrate inhibitors (KHIs) – have seen increasing use as a cost effective technology for gas hydrate control in the oil and gas industry, offering significant CAPEX/OPEX advantages when compared with traditional thermodynamic inhibitors (e.g. methanol, glycols). While AAs prevent agglomeration/plugging, KHIs are primarily understood to be nucleation inhibitors, inducing an extended ‘induction time’ at a specific subcooled condition before hydrate nucleation can proceed to growth. The best known KHIs are water soluble poly-n-vinylamides such as poly-n-vinylcaprolactam (PVCap), poly-n-vinylpyrrolidone (PVP) and related polymers. As KHIs are seen primarily as ‘nucleation delayers’, evaluation is typically undertaken through measurement of induction times as a function of various parameters at the conditions of interest. However, as nucleation is stochastic by nature, obtaining repeatable/transferrable data is often highly problematic and time-consuming, making robust evaluation difficult. Here, we demonstrate that less well investigated aspect of KHI polymers – their ability to inhibit crystal growth – is considerably simpler to quantify than nucleation inhibition. Beginning at low aqueous concentrations (e.g. > 0.1 mass% aqueous), PVCap and other KHI polymers induce a number of highly repeatable, well-defined hydrate crystal growth inhibition (CGI) 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, CGI regions are readily measurable using conventional hydrate laboratory equipment, with subcooling extents – which it is speculated are polymer crystal surface absorption related phenomena – providing a means to assess KHIs more rapidly and reliably, while giving a increased confidence in performance under worst case scenario (hydrate present) field conditions.

Keywords: gas hydrates, KHI, methane, natural gas, experimental data, crystal growth, inhibition

* Corresponding author: Phone: +44 (0)131 451 3798 Fax +44 (0)131 451 3127 E-mail: ross.anderson@pet.hw.ac.uk
**NOMENCLATURE**

- $\Delta T_{s-I}$: Temperature difference from s-I hydrate phase boundary [°C]
- $\Delta T_{s-II}$: Temperature difference from s-II hydrate phase boundary [°C]
- $\Delta P_h$: Change in pressure due to hydrate formation [bar]
- CIR: Complete (hydrate) Inhibition Region
- CGI: Crystal Growth Inhibition
- KHI: Kinetic Hydrate Inhibitor
- PVCap: Poly-n-vinylcaprolactam
- PVP: Poly-n-vinylpyrrolidone
- RFR: Rapid (KHI) Failure Region
- RGR: Reduced (hydrate) Growth (rate) Region
- SDR: Slow (abnormally, hydrate) Dissociation Region
- SG: Second Germination (KHI test method)
- $t_i$: Hydrate nucleation induction time [hrs]

**INTRODUCTION**

Low dosage Kinetic Hydrate Inhibitors (KHIs) have seen increasing use as a cost effective technology for gas hydrate control in the oil and gas industry, offering significant CAPEX/OPEX advantages over traditional thermodynamic inhibitors (e.g. methanol, glycols) [1-3]. The widespread understanding within the industry and academia is that KHI polymers (e.g. PVCap, poly-n-vinylcaprolactam) delay/slow down/interfere with the process of hydrate nucleation by surface adsorption on nuclei [4-7], forcing in an increased ‘induction’ or ‘hold’ time, $t_i$; the time that passes at a specific subcooling ($\Delta T$ from the hydrate phase boundary at pressure, $P$) within the hydrate stability zone (HSZ) before critical nuclei are achieved and hydrate nucleation to proceed to growth. In theory, if the KHI-induced induction time, $t_i$, at $\Delta T,P$ is greater than the pipeline fluid residence time at that condition, then the KHI should be able to prevent hydrate nucleation / growth, whereby avoiding plugging.

As KHIs are primarily considered ‘nucleation inhibitors’, they are generally developed and tested through laboratory induction/hold time studies [1-3]. The same applies for determining the effects of various parameters including pressure, presence of synergists, salts, liquid hydrocarbons (condensate, oil) and other oilfield chemicals (e.g. corrosion and scale inhibitors). However, there is an inherent problem induction time measurements; nucleation is very sensitive and probabilistic by nature, meaning test results are often highly stochastic and poorly transferable [1-3,8-10]. Furthermore, this tendency to focus on KHIs as nucleation inhibitors often leads to the mistaken impression that the moment a hydrate crystal appears in a KHI inhibited system, the inhibitor has failed. These issues have resulted in low operator confidence in KHIs, restricting uptake by the industry, even though they are now being used successfully in the field [1,2].

