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Brochure and Presentation Slide Copy

Pushing the Hydrate Phase Envelope

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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.

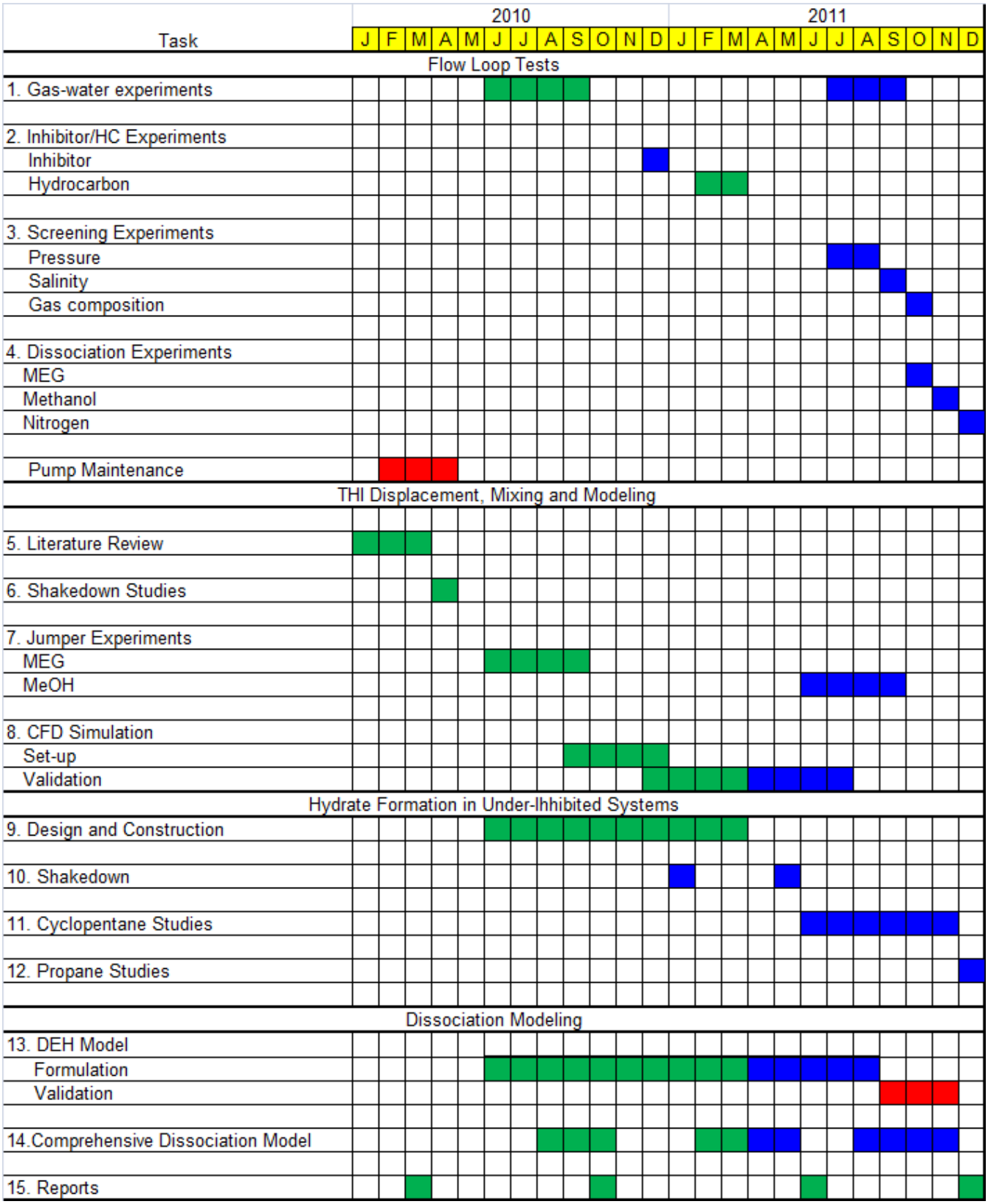

Figure 1.1 – Task Chart for Pushing the Hydrate Phase Envelope Studies

1.3 Activity Summary

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.

A total of 12 experiments were conducted. All tests were conducted at a base pressure of 1500 psia, liquid loading of 62.5%, a mixture velocity of 3.9 ft/s (750 RPM) and a 40°F/hr cooling rate unless specified. Tests were run in different environments gas-water, gas-oil-water and gas-oil-water-2%AA. The purpose of these tests was to study the effect of parameters such as cooling rate, velocity, gas addition on the transportability of hydrates; to identify conditions under which hydrates are transportable from pressure, temperature, pressure drop measurements and densitometer scans and to understand deposition in different environments (Gas-water & Gas-oil-water).

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.

Forty eight experiments using MEG and fresh water 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 the experimental runs with 12% brine and the CFD simulations that were performed using FLUENT 5.3 and STAR CCM+..

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 to house the test apparatus was completed. The experimental facility was designed and components were ordered. The test apparatus is currently being assembled. A high speed video camera was tested using a cyclopentane – water mixtures and a preliminary test matrix was developed.

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.

