EVALUATION OF HYDRATE NUCLEATION TRENDS AND KINETIC HYDRATE INHIBITOR PERFORMANCE BY HIGH-PRESSURE DIFFERENTIAL SCANNING CALORIMETRY

Kevin McNamee
Nalco
7705 Hwy 90A, Sugar Land, Texas
UNITED STATES of AMERICA

ABSTRACT
Due to the large number of tests, fluid volumes, and test times for traditional KHI evaluation; it was desirable to develop a quicker KHI performance-screening tool. This paper discusses a potential new method for evaluating KHI performance, which utilizes a high-pressure differential scanning calorimeter to study the nucleation of hydrates. Although the limits of the DSC method do not allow testing under exact field conditions, nor under shear conditions, it could be used to facilitate quicker initial screening of KHIs and evaluate KHI compatibility trends with other chemicals/fluids.

Since hydrate formation is a stochastic event a large number of long traditional experiments are required to account for the dispersion of nucleation times. HP-DSC tests are significantly shorter, resulting in a higher output of data in a shorter time frame. Two DSC methods were explored to develop a quicker KHI screening tool. The first method utilized a stable water-in-oil emulsion to provide a large number of primarily independent nucleation events with uniform nucleation probability, in a single test. This method provides a very high statistical output in a single test, as each droplet can be treated as an individual nucleation event, analogous to a single rocking-cell or autoclave test. The second method was conducted in 100% water-cut systems. Both methods reduce the overall test time required for KHI performance evaluation.

In parallel studies at Nalco and CSM the hydrate nucleation trends were examined on a HP-DSC, for uninhibited and KHI inhibited fluids. The data from a select number of tests will be presented to illustrate the effectiveness of using the DSC for evaluating hydrate nucleation and KHI performance trends. This paper will also provide comparative data between traditional autoclave testing performed at Nalco, and the HP-DSC experiments, in an effort to develop a faster means to evaluate KHI performance.

Keywords: gas hydrates, kinetic inhibitors, hydrate nucleation

NOMENCLATURE
CSM Colorado School of Mines
DSC Differential scanning calorimeter
GHA Gas hydrate autoclave
HET Hydrate equilibrium temperature [°C]
HP High-pressure
KHI(s) Kinetic hydrate inhibitor(s)
KHI-A Proprietary KHI polymer A
KHI-B Proprietary KHI polymer B
Q(t) Heat of formation at time, t [J]
Q_∞ Total heat of formation of peak [J]
PVCap Poly(N-vinyl caprolactam) KHI
R_d Water droplet diameter [microns]
%RSD Percent relative standard deviation
SC Sub-cooling [°C]
INTRODUCTION

Kinetic hydrate inhibitors (KHI) are commonly used for management of hydrates during the production of petroleum fluids [1-3]. KHI inhibition of hydrates is achieved by effectively delaying the nucleation and crystal growth phases of hydrate formation. Traditionally KHI performance is evaluated by various high-pressure testing apparatuses such as rocking-cells, autoclaves and flow-loops. These traditional test methods for KHI evaluation can require large fluid volumes and long test times. Additionally the stochastic nature of hydrate formation results in high dispersion of hydrate formation times, hold-times. For statistical analysis of KHI performance numerous runs are required as a direct result of the large variation in observed hold-times. During the development of new KHIs the long test time and high run requirements can produce a bottleneck in development of new products and analysis of parameters affecting KHI performance. Therefore, it is highly desirable to develop new test methods to improve statistical throughput and decrease test duration. By using a high-pressure differential scanning calorimeter (DSC) new methods for studying hydrate nucleation/formation and KHI performance trends were explored in collaboration with the Center for Hydrate Research at Colorado School of Mines (CSM).

