1.0 Executive Summary

Mike Volk

Hydrate transportability studies: During the last reporting period, a final report was generated. This report summarizes the main findings.

These studies showed that repeatable experiments could be conducted when the temperature profiles were repeatable for the gas-water and gas-oil-water experiments. The standard deviation for these experiments varied from 5 to 20%. Above about 10% solid-liquid ratio, the pressure drop becomes strongly affected by other phenomena such as slugging, possible accumulation or deposition of hydrates, etc. In contrast to gas-water tests, tests that were oil continuous at 50% water cut exhibited a higher pressure drop and a flow curve typical of homogeneous flow. The flow curves do not behave in a way that indicates settling. However, some sloughing and what appears to be deposition or re-dispersion of particles were noticed. Samples of fluid taken also confirm that not all hydrates were present in the flowing phase in some cases; therefore the slurries generated may not be completely homogeneous. Additional tools to help “see” inside the high pressure flow loop are needed to interpret hydrate experiments with a good level of confidence. Efforts to advance instrumentation in this area are underway in the current project phase that began in January 2012.

Slurry characterization and modeling: From the analysis of flow loop experiments at high-liquid loading, two models have been proposed to describe the behavior of slurries using a generalized two parameter model. One model describes the settling region while the other focuses on the dispersed region. The dispersed model reasonably agrees with experimental data, while the segregating model represents the behavior at low velocities and high hydrate fractions. However, the magnitude for the latter model was not representing the experimental data very well. As the study progresses, a combination of these two approaches may be necessary to properly predict the behavior of slurries over the entire range of velocity and hydrate fractions. A critical shear rate or critical velocity criteria for full dispersion of slurries has also been defined from experimental data.

Gas restarts in jumpers using low pressure hydrate formers: To understand the conditions leading to hydrate plugging in jumper type configurations and to verify the hypothesis related to higher hydrate risk at certain locations in the jumper facility, three additional gas restart tests in the jumper were conducted on very cold days in February. Cyclopentane was chosen as the hydrate former because of its ability to form hydrates at atmospheric conditions. A preliminary experiment with water bridging the 1st low spot to test the feasibility of forming hydrates in low pressure jumper configurations was also conducted by Susana Mele in 2009. Two sets of additional experiments were conducted in 2012 using the same configuration. These tests were low superficial velocity tests where less water was removed and inhibited against hydrate. The intent was to determine if restarts could be successfully attempted under these conditions. A third run was conducted with both low spots bridged with liquid and cyclopentane. In all tests, hydrates grew rapidly after nucleating at the cyclopentane-water interface. In a short period of time a slurry mass formed in the 1st elbow that was permeable to gas but not liquid. The wall of the riser was also coated with a hydrate layer. Restarts at higher velocities displaced the slush to the 1st high spot and 2nd low spot. Restarts with only water (fresh or 3.5% brine) in the first low spot had a lower potential for plugging without inhibitor but the risk appears to be much higher when both low spots are bridged with water upon restart.
**Monitoring of hydrates in pipelines:** Recent transportability studies in the flow loop have pointed to a lack of proper instrumentation to identify phenomena taking place inside the pipe. View ports and basic instrumentation, such as pressure drop or temperature measurements, are not sufficient to properly identify flow patterns, settling of hydrate particles or deposition at the wall. It has become clear that to further advance research in hydrate transportability in pipelines, new tools must be developed. Such tools would be invaluable in interpreting flow loop experiments and might later be required in the field to properly monitor hydrate slurries should the technology ever be deployed. This project aims at identifying new and existing technologies that can be helpful in the monitoring of hydrates in flow lines.

In 2011, contacts with Mettler-Toledo were made and a non-contractual agreement was finalized. Mettler-Toledo (MT) provided the high-pressure FBRM and PVM probes that were installed on the flow loop and TU provided the flow loop and staff to reproduce a few test conditions with hydrate particles in the flow line. The common goal was to evaluate the probes’ performance to visualize and monitor hydrate particles flowing in the flow loop. Results from these tests are presented in this report. The PVM probe was able to observe phenomena never observed on that scale in the flow loop. However, it is only capturing phenomena on a 1mm² field of view. Larger scale phenomena cannot be observed with the PVM or the FBRM. Other types of technology must be developed to investigate multiphase flow parameters such as phase velocities, particle settling…etc.

Efforts to investigate and list other technologies have begun. Current technologies investigated so far include some tomographic techniques, sand monitoring technologies and ultrasonic methods. Tomographic techniques are certainly the most interesting since they provide a visualization of the process inside the pipe. They are also the more complex and probably the most expensive. It is unknown whether these will be suitable for hydrate monitoring, but discussions with the technology providers, such as ITS, will continue and hopefully partnerships will evolve. Similar contacts will be pursued with ClampOn and other companies as well. The literature survey will continue to investigate other techniques of interest to advance hydrate monitoring technology. Some of these techniques include in-situ viscosity, multiphase flow meters, distributed fiber optic acoustic sensing and some other tomographic techniques. The survey should be completed by Summer 2012 and a few technologies will be selected to proceed to Phase 2 for evaluation.

