# HYDRATE INHIBITION VIA COLD FLOW - NO CHEMICALS OR INSULATION

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### ABSTRACT

Nonadhesive hydrate slurries have been shown to exhibit low viscosities in a field-scale flow loop when formed under appropriate conditions. The factors that favor formation of low-viscosity hydrate slurries include high Reynolds Number and Capillary Number, and high mass transfer and heat transfer rates. High liquid loading and high superficial fluid velocities are found to be conducive to the formation of low viscosity hydrate slurries. Dispersed bubble flow has been observed to facilitate flowable hydrate slurry production. Alternatively, the formation of nonadhesive hydrates at moderate superficial velocity is possible when a static mixer is used upstream of the hydrate formation location. For certain fields, low-viscosity hydrate slurry technology could eliminate the need for insulation and hydrate inhibitor chemicals.

Keywords: gas hydrates, static mixer, slurries, cold flow

### NOMENCLATURE

 $d_w$  water droplet diameter [micron] GVF gas void fraction [%] Nu Nusselt number Q flow rate [gpm] Re Reynolds number SM static mixer  $\langle v \rangle$  average liquid velocity [m/s] WAT wax appearance temperature [°F] WC water cut [%] WDT wax dissolution temperature[°F]  $\Delta P$  pressure drop [psi]  $\mu$  viscosity [cP]  $\mu_r$  relative viscosity of hydrate slurry

### INTRODUCTION

Hydrate slurries that flow have been pursued by the oil and gas production, refrigeration, natural gas transportation, separation, and  $CO_2$ sequestration industries. Flowable hydrate slurries are those in which the attractive forces between hydrate particles that lead to formation of large networks, have been minimized. The capillary force tends to be the most significant hydrate interparticle force in the presence of liquid hydrocarbons [1].

Hydrate slurries were first noted to have different morphologies given different flow conditions and history [2]. Hydrate formed under various flow regimes was described as "slurrylike", "slushlike" or "powderlike". One characteristic of slurrylike and powderlike hydrate is that it tends to flow easily compared to slushlike hydrate, which tends to aggregate.

Hydrate slurries form by several mechanisms such as shown in Figure 1. Water can be entrained into an oil phase as droplets. Hydrate initially forms as a shell of some thickness into the droplets, and if these droplets are large enough, the interior may not readily convert to hydrate. The hydrate shell creates a diffusive boundary that reduces additional water conversion. This initial boundary thickness has been observed to be approximately 5 microns [3], although the actual thickness is

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expected to depend on the solubility of hydrate guest components into water and is therefore a function of gas composition and pressure.



Figure 1 Some mechanisms for hydrate formation in flowing oil-gas-water

If water remains in a hydrate particle core, some can permeate out of small pores and cracks in the hydrate shell to create capillary bridging between colliding particles. Hydrate is less dense than water, and so as it forms, it expands, inducing a core pressure that further motivates permeation. Also, colliding particles can fracture and expose water that will lead to capillary attraction. Such aggregates can build into networks, greatly increasing viscosity. In turn, the flowing pressure drop increases and flow rate decreases.

A similar phenomenon can occur with a gas bubble when it achieves a hydrate layer. Aggregating gas bubbles can cause plugging at lower hydrate fractions, however, since trapped gas produces an effectively larger aggregate for the same hydrate fraction. Dispersed bubble flow is conducive to flowable hydrate formation since hydrate encrusted bubbles do not form networks. The aggregation of hydrate encrusted gas bubbles seems to be a problem primarily when there is a free gas zone where the aggregates can accumulate or foaming is occurring. For these reasons, flow that produces foam networks is expected to be antagonistic to flowable hydrate generation, whereas, dispersed bubble flow is not.

A process for generating flowable hydrate slurries by direct hydrate generation and also by injection of flowable hydrate seeds was developed by Lund et al. [4]. This paper describes an alternate process for directly generating flowable hydrate slurries as well as another process for seeding. Tajima et al. [5] disclosed a method using static mixers for production of carbon dioxide hydrate slurries for  $CO_2$  sequestration. This technology was also applied to concepts for production of hydrate slurries for gas separations [6]. Static mixers, like the one shown in Figure 2, are nonmechanical devices, the most effective of which mix flow in tubes by dividing flow, rotating the flow, and reversing the flow rotation [7]. Each mixer is composed of multiple elements, which are the locations of flow division and reversal.



