THE UNIVERSITY of TULSA

Office of Research and Sponsored Programs

Hydrate Formation Project

18th Semi-Annual Advisory Board Meeting

Brochure and Presentation Slide Copy

Pushing the Hydrate Phase Envelope

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October 2011

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1.0 Pushing the Hydrate Phase Envelope – Executive Summary

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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 qualified 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

    - Liquid droplet/hydrate particle interactions
- Adhesive forces measurements between under-inhibited water and hydrate formers (CSM)
- Relations between adhesive forces measurements and observations

Task 4: Improved dissociation modeling

- Conduct depressurization and inhibitor dissociation experiments
- Modify dissociation model to account for non-uniform pressure dissociation
- Develop a robust and reliable DEH dissociation model with outflow of dissociation products
- Convert first generation inhibitor model into a robust model

Desired results from this work include:

- Better definition of the operating envelope for hydrate transportability
- CFD model / engineering tool to assist in the design process of future jumper installations.
- Integrated dissociation model for heating, depressurization or inhibitors.

The schedule for completing the complex and interrelated tasks is shown in Figure 1.1. 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.

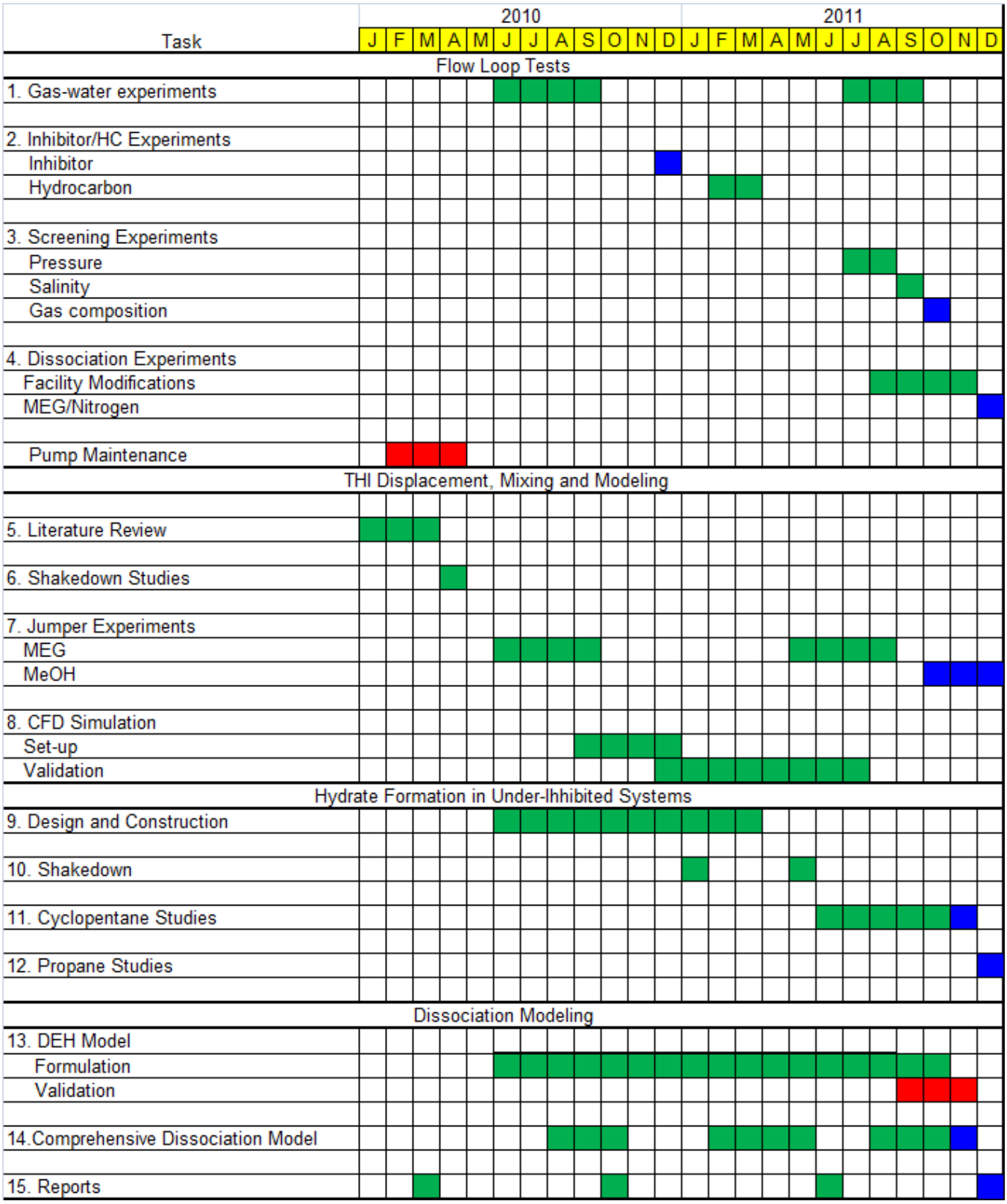

Figure 1.1 – Task Chart for Pushing the Hydrate Phase Envelope Studies

1.3 Activity Summary and Path Forward

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 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, and an increased confidence in the feasibility and limitations of hydrate transportability.

