THE UNIVERSITY of TULSA

Office of Research and Sponsored Programs

Hydrate Flow Performance JIP

15th Semi-Annual Advisory Board Meeting Brochure and Presentation Slide Copy Pushing the Hydrate Phase Envelope

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March 2010

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Pushing the Hydrate Phase Envelope – Executive Summary

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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 three 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.

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, Low salinity and 14%
    - 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: Improved dissociation modeling

- Conduct depressurization and inhibitor dissociation experiments
- Modify dissociation model to account for non-uniform pressure dissociation
- 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 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.

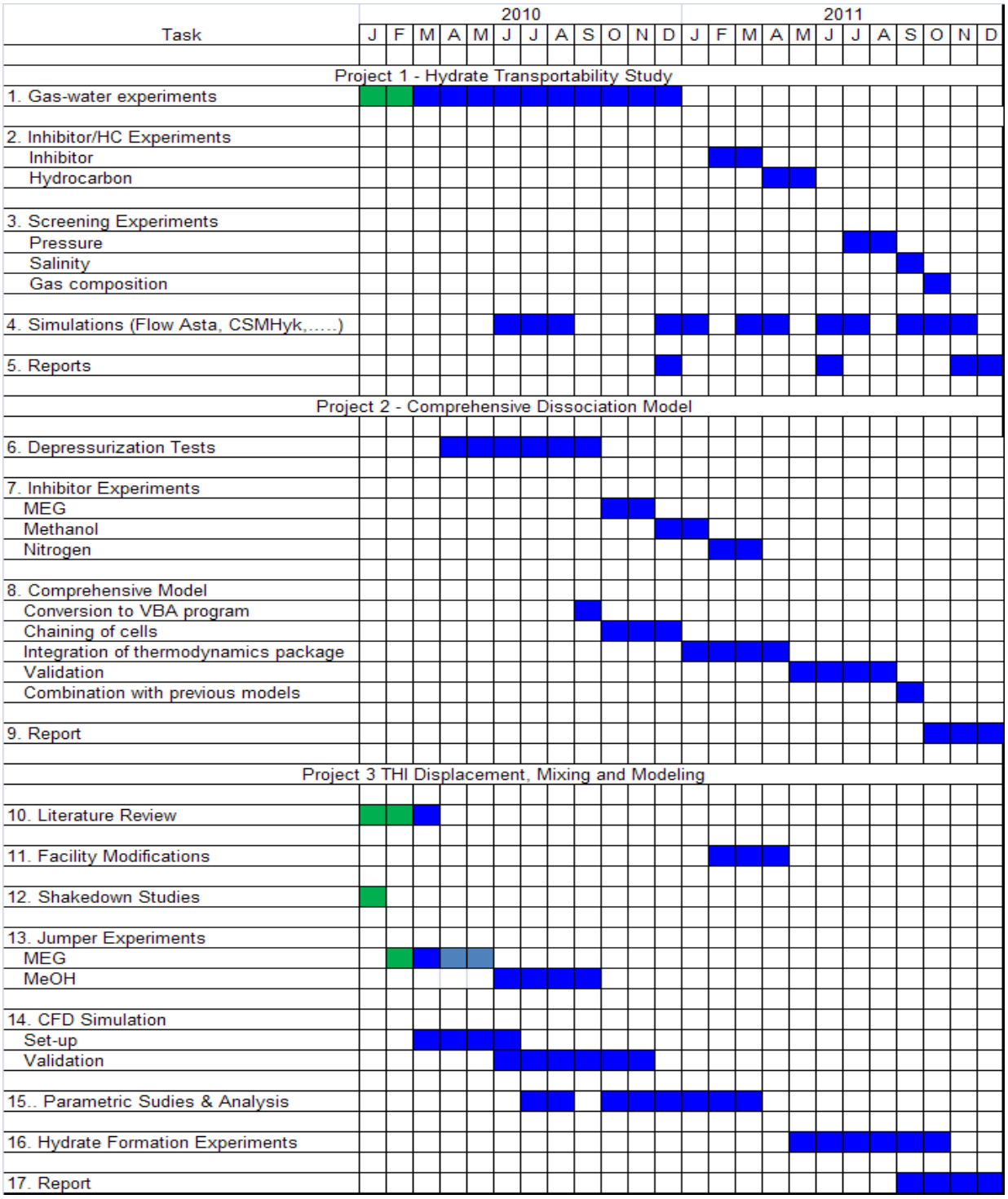

Figure 1 – Task Chart for Pushing the Hydrate Phase Envelope Studies

3. Activity Summary

The progress for the three 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.

Additional experiments with natural gas and water were conducted. The purpose of these experiments was to gather experimental data to validate existing models (CalSep FlowAsta and CSMHyk-OLGA), as well as establishing trends on the influence of parameters. Four constant pressure experiments were conducted for Colorado School of Mines model validation efforts and an additional 12 constant mass experiments were conducted for validation efforts with FlowAsta and to identify effects of parameters. Since the last ABM, five more tests were conducted focusing on the effect of the presence of a hydrocarbon phase, the presence of an under-inhibited thermodynamic inhibitor phase and the presence of both of these.

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 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

Three shakedown experiments using MEG have been conducted. For the low velocity experiment, thirty five (35) minutes were required to displace one (1) jumper volume of MEG. However, samples were taken at t = 10, 20 and 35 min in order to determine the inhibitor concentration profile at different stages during the test as well as to evaluate the transient behavior of the mixing process. At high velocities (0.45 and 0.9 ft/s), since less than five (5) min are needed to pump one (1) jumper volume, sampling was carried out at the end of each experimental run. Uniform MEG volume fractions along the system were obtained at high inhibitor velocities (> 0.45 ft/s). Under these flow conditions, the water is displaced as a slug and only the inhibitor remains in the jumper after flushing. At low velocities, a slow diffusion mechanism takes place and a mixing front is observed as MEG is injected into the system. In this case, a concentration gradient was obtained upon analysis of the samples and MEG fractions under 50% were measured in the 2nd low spot.

