Experimental Investigation of Deposition and Wall Growth in Water Saturated Hydrocarbon Pipelines in the Absence of Free Water

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ABSTRACT

Using a combination of micromechanical force and flowloop measurements, hydrate deposition on a pipe wall surface was investigated for ‘dry’ hydrates formed in the bulk phase and for hydrates growing on the pipe surface.

Cyclopentane ‘dry’ hydrates (without a free water phase) were used to predict whether hydrates, formed in a bulk condensate phase, would adhere to a pipe wall. Adhesion forces between cyclopentane hydrates and steel were measured using a micro-mechanical force apparatus. The average force of adhesion was measured to be very small, less than 0.01 N/m. This force was used in a particle force balance, predicting that hydrates formed in the bulk phase would not deposit on the pipe wall.

It was hypothesized that in the presence of a water saturated hydrocarbon, hydrates would grow on the pipe wall as the fluid cooled below its equilibrium temperature. This hypothesis was confirmed using a single pass condensate flowloop. Water was continuously dissolved into the flowloop inlet stream as water deposited in the flowloop test section, resulting in both a pressure drop and fluid temperature increase. This work illustrates the need for a hydrate wall growth model.

Keywords: hydrates, adhesion force, flow assurance, flowloop, wall growth, deposition

NOMENCLATURE

CS Carbon steel
CyC5 Cyclopentane hydrate
FA Adhesion force
FD Drag force
FL Lift force
MD External moment of surface stress

INTRODUCTION

Clathrate hydrates have hindered the oil and gas industry since 1934, when Hammerschmidt discovered hydrates were capable of plugging pipelines. Clathrate hydrates are crystalline inclusion compounds wherein hydrogen-bonded water molecules form cages containing guest...
molecules[1]. Hydrates form at high pressures and low temperatures, similar to conditions on the seafloor; because hydrocarbons act as guest molecules, offshore pipelines are prime candidates for hydrate formation and plugging. In addition to lost production and revenue, hydrates pose a significant safety hazard. In 1994 Linglem et al suggested that hydrates may deposit on the pipe wall, similar to a freezing water pipeline[2]. Further evidence of a deposition mechanism was also shown in a 2002 field study, conducted in the Werner Bolley field in Wyoming. A steady pressure drop was observed, which was then followed by a rapid pressure drop decrease, indicating hydrate was building up in the pipeline and then being released downstream[3].

Before developing a predictive hydrate deposition model, it was necessary to determine what conditions result in hydrate depositing on the pipe wall. This work investigates the feasibility of deposition from hydrates formed in the bulk phase and on the wall itself.

EXPERIMENTAL

Micromechanical force measurements

Taylor measured adhesive forces between two THF hydrate particles and conducted initial force measurements between THF hydrate and stainless steel using a micromechanical force (MMF) apparatus[4]. Taylor’s hydrate-steel forces were completed as a portion of a larger scoping study. This work combined Taylor’s experimental procedure with a more refined sample preparation method.

The MMF apparatus was used to measure the adhesive force by bringing a hydrate or ice particle in contact with a steel surface. Adhesive force was measured by first placing a hydrate particle onto a thin glass fiber, approximately 30 microns in diameter, with a known spring constant. The steel sample was contacted with the hydrate particle and then displaced until the hydrate particle was removed from the steel surface. Adhesive force was calculated via Hooke’s Law, by taking the product of the spring constant and the displacement of the glass fiber (Figure 1D), required to remove the hydrate particle from steel. A sample measurement is shown in Figure 1.

Figure 1. Hydrate-steel force measurement (reproduced from Taylor[4]). A) Hydrate particle and steel before measurement. B) Applying contact force to hydrate with steel sample. C) Applying removal force to hydrate particle by moving steel. D) Final displacement of glass cantilever after the particle was removed from the steel.

Carbon steel 318 (CS) samples were prepared in the CSM metallurgy laboratory by polishing 1 cm² pieces of steel and cutting small test samples using a high precision saw. Sample surfaces were polished using either 1 micron diamond polish or 240 grit sandpaper (corresponding to a surface roughness of approximately 59 microns).

