Project: Study of Soluble Scale Fouling Control in High Solids Black Liquor Concentrators (DE-FG36-99GO10387)

Milestones and Progress, Quarter 5 (October 1, 1999 – December 31, 1999)

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Summary

During this quarter, work has finally resumed on the black liquor solubility experiments (Task A.1), but no new data have yet been generated. The crystallization experiments with inorganic model solutions (Task B.1) have been completed, and crystallization experiments with kraft black liquor (Task B.2) have been started. The Annular Test Cell (ATC) apparatus is now fully operational, while construction of the falling film evaporator pilot plant (Task C.1) is nearly complete. Startup of this unit is planned for late in Quarter 6. In the CFD model development work (Task D.2), the relaxation of simplifying assumptions in the falling film model have been completed, and expressions were developed to estimate film velocity/film Reynolds number relations. Also, thin film data taken for a range of conventional fluids were compared to predictions using selected methods, and attempts were initiated to extrapolate to approximate black liquor evaporator conditions.

In an attempt to clarify the numbering of tasks in section D and alleviate some confusion, Task D.0, Literature Review (added by ORNL) has been renumbered Task D.1. The remaining Tasks in section D have also been renumbered accordingly.

Overall, steady progress is being made on this project, but it is currently behind schedule. The specific tasks that are behind schedule, the reasons for the delays, and the expected completion dates are discussed in the *Performance Variances and Open Items* section below. The remaining tasks are either on schedule, or have not been started.

Performance Variances and Open Items

Task A.1, Solubility experiments – one kraft black liquor (scheduled completion date: 6/99), and Task A.2, Solubility data obtained – other liquors (scheduled completion date: 9/99). Both of these tasks are behind schedule due to the aftereffects of the change in personnel, and unavailable technician support that were described previously. In addition, the modifications to the reactor, and testing of changes to the operating procedures have progressed much more slowly than expected. We plan to complete Task A.1 in Quarter 6 and Task A.2 in Quarter 7.

Task C.1, Pilot falling film evaporator operational (scheduled completion date: 9/99). This task is behind schedule due to slower than expected progress in installing the pilot evaporators. We expect to complete the installation of the pilot falling film evaporator, and have it operational by the end of Quarter 6.

Task D.2.3, Relax simplifying assumptions (scheduled completion date: 7/99), and Task D.2.4, Compare to experimental results: preliminary analysis (scheduled completion date: 9/99). These two tasks are behind schedule because of the change in personnel at ORNL that was described in the Quarter 3 report. We anticipate completing both tasks by the end of Quarter 6 (March 2000).

Status of Progress by Task

A.1. Solubility experiments – one kraft black liquor.
Scheduled completion date: 6/99.
Current status: **in progress-10% complete.**

Progress during the quarter:

Work has finally resumed on the black liquor solubility experiments, but no new data have yet been generated.

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A.2. Solubility data obtained – other liquors.

Scheduled completion date: 9/99.

Current status: **not begun.**

A.3. All solubility data analyzed.

Scheduled completion date: 1/00.

Current status: **not begun.**

B.1. Crystallization experiments – inorganic model solutions.

Scheduled completion date: 9/99.

Current status: **complete.**

Progress during the quarter:

Metastable zones have been measured for sodium carbonate and sodium sulfate, and the effects of sodium hydroxide and black liquor (1%) have been considered. Crystals have been confirmed to be Burkeite by x-ray powder diffraction. Experiments showed that Burkeite formed a solid solution with sodium sulfate or sodium carbonate, and the ratio of the two could change when kept in contact with the solution.

The evaporation process for an aqueous solution of sodium carbonate and sodium sulfate can be divided into four stages: (1) nucleation of sodium carbonate or sodium sulfate that occurs on liquid-air interfaces due to surface evaporation, and subsequent growth of the crystals, (2) nucleation of Burkeite crystals in the bulk solution due to supersaturation build-up, (3) predominantly secondary nucleation and crystal growth of Burkeite crystals, and (4) nucleation and crystal growth of sodium carbonate and Burkeite. The identity of the crystals formed has yet to be confirmed by x-ray powder diffraction.

B.2. Crystallization experiments – one kraft black liquor.

Scheduled completion date: 9/00.

Current status: **in progress-10% complete.**

Progress during the quarter:

Application of the Lasentec FBRM probe to crystallization in black liquor has been investigated. The method to convert cord length distribution, which is measured by the FBRM probe, to crystal size distribution, has been met with preliminary success. We are now able to convert the two for simple geometry crystals. The relationship between the number of particles per unit volume and the number of chords per unit time is still under investigation. The experimental crystallizer has been upgraded to handle black liquor, which is more viscous than aqueous solutions and causes problems for mixing and sampling. Other modifications to the crystallizer have also been started. These include the addition of a metering valve, PID temperature-control, cooling, and a data acquisition system.

B.3. Crystallization experiments – other kraft black liquors.

Scheduled completion date: 3/01.

Current status: **not begun.**

B.4. Crystallization data analyzed and modeled.

Scheduled completion date: 5/01.