Previous research has shown the ability to use a high-pressure DSC for studying natural gas hydrates [4-12]. Two new DSC methods were developed to evaluate nucleation/formation trends of gas hydrates in KHI inhibited and uninhibited type II hydrate systems. One method utilized a stable water-in-oil emulsion test matrix while the other was conducted in a 100 %WC system. In the first method, a stable water-in-oil emulsion was utilized to provide a high statistical output in a single run, as previously shown by Lechance et al. [8-10]. Using a low water-cut emulsion with a monomodal droplet distribution of < 10 microns, inter-droplet interactions can be drastically reduced. The minimization of inter-droplet interactions results in primarily independent droplet nucleation, while the monomodal droplet size distribution provides a uniform droplet nucleation probability. CSM has also shown that a droplet size of < 10 microns results in 100 % conversion of the droplets to hydrate upon nucleation. Combination of the small droplet size, uniform nucleation probability and minimal droplet interactions provides a test matrix in which each droplet nucleation can be treated as an individual nucleation event. These individual nucleation events occur primarily independent of each other resulting in a high statistical output in a single test. In addition to the high statistical output of the DSC emulsion method, the nucleation times were observed to be highly reproducible. This provides a highly efficient means for studying hydrate nucleation trends.

The second method for studying hydrate nucleation/formation was a 100 %WC system. Although the high statistical throughput was not retained from the emulsion test method, the 100 %WC method was also shown to be a good means of producing reproducible hydrate nucleation. The benefit of a 100 %WC system is the removal of any data discrepancies that could arise from KHI interactions with natural components present in the oil.

This paper describes the nucleation trends observed for the two DSC test methods for uninhibited and KHI inhibited systems. Both methods were observed to exhibit highly reproducible nucleation times in a dramatically quicker time frame than traditional test methods. Additionally, both methods were capable of differentiation between a KHI inhibited and an uninhibited sample. The DSC results were also compared to analogous autoclave testing in emulsion and 100 %WC systems, providing a glimpse at the mechanism for KHI hydrate inhibition.

EXPERIMENTAL

Instrumentation

A high-pressure µ-DSC VII (Setaram) was used to study hydrate formation and dissociation trends in water-in-oil emulsions and 100 %WC systems. The DSC was equipped with two 0.5 cm³
Hastelloy C276 high pressure vessels, with a maximum operating pressure of 400 bar. The operating temperature range of the DSC is from (−45 to 120) °C, with temperature accuracy of ± 0.1 oC, precision of ± 0.02 oC, and programmable heating/cooling rates of (0.001 to 5) oC/min. The pressure is controlled by a gas charging panel capable of charging to pressures from (5 to 1000) bar, with a pressure deviation of ± 0.5 bar.

Autoclave testing was conducted in 450 mL total volume, high-pressure gas hydrate autoclave to measure hydrate induction times in the presence and absence of KHI. The autoclave design used was a GHA 200 Gas Hydrate Autoclave system (PSL Systemtechnik). The 450 cc static chamber is equipped with a magnetically driven stirrer, a cooling jacket and chiller, and is fitted with a head containing a thermocouple, boroscope, analog pressure gauge, and pressure transducer. Software provided by PSL was used to control stirrer rate, and temperature variables. The software also collects pressure data as a function of time. A Nalco custom-built charging panel was used to deliver synthetic natural gas to set pressures. The autoclave temperature and pressure specifications are −10°C to 60°C (with an accuracy of 0.1°C) and a maximum pressure of 200 bar. The autoclave material is Stainless steel (AISI 316 Ti), with Viton® seals, and a sapphire-glass window (used for visual observations with a boroscope-camera).