Thirty seven experiments have been conducted.. The rheological behavior of the gas-water-oil tests was different from gas water tests in that the gas-water tests indicated formation of a bed whereas gas-water-oil tests indicated significant deposition that appeared to coat the walls of the pipe. The effect of mixture velocity on gas-water experiments indicated the formation of a hydrate layer in the pipe which results in a restriction and a reduction in the diameter available for the fluid to flow. Whether the hydrate layer forms at the top or the bottom of the pipe could not be determined, but an increase in the mixture velocity resulted in the erosion of the hydrate layer with the hydrate particles getting dispersed into the flowing fluid. Gas-oil-water tests showed increased deposition in the pipe (based on samples) that appears to be coating the pipe walls that was different than the hydrate layer observed in the gas-water tests. Determination of the pressure drop due to hydrates is a combination of the pressure drop due to deposition and the pressure drop due to slurry flow. However, to properly interpret the pressure drop build-up due to hydrates, it is necessary to determine the viscosity of the flowing fluid and also detect or measure any deposits that may form in the loop. Techniques to quantify what is taking place in the pipe is the focus of the next phase of study. From the flow loop experimental results, it has become obvious that we need a tool to properly simulate the phenomena, especially be able to compute the hydrate fraction at any given time and adjust the volume of the different phases accordingly. In order to do this, a closed-system simulation routine must be developed. Plans are to develop this simulator with re-useable components that could be easily extended into a dissociation model or flow model during the next phase of study

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 involved in jumper inhibition.

Seventy seven experiments using MEG, fresh water and brine have been conducted to date. 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. The focus this reporting period was on experimental runs with the focus of capturing the physics of both mixing and displacement. The set-up for the OLGA, Fluent and STAR-CCM+ simulators being utilized was completed. Comparison to experimental data was begun. These efforts will continue in the coming months as will experiments with MEOH and hydrate formation using cyclopentane as the hydrate former.

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

The goal of this project is to characterize 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 conditions. Induction times and system temperatures will be measured. Visual observations will determine whether or not the hydrates deposit on the pipe walls and aggregate shapes and sizes will be observed. 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 measurements will be related to experimental observations. Any hydrate plugs that form will be characterized (porosity and permeability) and dissociated with MEG or MeOH.

Construction of the facility and the experimental test facility was completed. Twelve shake down experiments were conducted. Although preliminary at this time, hydrates were found to form at the interface for un-inhibited systems. Deposition was observed on the pipe surface as well as the stainless steel thermowell centrally located in the pipe. Agglomeration was also observed that was captured with videos. Before the end of the year, the un-inhibited, inhibited and under inhibited tests as a function of salinity will be completed and the findings documented in a report. Plans are to extend these studies into the next phase where propane will be used as the hydrate former.

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. 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.

The existing Excel/Visual Basic program for dissociation by inhibitor injection was modified to chain five length cells in a row and to allow the flow and dilution of inhibitor from one cell to the next. Program modifications were initiated to allow for communication with PVTSim, in that the program allows the user to choose a database. At this point the model only deals with gas filled plugs. Future modeling efforts includes adding additional length segments, making the model more robust by accounting for changing porosity and permeability as a function of length, liquid filled plugs, additional hydrate formers and other inhibitors than MEG. The final step will be model validation.

As a first step towards developing a new DEH model, a 1-D dissociation code in FORTRAN was developed. The developed model can simulate the hydrate dissociation phenomenon with emphasis on estimation of pressure buildup before (due to thermal expansion) and during hydrate dissociation under quiescent conditions. The simulation results were qualitatively and quantitatively compared with those existing models and available literature data. While the 1- D simulations provide reasonable estimates of hydrate dissociation time which is insightful information in devising remediation strategies, a working 2 D model can help understand the physics of dissociation in a finite length of a plug which will be of more practical significance, thus justifying the need for a 2-D model. Work on the 2 D model is about 75% complete. The remaining work includes: (a) Incorporating pressure buildup due to thermal expansion in the fortran code (currently this calculation is done in a spreadsheet); (b) Heat transfer through gas if all the water is drained; (c) development of a 2- D grid of pipe cross section to capture asymmetric heat transfer through pipe circumference; (d) accounting for heat transfer through gas - water homogeneous mixture; (e) incorporation of multiphase flow correlation to calculate the outflow; (f) Interface with PVTSIM (for variable gas composition); and (g) a model to capture phase segregation and its effect on heat transfer and outflow calculations.

1.4 % of Total Projected Completed: 80%