Figure 2 Static mixer in main flow stream

Static mixers appear to enhance flowable hydrate production by each of the following mechanisms:

1. increased heat exchange with the pipe wall, faster hydrate formation, and more thorough conversion of water to hydrate,

2. more rapid reaction rates by increasing the transfer rate of gas to water,

3. diminishing droplet and bubble size, thereby increasing reaction surface area (and reaction rates) and decreasing hydrate shell thickness necessary for converting an entire droplet,

4. breaking apart hydrate particles that may have a water core, thereby exposing the water core to gas for more thorough conversion, and

5. breaking apart aggregates caused by hydrate inter-particle water bridges during conversion.

The simple patented process is shown in Figure 3 involving static mixers positioned within the pipeline where hydrate becomes stable [8]. Additional static mixers can be positioned at the proper distance to prevent excessive coalescence of unconverted water.



Figure 3 The flowable hydrate slurry generation process

A second patented process is shown in Figure 4, where a sidestream of the main stream utilizes a

static mixer to form flowable slurries, which are then used to seed the main stream [8].



Figure 4 The flowable hydrate slurry seeding process

In this study, the parameters important for production of flowable slurries in oil-dominated systems under cold temperatures and high pressures without chemical inhibition has been tested and production of such slurries has been promoted through the use of static mixers or powder-like seeds.

# **EXPERIMENTAL DESCRIPTION**

Three classes of experiments were tested:

- 1. hydrate slurries produced in bare piping,
- 2. hydrate slurries produced through static mixers, and
- 3. hydrate nucleation by seeds

The following operating conditions were expected to promote the formation of flowable slurries:

- Lower gas void fraction
- Lower water cut
- Higher liquid velocities
- Smaller water droplets/gas bubbles
- Higher viscosity oil
- Lower oil/water interfacial tension

# Description of Loops

The operating conditions were evaluated by using a large diameter (4") and small diameter ( $\frac{1}{2}$ ") loop. The  $\frac{1}{2}$ " diameter loop was connected to the 4" diameter loop in such a fashion that its contents could be transferred, thus enabling the formation of hydrate in the  $\frac{1}{2}$ " loop to seed 4" loop fluids.

Both loops were equipped with similar equipment: A sliding vane pump was used to minimize damage to the hydrate particles.

A hydraulically-controlled piston moved within a gas accumulator to maintain constant pressure

during gas consumption by hydrate formation, gas absorption, or thermal expansion.

Borosilica or sapphire sight glasses were present for viewing flow regime and hydrate morphology.

A Lasentec D600X Focused Beam Reflectance Method (FBRM) particle size analyzer measured chord length distributions (i.e., the line length from one edge of a particle to the other). The chord length distributions were converted into particle diameter distributions by assuming lognormal distributions of water droplets/hydrate particles [9] and then applying the Cahn and Fullman technique [10].

A MicroMotion DH100 Coriolis mass flow meter was used. The average liquid velocity,  $\langle v \rangle$  was taken as the flow rate divided by the crosssectional area of the tubing.

A Rosemount differential pressure transducer detected the pressure drop from the suction to discharge sides of the pump, which was equated to the pressure drop across the loop.

Figure 5 shows the 4" loop layout. The loop was contained in an environmental chamber with temperature controlled between 20 and 90°F by blowing conditioned air past six finned sections.



Figure 5 Diagram of the 4" flow loop with static mixer locations indicated.

The dimensions of the 4" loop are as follows:

312 ft / 275 ft *
3.826 in
185gal / 165gal *
245gal / 205gal *
1,200psig
20-90°F

Table 1. Characteristics of the 4" loop

\*with / without outside loop section

The 4" loop was configured in one of three ways: (1) no mixers, (2) one mixer with four elements (labeled "A"), and (3) a total of five static mixers with four elements each.

A  $\frac{1}{2}$ " loop was constructed for the purpose of generating powder-like hydrate seeds. The loop is shown in Figure 6.



Figure 6 Diagram of the 1/2" flow loop

The  $\frac{1}{2}$ " loop was connected to the 4" loop, but was isolated from content transfer by two block valves. The temperature was controlled by a water bath. The dimensions of the loop are as follows:

Table 2. Characteristics of the  $\frac{1}{2}$ " loop

Loop length	138 ft
Inner diameter	0.5 in
Loop-section volume	1.4gal
Total loop volume	4.7gal
Max. allowable working pressure	4,500psig
Temperature range	20-100°F

The  $\frac{1}{2}$ " loop was configured in one of three ways: (1) with no static mixers, (2) with one 4-element static mixer at the discharge of the pump, and (3) with five 4-element static mixers inserted prior to the bends of the loop.