To overcome the problem of poor reproducibility of KHI tests, TOTAL developed and used for a number of years a specific procedure in their semi-industrial hydrate flow loops they termed the “second germination” (SG) method. This proved to be very efficient in their hydrodynamic, through tubing flowing test conditions [8]. The procedure was subsequently applied in 2006 to autoclave cells with respect to tackling the ongoing problem of stochasticity in laboratory KHI data [9]. In Duchateau et al. [10,11] (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. In summary, the SG method involves forming first forming hydrate at high subcooling, then dissociating this hydrate before then re-cooling to measure $t_i$ and/or the subcooling of hydrate formation at constant cooling rate. By maintaining the temperature close to the hydrate phase boundary during the dissociation step, it was concluded that ‘nuclei’ of some form – related to the phenomenon of ‘hydrate history’ – were preserved, and that these aided more consistent nucleation/growth patterns when re-cooling to form hydrate (i.e. the ‘second germination’), resulting in much more repeatable data.

Beginning in late 2008, within the context of an ongoing Joint Industry Project (JIP), work began at Heriot-Watt University, UK, to develop a new crystal growth inhibition (CGI) based method for KHI evaluation. The goal of development was to circumvent the inherent problem of stochasticity in induction time data, and, building on the basic principles of the SG technique, to provide a more reliable means for KHI assessment. This work has proved very successful, yielding a novel, rapid and reliable means for KHI assessment in addition to
providing new insights into KHI inhibition mechanisms.

In the companion paper to this work [12], we report the application of this new CGI method to evaluate the relative hydrate inhibition performance of a number of commercial KHI + corrosion inhibitor (CI) formulations for a gas condensate system; the aim being to assess its suitability for KHI field evaluation studies. Here, the basis of the CGI approach and its development as a method for KHI evaluation is summarised.

BACKGROUND TO THE CGI METHOD

As noted, the primary goal of CGI method development was to bypass the stochasticity inherent to nucleation processes (thus induction time measurements) and instead focus on KHI inhibition properties that were more consistent (i.e. repeatable) / more readily quantifiable as a means for evaluation. Certainly, literature studies strongly suggested that such properties existed; the following three findings being particularly significant:

1. Observations from single crystal studies that KHI polymers can apparently completely inhibit hydrate crystal growth under certain PTX / subcooled conditions [13-15]
2. Reports that KHIs can induce abnormally slow dissociation / metastability of gas hydrates outside the thermodynamic stability region [16,17]
3. Demonstration that in systems where the aqueous phase has been ‘seeded’ with nuclei of some sort (hydrate history, i.e. SG method), KHIs can still significantly inhibit hydrate nucleation(?) and/or growth [8-11]

While individually each of these findings have their own specific implications – as discussed below – clearly, taken together they provide very strong evidence that KHI inhibition properties extend well beyond the nucleation phase, influencing hydrate behaviour throughout the entire growth–dissociation cycle. Following on from this, presuming heat/mass transfer in systems was not significantly limited, then observations support a strong thermodynamic component to KHI controls on hydrate phase behaviour. Given that adsorption of polymers on hydrate crystal surfaces is generally accepted as the primary mechanism of KHI inhibition, and surface adsorption is thermodynamic process, it follows that such behaviour should not be unexpected.

In terms of specific implications of each finding, with respect to (1), it can be readily concluded that if KHI polymers can completely inhibit the growth of hydrates in water soluble organic liquid hydrate forming systems, then the same should likely apply in more ‘realistic’ hydrocarbon gaseous (e.g. methane, natural gas) hydrate forming systems; a highly desirable property should this be the case.

Finding (2) indicates that hydrate formed in KHI systems may not be structurally/compositionally identical to that formed in KHI-free systems; abnormally slow dissociation equates to metastability which implies a ‘more stable than normal’ solid clathrate type phase, e.g. a polymer-hydrate complex. Certainly, if KHI polymers do strongly absorb on hydrate surfaces in a regular fashion, this seems perfectly plausible.

Finally, finding (3) suggests that if ‘hydrate history’ does represent hydrate ‘nuclei’ of some form, then this could potentially be construed as KHIs strongly inhibiting after nucleation, adding further support to (1).

Based on the above considerations, as part of method development, it seemed logical to examine in more detail the ability of KHIs to inhibit hydrate growth in gaseous hydrocarbon systems when viable crystals were actually present; i.e. taking the SG method one step further and testing under ‘worst case scenario’ conditions.