Ice particles used in the ice-carbon steel (CS) measurements were formed by placing a water droplet on the end of the glass fiber and quenching the droplet in liquid nitrogen. The ice particle was then placed in the MMF cooling chamber, containing n-decane. Cyclopentane hydrate (sII) particles were formed using a similar procedure, except cyclopentane (CyC5) was used as a bulk fluid instead of n-decane. The quenched ice particles were placed in the cell with the CyC5 fluid below 0°C. The CyC5 was then slowly raised above freezing, allowing the ice particles to convert to cyclopentane hydrate over 30 – 60 minutes.
Single pass flowloop

Figure 2 shows the schematic of the single pass flowloop.

The flowloop consisted of a cooling section, test section, and reheat section. The cooling and reheat sections were each 60 ft in length, while the test section was 280 ft in length, parsed into seven 40 ft sections. The flowloop was constructed using a series of 20 ft long, coiled, pipe-in-pipe heat exchangers with an inner diameter of 0.37 inches.

The water concentration was measured prior to the cooling section and after the reheat section using GE moisture probes. Moisture content was maintained throughout the course of the experiment using an ultrasonic mixing system upstream of the separator. The flowloop was operated using 100% liquid loading and a flow rate of 0.75 gallons per minute.

RESULTS

MMF measurements

Initial experiments measured adhesive forces between ice and carbon steel. Measurements were conducted using both the 1 micron and 240 grit polished samples. Each steel sample was measured at three different temperatures, using a new particle for each measurement. The contact force between the ice particle and the steel sample (Figure 1B) ranged from 1.37 – 2.77 mN. Figure 3 shows that adhesive force increases with increasing temperature (decreasing subcooling), as shown in previous work by this laboratory [4]. It is important to note that the adhesive forces are normalized using the mean harmonic radius [4].

Figure 3. Cumulative probability distributions of measured adhesive forces between carbon steel and ice.

Cumulative force distributions shown in Figure 3 indicate the steel surface roughness did not affect forces within the range tested.

Figure 4 compares cyclopentane (CyC5) hydrate-CS forces with ice-CS and CyC5-CyC5 measurements. Measurements were completed at various subcoolings for each system, where subcooling is defined as the melting temperature minus the experimental temperature.

Figure 4. Adhesive force comparisons for various subcoolings. CyC5 represents cyclopentane hydrates and CS corresponds to carbon steel with varying surface roughness. Error bars show the range of data measured (0% and 100% in Figure 3).

Figure 4 shows that CyC5-CyC5 forces are substantially higher than either ice or hydrate forces with carbon steel. Furthermore, CyC5-CS measurements are substantially lower than ice-CS forces. CyC5-CS force are only measurable at low
subcoolings, near the dissociation temperature. CyC5-CS forces also appear to decrease with increasing CS surface roughness, which would decrease the contact area for capillary forces[4].

**Applying MMF Measurements to a Force Balance**

This work assumes that hydrate particles, formed from dissolved water, will have a diameter of approximately 10 microns or less and will be within the laminar sub-boundary layer in the pipeline. The force balance used in this section is similar to work conducted in the colloidal literature[5, 6]

A particle on a surface can be removed by three different mechanisms: (1) rolling, (2) sliding, and (3) lifting. The first step in predicting the removal mechanism is to develop a force balance on the particle [5-8]. Figure 5 shows the force balance used by Burdick et al. [5, 6].

![Figure 5. Force balance on a particle in laminar fluid flow.](image)

Adhesion force ($F_A$), drag force ($F_D$), and lift force ($F_L$), all act on the particle of diameter, d. Additionally, there is one external moment of surface stresses ($M_D$), acting through the center of the particle. Predicting $F_A$ is typically a key parameter in the colloidal literature; however, this study simply used the adhesive forces measured in the micromechanical apparatus.