HET Test Procedure
Emulsions were prepared by the method described by Koh et al. [5, 8-10]. For emulsion and 100 %WC testing ≥ 30 mg of sample was introduced into the sample cell, while keeping the reference cell empty. For 100 %WC tests a small section of copper wire was also added to the sample cell to facilitate higher probability hydrate nucleation. Each test method utilized a temperature equilibration and gas purge step (using 10 bar Green Canyon gas, Table 1) at 35 °C. The gas purge was conducted with a charging and depressurization rate of 1 bar/min to assure no introduction of gas pockets (charging) or splashing of the samples (depressurization). For HET determination and 100 %WC tests the cells were pressurized to the desired test pressure (100 bar) by the following: a slow gas charging rate of 1 bar/min was used for the first 10 bar, followed by a charging rate of 5 bar/min from 10 to 100 bar. After reaching 100 bar the cell was sealed and allowed to equilibrate for 3.5 h. After equilibration the cell was cooled at a rate of 1 °C/min to the desired temperature, -45 °C for emulsions and -10 °C for 100 %WC, and held for 24 h to assure as close to complete conversion to hydrates as possible. After reaching the desired temperature the temperature was ramped back to 35 °C at a rate of 0.5 °C/min. HET values were determined from the temperature at the minimum of the endothermic dissociation peak. The HET values for each test method are shown in Table 2.

HET values in the autoclave were determined as follows: 200 mL of total fluids were added to the autoclave, the cell was sealed, purged with gas, and charged to the desired pressure at 35 °C. The pressure was boosted as required until the pressure equilibrated. Subsequently, the autoclave was cooled over a 7 h period to 4 °C, held at 4 °C for 24 h, and heated back to 35 °C at a rate of 0.5 °C/h. HET values were determined from the pressure vs. temperature relationship of the dissociation phase. Autoclave HET values are shown in Table 2.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>0.39</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>---</td>
</tr>
<tr>
<td>Methane</td>
<td>87.26</td>
</tr>
<tr>
<td>Ethane</td>
<td>7.57</td>
</tr>
<tr>
<td>Propane</td>
<td>3.10</td>
</tr>
<tr>
<td>iso-Butane</td>
<td>0.49</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.79</td>
</tr>
<tr>
<td>iso-Pentane</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Table 1. Green Canyon gas composition.

 Isothermal Test Procedure
An isothermal test method was conducted for both 100 %WC and emulsion samples in the DSC as follows: After the equilibrium step described in the HET procedure the cells were cooled at a rate of 1 °C/min to the desired isothermal temperature. After reaching the isothermal test temperature the temperature was held for 5-10 h, before heating the cells back to 35 °C.

Autoclave isothermal testing was conducted by charging the loading and charging the cell as per the HET procedure, followed by cooling the cell over a 1 h period to the desired isothermal temperature. After reaching the test temperature
the isotherm was held until hydrate formation was detected by a pressure drop of > 0.2 bar.

**DSC Emulsion Ice-Memory Effect Method**

In an adaptation of a method utilized by Takeya et al. [12] an ice-memory effect method was utilized in the DSC for evaluating nucleation trends in an emulsion. The cells were loaded and purged as per the isothermal DSC procedure followed by an ice cycle conducted as follows: The temperature was ramped from 35 °C to -45 °C and then from -45 °C to 1 °C, at a rate of 1 °C/min. After gas saturation was completed the cell was cooled to the desired isothermal temperature at a rate of 1 °C/min and held for a duration of 5-10 h. Following the isothermal hydrate formation phase the cell was heated to 35 °C at 0.5 °C/min, to dissociate hydrates.

**RESULTS AND DISCUSSION**

**Emulsion Stability**

A highly stable water-in-oil (W/O) emulsion was desired for DSC hydrate testing. Using a stable emulsion with low water-cut and a monomodal droplet size of < 10 microns, inter-droplet interactions are greatly minimized. The reduction in inter-droplet interactions results in primarily independent droplet nucleation, allowing for a high statistical output per test. The monomodal droplet size results in a uniform droplet nucleation probability, due to the uniformity of droplet surface area. Additionally, the < 10 micron droplet size produces 100 % conversion of water droplets to hydrate upon hydrate nucleation, eliminating any discrepancies between exothermic peaks being from nucleation or growth of hydrates in a water droplet. As hydrates form at the water-oil interface a shell will surround the water droplets upon nucleation, which in turn will convert the entire droplet if its diameter is < 10 microns. Emulsion stability was determined by conducting ice formation-dissociation cycles on the emulsions. A stable emulsion is one in which a single peak will occur for ice formation and will remain unchanged upon multiple ice formation-dissociation cycles as shown by Lechance et al. [8]. Clausse et al. [13] have shown that the DSC can be used to determine the droplet size in an emulsion by equation (1).

