Microscale Detection of Hydrate Blockage
Onset in High-Pressure Gas-Water Systems

Masoumeh Akhfash\textsuperscript{a}, Zachary M. Aman\textsuperscript{a}, Jianwei Du\textsuperscript{a,b}, Paul F. Pickering\textsuperscript{a}, Michael L. Johns\textsuperscript{a}, Carolyn A. Koh\textsuperscript{b}, Eric F. May\textsuperscript{a,*}

\textsuperscript{a}. Fluid Science & Resources Division, School of Mechanical and Chemical Engineering, University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia
\textsuperscript{b}. Center for Hydrate Research, Chemical Engineering Department, Colorado School of Mines, 1500 Illinois St, Golden, CO 80401, United States.

A high-pressure stirred autoclave cell equipped with a focused beam reflectance measurement (FBRM) probe and a particle video microscope (PVM) was used to study hydrate formation and plugging in gas-water systems as a function of shear rate. These probes allowed estimates of the mean hydrate particle size and number of hydrate particles to be correlated with the hydrate volume fraction and the hydrate slurry’s resistance-to-flow. Before reaching the hydrate volume fraction $\phi_{\text{transition}}$ at which the hydrate slurry first exhibits a measurable increase in resistance-to-flow at $\approx (16 \pm 2) \text{ vol\%}$, clear changes in the measured number and size of the hydrate particles were observed. Initially, hydrate particles within the FBRM probe’s field of view decreased in size and increased in number until a maximum was reached at concentrations of 2 to 9 vol\% (increasing with shear rate). However, with continued hydrate growth, the number of particles within the FBRM probe’s field of view unexpectedly decreased and eventually plateaued at hydrate volume fractions approaching

\textsuperscript{*} Corresponding (Eric F. May). Email address: eric.may@uwa.edu.au, telephone: +61 8 6488 2954, Facsimile: +61 8 6488 1024
We propose that, following nucleation, particle numbers in the bulk liquid increased until the average particle size and separation became comparable, after which the particles began to interact and, driven by buoyancy forces, formed a moving particle bed located near the gas-water interface. Such findings could facilitate development of a scaling relationship for predicting the onset of hydrate plugging behaviour in water-continuous systems.

*Keywords: Gas hydrates, high-pressure autoclave, heterogeneous particle distributions, particle bedding, focused beam reflectance measurement*
1 Introduction

Gas hydrates are ice-like solids comprised of water and light hydrocarbon gas molecules (e.g. methane) that are typically stable under high pressure and low temperature conditions. Deep water oil and gas flowlines are inherently at high risk of hydrate formation and subsequent potential blockage, the prevention of which has been identified as the leading flow assurance concern for offshore assets \(^1\). However, the use of thermodynamic inhibitors to prevent hydrate formation and blockage (e.g. during shutdowns and start-ups) may not be economically feasible for deep-water fields and/or mature reservoirs nearing the end of their production life which produce large volumes of water. This economic reality has motivated the development of hydrate management strategies \(^2\), where hydrate is allowed to form as a transportable suspension in oil. The design of such hydrate management strategies is informed by experimental efforts conducted over the past three decades to develop conceptual mechanisms for hydrate blockage formation in oil-, gas- and water-dominated systems \(^3\). Plug formation mechanisms in oil-dominated systems are well-established \(^4\), but the multi-phase mixture in the flowline may transition to water-continuous \(^5\) as the amount of produced water increases with field life \(^1\).

Investigations of hydrate formation in gas-water systems using flowloops and autoclaves \(^6, 7, 8, 9\), have suggested that a critical stage in the formation of blockages is the buoyant collection of hydrate particles to form a moving bed near the gas-water interface. Joshi, et al. \(^6\) performed several flowloop studies of high water cut systems (including 100% water cut) at different fluid velocities and liquid loading. The behaviour of the pressure drop across the flowloop during hydrate growth resulted in a three-stage conceptual model for hydrate blockage formation (Figure 1). During the initial stages of hydrate formation in these flowloop tests no increase in pressure drop was observed, which was assumed to correspond
with a homogeneous distribution of solid particles in the aqueous phase. Continued hydrate growth resulted in an increased pressure drop, consistent with the formation of a moving hydrate bed near the gas-water interface; in this condition, the particles are heterogeneously distributed throughout the cross-section of the aqueous phase. Joshi, et al. \(^6\) labelled the hydrate volume fraction at which this heterogeneous behaviour was first observed as \(\phi_{\text{transition}}\). This transition from a homogeneous to a heterogeneous hydrate-in-water particle distribution preceded the ability for hydrate particles to form a stationary bed and deposit on the flowline wall, as the final stage in this mechanism. In this latter stage, the frictional pressure drop in the flowloop increased by at least one order of magnitude.

![Conceptual mechanism for hydrate plugging in a gas-water system](image)

**Figure 1.** Conceptual mechanism for hydrate plugging in a gas-water system, developed by Joshi, et al. \(^6\)

Akhfash, et al. \(^7\) and Aman, et al. \(^8\) observed similar patterns to Joshi, et al. \(^6\)’s flowloop data through resistance-to-flow (torque or motor current) behaviour in a sapphire visual autoclave, where resistance-to-flow was measured to increase significantly only above a critical hydrate volume fraction (\(\phi_{\text{transition}}\)). These measurements provided a new visual method to detect hydrate bed formation in the autoclave geometry, and delivered visual
observations confirming the onset of a heterogeneous particle distribution prior to severe hydrate blockage formation.