To do this, instead of allowing all hydrate to dissociate leaving only hydrate history as per the SG method, a small, but measurable fraction of hydrate could be retained (typically > 0.5% of aqueous phase as hydrate) following the first growth-dissociation cycle, ahead of cooling back into the hydrate region to observe growth patterns. In this sense, all primary ‘nucleation’ processes would be circumvented, with hydrate growth patterns solely representing the ability of the KHI polymer to inhibit further development of existing, viable crystals.

Upon undertaking such studies, it was found that, far from the KHI having ‘failed’ in the sense that crystals were present, instead, at low hydrate fractions (typically > 0.5% of water converted)
KHI polymers (PVCap, PVP, commercial polymers) were found to be able to completely inhibit growth (in agreement with findings for THF systems at atmospheric pressure) and/or induce hydrate dissociation within the normal thermodynamic stability region to significant subcoolings. Furthermore, this powerful crystal growth inhibition property extend to higher subcoolings, manifesting as severe to increasingly reducing growth rate suppression before hydrate growth patterns finally reverted to those for KHI-free systems. Significantly, in the majority of cases, the boundaries between different inhibition regions were found to be clearly definable, typically by order of magnitude step changes in growth rates as they were crossed, facilitating mapping of relative boundary subcooling positions for comparative performance evaluation purposes.

While it is outwith the context of this work to discuss in detail the origins of these crystal growth inhibition ‘regions’, it is currently understood that they result from variable polymer interference – namely by adsorption on those faces favoured for crystal development, as originally observed in single crystal literature studies [13-15] – in the normal process of hydrate crystal growth as a function of subcooling/driving force.

Whatever the exact mechanisms responsible for the observed behaviour are – investigations are ongoing – regions are clearly discernible and have been defined internally (within the JIP research project) as follows:

**Complete Inhibition Region (CIR)**
Hydrate growth, even when crystals are present (in small fractions) is inhibited indefinitely and hydrates initially formed at high subcoolings may dissociate if taken into this region even though they would be expected to be thermodynamically stable.

**Reduced Growth rate Region (RGR)**
Hydrate growth is consistent, but growth rates clearly are inhibited by the polymer. Variability in degree of inhibition is high, ranging from severe (growth rates a number of orders of magnitude less than for a KHI-free system) to limited as subcooling increases. This region may be further subdivided based on clear changes in growth rates within it (e.g. very slow, slow, moderate).

**Typical growth rates order of magnitude (% water / hr) Growth rate description**

<table>
<thead>
<tr>
<th>Region</th>
<th>Growth rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIR</td>
<td>0.00</td>
</tr>
<tr>
<td>RGR (VS)</td>
<td>0.01 (&lt; 0.05)</td>
</tr>
<tr>
<td>(S)</td>
<td>0.1 (≥ 0.05 to &lt; 0.5)</td>
</tr>
<tr>
<td>(M)</td>
<td>1 (≥ 0.5 to &lt; 5)</td>
</tr>
<tr>
<td>RFR</td>
<td>10 (≥ 5)</td>
</tr>
<tr>
<td>SDR</td>
<td>Dissociation rate one order of magnitude less than for no KHI</td>
</tr>
</tbody>
</table>

Table 1. Classification of crystal growth inhibition (CGI) regions based on orders of magnitude change in hydrate growth rates (% water converted to hydrate per hour), as commonly observed across region boundaries.

Defining characteristics of the hydrate slow dissociation region (SDR), which corresponds to the ‘history’ region are also shown.

**Rapid Failure Region (RFR)**
Growth rates appear largely unaffected by the presence of the polymer and are essentially comparable with those for the KHI-free system.

**Slow Dissociation rate Region**
In addition to crystal growth inhibition regions, the region of anomalously slow hydrate dissociation (in the presence of KIH polymers) outside the hydrate phase boundary for systems previously reported in the literature [16,17] has been similarly found to be clearly definable by order of magnitude increases in dissociation rates (i.e. return to normal, KHI-free rates) at its boundary. This has been found to correspond to the ‘history’ region as previously reported by others [8-11].

In terms of delineating specific CGI regions experimentally, while identification of clear changes in growth rate at particular subcoolings is generally straightforward, classification within defined regions according to growth rate – a ‘relative’ property – is not as simple. Table 2 shows the classification approach adopted here.