\[ R_d = 450 \cdot e^{\left( \frac{T_{\text{ice}}}{450} \right)} \]  

Where \( R_d \) is the droplet diameter (μm) and \( T_{\text{ice}} \) is the temperature at the maximum of the exothermic ice formation peak. It was previously reported that in W/O emulsions the peak maximum is indicative of the ice formation temperature, in contrast to using the onset temperature for bulk water [13].

**HET Determination**

The HET values for the emulsions and 100 %WC systems for the DSC and autoclave were compared to determine any similarities or differences between the two instruments (Table 2). The results show good agreement between tests conducted in the DSC and autoclave with an average deviation of < 0.4 °C between the results for DSC and autoclave HET values for both the 100 %WC and emulsion samples.

<table>
<thead>
<tr>
<th>Test Method</th>
<th>HET (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSC Emulsion</td>
<td>19.7</td>
</tr>
<tr>
<td>DSC 100 %WC</td>
<td>21.0</td>
</tr>
<tr>
<td>Autoclave Emulsion</td>
<td>19.9</td>
</tr>
<tr>
<td>Autoclave 100 %WC</td>
<td>21.4</td>
</tr>
</tbody>
</table>

Table 2. HET values for autoclave and DSC testing.

**DSC Isothermal Emulsion Testing**

An isothermal test method was used to determine the hydrate nucleation times for emulsions in the DSC. The time until hydrate formation occurred, hold-time, was determined by the exothermic hydrate formation peak. Integration of the heat output with respect to time was used to determine the %hydrate conversion:

\[ \%\text{HydrateConversion} = \frac{Q(t)}{Q_{\infty}} \]  

Where \( Q(t) \) is the energy of formation at time \( t \), and \( Q_{\infty} \) is the total energy of formation for the hydrate formation peak. For emulsion testing the hold-times were recorded as the time until 50 % of the sample was converted to hydrates, \( t_{50} \). As the sample is expected to exhibit primarily independent nucleation with close to uniform droplet nucleation probability, \( t_{50} \) is the best
statistical representation of the hold-time for the sample. Due to the Gaussian nature of the droplet size distribution, the first and last observed nucleation times will be skewed by slightly different nucleation probabilities, resulting in a higher dispersion in hold-times for those values. Comparison of the $t_{50}$ values for uninhibited samples and the %Relative Standard Deviation (%RSD), equation (3), for variable sub-cooling tests are shown in Table 3:

\[
\text{%RSD} = \frac{\sigma}{t_{50}}
\]  

(3)

Where $\sigma$ is the standard deviation of $t_{50}$. By using %RSD the reproducibility of hold-times can be statistically evaluated without being skewed by hold-time scaling.

Analysis of the observed hold-times of the isothermal emulsion testing in the DSC showed some discrepancies in hold-times. Hold-times from replicate tests showed a high degree of dispersion, as well as a large number of non-nucleating runs. These non-nucleating runs were observed even at a sub-cooling shown to provide failures within a few hours in replicate tests. It has been reported in the literature that a very high sub-cooling is required to gain 100% nucleation probability when conducting hydrate nucleation experiments in the DSC [5, 15]. The scatter in hold-times and occurrence of non-nucleating runs was observed to become worse when introducing a KHI into the system, as a direct result of decreasing the probability of hydrate nucleation. Although at much higher sub-cooling the dispersion of hold-times and occurrence of non-nucleating runs decreased, other factors made using the isothermal method inadequate for studying KHI performance trends. These included the competition of ice formation and/or the inability to differentiate between a blank and a KHI inhibited system. In order to more accurately study the nucleation and KHI performance trends in the DSC a new method was developed for testing.

