RE: 4258

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

Milestones and Progress, Quarter 6 (January 1, 2000 – March 31, 2000)

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Summary

For Task A.1, some shakedown runs (both successful and unsuccessful ones) for black liquor solubility have been completed. Based on these, the experimental apparatus and operating procedures have been continually modified to attempt to overcome the persistent experimental problems associated with collecting samples of filtered black liquor at high solids. The crystallization experiments with kraft black liquor (Task B.2) are well under way. The falling film plate evaporator is now fully operational (Task C.1), and has been tested with water. In the CFD model development work (Task D.2.4), a preliminary comparison of flow dynamics models to experimental results was completed, and heat transfer models with simplifying assumptions have been completed (Task D.3).

The project review meeting was held via videoconference on March 17, 2000, and was attended by the principal investigators and members of the Industrial Advisory Group.

Steady progress is being made on this project, except for the black liquor solubility work, which is seriously 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.

Performance Variances and Open Items

Task A.1, Solubility experiments – one kraft black liquor (scheduled completion date: 6/99), Task A.2, Solubility data obtained – other liquors (scheduled completion date: 9/99), and Task A.3, All solubility data analyzed (scheduled completion date: 1/00). All three of these tasks are behind schedule due to the ongoing experimental problems encountered in collecting filtered black liquor samples at higher total solids levels (> 65 wt. %) for Task A.1. We expect to finally resolve these sampling issues during Quarter 7, and then proceed to complete Task A.1 in Quarter 8.

Task C.1, Pilot falling film evaporator operational (scheduled completion date: 9/99). Construction of the falling film plate evaporator has been completed, and the system is now fully functional. However, additional modifications are being made to improve the operation of the unit and increase the accuracy of the data that can be obtained from this system. We expect these modifications to be underway during Quarter 7, and completed during Quarter 8.

Status of Progress by Task

A.1. Solubility experiments – one kraft black liquor.
Scheduled completion date: 6/99.
Current status: **in progress-15% complete.**

Progress during the quarter:

The black liquor solubility work has been beset by persistent experimental problems associated with sampling black liquor through a series of 60 + 15 + 2 μ m filters. Filtered samples have been successfully collected at 57 and 63 wt. % total solids, but liquor sampling at higher solids has been unsuccessful because of filter plugging.

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The analytical data for the two successful runs is not very consistent. The liquor composition (Na, K, S, and SO_4^{2-}) appears to reach equilibrium within one hour after the evaporation is stopped, but then drifts lower with time. These results may be due to the specific sampling procedure that was followed at the time.

Based on the numerous shakedown runs that we have completed (both successful and unsuccessful ones), we have continually modified (and continue to do so) the experimental apparatus and the evaporation and sampling procedures in somewhat of a trial-and-error approach:

1. We have assembled two additional sampling lines with the $60 + 15 + 2 \mu\text{m}$ inline filters giving us a total of three complete sampling lines. By switching the sampling line after each sample is collected, we use each filter assembly only once and then clean it offline with hot water. Previously with only the one sampling line, we believe that we were concentrating liquor that was trapped in the line between samplings. Also, we had to blow nitrogen back through the filters to clean them, but this probably only created a narrow void space for the gas to pass through. We were not completely cleaning out the filters, and they subsequently plugged immediately during the next attempt to collect a sample.
2. Thermocouples have been installed into the liquor sampling line before and after the $2 \mu\text{m}$ inline filter. This allows us to monitor the actual liquor temperature in the sample line. Previously, we had been monitoring the skin temperature of the $2 \mu\text{m}$ filter, and discovered that the actual liquor temperature was $10\text{--}15^\circ\text{C}$ higher. This probably further contributed to liquor concentration in the sample line.
3. We have purchased a much larger (seven times the surface area) $2 \mu\text{m}$ inline filter should we need to install it.
4. The liquor heat up is now run with a low heating rate, a slow stirring speed, and the vapor valve open to allow the liquor to degas and avoid pressure buildup in the reactor and liquor carryover into the condensate lines.

Our ultimate goal is to collect, and analyze filtered black liquor samples at up to 80 wt. % total solids.

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.**

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

Scheduled completion date: 9/00.

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

Progress during the quarter:

The modification to the experimental apparatus has been partially completed: a metering valve, PID temperature-control, a cooling system, and a data acquisition system have been installed. The Lasentec FBRM probe has been used to further investigate crystallization in black liquor. This system has two modes of measurement: the C mode (filtered signals), and the F mode (unfiltered signals). The C mode is more sensitive to changes in the large particles, and is thus more suitable for monitoring crystal growth, whereas the F mode is more sensitive to changes in the fine particles, and is thus a better indicator of the nucleation point.

For solutions of various sodium carbonate to sodium sulfate ratios, the crystals formed during Phase I of the evaporation experiment, i.e. before massive nucleation of Burkeite, have been analyzed for composition. Depending on the solution composition, pure sodium carbonate or sodium sulfate crystals, or solid solutions of Burkeite with sodium carbonate or sodium sulfate could form during Phase I.

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-85% complete.**

Progress during the quarter:

The major parts of the falling film Plate Evaporator have now been installed. The system was successfully tested with water and determined to be fully functional. However, additional modifications are being made to improve the operation of the unit and increase the accuracy of the data that can be obtained from this system.