In summary, the properties of the complete inhibition (CIR) and rapid failure regions (RFR) can be very specifically defined; for the former, growth is indefinitely inhibited (with potential hydrate dissociation) and in the latter, growth is at least equal to that for the same system in the absence of a KHI. Likewise the region where reduced growth rate (RGR) is observed can be
simply defined as ‘growth being slower than the KHI-free system’ for the same PTX conditions. However, subdivision of the RGR – which has proven important given the wide range of inhibited growth rates observed – requires some specification of actual/relative growth rates. For simplicity, a growth rate order of magnitude classification has been adopted, which is deemed appropriate based on results to date and the obvious apparent relationship between CGI regions and exponential-like induction time trends, as discussed later in this manuscript. As an example, a growth rate of 0.03% water converted per hour would be classed as ‘very slow’ (VS), 0.07% / hr would be slow (S) and 0.6% / hr would be medium (M), so long as the value is less than that for the no KHI case. If the value is equal to that for no KHI, behaviour is classed as RFR (rapid failure), i.e. the KHI is failing to appreciably inhibit hydrate growth.

EXPERIMENTAL

Equipment and Materials
Over the past 2.5 years, tests using the CGI method have been carried out on a wide range of gas–aqueous and gas–aqueous–liquid hydrocarbon systems in the presence of KHI polymers, as listed in Table 3. Here, example results are reported for methane–water and standard North Sea natural gas (NG)–water systems with PVCap aqueous.

Tests described here were carried out by constant volume methods (although constant pressure gas consumption tests have yielded identical results); i.e. hydrate detection was by change in pressure due to gas consumption. Tests were conducted on in-house (Hydrafact / Heriot-Watt University) designed / built 280 ml volume high pressure (max 410 bar) stainless steel or titanium (salt compatible) autoclave cells, as illustrated in Figure 1 (tests have also been repeated successfully in rocking cells, confirming transferability). For these set-ups, cell temperature is controlled by circulating coolant from a programmable cryostat through a jacket surrounding cells. Temperature is determined by platinum resistance thermometers (PRT, ± 0.1 °C), with pressure measured by either strain standard gauge (± 0.07 bar) or precision Quartzdyne (± 0.0007 bar) transducers; these being regularly calibrated against a dead weight tester. Cell pressure and temperature are continually monitored and recorded by computer.

The PVCap used in experiments was Luvicap-EG base polymer (average molecular weight / AMW = ~7000) with the ethylene glycol solvent removed by vacuum oven drying (supplied by BASF). Methane, supplied by BOC, was 99.995% pure. The composition of the natural gas used (also supplied by BOC) is given in Table 2. Deionised water was used in all tests, with aqueous PVCap solutions prepared gravimetrically.

![Figure 1. Schematic illustration of the 280 ml high pressure (max 410 bar) autoclave cells used in experiments.](image)

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>89.41</td>
</tr>
<tr>
<td>Ethane</td>
<td>5.08</td>
</tr>
<tr>
<td>Propane</td>
<td>1.45</td>
</tr>
<tr>
<td>i-Butane</td>
<td>0.18</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.26</td>
</tr>
<tr>
<td>i-Pentane</td>
<td>0.06</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.55</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.93</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>0.06</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.02</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>
Cell aqueous liquids volume fractions were typically 0.80-0.85. The reason for using quite high liquid volume fractions was twofold: (1) to give high sensitivity for detection of hydrate (the smaller the gas head/moles of gas, the greater the pressure change due hydrate formation) and (2) to minimise dead volume / aqueous phase unwetted internal cell surfaces where hydrate might be able to grow slowly from polymer-free condensed water (e.g. a disequilibrium ‘top of line condensed hydrates’ type scenario). To aid further in the latter and ensure mass transfer/reaction rates were maximised, impeller speed was typically set at 750 rpm, giving good shearing/co-mingling of aqueous and gaseous phases.