**DSC Ice-Memory Effect Method Validation**

The freezing-memory effect of water [12] and the hydrate-memory effect [16] have been used to increase the probability of hydrate formation and decrease the dispersion of hold-times, without altering the sub-cooling of the system. In order to maintain the high statistical output from using an emulsion, an ice-memory effect method was developed on the DSC. The hydrate-memory effect could not be used as Lechance et al.[8-9] and Palermo et al.[12] have shown that hydrate formation-dissociation cycles destabilize emulsions. This destabilization is even more pronounced with sII hydrates in comparison to sI hydrates. A modification to the ice-memory effect method used by Takeya et al.[13] to study hydrate formation by high-pressure x-ray diffraction was developed for the DSC.

The ice-memory effect method was conducted by first converting the water droplets into ice, followed by heating just above the ice melting point (1 °C) to retain some residual ice structure. The sample was then pressurized to a level at which saturation could be achieved without hydrate formation occurring. After saturation was achieved the sample was cooled to the desired isothermal temperature and held until hydrate formation occurred. A depiction of the ice-memory effect method is shown in Figure 1. The results of the ice-memory effect method are shown in Table 3 and Table 4.

![Figure 1. DSC ice-memory effect method](image)

Runs conducted with the ice-memory effect method at a sub-cooling of ≤ 27 °C resulted in the occurrence of either no hydrate formation during the test duration or non-nucleating runs in replicate tests. These non-nucleating runs indicated that the probability of hydrate nucleation was below 100%. Increasing the sub-cooling to ≥ 29 °C resulted in the absence of non-nucleating runs. At 29.3 °C
sub-cooling an improvement in results was seen in
the memory effect method, as the isothermal
method was observed to exhibit non-nucleating
runs at equivalent sub-cooling. A summary of the
hold-times vs. sub-cooling in the ice-memory
effect DSC tests is shown in Table 3.

<table>
<thead>
<tr>
<th>SC (°C)</th>
<th>t50 (h)</th>
<th>σa</th>
<th>%RSD50 b</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.7</td>
<td>n/a</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>29.2</td>
<td>2.81</td>
<td>0.966</td>
<td>34.4</td>
</tr>
<tr>
<td>29.3</td>
<td>2.05</td>
<td>0.383</td>
<td>18.7</td>
</tr>
<tr>
<td>29.5</td>
<td>0.43</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

*Standard deviation of hold-times (t50)

Relative Standard Deviation (%RSD) calculated by:

$$\text{(%RSD)} = \left( \frac{\sigma}{t_50} \right) \times 100$$

c No hydrate formation observed after 10 h.

d Data from only a single run

Table 3. Ice-Memory Effect DSC Results.

As expected, it was observed that as sub-cooling
was increased hold-time dispersion decreased, as
indicated by the decrease in %RSD (Table 3). The
low %RSD indicates a high degree of reproducibility of the results. Additionally the
hold-time was also observed to decrease. A hold-
time of \( \approx 1-2 \) h for the uninhibited emulsion was
desired to enable better differentiation between the
uninhibited and KHI inhibited emulsions. From
the results a sub-cooling of 29.3 °C was chosen as
the sub-cooling for evaluation of KHI
performance, as it had both a low %RSD and a
hold-time in the target range. The results of DSC
testing were confirmed to be highly repeatable with both Nalco and CSM producing statistically
equivalent hold-times using the ice-memory effect
method in separate labs with the same emulsion composition.

**DSC Ice-Memory Effect Testing with KHI**

Using the optimal sub-cooling determined from the
uninhibited emulsion testing (29.3 °C), DSC
ice-memory effect testing was conducted on KHI
inhibited emulsions. Emulsions inhibited with 0.2
wt% PVCap were tested to evaluate the ability to
differentiate between an uninhibited and KHI
inhibited emulsion by the ice-memory effect DSC
method. At 29.3 °C sub-cooling the results indicated some degree of inhibition of the PVCap
compared to the uninhibited emulsion (Table 4,
Figure 2). Figure 2 shows the comparison of the
average blank hold-time (Figure 2-Red) vs. the
average 0.2 wt% PVCap inhibited hold-time
(Figure 2-Black). Also depicted in Figure 2, is a
select number of replicate runs conducted by CSM
(Figure 2-Blue) and Nalco (Figure 2-Purple). The
similarity in hold-times from both labs further indicates the high reproducibility of the method and the ability to distinguish between an
uninhibited emulsion and a traditional KHI,
PVCap.

