Hydrate Flow Performance JIP

16th Semi-Annual Advisory Board Meeting
Brochure and Presentation Slide Copy
Pushing the Hydrate Phase Envelope

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Confidential
1.0 Pushing the Hydrate Phase Envelope – Executive Summary

Mike Volk

1.1 Scope of Work

The results from the prior phase of study show that to some degree hydrates can be transported and there may be a “safe zone” of operation where hydrates could be transported in the hydrate domain. The gas and liquid restart studies showed that liquid holdup was over estimated with current simulators while the low pressure hydrate formation tests in the jumper showed being able to predict this hold up is critical in that a relatively small amount of water plugged the jumper upon restart and little is known about mixing of the inhibitors upon displacement. CFD models were developed and the holdup predictions were improved by 50 % showing promise for further development.

Hydrate plugs were characterized and dissociated. Current models were found to be adequate for dissociation by heating but the depressurization model was not applicable because the dissociation was not uniform. No inhibitor model exists but a first generation model was developed during the prior phase of study.

The prior phase of study quantified the hydrate plugging risks while the work in this phase of study will try to quantify how far into the hydrate envelope production can go. The work consists of four tasks supported by 40 experimental runs with the hydrate flow loop and 90 runs in the jumper facility. The experimental work will be performed in the University of Tulsa’s Hydrate Flow Loop Testing Facility.

1.2 Tasks

**Task 1: Hydrate transportability during steady-state operations**
- Determine parameters affecting transportability
- Determine maximum transportable hydrate fraction with & without use of chemicals
- Determine and correlate pressure drops

**Task 2: Hydrate risk and inhibition during restart operations**
- Conduct inhibitor displacement experiments in the 3” jumper facility
  - MEG and MeOH
  - Brine: Fresh and 14% salinity
  - THI superficial velocity: 0.05 to 1 ft/s
- Measure THI concentration profile in jumper
- Compare experimental data with CFD simulations
- Validate findings with hydrate experiments

**Task 3: Conduct Hydrate Formation Studies on Under-inhibited Systems**
- Interface development and hydrate growth
  - Cyclopentane and propane
  - Un-inhibited, under inhibited and inhibited systems
  - MEG and MeOH
  - Induction time
  - Wall deposition and aggregate size distributions
o Liquid droplet/hydrate particle interactions
  • Adhesive forces between under-inhibited water and hydrate formers (CSM)
  • Relations between forces and observations

Task 4: Improved dissociation modeling
  • Conduct depressurization and inhibitor dissociation experiments
  • Modify dissociation model to account for non-uniform pressure dissociation
  • Develop robust and reliable DEH dissociation model that can analyze and quantify the risk involved
  • Convert first generation inhibitor model into a robust model

Desired results from this work include:
  • Operating envelope for hydrate transportability
  • CFD model / engineering tool to assist in the design process of future jumper installations.
  • Universal dissociation model for heating, depressurization or inhibitors.

The schedule for completing the complex and interrelated tasks is shown in Figure 1. The study will last two years, finishing in 2011. Figure 1.1 also shows when significant deliverables in the form of reports, model validations, and data will be provided to the participants. Those activities colored in green are completed while those colored in blue are scheduled.
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*Figure 1.1 – Task Chart for Pushing the Hydrate Phase Envelope Studies*
1.3 Activity Summary

The progress for the four projects is discussed below.

**Project 1 – Hydrate Transportability**

From recent flow loop studies conducted at the University of Tulsa, as well as analysis of past experiments, it appears that hydrates can be transported safely, without inhibitor, with a solid fraction between 5% and 25% depending on operating conditions. Accurate predictions of pressure drops and maximum transportable hydrate solid fractions are a necessary step for integration into existing simulation codes and a critical step towards slurry flow technology. Better confidence in these predictions and existing slurry flow models is needed before such technology can be deployed in the field. The purpose of this study is to provide this increased confidence level in slurry flow technology by focusing on the following aspects:

- Identify the operating parameters that have a strong effect on flowing pressure drops.
- Identify a safe maximum transportable hydrate fraction and its dependency on operating parameters.
- Correlate when possible the frictional pressure drops with solid hydrate fraction in the flow stream and other relevant parameters if needed.

These findings would result in better use of existing models and better pressure drop modeling, in an increased confidence in the feasibility and limitations of hydrate transportability.