Experiments conducted in both flowloops \(^6\) and autoclaves \(^8\) showed that an increase in shear rate (flow velocity or impeller speed, respectively) delayed the onset of hydrate bed formation to higher values of \(\phi_{\text{transition}}\). Further, Joshi \(^{10}\) suggested that the formation of a moving hydrate bed was irreversible, which may have been the consequence of initial wall film growth visually observed by Aman, et al. \(^8\). However, while qualitative agreement in the shear-dependence of \(\phi_{\text{transition}}\) was observed between experiments in different autoclaves and flowloops, significant inconsistencies are found when any dependence of \(\phi_{\text{transition}}\) on Reynolds number is considered, where the latter dimensionless group might be expected to provide a quantitative measure of the shear force that is independent of flow geometry. As discussed by Aman, et al. \(^8\), this suggests that the various length scales used in the calculation of Reynolds number within different geometries are not suitable for the generalised prediction of hydrate bed formation. To build such a relation, more information about the relevant length scales at which hydrate particles begin to interact in water-continuous systems is needed.

In assessing a system’s propensity for forming a moving hydrate bed, the dispersed particle size is a critical parameter. Focused Beam Reflectance Measurements (FBRM) are commonly used to study this property; an FBRM probe measures the number and size of chord lengths at a particular point in space, enabling the generation of a chord length distribution (CLD). Examples of FBRM experiments include characterising emulsions and droplet size distributions in oil \(^{11, 12, 13, 14, 15}\), describing hydrate nucleation and growth behaviour \(^{11, 16, 17}\), analysing the performance of anti-agglomerant chemical additives \(^{18, 19, 20, 21, 22}\), and modelling the rate of hydrate formation and dissociation in gas-water systems \(^{23, 24}\).
An FBRM probe enables *in situ* measurements of particle size in opaque or dark surroundings and in suspensions at high solid concentrations. It does not require an assumption of particle shape to calculate the CLD, although refinements can be made using additional information about the particle size distribution (PSD) that may be available as discussed by several authors \(^{25, 26, 27, 28, 29, 30}\). Further to this, Heath, et al. \(^{31}\) highlighted the use of different weighting functions (no weight, length weight, square weight and cube weight) that can be applied to FBRM measurements, which may be used to correct for measurement bias when reporting statistical parameters of the distribution. Heath, et al. \(^{31}\) reported FBRM measurements for well-known particle size distributions between 50 and 400 microns, and concluded that the mean square weighted chord length provided the best estimate of the actual mean particle size. This square weighted function was therefore applied to all the experimental results discussed in this paper. However, while the measured CLDs are assumed to be close representations of the hydrate PSD, the objective of this work was to study the *evolution* of those distributions rather than their particular numerical values.

A review of the existing literature indicates numerous uses of the FBRM technique in oil continuous systems, such as works from Greaves, et al. \(^{11}\), Boxall, et al. \(^{12, 14}\), Less and Vilagines \(^{15}\) and Turner, et al. \(^{16}\). For instance, Turner, et al. \(^{16}\) utilized an FBRM probe in an autoclave to monitor the changes in the size distribution of water droplets in the oil as hydrate grew in the system. Apart from a minor increase in the population density of large particle sizes during hydrate nucleation, Turner et al. observed no change in CLD until the end of the experiment, validating the hypothesis that water droplets gradually convert to hydrate.

In another oil study, Leba, et al. \(^{18}\) and Cameirao, et al. \(^{19}\) combined *in situ* FBRM measurements with pressure drop and temperature signals from flowloop experiments, to study agglomeration processes in water-in-oil emulsions at low water cuts. In both studies no
increase in the mean chord length signal (un-weighted or square-weighted) was observed during early stages of hydrate formation, indicating no change in the size of water droplets/hydrate particles. Approximately 50 minutes after hydrate nucleation, the FBRM chord length measurements suddenly increased, which was considered to indicate the onset of particle agglomeration. This shift in the FBRM CLD was also consistent with an increase in the measured pressure drop across the flowloop. A model for hydrate aggregation based on a monodispersed population of water droplets in water-in-oil emulsions was then proposed \(^{18}\), which was subsequently improved by Cameirao, et al. \(^{19}\) by considering a polydispersed log-normal distribution of water droplets \(^{14, 32}\). Simulated CLDs were then compared to experimental measurements of CLD obtained from the FBRM at different levels of agglomeration, to adjust the fractal dimension and number of hydrate primary particles contained within the agglomerates \(^{19}\).

However, few studies are available on the use of FBRM probes to characterise water continuous systems. Clarke and Bishnoi \(^{23, 24}\) used FBRM size measurements to define the moments of the particle size distributions, in order to model the rate of gas hydrate formation and dissociation in a gas-water system. They assumed that mixing in the stirred tank was sufficiently high to consider the FBRM readings representative of the whole system, and that the FBRM probe scanned all the particles in the field of view. Reasonable agreement was obtained between the predicted and experimental formation/dissociation rates based on their FBRM measurements.

In this work, a stainless steel autoclave equipped with an FBRM probe was used to monitor the changes in the distribution of hydrate particles in gas-water systems over a range of mixing speeds (50 to 700 RPM). The FBRM data were coupled with resistance-to-flow (motor current) measurements to explore the relationship between hydrate particle
distribution and bed formation. From our knowledge of the published literature, this study represents the first use of FBRM measurements to investigate the onset of hydrate bed formation ($\phi_{\text{transition}}$). Further, in a few experiments, the FBRM probe was used together with a Particle Video Microscopy (PVM) probe, which provided some visual information about the size and morphology of the hydrate crystals and aggregates.