CGI Experimental Procedure
In the companion paper to this work [12], a standardised CGI experimental procedure (e.g. for commercial formulation assessment) is described. Tests described here followed the same general methodology, albeit with some variations (e.g. in heating cooling rates, hydrate fraction present) as systems were explored in detail from a more specific R&D perspective. In summary, the general methods used were as follows:

1. Following gas charging to initial pressure at a temperature outside the hydrate region, the system was first cooled rapidly to a high subcooling to induce hydrate formation
2. Following initial rapid hydrate formation, the system was then warmed in steps to dissociate most of the hydrate formed, leaving only a small fraction remaining (typically < 0.5% of water converted), while assessing the extent of any anomalously slow dissociation behaviour
3. Cell temperature was then reduced again at a constant cooling rate (typically 1.0 °C / hr, but both slower and faster rates were commonly employed as part of investigations) to observe clear changes in growth rate as a function of subcooling
4. Steps 2-3 were repeated a number of times to examine repeatability
5. Finally, following a repeat of Step 2, the system was step-cooled with a small fraction of hydrate present to confirm the extent of the complete inhibition and very slow growth regions where appropriate

From PT data generated using the above procedure, changes in relative growth rates were used to delineate obvious changes in KHI-induced crystal growth inhibition regions, allowing mapping and description of these for the systems under study. In all cases, the fraction of hydrate present at a given condition was calculated from system composition and volumetric data using the in-house HydraFLASH® thermodynamic model [18].

RESULTS AND DISCUSSION
As noted, CGI experiments have been carried out on a wide range of systems within the context of the current JIP; these are listed in Table 3. Here, to present the method, we use example results for methane–water–PVCap and natural gas–water–PVCap systems. Ahead of this, to put KHI inhibited system behaviour in context, we show results for a simple PVCap-free methane–water system carried out in the same autoclave set-up type following the same procedures.

KHI-Free Methane–Water System
Figure 2 shows example cooling and heating curves for the blank (no PVCap) methane–water system plotted as pressure versus temperature. The s-I methane hydrate phase boundary (literature experimental data interpolation) is shown for comparison. On the first cooling run, as there is no ‘hydrate history’ in the system, nucleation occurs at a subcooling; in this case at $\Delta T = -5.5$ °C. Growth is then rapid (14.2% water converted per hour) and equilibrium achieved in around 20 minutes.

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![Figure 2. PT plot showing typical hydrate nucleation / growth and subsequent growth / dissociation behaviour in response to temperature changes for a well mixed methane–water system (one degree of freedom in the presence of hydrate). Points are every 5 minutes.](image-url)
As the system is two component (C), if three phases (P) are present (Hydrate + Liquid + Gas) there is one degree of freedom (F), meaning PT conditions will follow the hydrate phase boundary (unless the system is component, heat or mass transfer limited). As can be seen, this is what occurs upon hydrate growth; PT conditions follow the phase boundary upon further cooling. When heated rapidly, hydrate dissociation occurs rapidly in response as the system attempts to regain equilibrium. When heating is stopped and re-cooling initiated with a small fraction of hydrate present (1.4% of water), hydrate growth begins again the instant PT conditions enter the stability region and subsequently follow the phase boundary as expected.

Example Results: Methane with PVCap
As part of the ongoing JIP project, hydrate growth and dissociation patterns in the presence of PVCap have been studied for a range of concentrations from 0.1 to 5.0 mass% aqueous. Here, example data for 0.25 and 0.50 mass% PVCap aqueous are presented.

Figure 3 shows example experimental cooling and heating curves for methane–water–PVCap (0.25 mass% aqueous) plotted as pressure versus temperature. The s-I methane hydrate phase boundary is shown for comparison. On the first cooling run with no history (1.0 °C / hr) nucleation eventually occurs some six hours after PT conditions entered the hydrate region at ΔT_{s-I} = −5.6 °C; a similar subcooling / pressure to the KHI free case presented in Figure 2. However, in contrast to the KHI-free case, subsequent hydrate growth is not rapid, but rather is slow and controlled, with PT conditions apparently closely following a ‘boundary’ which parallels the hydrate phase boundary for the system at a generally fixed subcooling of −5.2 °C. This pattern continues until more than 3% of water is converted to hydrate, at which point the cell temperature was heated rapidly to dissociate the hydrate present.

Upon heating, dissociation only becomes marked at a temperature some 3.5 °C higher than the phase boundary. When cooled to give ΔT_{s-I} = < +3.5 °C, the dissociation rate reduces abruptly.

Following the above, the temperature of the system was then cooled back into the hydrate region and held there in preparation for a cooling run with a small fraction of hydrate present. However, as can be seen in Figure 3, even though PT conditions were within the thermodynamic hydrate stability region for the system, dissociation continued, albeit at a very slow rate.

