Project: Control of the Accumulation of Non-Process Elements and Organic Compounds in Pulp Mills with Bleach Filtrate Reuse (DE-FC07-96ID13441)

Milestones and Progress, Quarter 8 (April 1, 1998 - June 30, 1998)

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Summary

Overall, this project is on schedule and proceeding as planned.

Two approach changes are recommended. One is to rely on commercially developed software, in particular that developed by OLI Systems, Inc. and now being expanded in a collaborative effort between OLI Systems inc. and IPST to provide a simulation package for the pulp and paper industry and to integrate it with existing process simulation tools used by that industry. The second is the development of a detailed brownstock/bleached fiber washer model as a tool to evaluate the data and methods developed in this study, and to demonstrate its utility to industry. Both of these are discussed in more detail in the *Approach Changes* section of this report.

Two tasks are behind schedule They are Task A-2.3, Measurement of stability constants for wood organics with metal ions (scheduled completion date: 6/98), and Task C-1.2, Estimation of unavailable thermodynamic parameters (scheduled completion date: 12/97) The reasons and expected completion dates for these tasks are discussed in the *Performance Variances and Open Items* section of this report. All other tasks are either completed, or on or ahead of schedule.

Approach Changes

Chemical Equilibrium Solver and Databases: The original plan for this project was to use a chemical equilibrium simulator, NAEELS, developed by Sinquefield (1991) at Oregon State University, as the basis for this project. However, as the result of two recent developments we are recommending a change IN this plan.

The first of developments is that IPST and OLI Systems, Inc. have agreed to develop a chemical equilibrium simulator for pulp and paper manufacturing processes. OLI Systems, Inc. (OLI) is a leading developer of chemical equilibrium software, and their products are used extensively by a number of industries world-wide over the past two decades. OLI and IPST are working to develop an equilibrium simulator (PPSE) for the pulp and paper industry. PPSE will include adsorption equilibrium for metal ions on wood pulp fibers and complexation metal ions with of dissolved organic matter, as well as OLI's extensive inorganic ions and compounds databases, updated to include all inorganic species of interest to the pulp and paper industry, based in part on data developed as part of the current DOE-sponsored project. Further, OLI Systems Inc. has agreements with the two leading providers of process simulation tools for the pulp and paper industry (Pacific Simulation, Inc. and H. A. Simons, Inc.) to develop an interface between those simulators (WinGEMS and IDEAS, respectively) and OLI's chemical equilibrium simulator. As a result, PPSE will make the data from the current project available to the pulp and paper industry in the form that is most useful to them (coupled with a process simulation capability), and through commercial suppliers who will be able to support the software.

The second development is the release of an updated version of NAEELS (hereafter referred to as Weyerhaeuser-NAEELS) to IPST for use in the current project. Weyerhaeuser Company, one of the sponsors of the development of NAEELS at Oregon State University, further developed the software,

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greatly expanding its inorganic compounds database and its database management, and adding a Windows front end.

As a result, we are recommending that these two chemical equilibrium simulators for most of the development work in this project, rather than to upgrade NAELS first. Because NAELS is a DOS-based code with no graphical interface (and incorporation of one is not part of this project), it is likely that industrial users of chemical equilibrium simulators would prefer software with a more advanced interface. The issue of whether to provide an upgraded version of NAELS as a product of the current project, or instead to focus on expanding existing, commercially developed chemical equilibrium simulators will be discussed with the AF&PA Environmental Effectiveness Committee and others from industry, and a recommendation submitted to DOE during the 9th (current) quarter of this project.

Evaluation of the Estimation Procedure. Dr. Greg Rorrer of Oregon State University will spend between three and four months of his sabbatical leave at IPST, starting on or about April 1, 1999. While at IPST, Dr. Rorrer will develop a detailed model for the adsorption of metal ions on wood pulp fibers. This model will include transport effects as well as adsorption equilibrium. This model will be combined with a brownstock washer model to evaluate its predictive capability in comparison with mill data, and to demonstrate the applicability of the results obtained in this project. Because of this, we request a change in the completion date of this task from 3/99 to 8/99, a concurrent no-cost extension of the project completion date, and an extension of the final report due date to 9/99.

Performance Variances and Open Items

Task A-2.3, Measurement of stability constants for wood organics with metal ions. (Scheduled completion date: 6/98). This task is behind schedule for two reasons. The first is that, as originally proposed, it was to be the responsibility of Dr. Jim Frederick, the project PI. However, as a result of Dr. Frederick's move from Oregon State University to IPST in January, 1997, and the addition of Dr. Alan Rudie as a co-PI for this project, there was a delay in beginning this task. Second, the experimental methods that were planned for this task required more development time than was earlier expected. As a result, this project is behind schedule. The experimental methods needed have now been developed, and we anticipate completing the task within the next nine months.