2 Materials and Methods

2.1. Apparatus

A simplified schematic diagram of the high-pressure autoclave apparatus is shown in Figure 2. The apparatus used in this study was essentially identical to that used by Greaves $^{33}$ and Boxall $^{34}$, so only the differences to the original apparatus and a summary of its key features are described here. The autoclave was constructed by Challenger Manufacturing using 316 stainless steel, with a 10.2 cm internal diameter (four inches) and a 22.9 cm height (nine-inches). The internal volume of the cell was 1775 ml, and the cell was rated to the maximum operating pressure of 83 bar (1200 psi). The cell contents were agitated using an anchor-type impeller with a 6.5 cm diameter. The autoclave apparatus consisted of a magnetic drive shaft with maximum torque of 15 kg.cm, connected to an AC drive motor with a maximum rotational speed up to 2000 RPM, provided by Sejin Young Tech, Korea. The cell was connected to a high-pressure gas reservoir (2286 ml) through a pressure control valve. All experiments in this work were performed under isobaric conditions, using the gas injection port at the top of the cell; the amount of gas consumed as hydrates formed in the autoclave cell was determined from the change in pressure of a constant volume reservoir that supplied the gas. The autoclave cell was submerged in a water-glycol bath, where the bath fluid was continuously circulated through two Fisher Scientific chillers to control cell
temperature and remove heat during the exothermic process of hydrate formation. To help maintain isothermal conditions, injection gas from the high-pressure reservoir passed through 10 meters of 1/8 inch stainless steel tubing located inside the glycol bath before injection into the autoclave. The temperatures of the autoclave cell and bath were measured using two 1/8 inch T-Type thermocouples from Omega Engineering, where the cell thermocouple was positioned about 2 cm inside the liquid phase. Two Omega transducers (0-207 bar) with a resolution of ± 0.1 bar monitored the cell and reservoir pressures. A LabVIEW data acquisition system (DAQ) was used to record cell and bath temperatures, cell and reservoir pressures, and the motor current required to maintain a constant mixing velocity within the cell (e.g. 300 RPM) at 5 s interval over the entire period of the experiments.

Figure 2. Simplified sketch (left) and picture (right) of the high-pressure autoclave cell.

The FBRM probe used in this study was a Mettler-Toledo Lasentec D600X particle size analyser. The FBRM probe was directly in contact with the fluids throughout the experiment. The FBRM functions by emitting a class I, 3 mW laser beam with wavelength 791.8 nm through the probe tip at the sapphire window (Figure 3). The optical system rotated at a speed of 2123 RPM, corresponding to a linear velocity of 2 m/s (by considering a tip (scanning) diameter of 18 mm), allowing the laser to scan across the surface of particles in
front of the sapphire window; the laser was reflected when it scanned the surface of a particle. The scanned chord length was calculated based on the measured reflectance time and the known rotational speed. Generally, thousands of particles were scanned per second, generating a detailed chord length distribution in real time. The measured data were analysed to determine the mean chord length and number of chord counts as a function of time. Chord length distributions were analysed for the range of 1 to 1000 μm on a logarithmic basis.

The PVM probe used in this work was a Mettler-Toledo Lasentec model V800S. The PVM used a high-resolution camera and six lasers to illuminate the material in front of the probe window, to obtain high-resolution images of particle suspensions or emulsions (Figure 3). The PVM field-of-view was 860 by 645 μm, with a minimum resolution of 20 μm.

The FBRM and PVM probes were inserted at angles of 45° into the cell to maximize the flow across their windows and to allow representative particle sampling. The position of the probes in the autoclave was determined based on the simulation of the flow behaviour inside the autoclave, where the details are discussed by Greaves.
Figure 3. (a) FBRM probe assembly; (b) the procedure of FBRM chord length measurements; (c) PVM probe assembly; (d) an example of PVM imaging: methane gas bubbles in water after hydrate dissociation, captured from one of the experiments performed in this work. Sketches (a) – (c) are redrawn based on information from Mettler-Toledo-Autochem\textsuperscript{35}.

2.2. Experimental Procedure

Gas hydrate was formed in the high-pressure autoclave apparatus according to the following procedure:
(1) The cell was thoroughly cleaned with acetone, rinsed with deionized water (DI), and dried completely with compressed air.

(2) To calibrate FBRM and PVM readings prior to each experiment, the probes were cleaned with DI water and acetone, then dried carefully until the total chord counts in the FBRM reading was reduced below 100 (over 10 s) and no particle was visible in the PVM window. To decrease the hydrate deposition/accumulation on the sapphire windows of the FBRM and PVM, a silane-based hydrophobic surface treatment was applied to the surface of the probes, as discussed by Greaves \(^{33}\) and Boxall \(^{34}\).

(3) The cell was loaded with 900 ml deionized water to completely cover the impeller blade, after which the cell was loaded into the water/glycol bath.

(5) The cell was flushed with high purity methane gas (99.999%) at 20 bar to remove any remaining air from the system.

(6) The bath temperature was maintained at 20 °C and the cell was pressurized to 65 bar and leak-tested for at least two hours.

(7) The motor speed was set at a pre-defined rotational speed (e.g. 300 RPM); all valves between the cell and gas reservoir were set to the required configurations for constant-pressure operation, and the system was left overnight to ensure complete saturation of water occurred prior to hydrate formation.