CFD simulations were carried out using FLUENT 5.3. The calculated trends from the numerical simulations show good agreement with the empirical concentration profile. However, a considerable difference (>40% error) on certain local values was obtained, in particular, the corresponding MEG fractions measured from the middle point of the first riser to the lowest sampling port of the last vertical section. A sensitivity analysis was performed in order to assess the effect of the ethylene glycol diffusion coefficient on the concentration gradient predicted by the numerical simulation. When the ethylene glycol mass fraction effects were taken into account the predicted concentration profile comes closer to the experimental gradient. In this case, the empirical trends were reproduced with an average deviation of approximately ±20%.

Project 3 – 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. Therefore, the objectives of this study are:

- Conduct depressurization and inhibitor dissociation experiments
- Modify depressurization dissociation model based on experimental results, if necessary
- Convert first generation inhibitor model into a robust model

Thirty seven (37) tests were conducted in the prior phase to form hydrate deposits for characterization and dissociation studies. Dissociation was conducted using heat, two sided depressurization and inhibitors (MEG and Nitrogen). The results from these tests were compared to model predictions in an attempt to validate the models. A draft of the final report was written.

4. % Completed: 5%

5. Conclusions/Observations

Hydrate formation rate constants were calculated from 55 pumping experiments with different fluids. Results indicate that the flow velocity has a much larger impact than the other variables.

Additional experiments were conducted with gas-water. Higher velocities increased hydrate formation rate and hydrate transportability, possibly because of the non-Newtonian properties of the hydrate slurry. Higher liquid loadings also showed improved transportability, especially 90%. Liquid loading between 50% and 75% all show similar pressure drop buildup for hydrate fractions up to about 6-10%. Higher cooling rates show a larger pressure drop buildup than lower cooling rates. When 10% dodecane was added to the water phase, hydrates were visually observed to deposit at the bottom of the pipe. This was not observed when both dodecane and MEG were present. Results were somewhat inconclusive regarding the addition of MEG to the water phase. Differential pressures were similar to the blank case. A higher formation rate was however observed.

For the transient studies, higher inhibitor velocities contribute to displacement of the water as a slug. Uniform MEG concentrations along the jumper length were achieved under these conditions. Lower velocities promoted mixing of ethylene glycol with water. Concentrations gradients were observed and MEG fractions under 50% were measured in the 2nd low spot. Preliminary 2D simulations were used to model the diffusion mechanism of MEG in a 3” jumper configuration. Experimental trends were reproduced with a deviation of ±20%.

For the hydrate characterization studies, the pumping test plugs were formed when the flowing mixture stalled due to friction at the pipe wall. The deposits were not uniform and only 2 of the 18 made plugs. These were slurry like and were impermeable. The other 16 deposits had channels or voids in them making permeability measurements inappropriate. Porosity of the hydrate itself could not be measured because the pores were liquid filled and could not be drained. As a result of these findings, plugs were then made in a low spot configuration. The permeability of the plugs formed varied from 2 to 15 Darcies when measured, but these permeabilities were found to continually decrease as water saturated gas

continued to flow through them. It is hypothesized that these plugs would have become impermeable to gas if the gas flow was continued for a longer duration. The plugs were also formed in a reproducible manner.

The plugs from the pumping tests were dissociated by heating. Since the driving force for the pumping dissociation tests was so large the hydrate plug collapsed very quickly, causing the end of collection of useful data. The insight gained from these tests led to a mature dissociation method that was used during dissociation of the plugs created in the low spot configuration. The plugs dissociated uniformly for heating as the model predicts; however, the depressurization experiments did not dissociate uniformly as the model predicted. The inhibitors were found to dissociate where they were in contact with the hydrate mass. Nitrogen was found to be effective but slow, possibly because of the large dilution of the nitrogen once hydrates dissociate. However, it should be noted that the nitrogen injection rate (0.1 lb/min) was fairly low. The model predictions were improved when both temperature and pressure were used as inputs for the model.

6. Future Work

In Phase IV, it is proposed to continue the investigation and quantification of operating parameters on transportability (pressure drops and hydrate fractions) in gas-water systems. Detailed work will be carried out on the effect of velocity, liquid loading and cooling rates in order to derive trends. Screening work will also be conducted to check whether other parameters could have an impact in the established trends. The parameters of interests will be the presence of an under-inhibited MEG or methanol phase, the presence of a hydrocarbon phase, salinity, gas composition and system pressure. Consideration will be given to how these trends extrapolate to the field as data is generated. Ways to improve the detection on plugging/accumulation onset will also be considered. Development of a simulator based on PVTSim open-structure will also continue in order to optimize the design of experimental conditions.

The MEG and MeOH transient experiments will continue in order to determine the effect of jumper volumes displaced, velocity and liquid loading on jumper inhibition procedures. Additional CFD simulations will be conducted to improve the modeling of the mixing and displacement process with hydrate inhibitors. Sensitivity analyses on mixture properties, grid size and thermodynamic conditions (pressure and temperature) will be conducted and their effect on simulation results will be evaluated. Scale up studies using larger geometries will be conducted once the model is validated.

The characterization and dissociation studies report for the prior phase will be completed and posted on the web site for the project. Dissociation studies for the new phase are not scheduled to begin until the second quarter. 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. 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.