KHI-A was tested by the DSC ice-memory effect
testing at 29.3 °C sub-cooling:

- (Red) uninhibited blank;
- (Blue) 0.2 wt% PVCap, runs conducted by CSM;
- (Purple) 0.2 wt% PVCap, runs conducted by Nalco;
- (Black) average 0.2 wt% PVCap

100  %WC testing was conducted in the DSC to
assess the possibility of side interactions leading to
KHI performance differences between the DSC and autoclave testing of emulsions. If the 100
%WC tests show similar trends in performance to the
autoclave then other interactions could be
causing the change in performance in the ice-memory effect testing. One possibility is different degrees of interaction of the PVCap and KHI-A with either the components of the crude or the ice particles. In order to test without interactions an isothermal method was used with 100 % DI water with and without KHI.

<table>
<thead>
<tr>
<th>KHI</th>
<th>SC (°C)</th>
<th>$t_{50}$ (h)</th>
<th>$\sigma$ (h)</th>
<th>%RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>29.3</td>
<td>2.08</td>
<td>0.34</td>
<td>16.5</td>
</tr>
<tr>
<td>PVCap</td>
<td>29.3</td>
<td>3.24</td>
<td>0.49</td>
<td>15.0</td>
</tr>
<tr>
<td>KHI-A</td>
<td>29.3</td>
<td>1.38</td>
<td>0.51</td>
<td>37.1</td>
</tr>
</tbody>
</table>

*Where KHI dose was 0.2 wt%*

$^a$Standard deviation of hold-time ($t_{50}$)

$^b$Relative Standard Deviation (%RSD) calculated by:

$$\frac{(100\%) \sigma}{(t_{n} - t_{50})}$$

Table 4. Ice-memory effect DSC results with KHI at 29.3 °C sub-cooling.

As initial isothermal DSC testing was observed to have inconsistencies in the results, modifications to the test were conducted to improve nucleation probability. A small copper wire was added to the sample cell to enhance the nucleation probability. Rensing et al. discovered in their hydrate rheology experiments that the addition of a copper wire resulted in higher nucleation probability and enhanced data reproducibility[17]. Using this method lower sub-cooling could be tested in the DSC, allowing for a higher chance of differentiating KHI performance, without an inherent increase in %RSD.

After optimization of the sub-cooling to provide the target hold-time of $\approx 0.5$ h, testing was conducted with three different KHIs (PVCap, KHI-A, and KHI-B). Autoclave performance trends of the three KHIs is on the order of uninhibited $\ll$ PVCap $\ll$ KHI-B $<$ KHI-A (Figure 3). The results of the 100 %WC isothermal DSC tests are shown in Figure 3. As can be seen in Figure 3, 0.8 wt% PVCap was shown to have a longer hold-time (3.4 h) vs. the uninhibited sample (0.3 h), without an overlap of the %RSD, indicating some degree of inhibition. KHI-A and KHI-B, both high performance KHIs, were observed to have statistically equivalent performance to PVCap. Comparing the results from the 100 %WC DSC tests (Figure 3) to analogous 100 %WC autoclave tests (Figure 4) shows a large difference in observed KHI performance trends.

![Figure 3. 100 %WC DSC isothermal test hold-times at 26 °C sub-cooling: (White) no inhibitor; (Red) 0.8 wt% PVCap; (Blue) 0.8 wt% KHI-A; (Green) 0.8 wt% KHI-B; (Black) average of all KHI runs at 0.8 wt%.