(8) The bath temperature was cooled to 1 °C to allow for hydrate formation, with the chillers working at their maximum capacity to deliver a cooling rate of 8 °C/h. Hydrate nucleated within 30-60 minutes after the system crossed over the equilibrium point for Experiments 2-8 (listed in
Table 1). However, for Experiment 1 at 50 RPM, nucleation occurred after 13 h. Experiments typically required 7 to 24 h to reach a steady state pressure signal.

After the hydrate formation process ceased, the system was heated to 20 °C in a stepwise manner to dissociate hydrate in a constant-pressure mode. Finally, a mass balance was performed by calculating the number of moles of gas in the dissociation reservoir with respect to the number of moles consumed during hydrate formation.

In the present study, experiments were initiated at ambient temperature (22 ± 1 °C) and with a constant cell pressure of 65.3 ± 0.5 bar. Hydrate formation was identified from a slope change in the measured pressure signal with time, due to gas consumption. The amount of hydrate formed in the cell was calculated through the measured pressure decrease of the reservoir. Multiflash 4.2 using the cubic plus association (CPA) model set was used to calculate water and hydrate phase densities and the methane compressibility factor, while the methane hydration number was assumed to be a constant 5.75. The initial Reynolds number ($Re_{initial}$) of the water phase was calculated at 21 °C and 65 bar (a common initial state) for each mixing condition, using the standard definition for stirred tanks:

$$Re = \frac{\bar{N} \rho D^2}{\mu} \quad (1)$$

where $\bar{N}$ is the impeller rotational speed ($s^{-1}$), $D$ is the impeller diameter (m), and $\rho$ and $\mu$ are, respectively, the density (kg/m$^3$) and viscosity (kg/m/s) of the water phase. The hydrate volume fractions reported hereafter were calculated based on the total volume of the hydrate, $V_H$, and water, $V_W$, phases: i.e. $\phi = V_H / (V_H + V_W)$. The reproducibility of the results obtained at various shear rates was checked by conducting two repeat tests.
3 Results

3.1 Resistance-to-flow measurements

Eight experiments were performed in the autoclave cell (listed in Table 1) at different motor speeds ranging from 50 to 700 RPM; the initial Reynolds numbers ranged from 3500 to 49000. Hydrate nucleated at temperatures ranging from 1.5 to 6.2 °C, equivalent to a subcooling range of 3 to 7.5 °C for pure methane gas, where the hydrate equilibrium temperatures (reported in Table 1) were predicted from the measured pressure using the Cubic Plus Association model set implemented in Multiflash 4.2. While the final set point for the bath temperature was fixed at 1 °C, the temperature observed during the latter stages of each experiment ranged between 6.5 and 8.7 °C. This indicates that once hydrate formed the cooler’s power was insufficient for the thermal mass of the system and the heat transfer from the environment for it to reach the bath temperature within the experimental timeframe. However, this is unlikely to have any significant impact on the results observed here, given that sufficient hydrate growth always occurred over the experiment’s duration to achieve hydrate volume fractions much larger than $\phi_{\text{transition}}$. Table 1 also shows maximum amount of hydrate formed in each experiment.
Table 1. Summary of experiments conducted in the autoclave cell. In all experiments, the hydrate equilibrium temperature was 9.0 ± 0.1 °C. The hydrate volume fraction in the liquid phase at the end of each experiment is denoted \( \phi_{\text{final}} \). The relative motor current (R.M.C.) was calculated based on the ratio of the instantaneous motor current (post nucleation) to the average motor current measured prior to nucleation. The quantities \( \phi_{\text{transition}} \) and \( \phi_{+\text{transition}} \) represent the average and maximum hydrate volume fractions at which an increase in relative motor current above R.M.C.\(_{\text{ave}}\) + u and R.M.C.\(_{\text{ave}}\) + 3u was observed, respectively, where u is the standard deviation of the relative motor current measured prior to \( \phi_{\text{transition}} \).

<table>
<thead>
<tr>
<th>Exp.</th>
<th>RPM</th>
<th>( Re_{\text{initial}} )</th>
<th>( T_{\text{nucleation}} ) (°C)</th>
<th>( T_{\text{final}} ) (°C)</th>
<th>( \Delta P_{\text{consumed}} ) (bar)</th>
<th>( \phi_{\text{final}} ) (vol%)</th>
<th>R.M.C.(<em>{\text{ave}}) before ( \phi</em>{\text{transition}} )</th>
<th>R.M.C.(<em>{\text{ave}}) before ( \phi</em>{+\text{transition}} )</th>
<th>( \phi_{\text{transition}} )</th>
<th>( \phi_{+\text{transition}} )</th>
<th>Maximum R.M.C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>3525</td>
<td>1.5</td>
<td>5.6</td>
<td>21.1</td>
<td>36.9</td>
<td>*</td>
<td>*</td>
<td>1.08</td>
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<td>100</td>
<td>7050</td>
<td>3.9</td>
<td>6.1</td>
<td>22.7</td>
<td>40.0</td>
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<td>21149</td>
<td>6.2</td>
<td>6.6</td>
<td>24.7</td>
<td>42.8</td>
<td>1.05</td>
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</tr>
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<td>21149</td>
<td>5.3</td>
<td>8.0</td>
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<td>0.03</td>
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</table>

*: Not able to be specified due to significant fluctuations in motor current observed in Experiment 1 at low hydrate volume fractions.

**: Not able to be specified, as the amount of water in the cell was not measured accurately. The result is reported because in Experiment 8, both the FBRM and PVM probes were in service.