Task C-1.2, Estimation of unavailable thermodynamic parameters. (Scheduled completion date: 12/97)

Estimation methods for both thermodynamic properties of ions in aqueous solutions and their activity coefficients have been collected from the literature. All of these methods except one are currently part of the OLI Systems software. Evaluation of the methods has therefore been coupled with task D-2.1 as a result of the collaboration with OLI Systems Inc. It will be completed by 3/99.

Status of Progress by Task

A-1.1. Recovery of organic matter from bleach effluents and black liquors.

Scheduled completion date: 6/97

Current status: **complete**

A-1.2. Separation of carbohydrates and lignin degradation products.

Scheduled completion date: 12/97

Current status: **complete**

A-1.3. Analysis of functional groups.

Scheduled completion date: 6/98

Current status: **complete**

A-1.4. Characterization of carbohydrate polymers.

Scheduled completion date: 12/98

Current status: in progress

Progress during the quarter: Additional filtrate samples from a totally chlorine free (TCF) bleaching run (labeled #1BS, #2BS, Decker, CB, PO2, Q, Eop, P1, P2, and P3) were received from the Louisiana-Pacific pulp mill in Samoa, CA. The solids contents of these samples were determined: #1BS, 7.28%; #2 BS, 6.87%; P1, 1.46%; and P2, 0.07%. The filtrate samples labeled #2BS, Decker, CB, PO2, Q, and P3 were freeze-dried and the solids recovered. The freeze-dried solids from samples #2BS and CB were dialyzed to remove the inorganic materials. The organics were acetylated with carbon-13 enriched acetyl chloride for NMR spectroscopy. The NMR results for the #2BS organics showed a peak for primary hydroxyls at 170.291 ppm, essentially no peak for secondary hydroxyls, and a peak for phenolic hydroxyls at 168.661 ppm. The solids from the CB sample showed no peaks by NMR. The samples labeled Q, PO2, and Decker did not have enough solids after freeze-drying to allow for dialysis. NMR analysis of these solids without dialysis showed no NMR peaks. This is attributed to a small lignin content (0.6% for sample Q and 0.4% for sample PO2) which may be too little for detection by NMR.

A-2.1. Selection of model compounds.

Scheduled completion date: 6/97

Current status: **complete**

A-2.2. Measurement of stability constants for model compounds with metal ions.

Scheduled completion date: 12/97

Current status: **complete**

A-2.3. Measurement of stability constants for wood organics with metal ions.

Scheduled completion date: 6/98

Current status: in progress

Progress during the quarter: An initial evaluation of black liquor complexation of calcium has been completed using the complexation indicator murexide. At pH 9, acid precipitated black liquor solids gave a slow transition to the bound state, suggesting that it is really not just one compound--which is consistent with the pH behavior and was expected. The initial estimate of the formation constant is $k = 3,700$ ($\log(k) = 3.5$). This is quite a bit lower than the calcium formation constant measured for the model compound vanillin: $k=95,000$ ($\log(k) = 4.9$). Current efforts are targeted at measuring the formation constant at higher pH. At pH 9, the murexide indicator is well behaved, but the black liquor will be only partially dissociated. The competition with hydrogen will result in a low formation constant and a broad observed transition.

A-2.4. Correlation of stability constants with chemical properties of organic matter.

Scheduled completion date: 12/98

Current status: not begun

B-1.1 Obtain wood pulp samples from an operating pulp mill.

Scheduled completion date: 9/96

Current status: **complete**

B-1.2 Determine the metals content in the pulp samples.

Scheduled completion date: 12/96

Current status: **complete**

B-1.3 Determine the residual lignin content in the pulp samples.

Scheduled completion date: 12/96

Current status: **complete**

B-1.4 Determine the residual hemicellulose content in the pulp samples.

Scheduled completion date: 4/97

Current status: **complete**

B-2.1 Measure metal adsorption isotherms on wood pulp.

Scheduled completion date: 9/97

Current status: **complete**

Progress during the quarter: The re-adsorption of calcium ions on the nickel-adsorbed LP-Samoa brownstock pulp was investigated. The nickel-adsorbed pulp was washed with distilled water similar to the final preparation procedure for the calcium-exchanged pulp described in earlier reports. An adsorption isotherm at 25°C for calcium ion adsorption and nickel-ion release from nickel-adsorbed pulp was developed, and the maximum adsorption capacity of calcium ions was 0.09 mmol/g dry pulp, similar to the saturation adsorption capacity for nickel on calcium exchanged pulp. However, the maximum equivalent nickel ion release was 0.03 mmol/g dry pulp. Material balance measurements showed that nickel ions were entrained in the water (void) fraction associated with the wet pulp, equivalent to 0.03 mmol/g pulp. This is a significant fraction of the total saturation adsorption capacity of 0.08 mmol Ni/g dry pulp.