Work on the 1D-model is approximately 90% complete. For a 2.9" pipe (size of inner pipe in FAL loop), model predictions were made for the amount of time to warm water, time to dissociate plugs with different power inputs, the volume of gas released as a function of time, the effect of insulation and an oil phase on dissociation and the pressure buildup before hydrate dissociation. Work on the 2D-model was also initiated.

1.4 % Completed: 50%

1.5 Conclusions/Observations

Hydrate Transportability: The focus of the flow loop tests this period were on gaining an understanding of deposition in gas-water and gas-oil-water experiments. The gas-water-oil tests showed increased deposition in comparison with the gas water experiments because of higher amounts of gas addition. 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. Additional studies are needed before any conclusions can be drawn. A technique, such as inserting a boroscope in the pipe, would be beneficial in gaining an understanding of the deposition taking place in the pipe.

From the latest 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. Details on this implementation are given in Section 7.

THI Mixing and Displacement: The mixing process between the glycol solution and 12% salinity water was found to be directly proportional to the flow velocity. Since elevated injection rates generate more mechanical or hydrodynamic dispersion into the jumper system, a better distribution of MEG into the brine phase is achieved. On the other hand, low velocities (which are associated to a reduced momentum) are less effective at fully contacting the salt-water homogenous mixture on restart. Density differences between the displacing and the displaced fluids play an important role on the overall inhibitor dispersion mechanism, which agrees with the results obtained by Valberg (2006). As the buoyancy force decreases (i.e. the density difference between the MEG and the aqueous phase or brine becomes smaller), gravity-driven convection is reduced. Therefore, a less efficient spreading process of the glycol solution is tracked upon restart.

CFD simulations employing the Species Transport equations provided correct modeling of the mixing process between MEG and water at low flushing velocities (0.05 ft/s). Inhibitor concentration gradients based on numerical predictions showed good agreement with experimental measurements. Performance of the OLGA® MEG Tracking Module on estimating inhibitor concentration profiles along the jumper axial direction was demonstrated to be unsatisfactory.

Dissociation Studies: The shortcomings of existing DEH models were identified. These models do not account for variable porosity and permeability over a given length of the plug, effect of trapped phases, effect of hot spots or uneven heating, and gas pockets are identified. Assumptions in Mehta's (2001) pressure buildup model may not represent the worst case scenario and has not been validated against experimental data. A model by Sintef was also identified; however, information on its full capabilities is not available. A need was identified for significant research as well as a new and improved model.

As a first step towards developing a new model, a 1-D dissociation code in FORTRAN was developed that is similar to CSMPLUG. Some of the new additional features worth mentioning are:

- Inclusion of overall heat transfer coefficient to account for heat loss to surroundings
- Step heating [DEH power input in steps]
- Inclusion of oil phase as trapped fluid in the plug
- Calculate pressure buildup due to thermal expansion of individual phases (water, oil, gas and hydrate)
- Simplified approach to calculate pressure buildup during dissociation
- Inclusion of hydrate equilibrium curve as an input to account for changing hydrate dissociation temperature as pressure builds up

A 2-D model is under development that will specifically focus on the pressure buildup during hydrate dissociation. This model will attempt to address specifically on the shortcomings of the existing models discussed in the future work.

1.6 Future Work

Hydrate Transportability: Gas-water tests indicated formation of a bed layer. These results would need to be compared to Hernandez' slurry flow model. . Additional experiments on the use of anti-

agglomerants in order to prevent deposit build up on the pipe will be considered. There will be focus on gas-water-oil experiments to improve repeatability. Challenges are to identify the onset of deposit buildup from available measurements such as pressure drops, densities and temperatures.

THI Mixing and Displacement: Experimentally, focus will be given on MEG and MeOH experiments in order to determine the effect of jumper volumes displaced, velocity and liquid loading on jumper inhibition procedures. For the modeling effort, additional CFD simulations will be conducted to improve the modeling of the mixing and displacement process with hydrate inhibitors. CD-Adapco will run 3-D simulation by using STAR-CCM+. A sensitivity analysis with respect to grid size will be conducted to evaluate the effect of the aspect ratio on the prediction of the concentration profile of THI along the jumper. The performance of the CFD model on predicting inhibitor concentration profiles over a certain range of geometrical configurations will be assessed. The impact of time step (Courant number) on the accuracy and validity of the results obtained by means of the 2D simulations will be assessed. 3D simulations will be performed to determine the combined effect of the radial and axial velocity profile on the concentration distribution of THI's along the pipeline

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 un – inhibited and inhibited systems. The independent variables that will be studied are water cut, inhibitor concentration, sub cooling level and mixing rate. Experiments at low 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: Later this year 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 first generation inhibitor model will be converted into a more robust model and then validated using the results of the experiments discussed above.

DEH Studies: Development of a 2-D model that provides conservative predictions of pressure buildup before and after dissociation will continue. This model should:

- ✓ Allow pressure buildup and account for changing dissociation temperature,
- ✓ Interface with PVTSIM (for variable gas composition),
- ✓ Account for the effect of variable porosity, permeability changing with space, and
- ✓ Account for thermal mass, non uniform heating or hot spots.