The focus of the experiments this reporting period was to understand the effects of different parameters on hydrate transportability for Natural Gas-Water experiments. Natural Gas-Water tests were chosen to segregate the effects of oil chemistry on transportability. Twenty-two steady state experiments were run and pressure drops were plotted as a function of hydrates in the liquid for each of these experiments. From the shortcomings in analysis, modifications were made to the flow loop, new experimental procedures were determined and additional experiments were run to characterize the fluid and also check for the effect of heat transfer. Experiments to understand rheology were also conducted.

**Project 2 – THI Displacement: Mixing and Modeling**

The risk of hydrate formation causing blockage of production lines and subsea equipment has become a matter of major concern during the last few years as offshore developments move into deeper waters with lower seabed temperatures and higher fluid pressures. Subsea jumpers are particularly susceptible to hydrate plugging due to their characteristic configuration, which consist of small diameters (in comparison with production and distribution lines) and low spots where the water is prone to accumulate and eventually form hydrates. Current operational procedures to avoid hydrate plugging of subsea jumpers include insulation, electrical heating, dead crude oil displacement and injection of thermodynamic inhibitors. The latter is the most common of these methods, and solutions of methanol and glycol (MEG) are often employed.
Design procedures are needed that reduce the risk of hydrate plugging, protects system integrity and offers a means to control the amount of chemicals to be used, while keeping the CAPEX and OPEX within acceptable project economic limits.

The objectives of these THI displacement, mixing and CFD model development studies are:

- Conduct jumper experiments to gain a better understanding of the interactions between density difference and viscosity for thermodynamic inhibitors.
- Quantify the suitability and effectiveness of MEG and methanol in jumper flushing procedures.
- Utilize CFD modeling to obtain better insight into the complex physical phenomena of jumper inhibition.

Modifications to the previous jumper facility were completed this period in order to begin the THI – water mixing experiments as well as the hydrate tests using cyclopentane. A stainless steel tank was set for holding the methanol and MEG and a chemical resistant gear pump and a Micromotion flowmeter were connected to complete the inhibitors injection system.

Twenty four experiments using MEG and fresh water have been conducted. The initial water volumes for all tests were approximately 34 and 17 gallons, which correspond to full and half liquid loading conditions, respectively. Inhibitor velocities varied from 0.05 ft/s (1 gpm) to 0.91 ft/s (20 gpm) and equivalent volumes of 1 and ½ jumper were injected for each case.

CFD simulations were performed using FLUENT 5.3 and the model was set up using the Species Transport equations. The computational mesh uses 592,000 cells. A 2D structured grid was considered, which consists of quadrilateral cells only. This particular type of mesh is recommended for regions of high gradients in the flow field. At the zone near the inhibitor inlet, the mesh is denser to capture the features associated to the entrance of the fluid to the jumper; while in the rest of the geometry the grid is coarser. The meshing process was carried out using Gambit 5.0.

**Project 3 – Understanding Hydrate Formation Mechanisms in Under-inhibited Systems**

This project characterizes interface development and hydrate growth in under-inhibited conditions with cyclopentane and propane. Tests will be run in a clear pipe at low pressure. Independent variables will be water cut, inhibitor concentration, subcooling level, and mixing rate. We will look at the induction time, total formation time, and formation rate. We will determine whether or not the hydrates deposit on the pipe walls and measure aggregate sizes and size distribution as visibility allows. Adhesion forces between under-inhibited water and cyclopentane will be measured through a sub-contract with Colorado School of Mines. Interactions between liquid droplets and hydrate particles will be recorded with high-speed video. The adhesion forces will be related to experimental observations. Any hydrate plugs that form will be characterized (porosity and permeability) and dissociated with MEG or MeOH.

The literature review on under inhibition of hydrates was completed this period. Taking the results from the literature into account, an experimental program was developed for the propose project. The design of the facility was completed and bids for construction of the facility were sought. The bids were reviewed and a contractor was chosen. Construction will begin in November. This facility includes an 8’ long, 3” ID glass test section which is jacketed by a 7’ long, 6” ID pyrex pipe. The test section can be
rocked (in horizontal position) or bubbled (in vertical position). The material for the test cell was ordered.