Additional pulp samples were obtained from the Pope & Talbot pulp mill in Halsey, Oregon. Five one-kg pulp samples from each of the following points were obtained: brownstock washer, bleach plant HOCL #1, bleach plant EOP, bleach plant HOCL #2, and bleach plant high-pressure peroxide. These pulp samples will be used for future experiments, and will provide a comparison of adsorption of metal ions on TCF-bleached pulps versus pulps bleached with chlorine-based chemicals. The pulp samples were analyzed for carboxylic acid group and phenolic hydroxyl group functional analysis at IPST.

B-2.2 Correlate metal adsorption isotherm parameters to wood pulp constituents.

Scheduled completion date: 12/97

Current status: **complete**

B-2.3 Measure metal ion adsorption kinetics for strongly adsorbing metal species.

Scheduled completion date: 3/98

Current status: **complete**

Progress during the quarter: Kinetic studies of the ion exchange process for nickel ion adsorption on calcium-exchanged LP-Samoa brownstock pulp were completed. The kinetic experiments were performed at 25 and 75°C with initial nickel ion concentrations ranging from 60 to 600 mg/L in solution (ppm). The pulp consistency was 1.0%. At an initial nickel ion concentration of 60 ppm, temperature had no effect on the kinetics of nickel ion adsorption and calcium ion release, and the equilibrated nickel ion adsorption capacities at both temperatures were 0.03 mmol/g dry pulp. The equivalent calcium ion release was also 0.03 mmol/g dry pulp. However, if the initial nickel ion concentration in solution was increased to 600 ppm, and the equilibrated nickel ion adsorption capacity was 0.07 mmol/g dry pulp at 25°C compared to 0.04 mmol/g dry pulp at 75°C, but the equivalent calcium ion release was unchanged at 0.03 mmol/g dry pulp.

The kinetics data for the ion exchange of nickel ions on calcium-exchanged LP-Samoa brownstock pulp were analyzed. A rate model was developed for this process assuming that 1) the process is carried out in a batch contactor as a closed system; 2) the external film mass transfer rate between the fiber surface and the contacting metal ion solution limits the adsorption rate; 3) adsorption isotherm used to determine the partitioning between the metal ion in the pulp and in solution is described by the Freundlich model. The resulting material balance equations for Ni adsorption and Ca release were nonlinear and integrated numerically to estimate the loading of Ni and Ca on the pulp as a function of adsorption time and input process parameters including pulp consistency, initial metal ion concentrations in the pulp and metal ion solution in contact with the pulp, Freundlich isotherm parameters (K and n), external surface area of pulp per volume of solution, and the film mass transfer coefficient. Since the mass transfer coefficient was unknown, it was backed out by fitting the kinetics data to the model using a nonlinear regression technique. This basic model can be extended to flow systems representing washing equipment in pulp mill operations such as decker washers or tower washers in the future.

A journal paper comparing the adsorption isotherms and adsorption kinetics of calcium and nickel-ion exchange processes on LP-Samoa unbleached pulp with LP-Samoa bleached pulp from two other stages in the TCF bleaching process (EOP, P) was partially completed.

C-1.1. Development of a database for inorganic ions.

Scheduled completion date: 6/97

Current status: **complete**

C-1.2. Estimation of unavailable thermodynamic parameters.

Scheduled completion date: 12/97

Current status: in progress

Progress during the quarter: Estimation methods have been taken from the literature for both enthalpy of formation as a function of temperature and for activity coefficients. Criss and Cobble's method is used for estimation of the heat capacity of ions as a function of temperature. The enthalpy of an ion is then estimated by integrating the heat capacity equation from 25°C to the desired temperature. This of course requires that the standard enthalpy of formation be known at 25°C. Alternately, Helgeson's equation of state relationships can be used to estimate the standard state thermodynamic properties of ions (enthalpy, entropy, free energy, heat capacity, and molar volume).

For activity coefficient estimation, several methods have been identified and will be evaluated. Kim's correlation of binary interaction parameters with ionic properties can be used to estimate these parameters for the Pitzer method of activity coefficient estimation. Both Bromley's and Meissner's methods are available to estimate mean activity coefficients for ion pairs. Binary interaction parameters for the Pitzer's equations are then extracted from these mean activity coefficients.