As discussed above, the measured increase in motor current provides a resistance-to-flow metric analogous to pressure drop in a flowloop or pipeline, and is generally a function of hydrate volume fraction in the system. As explained in detail by Joshi, et al. 6, Akhfash, et al. 7 and Aman, et al. 8, hydrate particles impose a negligible amount of resistance-to-flow on the system as long as they are distributed uniformly in the aqueous phase and at low concentration. Eventually, particle interaction and bed formation result in a heterogeneous particle distribution throughout the system and the measured resistance-to-flow increases. Figure 4 shows an example of relative motor current as a function of hydrate volume fraction,
as observed for experiment 4 listed in Table 1 (300 RPM). The relative motor current was calculated based on the ratio of the instantaneous motor current in the presence of hydrates to the average motor current prior to nucleation. In Figure 4, the initial increase in relative motor current above the baseline (R.M.C.ave line in Figure 4) was used to estimate the value of $\phi_{\text{transition}}$. This was done by calculating the standard deviation of the baseline relative motor current $u(\text{R.M.C.ave})$ (i.e. measured well before any consistent increase in current occurred). A threshold value of three times $u(\text{R.M.C.ave})$ was taken to be the point at which an unambiguous change in the relative motor current had occurred. By fitting a line to the relative motor current data measured above (and in the vicinity of) this threshold, $\phi_{\text{transition}}$ was estimated to be the point of intersection between $\text{R.M.C.ave}+u(\text{R.M.C.ave})$ and the fitted line. The uncertainty in the determination of $\phi_{\text{transition}}$ by this method was estimated from the intersection of the fitted line with the threshold $\text{R.M.C.ave}+3u(\text{R.M.C.ave})$. For the particular experiment at 300 RPM shown in Figure 4, $\phi_{\text{transition}}$ was estimated to be about 15.8 vol% hydrate with $\phi_{\text{transition}}^*$ estimated to be 16.7%. This increase in resistance-to-flow continued until about 35 vol% hydrate formed in the cell (see Figure 4). At these later stages of hydrate formation, rapid fluctuations in motor current were interpreted as being a result of particle jamming and stationary bed formation (or particle deposition) throughout the experimental cell.
**Figure 4.** Relative motor current (resistance-to-flow) as a function of hydrate volume fraction for a gas-water system at 300 RPM (experiment 4). The insert figure contains the same data with a magnified ordinate range to schematically show how $\phi_{\text{transition}}$ and $\phi^+$ were calculated. The values reported in Table 1 were obtained based on the intersection of the fitted lines.

Two main observations may be derived from the resistance-to-flow and $\phi_{\text{transition}}$ results presented in Table 1. First, there was no statistically significant difference in the values of $\phi_{\text{transition}}$ obtained for experiments performed at different shear rates (16±2 vol% hydrate), within the confidence assigned to the motor current measurements. Although some previous observations \(^7\, 8\, 10\) showed a direct dependence of $\phi_{\text{transition}}$ with the degree of turbulence in the system, this trend was not clear within the range of shear rates applied in this study, potentially because of the limited resolution of the motor current measurements.
As discussed below, $\phi_{\text{transition}} \approx 16 \, \text{vol}\%$ may correspond to the upper threshold for hydrate particle transport in water, if the system is to maintain minimal interparticle interactions. Second, the maximum relative resistance-to-flow achieved in the system (during the later stages of plug formation) decreased as shear rate increased, despite the conversion of additional water to hydrate, as was observed and discussed in detail by Aman, et al.\textsuperscript{8}. Table 1 shows that the maximum resistance-to-flow reduced by a factor of 8 as the mixing speed was increased from 100 to 700 RPM. At low shear rates (e.g. experiment 2, 100 RPM), 40 vol% hydrate in the aqueous phase was sufficient to stop the impeller rotation, but at higher shear rates (e.g. 300 and 700 RPM), between 56 and 78 vol% hydrate was required to achieve a plugging condition.

The values of $\phi_{\text{transition}}$ derived from these motor current measurements agree with observations from the literature for water/gas systems. Joshi\textsuperscript{10} reported $\phi_{\text{transition}}$ in the range of 12-19 vol% for three methane-water experiments performed in a 4-inch autoclave cell with a vane-blade impeller geometry over the range of 35000 to 60000 Reynolds number (calculated using eq. 1), which corresponded to a shear rate of 300-500 RPM. The present observations are also in qualitative agreement with the observations of Akhfash, et al.\textsuperscript{7} and Aman, et al.\textsuperscript{8} in a 1 inch sapphire autoclave cell, where $\phi_{\text{transition}}$ was found to be in the range of 15-22 vol% for shear rates of 50-400 RPM. However, because of the smaller ID, these shear rates correspond to a Reynold’s number range of only 300-2400, which are an order of magnitude below those observed in the larger autoclave and flow loop experiments. This suggests that while shear rate affects the value of $\phi_{\text{transition}}$, the Reynolds number as defined by eq (1) and/or the length scale therein are not generally relevant to the onset of hydrate bed formation.
3.2 In Situ Images of Hydrate Formation

In addition to resistance-to-flow observations (Section 3.1), the morphology and diameter of hydrate crystals were monitored in some experiments with a PVM probe inserted in the autoclave cell. Figure 5 illustrates sample PVM images captured at different times after nucleation for experiment 8 (300 RPM). The PVM images did not clearly show solid hydrate particles until five minutes after nucleation, presumably because the microscope’s objective lens limited the PVM’s ability to resolve particles smaller than 20 micron. In Figure 5, images are only shown up to 40 minutes after nucleation because at that point a large mass of hydrate adhered to the PVM objective lens, preventing any further meaningful measurements.
While the PVM provided an approximate range of 50 to 700 microns for the size of hydrate particles, it did not provide any quantitative information on their spatial distribution in the aqueous phase nor any evidence for the formation of a hydrate bed. In contrast, the FBRM was able to identify particle sizes as small as 0.5 microns, providing a 40-fold
improvement from the minimum detectable size by the PVM. The FBRM was used to measure particle number concentrations and size distributions in the water phase as a function of time.