The specific removal mechanism can be predicted using the force balance shown in Figure 5. The lifting mechanism occurs when

$$F_L \geq F_A$$ (1)

whereby the particle is removed in the vertical direction. The sliding criterion,

$$F_D \geq \mu(|F_A| - F_L)$$ (2)

is derived from the force balance in the horizontal direction, where $\mu$ is the static coefficient of friction between the particle and surface. The criterion for rolling is,

$$M_D + F_D \cdot l_1 + F_L \cdot l_2 \geq F_A \cdot l_2$$ (3)

where $l_1$ and $l_2$ are the vertical and horizontal moment arms, respectively [5, 6].

**Force Balance Results**

Calculations using the force balance model were completed using an adhesive force of 0.002 N/m, which is slightly higher than any forces measured between CyC5 and carbon steel. A particle diameter of 10 microns was used, ensuring the particle is within the laminar sub-boundary layer and Figure 5 remains accurate. Using these parameters, Equations 1-6 predict hydrate particles will roll off the surface at velocities of 3 ft/s and 6 ft/s for condensate and methane systems, respectively.

The MMF measurements and subsequent calculations predict that hydrates formed in the bulk fluid phase will not deposit on the pipe wall, in the absence of free water, under normal operating conditions. This prediction is also consistent with cold flow technologies.

It is important to note that this study only pertains to pipelines with fully converted water. In presence of free water, which may occur when a water saturated gas stream cools, it is possible for hydrates to grow on the pipe wall.
Flowloop results

A liquid condensate containing dissolved water was circulated through the flowloop at 1000 psia. The inlet condensate temperature was held at 15°C and the test section temperature was maintained at -21°C. After passing through the test section the condensate was reheated to 15°C. The test section inlet water concentration was maintained at approximately 25 parts per million by weight (ppmw) and the outlet concentration was in equilibrium with the solid deposit on the flowloop wall (~7ppmw). Figure 6 shows the water system originally in equilibrium, before water injection was started, which is denoted by the increase in the inlet moisture concentration.

The deposit initially grew in the first 40 ft of the test section, as shown in Figure 7.

As the condensate passed through the test section, the fluid was cooled below the ice/hydrate equilibrium concentration. Consequently, dissolved water formed a solid deposit on the flowloop wall and a pressure drop increase was observed as illustrated in Figure 6.

The step changes in flow rate were a result of increasing pump speed. As pressure drop increased, flow rate decreased and the pump speed was manually increased to maintain a flow rate near 0.75 gpm. Figure 7 shows the initial increase in pressure drop occurred primarily in the first 40 ft of the test section. But as time increased, the gap between the 40 ft and 80 ft line began to broaden, indicating hydrate/ice was propagating downstream. This was also observed in the gap between 80 ft and 120 ft.

The explanation for this behavior is shown in Figure 8.
insulation. This temperature increase shifted the equilibrium curve further downstream, which resulted in the solid deposit moving downstream as illustrated in Figure 7.

This experiment validates the hypothesis of hydrate/ice forming on the pipe wall. A gas condensate fluid was cooled below the hydrate/ice saturation temperature and the excess water deposited on the pipe wall. This work exhibits the need for a wall growth model in water saturated hydrocarbon systems. Such a model would also serve as a starting point for modeling wall growth or deposition in a more complicated system containing free water.

**CONCLUSIONS**

Cyclopentane hydrates were used to investigate whether hydrates, formed in a bulk condensate phase, would adhere to a pipe wall. Adhesion forces between cyclopentane hydrates and steel were measured using a micro-mechanical force apparatus. The average force of adhesion was measured to be less than 0.002 N/m. This force was used in a particle force balance, predicting ‘dry’ hydrates (without a free water) formed in the bulk phase would not deposit on the pipe wall.

It was hypothesized that in the presence of a water saturated hydrocarbon, hydrates would grow on the pipe wall as the fluid cooled below its equilibrium temperature. This hypothesis was confirmed using a single pass condensate flowloop. Water was continuously dissolved into the flowloop inlet stream as water deposited in the flowloop test section, resulting in both a pressure drop and fluid temperature increase. This work illustrates the need for a hydrate wall growth model.

**References**


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