**Project 4 – Comprehensive Dissociation Model**

Work on hydrate dissociation modeling is limited. Peters (1999) modeled the two-sided hydrate dissociation with a radial moving boundary. The model is capable of predicting the hydrate dissociation time and the total time for plug melting. CSMPlug is the plug dissociation computer program generated out of the initial two-sided dissociation model of Peters, extended by Bollavaram (2003) for one-sided dissociation and for electrical heating by Davies et al (2005). The model is based on Fourier’s law of heat transfer in cylindrical coordinates and takes into account hydrate, ice, and water phases. This model is used by industry. The University of Tulsa has developed an extensive hydrate plug database for melting, depressurization and inhibitors. Comparison of CSMPlug predictions to this database shows good agreement for heat dissociation but not for depressurization because the experiments show non-uniform dissociation. No model is available for inhibitors.

This project will develop a numerical model to simulate and understand the physics and risks of hydrate remediation processes by electrical heating/thermal dissociation. The starting point is TU’s heating dissociation model. The proposed model will eventually account for changes in porosity and permeability of hydrates during dissociation. Pressure buildup, accompanying equilibrium changes, and hydrate thermal expansivity will be included. A thermodynamics package will be incorporated, and water will be allowed to refreeze. Two modes will be available: constant pressure and pressure buildup. A comprehensive analysis will be conducted to study the risk of pressure buildup in the pipelines that are perceived to be associated with the direct electrical heating techniques for hydrate remediation.

An overall dissociation model will be developed that will include an inhibitor model and combine all of TU’s models into one program. The inhibitor model will be guided from knowledge gained in Project 3. TU’s current heating model will be replaced by the model developed in this study when it is demonstrated to be better than the current model. Validation experiments will be done in the flow loop for dissociation by inhibitors and depressurization, and the models will be improved based on these tests. Then the heating, depressurization, and inhibitor models will be packaged together into one program.

A literature review related to the available DEH techniques and models was conducted. Two commonly referred to models were identified; one by CSM and the other by Mehta at Shell. The assumptions and limitations were identified and an effort to develop a 2D model that provides conservative predictions of pressure buildup before and after dissociation was begun.

**1.4 % Completed: 40%**

**1.5 Conclusions/Observations**

**Hydrate Transportability:** Repeatability of experiments was between 20-37% for hydrate fractions up to 8% for the 62.5% liquid loading, 3.9 ft/s mixture velocity, 40°F/hr cooling rate, constant mass tests. The experiments were repeatable provided the pressure-temperature profile was repeatable. The sub-cooling at hydrate onset is uncontrollable and this led to the variation in results. The phenomenon
observed in the tests which slug is similar to what is observed with heavy oil flow in that there is no flow between slugs. Hydrate transportability for 90% liquid loading tests was increased to a Solid Liquid Ratio of around 60% through constant mass – stage gas/mass addition experiments. This indicates that Solid Liquid Ratio and pressure drop cannot be criteria to determine up to what fraction hydrates are transportable.

The effect of heat transfer on the flow loop for experiments with one leg chilled and with the other leg quasi-insulated appeared to be insignificant other than at hydrate onset; that is, there was no significant wall effect seen due to heat transfer.

New phenomena were observed for tests with gas injection from the bottom for 90% Liquid loading. Gas bubbles are coated with hydrates by the time they reach the gas water interface. Once they reach the interface, jamming phenomenon is observed in the gas portion of the pipe. Rheology experiments for natural gas-water hydrate slurries exhibited pseudo plastic behavior at mixture velocities below 6 ft/s and above 6 ft/s; the mixture adhered to the Bingham plastic model.

**THI Mixing and Displacement:** Experimentally, higher inhibitor velocities (v > 0.45 ft/s) contributed to displacement of the water as a slug. Uniform radial MEG concentrations were measured in the 2nd low spot at high injection rates. However, lower velocities (v < 0.2 ft/s) promoted mixing of the inhibitor with the water phase. Concentration profiles over time fit the classical trend given by the convection-diffusion equation. The repeatability assessment showed that the current sampling procedure allowed obtaining experimental concentration data within 5% and 11% uncertainty. For MEG displacement equivalent to ½ a jumper volume, lower velocities contributed to a better inhibition of the water present in the low spots. Since the mixing front is longer at low injection rates, the dispersion of the ethylene glycol is greater.

CFD 2D simulations employed the species transport equations allowing modeling the mixing phenomenon of MEG and water at low velocities (0.05 ft/s) during jumper restart. Experimental trends were reproduced with a deviation of ± 10%. Conversely, large errors were obtained at intermediate and high injection rates. Diffusion effects were found to be significant at short times, whereas at longer times transport of MEG into the water phase dominated the inhibition mechanism.