![Figure 4. 100 %WC autoclave sub-cooling vs. hold-time curves: (Black) uninhibited emulsion for comparison to 100 %WC test; (White) uninhibited 100 %WC; (Green) 0.8 wt% PVCap; (Blue) 0.8 wt% KHI-A; (Red) 0.8 wt% KHI-B.

Examination of the dissociation peaks of the 100 %WC DSC testing also showed differences between the uninhibited and KHI inhibited samples. Although previous experimental evidence has shown the presence of KHI is expected to shift the dissociation temperature by a few degrees at most, other differences were observed in the DSC dissociation phases. When KHI was present (PVCap, KHI-A, or KHI-B) multiple peaks were observed during hydrate dissociation (Figure 5b). In contrast, uninhibited samples had a single dissociation peak at the expected HET value (Figure 5a). Analysis of the ice-memory effect dissociation peaks also showed differences between the uninhibited dissociation
(Figure 5c) and KHI inhibited dissociation (Figure 5d).

Peak broadening is likely causing a melding of the multiple peaks in the emulsion tests, where peaks are distinctly separated in the 100 %WC tests. Since the droplet size distribution is not perfectly monomodal and the droplets act independently, it is reasonable to assume that each droplet will dissociate independently and at slightly different temperatures (with the bulk of the sample dissocating at the expected HET value). The result is a broadening of the emulsion dissociation peak (Figure 6a) over the narrower 100 %WC peak (Figure 5a) as can be seen when comparing the dissociation peaks of the uninhibited samples by each method. It is possible that this peak broadening from the emulsion results in a melding of the multiple peaks when KHI is present (Figure 6b). There is a similarity between the location of the individual dissociation peaks of the 100 %WC KHI test (Figure 5b) and the location of the bumps in the emulsion test (Figure 6b), indicating the possibility of the melding of multiple peaks in the emulsion test with KHI.

Previous research by Ohno et al. has shown the occurrence of both the metastable hydrate phase and stable hydrate phase in a multicomponent gas system [18]. It is possible that the DSC tests with KHI present have a similar occurrence of hydrate metastability. Evidence for this is in the dissociation temperature values of the two peaks, where the first peak aligns with the expected sI dissociation temperature, and the second peak the sII dissociation temperature. Ohno et al. described a significant delay in the shift from the metastable to stable phase when as low as 0.02 wt% PVCap was present, over an uninhibited sample. In the absence of KHI the transition to 100 % thermodynamically preferred phase was observed by Ohno et al. to be very rapid. In the DSC tests this shift in transition time to the completely stable hydrate phase can explain the occurrence of multiple peaks in the KHI inhibited samples and only a single peak in the uninhibited samples. Based on the findings of Ohno et al. it is feasible...
that the uninhibited DSC tests show purely sII dissociation as a result of the test duration exceeding the time to fully convert to the stable phase. Further testing is needed to fully support the occurrence of metastability in the DSC testing.

The peaks above the sII dissociation value are presumed to be caused by KHI interactions with the melting hydrate. CSM has observed similar findings in pure methane hydrate experiments with PVCap [8]. Although, CSM observed multiple peaks only one aligned with sI dissociation, while none were seen at the expected sII dissociation temperature. Due to the lack of peak alignment with the sII dissociation value, the extra peak was presumed to be a result of KHI interactions. CSM supported these findings with visual testing on a melted hydrate particle with and without PVCap[19].

DSC vs. Autoclave Testing
In an effort to explain the differences in KHI performance trends in analogous autoclave and DSC testing further examination of the experimental conditions were conducted. One possibility for the different performance trends is the sensitivity of the test apparatuses. The DSC can detect hydrate formation at a much earlier stage than the bulk autoclave test. It is possible that the hold-time results from the two instruments are actually from detection two different phases of hydrate formation. The higher sensitivity of the DSC results in the detection of hydrates closer to the critical nucleation stage of formation. The autoclave cannot distinguish hydrate formation until a large fraction of hydrates occurs. This delay in detection in the autoclave could result in the detected formation phase being hydrate growth rather than hydrate nucleation.