All of these methods except Kim's are currently part of the OLI Systems software. Evaluation of the methods has therefore been coupled with task D-2.1 as a result of the collaboration with OLI Systems Inc. It will be completed by 3/99.

C-1.3. Evaluation of the inorganic database.

Scheduled completion date: 6/98

Current status: **complete**

C-2.1. Develop an organometal equilibrium calculator.

Scheduled completion date: 12/98

Current status: in progress

Progress during the quarter: Methods for regressing adsorption data for metal ions on wood pulp, and for regressing complexation data for metal ions with dissolved organic matter, were established by OLI Systems Inc. and provided to IPST. Data from OSU on the adsorption of calcium and manganese on wood pulps, and on the functional group content (carboxylic acid and phenolic hydroxyl) were assembled for correlation. A parallel set of data for complexation of calcium and manganese with dissolved organic matter with the same two functional groups, and the concentrations of these functional groups on dissolved organic matter were collected. The regressed data will be used in simple mass balance and equilibrium calculations with the OLI Systems software to simulate the accumulation of calcium and manganese in a brownstock washer. These calculations are the first step in evaluating the overall model for the distribution of metal ions between pulp fibers, organometal complexes, inorganic ions, and inorganic precipitates (see task D-2.1).

D-1.1. Analysis of mill liquor, bleach filtrates, and pulp streams.

Scheduled completion date: 12/98

Current status: **completed**

D-1.2. Solubility limits of metals in mill liquor and bleach filtrate streams.

Scheduled completion date: 3/99

Current status: in progress

Progress during the quarter: Simulations of metal ion solubility in green and white liquors were run on the OLI Systems Software (ESP version 6.0) as an extension of the work reported in the September, 1997 report. Aluminum, Ba, Ca, Mg, Mn, and Si were studied, and the composition of the model liquors also included potassium (as K_2CO_3 in the green liquor and as KOH in the white liquor) at 2.5 atom % of the total sodium present. The metals were added as carbonates or sulfates, except for Al and Si which were added as $AlCl_3$, and Dickite: $Al_2Si_2O_5(OH)_4$.

The predicted saturated solution concentrations differed greatly (for some metals) from experimentally measured data for mill sampled clear liquors, corrected for suspended solids. In green liquor, predicted metal concentrations relative to measured values are as follows: Ba -4%, Ca 50x less, Mg 10^4 x less, and Mn +10%. In white liquor, the predicted metal concentrations (relative to measured values) are Ba +160%, Ca 14x less, Mg 3×10^4 x less, and Mn 60x higher. The predicted solid phases were $BaSO_4$, $CaCO_3$, $Mg(OH)_2$, and $Mn(OH)_2$ in both the green and white liquors. Both Al and Si remained soluble under the simulation conditions, which is contrary to experimental data, and is probably due to a poor choice of aluminosilicate compound used in the simulations. These large discrepancies point out the need to resample mill green and white liquors and investigate hot and cold sample filtration to remove suspended fine solids.

D-2.1. Evaluation of the estimation procedure.

Scheduled completion date: 3/99

Current status: in progress

Progress during the quarter: Preliminary development was begun for a process model for predicting the distribution of NPE's in a brownstock washer operating with recycled bleach effluent. In this preliminary model, only equilibrium effects are considered. Kinetics of metal ion adsorption and diffusion limitations will be incorporated in modeling work to be conducted by Dr. Greg Rorrer in 1999.

Goals For The Period July 1 – September 30, 1998

Task A.1

1. Continue the NMR characterization of dissolved organic matter. The research will concentrate on determination of the number of functional groups per phenylpropane unit in the lignin fragments.

Task A.2

1. Measure formation constants for calcium--black liquor organics at pH 10 and 11.

Task B

1. Finish journal paper summarizing results from Ni/Ca isotherm and adsorption kinetics experiments on brownstock and bleached pulp.

2. Complete the conductivity detector upgrade on IC unit, then calibrate the IC system for quantitative analysis of alkali/alkaline earth metal ions.

Task C

1. Upgrade the OLI database to include insoluble aluminosilicate, aluminate, and silicate species that were identified in the recent study by Wannenmacher and Frederick. Redo the simulations, using the updated database.

Task D

1. Conduct green and white liquor sampling experiments at a local mill, using both hot sample filtration to remove ultrafine, suspended inorganic particles.
2. Complete the preliminary simulation of a brownstock washer using recycled bleach filtrate as wash water, to evaluate calcium and manganese accumulation.