# **Determining Relative Viscosity**

Relative viscosity,  $\mu_r$  was used as a criterion for determining the ability to flow hydrate slurries. A flowable slurry has a low relative viscosity, while that of a plugging slurry will be higher.

The viscosity,  $\mu$  tends to be directly proportional to the pressure drop which induces flow,  $\Delta P$  and inversely proportional to the flow rate, Q:

$$\mu \propto \frac{\Delta P}{Q} \tag{1}.$$

Therefore, the relative viscosity was estimated as the ratio of the maximum viscosity of the circulating fluid slurry during water conversion to hydrate (subscript "max") to the fluid viscosity prior to hydrate nucleation (subscript "i"):

$$\mu_{r} \approx \frac{\left[\frac{\Delta P_{0}}{2}\right]_{\max}}{\left[\frac{\Delta P_{0}}{2}\right]_{i}}$$
(2).

### Description of the tested hydrocarbon liquids

To avoid shifting equilibria during slurry formation, greater than 99.9mol% methane was used in most experiments. The experimental conditions varied, but 1,000psig and 40°F was typical in the 4" loop, while 3,000psig and 40°F was typical for the  $\frac{1}{2}$ " loop. The methane hydrate equilibrium is well known and is predicted by CSMGem to be sI at 49.4°F for a pressure of 1,000psig. At 3,000psig, the predicted methane hydrate equilibrium temperature is 66.0°F.

Several different hydrocarbon liquids were used in the study, including dodecane, King Ranch Condensate, and Conroe Crude. Some of the physical properties and characteristics for the hydrocarbons are tabulated:

Fluid	$\hat{\Gamma}_{ow}$ mN/m <sup>2</sup>	μ cP	ρ kg/m <sup>3</sup>	WAT/ WDT °F/°F	Appear- ance
dodecane	51	2.0	790	N/A	clear
KRC	38	0.4	683	N/A	clear
Conroe	25	6-11	845	54.5/	dark
				70.7	

Table 3. Properties of tested liquid hydrocarbons\*

\*properties estimated at 40°F.

#### Description of Experimental Methodology

Hydrate was generally formed by loading the loop with the desired water and oil, pressurizing the loop to the experimental pressure with methane while pumping the liquids at the experimental pump motor speed, and then cooling the loop to the experimental temperature. The flow rate, hold temperature (subcooling), and water/hydrocarbon liquid loading were varied between experiments to determine hydrate slurry flow dependency on these factors.

For seeding experiments, flowable hydrate seeds were first generated in the  $\frac{1}{2}$ " loop by repeating a previously successful experiment. Simultaneously, hydrocarbon liquids, circulated at the desired pump rate and pressurized to 1,000psig with methane, were cooled in the large loop to the experimental temperature of about 40°F. No water was added to the 4" loop at this point to avoid premature hydrate formation before seeding. The transfer of flowable hydrate seeds was made to the 4" loop. Multiple transfers could be made by repeating the formation and transfer procedure until the desired seed amount was present in the 4" loop. Water was then injected into the loop at various rates to simulate seeding rates.

# **RESULTS AND DISCUSSION**

The effects of the operating parameters are discussed in this section. In particular, these effects included presence of static mixers, gas void fraction (GVF), water cut (WC), liquid velocity, droplet size, oil properties, salt concentration, hydrate structure, and the powder-like seeding process.

# Effect of gas void fraction and water cut

The GVF is equal to the ratio of average gas void area in a pipe cross section to the total crosssectional area. The effect of GVF and water cut on flowable hydrate formation was first observed in King Ranch Condensate in the 4" loop.

For an oil, greater water amount will tend to lead to larger pressure drops because more hydrate is produced; however, Figure 7 shows that by increasing liquid loading and decreasing the gas void fraction, lower pressure drop was observed during hydrate formation in 91 HC vol% King Ranch Condensate with 9 HC vol% Conroe crude. The lower pressure drop at 80% liquid loading is noteworthy since there was 36% more hydrate formed than in the 60% liquid loading. Therefore, by decreasing the gas void fraction, more flowable conditions were produced.