The experimental set-up and/or duration of the two DSC test methods could also lead to a lack of detection of the hydrate growth phase. Due to the static nature of the DSC the 100 %WC test will have very limited to no growth occurring as a result of diffusion limitations. This is evident in the lack of sample formation greater than a few percent in 100 %WC DSC tests. Growth is also limited or stopped in the emulsion tests as a result of the experimental design. The emulsion test matrix was developed to cause complete conversion of the water droplets to hydrates during the critical nucleation stage. Compounded with the independent nucleation of the droplets growth should be completely removed from the test. If any growth occurs in either method it will be very limited and will likely produce exotherms lower than the detection limits of the instrument.

The DSC and autoclave detecting different phases of hydrate formation could be leading to the observed KHI performance trend differences. The inhibition mechanism of KHI is presumed to be related to the ability of the KHI to inhibit the growth of a hydrate crystal. The inhibition of growth is thought to be from a combination of factors. The first factor for KHI inhibition is the interaction of a functional head group with the hydrate surface (i.e. the amide group of PVCap). Second is the incorporation of a functional side group in the forming hydrate cages, inhibiting the introduction of gas into the cage and delaying further growth. The pendant group of a KHI is generally designed to fill the hydrate cages (i.e. the ring structure of PVCap fills the large cage of sII hydrates). The third factor is the interaction of portions of the KHI with gas to delay incorporation of gas in a forming hydrate cage. The last factor is the inhibition of crystal growth by the backbone of the polymer. If these factors are the true mechanism for KHI inhibition then a KHI would be expected to work primarily as a hydrate growth inhibitor, with minimal nucleation inhibition. The KHI growth inhibition mechanism is supported by the observed differences in the KHI performance trends from DSC and autoclave testing.

CONCLUSION
Various techniques were explored to use a high-pressure DSC to study hydrate nucleation trends in the presence and absence of KHI. Both the copper wire induced nucleation in a100 %WC isothermal test and the ice-memory effect emulsion test methods resulted in highly reproducible nucleation times. Of the two methods, the ice-memory effect emulsion procedure had a higher degree of reproducibility and produced a high statistical output in a given test. Although the 100 %WC removes any discrepancies from KHI-ice or KHI-oil interactions, the sub-cooling range was very sensitive and the dispersion of hold-time data was higher.

Both DSC methods showed highly reproducible hydrate “nucleation” and some degree of
inhibition with KHI. Examination of the hold-times showed some discrepancy between the DSC tests and bulk autoclave tests. Those differences were attributed to differences in the hydrate formation phase being detected in each apparatus. The different formation phase detection arises from variations in experimental design and instrument sensitivity. In an autoclave test the degree of hydrate formation required before hydrates are detected is relatively large, resulting in the detection of hydrates during the growth phase of formation. DSC tests have a higher degree of sensitivity leading to detection of hydrates closer to the critical nucleation phase of formation. The experimental design of the DSC tests also limits the occurrence of hydrate growth. These differences in the DSC and autoclave tests result in different phases of hydrate formation being detected and directly affect the observed KHI performance trends.

Based on the reported theories of the KHI inhibition mechanism it would be expected that KHI inhibits growth rather than nucleation. As the DSC is detecting the “nucleation” phase of hydrate formation the limited inhibition observed in the tests with KHI should be expected. In the autoclave testing the “nucleation” phase passes without detection and the observed performance trends are from KHI inhibition of the “growth” phase of hydrate formation. Our experimental evidence indicates the mechanism for KHI performance is a growth inhibition mechanism.

Although the initial goal was to develop a method for fast screening of KHI performance, the ability to evaluate “nucleation” trends by the DSC shows potential for many areas of hydrate studies. This includes fundamental research of hydrate formation and metastability, which could prove particularly useful for hydrate gas storage and transportation applications.

ACKNOWLEDGEMENTS
The Center for Hydrate Research at the Colorado School of Mines for their collaborative efforts on the DSC test method development, experimentation, and result analysis.

REFERENCES