When cooling was subsequently initiated (0.2 °C / hr) with a small fraction (~0.15% water as hydrate) of hydrate present, no growth was observed until ΔT_{s-I} = −2.6 °C, at which point ΔP_h began to increase again, but only slowly. When ΔT_{s-I} reached −5.2 °C, growth rates picked up in earnest and again PT conditions steadily followed the ‘boundary’ which previously became apparent in the first run. Thus we can conclude from this data we apparently have at least 4 clear regions of KHI-induced growth/dissociation behaviour: (1) a region where no growth/dissociation is observed (2) a region where slow growth is observed, (3) a region where moderate growth is observed and (4) a region where slow dissociation is observed. These patterns can be observed over many repeat runs and regions are the CIR, RGR(S), RGR(M) and SDR respectively, as previously discussed.

Clearly, in the CIR, PVCap-induced complete hydrate growth inhibition is supported by the fact that hydrate was actually observed to dissociate. This is common to this region, but alone this behaviour at a single subcooling cannot be used to determine the total extent of the CIR.

![Figure 3](image-url)
In the CGI procedure, this is typically done by step-cooling with a small fraction of hydrate present. Figure 4 shows pressure drop due to hydrate formation ($\Delta P_h$) and temperature difference from the s-I hydrate phase boundary ($\Delta T_{s-I}$) data for a step cooling run with hydrate present for the 0.25% PVCap aqueous with methane example system at ~70 bar plotted as a function of time.

As can be seen, from 5 hours onwards, at a subcooling of 4.4 °C, growth is steady at 0.02% water converted per hour, indicating RGR(VS) conditions. Cooling to $\Delta T_{s-I} = -5.3$ °C results in a sudden increase in $\Delta P_h$ as hydrate begins to grow at a moderate pace, supporting constant cooling runs which defined the subcooling boundary for this as $\Delta T_{s-I} = -5.2$ °C. Subsequent heating to a temperature just outside the hydrate region at $t = 30$ hrs results in very slow dissociation (SDR) conditions. Recooling to a subcooling of 2.3 °C with 0.38% water present as hydrate at $t = 57$ hours results in no growth observed for 15 hours. Only when cooled further to $\Delta T_{s-I} = -2.7$ °C is very slow growth finally observed, confirming the extent of the CIR and supporting previous observations from constant cooling runs.

Clearly, the ability of PVCap at 0.25% to inhibit hydrate growth is limited beyond the RGR(S)/M boundary where PT conditions follow this boundary upon further cooling. However, rapid cooling runs indicate that some CGI properties are retained up until a subcooling of ~8 °C where for ‘seeded’ (history or hydrate present) conditions, growth typically immediately commences at a rapid rate; an example run being shown in Figure 3.

Figures 5 and 6 shows example CGI method cooling/heating curves for 0.5 mass% PVCap with methane where the same crystal growth inhibition behaviour can be observed. In Figure 5, PVCap induced hydrate dissociation is strongly evident; upon heating following initial hydrate formation (‘no history’ run), almost all hydrate which formed dissociates upon heating into the CIR even though PT conditions are within the hydrate stability region. This occurs to a significant extent again following a second cooling (‘with hydrate run’) / hydrate formation / heating into the CIR cycle, even though the temperature is over 4 °C within the hydrate region.

Figure 5. PT plot showing example CGI method cooling / heating curves for a methane–water system with 0.5 mass% PVCap aqueous. Points are every 5 minutes.

Figure 6. PT plot showing example CGI method cooling / heating curves for a methane–water system with 0.5 mass% PVCap aqueous. Points are every 5 minutes.
As seen for 0.25 mass% PVCap, there is also a boundary marking the end of PVCap crystal growth inhibition where rapid growth takes place (with hydrate run) immediately following this subcooling (~9.5 °C) being surpassed.

In Figure 6, this consistent rapid growth at $\Delta T_{s-I} = -9.5$ °C is similarly evident (‘no history’ and ‘with hydrate’ rapid cooling run). Likewise, for 0.25 mass%, with 0.5 mass% PVCap, growth rates during ‘with hydrate’ cooling runs (1 °C/hr) indicate both RGR(S) and (M) regions, with PT conditions in the latter case again following a clear CGI boundary as the system is cooled. In the case of 0.5 mass%, the higher polymer concentration results in the CIR, RGR(M) an RFR boundaries being shifted to higher subcoolings: $\Delta T_{s-I} = -5.2$, $-7.2$ and $-9.5$ °C compared to $\Delta T_{s-I} = -2.6$, $-5.2$ and $-8.0$ °C for 0.25 mass% PVCap respectively. Anomalously slow dissociation behaviour in the SDR is also very evident in Figure 6; following hydrate formation, heating into this region sees an initial dissociation spurt, following which growth rates reduce markedly (point clustering) at a condition far from the expected equilibrium one (e.g. compare with the KHI-free system in Figure 2).