Figure 7 Methane hydrate formation in 91 HC vol% King Ranch Condensate / 9 HC vol% Conroe crude in the 4" loop.

Figure 8 shows a comparison of slushy hydrate produced in 100 gallons of King Ranch Condensate and 5 gallons of fresh water, with flowing hydrate produced by injecting the 30 gallons of additional King Ranch Condensate, thereby decreasing the GVF and water cut. Other conditions of the test were 1.3m/s liquid velocity, 900psig pressurized with 76.4wt% methane and 23.6wt% propane, and hold temperature at 55°F.



Figure 8 Hydrate in King Ranch Condensate in the 4" loop. a) Shut-in slushy hydrate has the appearance of clumping b) Upon restart, the slushy hydrate agglomerates, producing plugging. c) Shut-in flowable hydrate slurry appears silty and does not self-adhere. d) Upon restart, the flowable slurry disperses into a fine suspension.

In Figure 8a, some gas space was observed in the loop, and large aggregates of hydrate were produced. Upon shut-in, these aggregates collected on the pipe bottom. Figure 8b shows how upon restart the aggregates rapidly collected into large

masses that drag and accumulate against the pipe walls. By contrast, Figure 8c shows the shut-in hydrate produced from low GVF, which has a silty appearance. Figure 8d shows how upon restart the silty hydrate disperses readily as a suspension, which does not collect on the pipe walls.

The slushy morphology is probably a result of gas bubble collection at the water droplet surface during hydrate formation, which leads to larger, hydrate coated gas bubbles and coalesced water droplets.

One benefit of high liquid loading is to carry the hydrate out of a pipeline. For this reason, flowable hydrate slurry generation is more suited to oil production than gas production.

Flowable hydrate has been shown to be produced in as high as 50% water cut in the Conroe oil. This was done at 30% GVF in the 4" loop at 1,000psig 75mol% methane/ 25mol% ethane mixture while circulating at a liquid velocity of 3.8m/s. It was done without the assistance of static mixers, the effects of which will be discussed later. Figure 9 shows how the pressure drop climbed slightly, but did not result in a maximum relative viscosity over 1.4.



Figure 9 Hydrate run in the 4" loop at 50% water cut in Conroe crude, with 30% GVF, 1,000psig of 75mol% methane / 25mol% ethane gas mix, 3.4m/s liquid velocity, 0 static mixer elements, 40°F hold.

Flowable hydrate has also been shown to be produced in GVFs as high as 46% at 5% water cut when no static mixers were present, giving a relative viscosity of 0.9. Neither the upper bound of GVF at the 5% water cut nor the upper bound of water cut at 46% GVF have been tested. Figure 10a shows how the pressure drop across the loop did not increase noticeably as 5% water cut was converted to hydrate at 735psig and 40°F, while circulating at 1.2m/s liquid velocity with no static mixers present. Other experiments at this lower circulation rate were observed to be plug with a relative viscosity of 9.5 at the moderate water cut of 35%, as shown in Figure 10b.



Figure 10 Runs in the 4" loop in Conroe crude, with 46% GVF, 735psig methane, 1.2m/s liquid velocity, no static mixer, and  $40^{\circ}$ F hold. a) non-plugging run with 5% WC and b) plugging run with 35% WC.

Figure 11 represents a map for plugging and nonplugging operation in the large loop, based on water cut and gas fraction for various flow rates. The limits for both water cut and gas fraction can be considered in the map: when water cut is 0, no hydrate can occur; likewise when the GVF is 0, mass transfer limitations produce little to no hydrate. The worst case for plugging is expected to be a case with high water cut and gas fraction; thus a hyperbolic shape is assumed in the map. Increased flow rate can be seen to enhance the non-plugging region.



Figure 11 Flow map of plugging and non-plugging regions at various flow rates in the 4" flow loop as a function of water cut and gas void fraction for the Conroe oil.

The relative viscosity as a function of water cut for all experiments are shown in Figure 12. From the figure, it can be seen that all of the data are bound between relative viscosity of 1 and some function which increases with water cut.



Figure 12 Hydrate slurry relative viscosity versus water cut

This upper bound limit function appears to be exponential and intercepts the axis at 1, i.e. as the water cut goes to zero, the viscosity remains unchanged:

$$1 \le \mu_{r,\max} \le \exp[11.2(WC)] \tag{7}$$

Figure 13 shows the relative viscosity as a function of the gas void fraction.