**Hydrate management for higher water cuts in oil systems:** The objective of this project is to conduct selected hydrate experiments in a flow loop under operating conditions representative of fields that are aquifer supported or those under late life conditions where water cut increases. As fields mature, lower GORs and higher water cuts create conditions where hydrate formation may be gas limited. The goal of the project is to start systematic definition of the safe operating window for production with hydrates without a significant risk of hydrate blockage. Different strategies, such as limited use of THI or AA or a combination of THI/AA would be tested experimentally. A ranking of the different strategies will be established based on pressure drops and evidence of hydrate transport morphology, e.g. accumulation. Laboratory screening, about 20 flow loop tests and simulation validation with existing tools are envisioned. The study will utilize model oil(s) and water to remove the chemistry inherent in field black oils, identified in previous DeepStar studies, as well as support clear visual observations of the hydrate formation and transport processes. Systematic addition of oil chemistry is envisioned for future work. Experiments will be targeted at un-inhibited conditions, as well as with utilization of THI and/or AAs. Model oil samples will be provided to chemical companies for screening and additive recommendations for flow loop testing. The scope of work for this project also includes selecting a mature field, a field with strong aquifer support or both from an operating company,
and utilize simulation tools and flow loop experiments to study different strategies aimed at extending field life. At a minimum, focus will be given to fields with high water cuts and low GOR.

Project discussions were held and a proposal was made to use food grade, mineral oils such as Puretol (Petro-Cananda) and LVT200 (ConocoPhillips) to construct model oils for hydrate transport studies. Properties of these fluids are being measured. Discussions with the chemical companies (Champion Technologies, Baker Petrolite, Nalco and Multichem (Halliburton)) to determine the additive concentrations required as a function of water cut were initiated. The goal is to have all the fluid testing complete by summer's end so flow loop testing can begin this fall.

**Direct electrical heating model:** The shortcomings of existing dissociation models were identified. The existing models do not account for variable porosity and permeability over a given length of plug, effect of trapped phases, effect of hot spots or uneven heating, and gas pocket. As a building block towards developing a 2-D model, a 1-D dissociation code in FORTRAN was developed that is similar to CSMPLUG. The following key additions were incorporated into TU's model.

- Inclusion of overall heat transfer coefficient to account for heat loss to surroundings
- Step heating option [DEH power input in steps]
- Inclusion of trapped phases
- Calculation of pressure buildup due to thermal expansion of individual phases (water, oil, gas and hydrate)
- Simplified approach to calculate pressure buildup due to gas released from hydrate dissociation
- Inclusion of hydrate equilibrium curve to account for changing hydrate dissociation temperature
- Elimination of tuning parameters such as critical gap requirement for pressure communication
- Use of a property table to calculate gas properties at any given pressure and temperature in the simulation

A 2-D model was developed to simulate the pressure buildup in a pipeline. The pipeline is divided into segments over which the 1-D model physics is applied. Gas released is allowed to migrate or accumulate depending on plug permeability, therefore allowing pressure buildup calculations. This pseudo 2-D model needs to be validated against experimental data. Both experimental and computational approaches are absolutely essential in obtaining meaningful interpretations and possibly establish safe DEH remediation procedures for a given condition. This model should be treated as a preliminary modeling effort to study the hydrate dissociation process in a finite length of plug. Substantial efforts are still required to check the robustness and correctness of the model. More detailed efforts are needed to build upon this model and address the current limitations. The model should also be validated against experimental data and a graphical user interface should be added. Coupling with a thermodynamic package would also be desired.

**Dissociation modeling and experimentation:** This project considers the dissociation of hydrate plugs by the injection of inhibitors. Ten experimental inhibitor tests will be conducted with plugs generated in the low spot configuration of the flow loop; 6 with nitrogen and 4 with MEG. These tests will be conducted this summer. However, before testing could begin several modifications to the test facilities were required. The range of the gamma scanner was extended by 10 feet to allow for evaluation of the front end of the plug and an online GC was installed so gas compositions could be taken every 9 minutes. Conducting hydrate plug dissociation experiments in the small scale facility using propane as the hydrate former is also being considered. The same inhibitors (MEG and nitrogen) will be used in these tests. The borosilicate glass section will help us to visually observe the hydrate plug dissociation.
The current TU inhibitor model is a first generation model. It calculates the dissociation time for
dissociation of a structure I methane/fresh water hydrate by nitrogen or MEG at 1500 psia. The hydrate
plug is only 1 ft long. Fourier’s law for heat conduction in cylindrical coordinates is used. The current
model was improved by chaining several 1-ft long cells to simulate a longer plug (longer cells will be
used for field simulations). The outlet gas or liquid from the first cell is the inlet gas or liquid for the
second cell, and so on down the chain. This allows for the dilution of the inhibitor as it moves through
the plug. By integrating the thermodynamics package into the model, the model now uses a
dissociation temperature calculated by PVTsim instead of one based on a curve fit to literature data.
The immediate future work for the modeling effort is to complete the integration of the thermodynamics
package. Right now, the model only gets the dissociation temperature from PVTsim. Other useful
properties include densities, heat capacities, thermal conductivities of the liquid and gas phases and
the hydrate structure. Getting these properties from PVTsim will allow the user to select any hydrate
formers or inhibitors. Modeling efforts will continue until 2013.