3.3 FBRM Measurements

The distribution of gas bubbles and hydrate particles in the liquid phase on a micron length scale was quantified through FBRM online measurements. The PVM and FBRM results were broadly consistent in terms of the size ranges of solid particles in the region where PVM was able to measure particle size. However, in addition to the larger range of measurable particle sizes, the FBRM was also successful in detecting hydrate nucleation through a sharp increase in the chord length and number of chord counts measured which corresponded directly to the decrease in the cell pressure caused by gas consumption upon hydrate formation.

The FBRM measurements provided valuable information on the size of entrained gas bubbles in water prior to hydrate formation. Figure 6 shows the mean square weighted chord length as a function of time after nucleation, where chord length can be taken as proportional to the size of gas bubbles and hydrate particles. Two important conclusions can be drawn from the data in Figure 6. First, the chord length of the entrained gas bubbles was measured in the range of 1 to 400 microns with no measurable dependence on shear rate prior to hydrate nucleation. This result may provide guidance as to a reasonable approximation of initial gas-water surface area estimates, which are central to hydrate growth rate calculations. Second, Figure 6 illustrates that upon initial hydrate nucleation, the diameter of the dispersed particles observable with the FBRM increased within a matter of minutes to a maximum value, and then decreased over a sustained period (tens of minutes).
Collectively, the data in Figure 6 suggest that the initial formation of hydrate in aqueous systems may include appreciable numbers of hydrate-encrusted gas bubbles \(^1\), and that following initial hydrate formation, the particles may experience shear-induced breakup, particularly since interparticle cohesive forces (which might balance the disruptive shear forces) are negligible in water continuous systems \(^{38}\). Figure 6e and f show that prior to hydrate formation, the total FBRM signal was small because of limited reflection of light by gas bubbles. The FBRM measurements are sensitive to the optical and surface properties of the particles being scanned, and the refractive index of gas bubbles is significantly lower than the refractive index of hydrate particles. Consequently, while the FBRM could detect a range of bubble sizes, the total number of counts observed before nucleation was much smaller than occurred afterwards. Following nucleation, the rapid increase in the size of detectable particles may have corresponded to the conversion of large, hard-to-detect bubbles to hydrate-encrusted bubbles, which can be easily observed with the FBRM. Figure 6d and f indicate that with increased shear (700 RPM), a wider range of bubble sizes were detectable as the number of counts increased several fold over the number and range of bubble sizes observed at low shear (100 RPM).
Figure 6. Mean square weighted chord lengths (a-d) and chord counts (e-f) of gas bubbles and hydrate particles measured by FBRM as a function of time post nucleation for various
impeller speeds. Prior to nucleation, the measured chord lengths and chord counts are indicative of the size and number of the gas bubbles detected by the FBRM.

As a particle size analyzer, the FBRM was also able to measure the chord length distribution during the hydrate growth phase. Figure 7 shows chord length distributions of the hydrate slurry at different hydrate volume fractions for both a low shear rate (experiment 2 at 100 RPM is shown in the left panel) and a high shear rate (experiment 6 at 700 RPM is shown in the right panel). The FBRM measurements were collected at 10 s intervals. The distributions shown in Figure 7 have been selected to show the trend in particle size distribution measured throughout the hydrate growth phase. In both the low and high speed mixing experiments, once hydrate nucleation was detected the measured chord counts immediately increased indicating the FBRM was successful at detecting hydrate growth. However, after about 3 vol% hydrate at 100 RPM, or 8 vol% hydrate at 700 RPM, an unexpected decrease in the number of counts was observed: as hydrate continued to form (based on the measured pressure drop) the number of counts decreased until a limiting hydrate volume fraction was reached (10 to 20 vol%). Above these limits, the FBRM was no longer sensitive to the amount of hydrate in the system, as the CLD no longer varied with time.
Figure 7. Chord counts-chord length distributions measured by FBRM, reported at different hydrate volume fractions for methane hydrate-in-water slurries. (Left panel): experiment 2 at 100 RPM and (right panel): experiment 6 at 700 RPM. Grey traces correspond to a sequence of distributions that increase in height with hydrate volume fraction, while coloured traces correspond to a sequence of distributions that decrease in height with increasing hydrate volume fraction. (For interpretation of the references to colour in this figure legend, refer to the web version of this article.)

On first consideration, it might be expected that the number of particles measured by the FBRM should have increased as hydrate continued to grow in the cell, and as larger particles were broken up due to shear. The observation of a consistent decrease in the number of chord counts at a relatively early stage of hydrate formation suggests that while particles still existed in the water phase they were not all detected by the FBRM probe.