Figure 13 Hydrate slurry relative viscosity versus gas void fraction

Similar to the water cut, there appears to be some exponential function that provides an upper boundary for relative viscosity with lower bound at 1. The function is of similar magnitude to that for the water cut and finds its intercept at 1, i.e. when no gas is available, the viscosity remains unchanged:

$$1 \le \mu_{r,\max} \le \exp[8.0(GVF)] \tag{8}$$

Effect of Liquid Velocity and Flow Regime

Liquid velocity was among the most influential parameters for forming flowable hydrate. For water cuts above ~20%, if the mixture was in what was observed to be a stratified wavy flow, a slushy and sticky hydrate often formed. As the liquid velocity was increased to greater than 1.7m/s, dispersed bubble flow was produced, which tended to more readily form flowable hydrate.

Higher velocities promote flowable hydrate by the same mechanisms previously mentioned for static mixers, i.e.

• higher shear rate is produced, resulting in smaller water droplets and gas bubbles, larger reaction surface area, and more thorough/rapid hydrate formation,

• higher shear rate also results in breaking aggregates that may form,

• heat transfer is increased, causing more rapid hydrate formation

• mass transfer is increased, thereby increasing hydrate formation rates, and

• smaller gas bubbles do not contribute to droplet coalescence as significantly as do large bubbles.

Figure 14a shows 35% water cut in Conroe crude in the 4" loop, pressurized to 735psig and 11% methane GVF, cooled to 40°F and circulating at 0.4m/s with no static mixers present. The relative viscosity produced was 24.7. Figure 14b shows a similar experiment where the liquid was circulated at 1.2m/s. The hydrate formation rate was 1.5 times faster than at the slower velocity, but the relative viscosity was only 2.3.



Figure 14 Runs in the 4" loop at 35% water cut in Conroe crude, with 11% GVF, 735psig methane, no static mixer, and 40°F hold. a) plugging run with 0.8m/s liquid velocity and b) non-plugging run with 1.2m/s liquid velocity.

Figure 15 shows the relative viscosity as a function of flow velocity. It can be seen that the tendency of velocity is to decrease the relative viscosity. All of the data are bound between unity and a power law function of the velocity:

$$1 \le \mu_{r,\max} \le 16.0 \langle v \rangle^{-20}$$
 [=] m/s (11).



Figure 15 Hydrate relative viscosity versus initial liquid velocity

Figure 16 shows how the droplet diameter diminishes as an exponential function of the velocity in the 4" loop. To achieve the desired droplet diameters of less than 20-30 microns, minimum flow velocities of 1.2-1.5m/s are required. Also shown in Figure 16 is the effect of static mixers, which is discussed in the "Effect of static mixers" section.



Figure 16 Initial droplet diameter with velocity for Conroe oil in the 4" loop for various experiments prior to nucleation.

# Effect of Oil Properties and Droplet Size

Oil viscosity and interfacial tension with water are known to play a role in the formation of a water droplet. Higher oil viscosity will produce smaller water droplets. The oil's viscosity dictates its initial resistance to flow and the resistance to allowing aggregates to form. A smaller water droplet will also be produced from a lower interfacial tension between water and oil.

Although interfacial tension between oil and water helps to dictate droplet size, it is the presence of surface active components which stabilize the droplet. Thus, under a certain shear rate, the interfacial tension is important for stabilizing a droplet, but once the shear is reduced, the water droplets can exist in a metastable state of hindered coalescence. Since small water droplets are desired for rapid and complete hydrate conversion, oils with surface active components are expected to produce flowable hydrate more easily than those without; i.e., fewer mixers are necessary to maintain droplet size during hydrate conversion.

One non-plugging experiment in the  $\frac{1}{2}$ " hydrate loop shown in Figure 17a was formed from 9% water cut in Conroe oil while circulating at 1.0m/s, charging to 3,000psig with methane, and cooling to 45°F. The resulting relative viscosity was 1.3. Figure 17b show how a similar experiment with dodecane had rapid viscosity increase to the point of plugging the loop. The relative viscosity prior to plugging was 18.0.



Figure 17 Runs in  $\frac{1}{2}$ " loop at 1.0 m/s with 9% WC at 45°F and 3,000psig with 4 static mixer elements with a) Conroe crude and b) dodecane.