**Dissociation Studies:** A dissociation model was built from first principles. From this effort it was concluded that it may be necessary to include the dissociation chemistry in the continuity and energy equations (to couple the diffusivity and energy equations). This will require a more complex solution procedure but should lead to better numerical stability and shorter computation times.

### 1.6 Future Work

**Hydrate Transportability:** Detailed analysis will include simulations run in OLG and Flowasta to check the various effects observed in the experiments. Simulations will include a sensitivity study of the effect of parameters such as sub-cooling, attractive forces, slip. Comparisons will be drawn between simulations and experimental data to try and point out the shortcomings of the existing models and the phenomenon that the existing models cannot capture. Further natural gas-water experiments will be conducted to check the effect of liquid loading, gas composition, pressure, salinity, velocity, under inhibited systems at low velocities and hydrocarbon phase on the transportability of hydrates. Additional experiments on cooling rate using the computer ramp will be considered. Extrapolation of experimental results will be made to real field situations to see how the results compare.
**THI Mixing and Displacement:** Experiments to evaluate the effect of brine salinity on MEG dispersion will be conducted as will gas restart cases when ½ jumper volume of inhibitor is displaced. The facility will then be modified to carry out static runs (bottom injection in riser, top injection in riser). The test apparatus will then be used to conduct low and high velocity experiments using methanol.

A CFD sensitivity analysis (Grid size) will be conducted. Simulations of the effect of temperature (25°C vs. 4°C) will be made as will a performance of the VOF (Volume of Fluid) model in predicting the displacement mechanism of the water phase at high inhibitor velocities. Once the methanol experiments have been run an evaluation of methanol behavior during jumper flushing at low and high rates will be conducted.

OLGA will be used to assess the performance of a transient 1D model in predicting the local concentration of thermodynamic inhibitors in the water phase during restart. Scale-up studies using larger geometries after the CFD model is validated will be conducted using 6”, 8” and 10” jumper configurations considering the same velocities and compare concentration profiles.

**Understanding Hydrate Formation Mechanisms in Under-inhibited Systems:** The construction of the test facility will be completed and shakedown experiments will be conducted. Experiments at atmospheric pressure (with hydrate former as cyclopentane) will be conducted in order to observe the interaction development and hydrate growth in uninhibited and inhibited systems. The independent variables that will be studied are water cut, inhibitor concentration, sub cooling level and mixing rate. Experiments at lower inhibitor concentrations using Methanol (MeOH) and mono ethylene glycol (MEG) will then be conducted. A high speed video camera will be used to record the hydrate formation and deposition.

**Dissociation Studies:** During this phase, additional depressurization tests will be conducted to verify the depressurization model. These will be followed by runs with extended MEG, methanol and nitrogen dissociation experiments using large volume of inhibitor with increased injection rates. The construction of the test facility will be completed and shakedown experiments will be conducted. Experiments at atmospheric pressure (with hydrate former as cyclopentane) will be conducted in order to observe the interaction development and hydrate growth in uninhibited and inhibited systems. The independent variable that will be studied are water cut, inhibitor concentration, sub cooling level and mixing rate. Experiments at lower inhibitor concentrations using Methanol (MeOH) and mono ethylene glycol (MEG) will then be conducted. A high speed video camera will be used to record the hydrate formation and deposition. For these experiments the density of MEG will be measured while draining liquid and for the nitrogen tests the composition of vented gas will be measured. The first generation inhibitor model will be converted into a more robust model and then validated using the results of the planned experiments.

For the comprehensive model the future work is running validation experiments in the flow loop and chaining individual cells together into a longer plug, to allow an inhibitor concentration gradient along the plug.

A 2-D DEH model will be developed that provides conservative predictions of pressure buildup before and after dissociation. This model will allow pressure buildup and account for changing dissociation
temperature, interface with PVTSIM (for variable gas composition), study the effect of variable porosity, permeability changing with space and account for thermal mass, non uniform heating or hot spot. The user will be able to define length to diameter ratio of the plug, type of hydrate structure, variable porosity, and permeability, mass of hydrate and trapped phases, heat flux, ambient temperature, initial temperature, and be able to introduce a hot spot in a given section of pipe. The user will be able to run the model in both the pressure buildup mode (closed system) and the constant pressure mode (controlled). Experiments will be conducted to form exclusively S-I and S-II hydrates in the 3" flow loop to obtain thermal dissociation data. The final step would be validation of the model to experimental data.