4. Discussion

The FBRM CLDs were used to estimate the total hydrate-water surface area, assuming spherically shaped hydrate particles. The measured mean chord lengths were
employed to estimate the surface area of an average particle, and then chord counts distributions were integrated numerically to obtain the total number of particles and, ultimately, the total hydrate surface area. This estimate was not intended to be rigorous but rather to help illustrate and interpret the acquired FBRM data and particularly the evolution of distributions such as those plotted in Figure 7. We note that the relation between FBRM chord length measurements and actual sizes of hydrate particles in oil systems has been discussed by Boxall. However, as this work mainly discusses the qualitative evolution of particle distributions (both in number and size) without focusing on the absolute values, those corrections have not been used in this work. Furthermore, additional calibrations would be required for those correlations to be applicable to the present measurements. In this context, Figure 8 is presented to summarise the evolution of hydrate surface area as a function of equivalent hydrate volume fraction for all experiments performed (100 to 700 RPM). A consistent behaviour was observed for each experiment in terms of the surface area increasing to a maximum followed by a decrease to a plateau: the hydrate volume fractions (φ) at which the maximum point and plateau were achieved are labelled φ₁ and φ₂, respectively.
Figure 8. Calculated hydrate surface area based on the FBRM chord lengths data as a function of hydrate volume fraction for six gas-water experiments at impeller speeds of 100 to 700 RPM.

Table 2 compares $\phi_1$ and $\phi_2$ with the value of $\phi_{\text{transition}}$ estimated based on the resistance-to-flow data. While $\phi_{\text{transition}}$ ranged from about 14 to 18 vol %, with any dependence on shear rate partially obscured by the measurement’s noise, $\phi_1$ varied from approximately 1.6 to 9.1 vol% for 100 to 700 RPM, respectively, while $\phi_2$ was about 10 vol% for experiments at 100-300 RPM, and about 20 % for experiments at 550-700 RPM.
Table 2. Hydrate volume fractions at which the peak ($\phi_1$) and the plateau ($\phi_2$) were achieved in the plots shown in Figure 8. Also listed are the values of $\phi_{\text{transition}}$ determined from motor current data in the same experiments as described in Section 3.1 and reported in Table 1.

<table>
<thead>
<tr>
<th>Exp</th>
<th>RPM</th>
<th>$\phi_1$</th>
<th>$\phi_2$</th>
<th>$\phi_{\text{transition}}$ bounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>100</td>
<td>1.6</td>
<td>10</td>
<td>15-16.8</td>
</tr>
<tr>
<td>3</td>
<td>300</td>
<td>2.2</td>
<td>11</td>
<td>14.1-16.1</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>2.8</td>
<td>11</td>
<td>15.8-16.7</td>
</tr>
<tr>
<td>5</td>
<td>550</td>
<td>2.4</td>
<td>19</td>
<td>16.4-17.7</td>
</tr>
<tr>
<td>6</td>
<td>700</td>
<td>5.5</td>
<td>20</td>
<td>14.3-16.0</td>
</tr>
<tr>
<td>7</td>
<td>700</td>
<td>9.1</td>
<td>20</td>
<td>14.3-17.9</td>
</tr>
</tbody>
</table>

The observed evolution in the CLDs measured with the FBRM is graphically summarized in Figure 9 and could be interpreted as follows: During the early stages of hydrate formation, particles were distributed homogenously in the water phase, so the FBRM measurements provided a representative sampling of the aqueous phase. With continued hydrate growth, the number of solid particles in the liquid phase became sufficient to enable particle interaction and this coincided with the maximum identified in Figure 9 at $\phi_1$. We hypothesise that this turning point in surface area represents the actual onset to a heterogeneous particle distribution in the aqueous phase, albeit at a level that has negligible effect on the macroscopic resistance to flow. At the highest shear rate tested (700 RPM) a homogeneous hydrate slurry was maintained at fractions up to 9 vol%, suggesting that the shear force exerted by the continuous water phase influences the point at which interparticle interaction becomes sufficient to affect the spatial distribution of particles. Above this threshold, particles are essentially removed from the FBRM’s field of view because, for example, they are buoyant and collect at the gas-water interface, and/or begin depositing on
the cell wall or impeller blades. A general comparison between the value of $\varphi_2$ and $\varphi_{\text{transition}}$ suggests that the point at which the FBRM-measured surface area of hydrate particles stopped decreasing and levelled off roughly corresponds to the point where the heterogeneous particle distribution begins to affect the slurry’s resistance-to-flow. At lower shear rates (100 – 300 RPM), the value of $\varphi_2$ determined from measurements at the micron length scale appears to occur slightly before the value of $\varphi_{\text{transition}}$ derived from macroscopic measurements, whereas at higher shear rates (550 – 700 RPM) $\varphi_2$ occurred slightly after $\varphi_{\text{transition}}$.

The mechanism discussed in Figure 9 is based on, and consistent with, the behaviour observed by Joshi, et al. 6, Akhfash, et al. 7 and Aman, et al. 8, which were all based on macroscopic measurements of pressure drop in a flowloop or motor current/torque in a visual autoclave. The FBRM data reveal that hydrate bed formation occurs as a process rather than having an onset at a point: the improved resolution indicates that hydrate bed formation is initiated at lower volume fractions (2-9 vol%) than previously considered. Potentially, resistance-to-flow measurements may only be able to resolve the point at which a moving hydrate bed has fully formed in the system. The results suggest that risk management strategies for high water cut systems may need to include an additional level of conservatism in estimating the maximum tolerable hydrate volume fraction, as particle interaction and bed formation may be initiated at lower hydrate fractions than detectable from (increases in) flowline pressure drop.
Figure 9. Schematic representation of hydrate particle distribution evolution in water continuous systems based on FBRM, pressure (this work) and visual measurements. Three regions of homogenous, heterogeneous and plugging conditions are considered; conceptual diagrams are shown for each stage to qualitatively represent the distribution of hydrate in the autoclave. In the autoclave schematics, white, green, and blue colours correspond to the hydrate, gas, and water phases, respectively. (For interpretation of the references to colour in this figure legend, refer to the web version of this article.)