Current status: **not begun.**

C.1. Pilot falling film evaporator operational.

Scheduled completion date: 9/99.

Current status: **in progress-90% complete.**

Progress during the quarter:

Assembly of the Annular Test Cell (ATC) apparatus has been completed. The finished unit has been tested using water and the entire system appeared to work as planned. The data acquisition system was also tested and found to work properly and all of the measured values were consistent. The measured overall heat transfer coefficient (U_o) in the annular heated zone ranged from 2,500 to 4,700 Watts/m²/°C (440 to 825 BTU/hr/ft²/°F). These numbers compare reasonably well to values measured in previous work with this type of system. An operating procedure has also been developed for this equipment.

Assembly of the larger Plate Evaporator unit is also nearing completion. The main mechanical components of the unit have now been assembled. This includes the piping for the black liquor feed system and the recycle loop, a hot water flush system, the steam feed control system, and condensate collection systems for both the steam and the black liquor vapor condensate streams. An electrical heat tracing system and insulation have been installed to maintain the liquor temperature throughout the loop. Instrumentation has also been installed to record the system operating conditions, including temperature, pressure and flow-rates. Preliminary testing with water only was performed and evaporation rates of 4-5 lb. H₂O/hr/ft² were measured.

C.2. Pilot evaporator data for fouling rate model completed.

Scheduled completion date: 9/00.

Current status: **in progress-10% complete.**

Progress during the quarter:

The batch experimental technique has been used to examine the second critical solids transition in one black liquor sample. Compositional analysis of scale samples pulled from the evaporator will be used to verify that the liquor has undergone the second critical solids transition as demonstrated by the data collection. After verification, this technique will be used to examine the effect of various evaporator operating parameters on high solids scaling.

C.3. Fouling rate model complete.

Scheduled completion date: 5/01.

Current status: **not begun.**

C.4. Pilot evaporator data – to evaluate fouling rate model.

Scheduled completion date: 5/01.

Current status: **not begun.**

D.1. Literature Review

Scheduled completion date: 1/99.

Current status: **complete.**

D.2.1. Assemble solution properties.

Scheduled completion date: 2/99.

Current status: **complete.**

D.2.2. Devise flow dynamics model with simplifying assumptions.

Scheduled completion date: 5/99.

Current status: **complete.**

D.2.3. Relax simplifying assumptions.

Scheduled completion date: 7/99.

Current status: **in progress-60% complete.**

Progress during the quarter:

Based on the available literature, comparisons were made of methods to account for factors that can cause departures from the simplifying falling film assumptions. Substantial differences were found in ways of accounting for effects such as waves, non-uniform distributions, and laminar/turbulent transitions. Expressions were developed

to estimate relations between film Reynolds number and film velocity for approximated black liquor evaporator conditions.

D.2.4. Compare to experimental results: preliminary analysis.

Scheduled completion date: 9/99.

Current status: **in progress-40% complete.**

Progress during the quarter:

Thin film experimental results for a range of conventional fluids were compared to predictions using selected methods. Extrapolations were attempted to approximate black liquor evaporator conditions. Based on IPST requests, additional discussions with instrumentation personnel at ORNL (experienced in liquid film measurement techniques based on electrical admittance principles and involved in water-cooled nuclear reactor accident simulation experiments) have not yet identified an accurate, reliable, and inexpensive method for adaptation to the indicated black liquor evaporator situation.

D.3. Heat transfer effects incorporated into CFD model.

Scheduled completion date: 9/00.

Current status: **not begun.**

D.4. CFD model for falling film evaporator fouling evaluated.

Scheduled completion date: 7/01.

Current status: **not begun.**

E.1. Monograph completed.

Scheduled completion date: 9/01.

Current status: **not begun.**

Goals For The Period January 1 - March 31, 1999

Task A.1.

1. Repeat the equilibrium study to establish the time required to reach equilibrium.
2. Run a critical solids evaporation experiment to as high a solids as possible.

Task B.2.

1. Continue modifying the experimental equipment.
2. Continue studying the application of the Lasentec FBRM probe.
3. Carry out preliminary experiments with black liquor.

Task C.1.

For the pilot-scale falling film plate evaporator:

- Complete Piping for the black liquor product discharge system. The black liquor product piping will include either a gear pump or a control valve to maintain the correct product flow for steady operation of the evaporator and an arrangement for collecting samples of the black liquor.
- Finish the installation, setup, and testing of the data acquisition system for this pilot unit.
- Perform preliminary testing on the system using water to verify the operation of all equipment (pumps, piping, heaters, instrumentation, and control systems).

- Perform additional testing on the system using $\text{Na}_2\text{CO}_3/\text{Na}_2\text{SO}_4$ solutions to verify that the system allows for the control and accurate measurement of heat transfer coefficients.

Task D.2.

1. Present task information at project review meeting scheduled for January 2000, and participate in the industry consortium meeting scheduled for February 2000.
2. Prepare preliminary DOE Field Work Proposal for continuation of funding.
3. Initiate compilation of thermodynamic properties for heat transfer effects.