The relative viscosity was plotted as a function of average droplet diameter in Figure 18. The relative viscosity can be seen to generally increase with increasing droplet size. Additionally, there is a bounded region of relative viscosity controlled by droplet diameter as expressed by the following approximation:

$$1 \le \mu_{r,\max} \le 5.0 d_{w}^{0.6}$$
 [=] micron (10).



Figure 18 Hydrate slurry relative viscosity versus mean droplet diameter.

The increase in relative viscosity with increasing droplet size is consistent with the concept of nonsticking hydrate particle generation. Smaller droplets will convert to hydrate thoroughly while larger droplets that are hindered by a hydrate shell may contain core water contributing to stickiness.

### Effect of static mixers

Although not always necessary, static mixers were observed to assist in flowable hydrate production. The optimal design for static mixers was studied by utilizing the FBRM particle size analyzer in the  $\frac{1}{2}$ " coalescence loop. The water droplet size distributions of 25% WC in Conroe oil and 25% WC in dodecane were tested with various combinations of flow rate, number of static mixer elements, distance from the end of the static mixer, and loop orientation. The dodecane contained 5vol% Conroe oil so that the particle size analyzer could discern hydrocarbon from water.

Four significant trends can be seen in Figure 16:

1. the static mixers cause the droplet size to decrease significantly, even at relatively low velocities,

2. there is little difference in droplet size when 4 elements are used versus 20 elements,

3. there is less effect on droplet size with increased velocity (above a threshold velocity of 1.0m/s) while using the static mixers, and

4. at large enough velocities ( $\sim 2.7$ m/s in the 4" loop) the droplet size produced with mixers is similar to that without, which suggests that drops produced from turbulence by wall shear have similar size to that produced by the static mixers. The effect of wall shear is seen in Figure 10, where no static mixer was needed to produce flowable hydrate at 3.8m/s.

The necessary velocity to produce a 20-30 micron diameter droplet is decreased by using static mixers from 1.2 - 1.5m/s to well below 1.0m/s.

Static mixers are beneficial in other ways than reducing droplet size, and additional elements may enhance flowable hydrate production. Static mixers can cause shedding of the hydrate shell, thereby increasing hydrate conversion. Continuous or periodically placed static mixer elements would reduce coalescence, thereby maintaining the small droplet size. Also, as wallinduced shear is diminished in scale-up to larger pipe size, the static mixers would play a more significant role to diminish droplet size.

Static mixers will reduce the size of gas bubbles in the same manner as they reduce water droplet size, which encourages dispersed bubble flow.

Also, the static mixers greatly increase mass and heat transfer from the surroundings, and so will encourage hydrate formation and growth. Heat transfer in laminar flow through static mixers is 2.5 to 3 times than that without:

$$Nu_{SM} = 2.5 Nu$$
,  $Re < 2000$  (13).

In turbulent flow, the heat transfer is more than 3 times greater with a static mixer present:

$$Nu_{SM} > 3 Nu$$
,  $Re > 2000$  (14).

Two tests were conducted under similar conditions:

1. one static mixer (containing 4 elements) located in the 1st position on Figure 5 and

2. with all five static mixers (a total of 20 elements) installed.

Both tests used 26% water cut and 27% gas void fraction, were pressurized to 1,000psig with methane, were circulated at 0.9m/s liquid velocity, and were cooled to 40°F.

In the first test, seen in Figure 19a, the effect of 4 static mixer elements was to produce a slurry with relative viscosity of 4.1. The test with an

additional 16 static mixer elements (20 total elements) is shown in Figure 19b. The effect of the additional elements was to reduce the produced relative viscosity by 72%, producing a slurry with relative viscosity equal to 1.2. It should be noted from the figures that flow through static mixers caused an increase in pressure drop as a function of flow rate. Thus the field and flow loop are different since no more additional pressure drop requirements are expected in the field once flowable hydrate slurries have been produced.



Figure 19 Runs in the 4" loop at 1.0m/s, 100gal Conroe crude in 26% WC, pressurized to 1,000psig with 27% GVF methane, held at  $40^{\circ}$ F. a) plugging with 4 SME b) no plugging with 20 SME.