At this point it is pertinent to comment on how, within the CIR, PVCap induces hydrate dissociation; polymer surface adsorption driven growth inhibition is well accepted, but at low concentrations, it is the widespread understanding that KHI do not sufficiently depress the activity of water to cause ‘thermodynamic-induced’ inhibition or hydrate dissociation. In addition to PVT data supporting this process, it has also been observed in visual tests carried out as part of the project. Currently, it is understood to be related to polymer interference with the normal process of hydrate reformation following initial rapid growth. It is well established that crystals formed at high subcoolings can adopt very high surface to volume morphologies (e.g. dendrites) as driving force is high. However, when subsequently taken to low subcoolings, crystals reform to more euhedral morphologies in an effort to reduce their surface area / surface free energy. This behaviour has been described for hydrates previously [19]. Reformation to lower surface to volume morphologies requires both a dissociation (on the long axis) and a growth (on short axes) component. It is assumed that the polymer permits the former but inhibits the latter, whereby causing a net volume loss of hydrate crystals, i.e. dissociation.

Using the CGI method to determine crystal growth inhibition boundaries at different pressures allows the delineation of these for the pressure range of interest, as illustrated in Figures 7 and 8 for 0.25 and 0.5 mass% PVCap aqueous with methane respectively. In both cases, boundaries are very consistent, commonly being present at a generally fixed subcooling from the phase boundary for a wide range of pressures (in these cases to 300 bar). For 0.25 mass%, polymer CGI performance improves with increasing pressure; the CIR consistently growing in extent. Studies on a wide variety of systems have shown this to be common; i.e. polymer CGI performance is better at higher pressures in terms to subcooling extent.
The same CGI measurement methodology can of course be readily applied to more complex multicomponent gas systems, including those containing liquid hydrocarbons (e.g. condensate), e.g. as detailed in the companion paper to this work [12]. As an example, CGI method results for a multicomponent North Sea natural gas with 0.5 mass% PVCap aqueous are shown in Figures 9-12.

As can be seen in Figure 9, constant rate ‘with hydrate’ present cooling curves (< 0.5% of water present as hydrate initially) show the same type of behaviour seen for pure methane systems, with no growth at low subcoolings, followed by slow growth then moderate growth with PT conditions then following a clear ‘CGI’ boundary at fixed subcooling as cooling/growth progresses. This data shows how consistent/repeatable this CGI behaviour is. In Figure 10, which shows various cooling/heat run types, this repeatability is particularly evident in cooling runs ‘with hydrate’ present at 1 °C/hr; there are two runs plotted which directly overly each other; i.e. growth patterns were identical in repeat runs.

Data for the step-cooling ‘with hydrate’ run to assess the extent of the CIR are shown in Figures 10 and 11. In Figure 11, it can be seen that at the first step where the subcooling was 7.7 °C, no growth (increasing ΔPₜₙ) was observed for approaching 30 hours. When subcooling was increased to 8.1 °C, ΔPₜₙ was seen to reduce, i.e. hydrate was dissociating, confirming complete inhibition (CIR) conditions. Only when the subcooling was increased further to 8.5 °C subcooling was very slow growth (RGR(S) 0.004% / hr) observed. When subcooling was increased to 10.2 °C, slow grow was observed, confirming initial observations from constant cooling runs. This behaviour is testament to the powerful crystal growth inhibition properties of PVCap; it was able to prevent any hydrate growth at subcoolings up to 8.1 °C for up to 50 hours, even inducing dissociation at this condition, with total active CGI extent exceeding 14 °C subcooling at pressures below 100 bar.

A significant finding of CGI studies is that region boundaries in binary and multicomponent s-II (most stable structure) forming systems typically (PVCap and various commercial polymers) parallel the s-I phase boundary for that gas, as shown in Figures 12 and 13.
This similarity in positioning of CGI boundaries as a function of subcooling suggests KHI crystal growth inhibition strength – presumably related to the strength of adsorption on specific crystal faces – is related to underlying changes in natural crystal growth patterns as a function of subcooling (e.g. favoured growth faces, morphologies).