After each FBRM measurement (every 10 s) prior to $\phi_{transition}$ (as determined from the motor current data), the mean separation distance between hydrate particles was estimated...
using a simplified approach that combined the FBRM data (mean chord lengths) with the measured hydrate volume fraction. By assuming that the particles were spherical and distributed homogeneously in the aqueous phase, the chord length data acquired at each time step was used to calculate the average volume for each particle. The total number of particles, N, was estimated by dividing the total volume of hydrate by this average particle volume. Finally, the total volume of the system (hydrate + water) was divided to N-volume elements. In this idealisation, each volume element was occupied by one hydrate particle at the centre, enabling estimation of the average distance separating two hydrate particles. This analysis was used to compare the calculated average separation distance between particles with the reported values of $\varphi_1$ in Table 2. That is, this estimation of average particle separation distance was used to assess whether the interpretation of $\varphi_1$ as being the onset of particle interaction was reasonable.

Figure 10 shows the results for the estimated edge-to-edge distance between particles. The hydrate volume fractions at which the chord counts decreased (the values of $\varphi_1$ reported in Table 2) correspond to hydrate particle separations in Figure 10 of 380, 395, 295, 460, 210 and 150 microns for experiments 2 to 7, respectively. The corresponding CLD-based average particle sizes at those hydrate volume fractions ($\varphi_1$) were measured to be 184, 240, 190, 260, 195 and 180 microns for experiments 2-7, respectively. The ratios of these values ranges from 2 at the lowest shear rate of 100 rpm, to 1.6 at 300-550 rpm, to 0.9 at the highest shear rate of 700 rpm. This qualitatively supports the interpretation that the onset of particle interaction starts to occur when the length scales of particle size and separation become comparable.
Figure 10. Calculated edge-to-edge distance between solid particles in the water phase based on a simplistic model for experiments 2 to 7 corresponding to mixing speeds of 100 to 700 RPM. (For interpretation of this colour figure, refer to the web version of this article.)

Our observation of a particle number concentration limit for the homogeneous state of a solid-liquid suspension is also consistent with the relevant literature. Studies of Einstein’s relation for dilute solid particle suspensions indicate that particle interaction starts occurring at around 5 vol%; particle collision and aggregation, together with shear rate should be considered for concentrated and non-dilute suspensions beyond this point. The shear rate above which a homogenous suspension is achieved for a given concentration of non-interacting solid particles can be estimated using the Zwietering correlation. Several studies with non-interacting solids have shown experimentally that for particle sizes, stirred tanks and mixing speeds comparable to those considered in this work homogenous suspensions are achieved for concentrations less than 10 vol%. In this work, we have extended such studies of solid suspensions by considering the evolution of hydrate particles, which are both interacting and less dense than the liquid phase.
4 Conclusions

In this study, we present a new method of characterising the onset to hydrate bed formation in a water-continuous system, through FBRM-based chord length distributions captured in a high-pressure autoclave cell over a range of mixing speeds (50-700 RPM). The results from the FBRM data provided a range of 1 to 400 microns for the chord length of entrained gas bubbles in the aqueous phase prior to nucleation. This is valuable as it can help guide first estimates of the initial gas-water surface area in water continuous systems, and might help improve the predictions of hydrate growth rate models.

The FBRM was effective in identifying hydrate nucleation, evidenced by clear changes in the measured number and size of the particles concurrent with the decrease in cell pressure. From the FBRM chord length and chord count distributions, it was possible to estimate the total hydrate surface area in the centre of the aqueous phase during the measurement. An increase in the total surface area was observed after hydrate nucleation; this surface area continued to increase until a maximum was reached between 2 and 9 vol\% hydrate for 100 to 700 RPM, after which the total surface area decreased rapidly, despite the fact that hydrate continued to grow in the cell. We hypothesise that this reduction in surface area measured by FBRM may correspond to the onset of particle interactions and evolution of a moving hydrate bed, which may not be detected in macroscopic (resistance-to-flow) measurements until hydrate volume fractions in excess of 14 vol\%. An increase in the measured motor current was detected at hydrate fractions above 16±2 vol\%, which has previously 6,7,8 been interpreted to correspond to the onset of spatially heterogeneous hydrate distribution and hence hydrate bed formation. Around these hydrate concentrations, the FBRM chord length signal reached a plateau at 10 vol\% for low shear rates (10-300 RPM) and 20 vol\% for high shear rates (550-700), which may correspond to the primary growth of
a moving hydrate bed with minimal particle entrainment in the bulk liquid phase. In general, the FBRM micron-scale measurements suggest that the onset of a moving hydrate bed may occur at much lower hydrate concentrations than those inferred from macroscopic measurement techniques (i.e. resistance-to-flow measurements).

A simplified model was used to estimate the mean particle distance between hydrate particles in the system by integrating the FBRM chord length distributions with the measured hydrate volume fraction. The results indicate the onset of a moving hydrate bed detected by FBRM corresponded to the point at which the average particle separation distance was comparable with the average particle size with the ratio varying from 2 to 1 as the shear rate increased.

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**References**


TOC/Abstract Graphic

PVM image
10 min after hydrate growth

FBRM distribution
8% hydrate

Resistence to Flow
(based on MC)

Motor Current (MC)

PVM probe

P

T

FBRM probe

HP gas-water systems