Effect of powder-like hydrate seed injection

Flowable hydrate onset by seeding was tested by first creating seeds in the  $\frac{1}{2}$ " loop, and then transferring them to the 4" loop. The transfer was performed by opening the valves which block the transfer line and by allowing the pressure differential to drive the powder-like hydrate slurry into the 4" loop. The seeds were transferred into the 4" loop while it was charged to experimental pressure with oil and gas and cooled to within the hydrate equilibrium region to ensure the seeds did not melt. No water was loaded into the loop prior to the transfer to keep hydrate from forming before seeding was possible. After transferring seeds to the 4" loop, fresh water was injected until the desired water cut was attained. Successive experiments at higher water cuts could be tested by injecting additional water to the 4" loop.

A baseline plugging experiment and a seeding experiment are seen in Figure 20a and Figure 20b, respectively. In both experiments, 34% water cut and 44% GVF in Conroe oil was circulated through 4 static mixer elements at 0.9m/s in the 4" loop, while pressurized to 1,000psig with methane and held at 40°F. In the baseline experiment, the relative viscosity reached 7.7, while the seeded experiment maintained a relative viscosity of 1.0.



Figure 20 Runs in 4" loop with 34% water cut, 44% GVF at 0.9m/s at 1,000psig methane, 4 static mixer elements, 40°F hold. a) plugging baseline run and b) non-plugging seeding experiment

These results suggest that seeding of a stream with powder-like hydrate promotes the growth of flowable hydrate slurries. The likely mechanism for this is that as a powder-like hydrate seed is coated by water, it seeds the droplet from within to convert the interior of a water droplet first and provides a hydrate core from the onset. Thus, no unconverted core exists to lead to aggregation. The maximum water injection rate was 2.0gpm, and all of the water could be injected within 11 minutes. The best seeding rate obtained was nearly 1:165 seeds to main stream by volume.

# Flowable slurries with wax

In some experiments in the  $\frac{1}{2}$ " loop, two exotherms were apparent, which indicated that wax was forming as well as hydrate. For the Conroe oil, the Wax Appearance Temperature (WAT) was found to be 54.5°F and the Wax Disappearance Temperature was 70.7°F at atmospheric pressure. At 3,000psig of methane pressure, the WAT is likely to shift lower by at most a few degrees.

Wax deposition on pipe walls is a gradual process compared to hydrate formation. In the flowable hydrate generation process, it is expected that hydrate will keep the pipe wall clear of wax deposition as it occurs through erosion. Preliminary observations indicate that hydrate erodes wax from a pipe wall particularly at high liquid velocities, and liquid loadings. It is also expected that increased water cut will enhance this effect, since more hydrate is produced.

Static mixers are also likely to contribute to reducing wax deposits. Wax precipitation is most rapid for laminar flow when a thermal gradient exists between the hydrocarbon and the pipe wall. Static mixers homogenize the temperature and eliminate thermal gradients, thereby reducing wax precipitation on the walls.

### Shutin/Restart

Flowable hydrate was observed to successfully restart after a 26-day shut-in period in the 4" loop without significant increase in pressure drop as shown in Figure 21. A hydrate slurry with relative viscosity of 1.0 was formed in 30% GVF of a methane ethane mixture in Conroe crude with 25% WC, while circulating the liquid at 2.6m/s through no static mixer elements, pressurized to 1,000psig with 75% methane/ 25% ethane mixture, and cooled to 40°F.



Figure 21 Twenty-six day shut-in restart of flowable slurry

After one day into the experiment, the pump was turned off for a period of 26 days while maintaining the temperature. After restart, the flow was fully restored with a maximum relative viscosity of 1.2.

# SUMMARY

Flowable hydrate slurries in oil were generated using two new processes. The following equipment and parameters were observed to have a positive influence on the formation of flowable hydrate:

- Static mixers in the main flow stream
- Lower gas void fraction
- Lower water cut
- Higher liquid flow rates
- A powderlike hydrate seeding process
- Smaller water droplets/gas bubbles
- Higher viscosity oil
- Lower oil/water interfacial tension

With some success, several of these influences can be diminished as the others are increased. Static mixers assist in generation of flowable hydrate slurries by the following processes:

- 1. Increased heat transfer causes more complete conversion of water to hydrate with shorter residence time,
- 2. Increased mass transfer of hydrate formers likewise increases water conversion rates,
- 3. Increased shear causes a reduction of water droplet size and increase in water surface area, further enhancing heat and mass transfer and water conversion rates,
- 4. Reduced water droplet size allows for more complete conversion to hydrate during

formation of an initial layer of certain thickness, and

5. Increased shear continuously separates converting particles to overcome capillary bridging and minimize hydrate bridge formation.

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