**CGI Region Relationship to Induction Times**

As KHI induced induction times are currently the primary factor in determining suitability for field use, as part of the JIP project, the relationship between \( t_i \) and CGI regions was investigated early on. Figures 14 and 15 show example plots of measured \( t_i \) data for the 0.5 mass% PVCap aqueous with methane and with the natural gas systems respectively. CGI region boundaries are shown for comparison. In both cases, \( t_i \) measurements were made following CGI tests. To measure \( t_i \), systems were heated to at least 15 °C higher than the phase boundary (although hydrate ‘history’ disappears rapidly outside the SDR region) and kept there for 2 hours before cooling rapidly to set point temperature. The induction time was taken as the time between cell temperature reaching within 0.2 °C of the set point temperature and the time when hydrate growth was first observed from pressure drop.

As can be seen, without knowledge of CGI region boundaries, \( t_i \) data would seem very scattered in that a very wide range of \( t_i \) values is observed for a narrow range of subcoolings (over 2–3 °C), as often observed in such tests. However, when CGI region boundaries are taken into account the reasons for this are clear; as growth rates increase in an order of magnitude type pattern from the CIR (zero growth even if hydrate present) to the RFR (rapid growth/as for KHI free), so induction times exponentially reduce from infinite in the CIR (never nucleates) through very long in the RGR to very short in the RFR, with this CGI region transition often occurring over a relatively small subcooling range. This pattern has so far been found to be ubiquitous in KHI systems (including commercial formulations with real gases, condensates, oils) and means CGI data can be used to assess likely \( t_i \) patterns ahead of making such measurements, increasing efficiency/eliminating needless runs (e.g. where PT conditions fall within the CIR there is no need for a long \( t_i \) measurement as nucleation will not occur).
CONCLUSIONS

In this work it has been demonstrated that less well investigated aspect of KHI polymers – their ability to inhibit crystal growth – is considerably simpler to quantify than nucleation inhibition. Results show that, in a well mixed, mass transfer / component unlimited system, beginning at low aqueous concentrations (e.g. > 0.1 mass% aqueous), KHI polymers induce a number of highly repeatable, well-defined hydrate crystal growth inhibition (CGI) 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, 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 reliably, while giving a increased confidence in performance under worst case scenario (hydrate present) field conditions.

Within the context of an ongoing industry sponsored JIP we have successfully used this method to determine the effects of a wide range of factors (e.g. gas composition, polymer type and concentration, presence of salts, alcohols, liquid hydrocarbons, Table 3) on KHI inhibition performance (extent of CGI regions), gaining new insights into inhibition mechanisms. We have also successfully applied this new method to evaluation of the relative hydrate inhibition performance of a number of commercial KHI + corrosion inhibitor (CI) formulations for an s-II forming gas condensate system as part of KHI field evaluation studies, as discussed in the companion paper to this work [12].

Table 3 List (non-exhaustive) of systems where CGI behaviour has been studies within the context of the ongoing Joint Industry Project (JIP).

<table>
<thead>
<tr>
<th>System</th>
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<tr>
<td>Methane–water–PVCap and –PVP</td>
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<tr>
<td>Methane–water–commercial polymers</td>
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<tr>
<td>Ethane–water–PVCap</td>
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<td>Propane–water–PVCap</td>
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<td>CO₂–water–PVCap</td>
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<td>Xenon–water–PVCap</td>
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<td>Methane–ethane–water–PVCap</td>
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<td>Methane–propane–water–PVCap</td>
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<td>Methane–ethane–propane–water–PVCap</td>
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<tr>
<td>Natural gas–water–PVCap</td>
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<tr>
<td>Natural gas–water–commercial polymers</td>
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<tr>
<td>Cyclopentane–methane–water–PVCap</td>
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<tr>
<td>Methylcyclohexane–methane–water–PVCap</td>
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<td>Methane–hexane–water–PVCap</td>
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<td>Methane–propane–condensate–water–PVCap</td>
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<td>Natural gas–condensate–water–PVCap</td>
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<td>Methane–water–methanol–PVCap</td>
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<td>Methane–water–ethanol–PVCap</td>
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<td>Methane–water–propanol–PVCap</td>
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<td>Methane–water–butanol–PVCap</td>
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<td>Methane–water–ethylene glycol–PVCap</td>
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<td>Methane–water–NaCl–PVCap</td>
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<td>Methane–water–2-butoxyethanol–PVCap</td>
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REFERENCES


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