The main mechanical components of the Plate Evaporator unit have been assembled. These includes the black liquor feed system and recycle loop, the steam feed control system, collection systems for both the steam condensate and the black liquor vapor condensate, and an electrical heat tracing system and insulation to maintain the liquor temperature throughout the loop. Instrumentation has been installed to record the system operating conditions, including temperature, pressure and flow-rates. A data acquisition system has been installed and set-up to record data from the instrumentation.

Tests were performed with water to measure the overall heat transfer coefficient. Additional tests were performed to check the flow distribution to the two sides of the dimple plate. The results indicated that flow on the left side of the plate was much higher than the right side of the plate. Therefore, modifications are being made to the distributor box to insure that the liquor flow is distributed evenly over the entire plate. Some changes were also made to the condensate collection set-up to insure that all of the vapor is condensed and adequately cooled. This will result in more accurate measurements of the heat transfer rates. New control systems for the inlet steam flow and the outlet vapor flow have been ordered and will be installed.

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

Scheduled completion date: 9/00.

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

Progress during the quarter:

A series of tests were performed with water to determine the overall heat transfer coefficient as a function of three variables: recycle flow-rate, delta-T, and waterside operating pressure. The test was performed as a 2^3 test matrix with three replicates of the center-point. The results were analyzed using a statistical package and an analysis of variance method. Both the recycle flow-rate and the delta-T had a significant impact on the heat transfer coefficient, the waterside operating pressure was not statistically significant, and there were no interaction effects. After the current slate of equipment modifications has been completed, additional testing will be performed 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.

Batch experimental work continued on the bench-top evaporators. The previous batch experimental work, which provided some insight into the second critical solids transition, has been verified using a compositional analysis of the scale material collected from the heat transfer surface after the two phases of the batch. Additional batch runs have been completed on various salt-water compositions with positive results. These runs have generated cleaner and more easily interpreted data, which will benefit this research as work progresses on defining second critical solids fouling.

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: **complete.**

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

Scheduled completion date: 9/99.

Current status: **complete.**

Progress during the quarter:

Ten analytical, semi-analytical, and correlational methods for falling film characterization were compared for water, propylene, and black liquor experimental conditions.

The effects of the very substantial viscosity variations among these fluids on characteristic length scales and dimensionless groups were evaluated. Using a selected semi-analytical method, typical film thicknesses were estimated, for given film Reynolds numbers, to be more than an order of magnitude greater for black liquor than for water. Corresponding average film velocities were estimated to be approximately five times greater for black liquor than for water. These results were presented at the industry consortium videoconference meeting on March 17.

D.3.1. Assemble thermodynamic properties.

Scheduled completion date: 1/00.

Current status: **complete.**

Progress during the quarter:

A preliminary compilation of thermodynamic and transport properties for comparative fluids to be used in heat transfer modeling was created.

D.3.2. Revise flow model to include heat effects with simplifying assumptions.

Scheduled completion date: 5/00.

Current status: **complete.**

Progress during the quarter:

Analytical methods for falling film evaporation heat transfer were formulated with simplifying assumptions.

D.3.3. Extend heat transfer models by relaxing simplifying assumptions.

Scheduled completion date: 6/00.

Current status: **in progress-50% complete.**

Progress during the quarter:

It was found that, for given temperatures, Prandtl numbers for black liquor are more than two orders of magnitude greater than those for water. Because these nondimensional groups are indicators of relative momentum and thermal diffusivities in fluids, this result may imply that certain heat transfer modeling methods developed mainly for water situations may not be reliable for black liquor situations.

D.3.4. Compare to experimental results.

Scheduled completion date: 8/00.

Current status: **not begun.**

D.3.5. Use test data to validate model.

Scheduled completion date: 8/00.

Current status: **not begun.**

D.3.6. Conduct simulation runs and analyze data.

Scheduled completion date: 8/00.

Current status: **not begun.**

D.3.7. Prepare Year 2 report.

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 April 1 - June 30, 2000

Task A.1.

1. Continue with shakedown runs to resolve the plugging problems of the sampling lines, and establish if different final filter elements (e.g. 15, 7, and 2 μm) affect the filtrate composition. Use the largest pore size final filter which does not allow suspended solids to pass through.
2. Repeat the equilibrium study to establish the time required to reach equilibrium at several solids levels.
3. Run a critical solids evaporation experiment to 80 wt. % total solids.

Task B.2.

1. Identify the crystal samples formed during evaporation by X-ray powder diffraction.
2. Start experiments with black liquor, and make any necessary modifications to the equipment.

Task C.1.

For the pilot-scale falling film plate evaporator:

- Complete modifications to the condensate collection systems.
- Install the automatic control system to maintain constant inlet steam pressure and constant vapor pressure on the liquor side of the unit.
- Fabricate a platform to allow easier access to the top of the pressure vessel for clean-up.
- Design, fabricate, and install a new distributor to give uniform flow over the entire dimple plate surface.
- Perform tests on the system using water to verify operation of the liquor distribution box.

- Perform additional testing on the system using $\text{Na}_2\text{CO}_3/\text{Na}_2\text{SO}_4$ solutions to verify the operation of the overall system, and to ensure that accurate measurement of heat transfer coefficients can be made.

Task D.3.

1. Participate in industry consortium meeting scheduled for June 2000.
2. Create and exercise appropriate extended heat transfer models.
3. Initiate efforts to use models to predict IPST water evaporation data.