DOE/ID/13441--721

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 9 (July 1, 1998 - September 30, 1998)

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Summary

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

The two approach changes that were discussed and recommended in the Quarter 8 (April 1 - June 30, 1998) progress report have been implemented in the current project plan. The OLI software has been used to develop a preliminary process model for predicting the distribution of NPE's in a two stage brownstock washer, and the OLI database has been upgraded to include improved chemical equilibrium data for metal-organic interactions. This exercise served as a tool to evaluate the data and methods developed in this study, and to demonstrate its utility to industry. The Weyerhaeuser-NAELS software has also been applied to predicting inorganic solubility behavior.

Task C-1.2, Estimation of unavailable thermodynamic parameters (scheduled completion date: 12/97), has been combined with Task D-2.1, Evaluation of the estimation procedure (scheduled completion date: 3/99) with a new scheduled completion date of 8/99. Dr. Greg Rorrer of Oregon State University will spend between three and four months of his sabbatical leave at IPST, starting in April 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, and 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.

Three tasks are behind schedule: Task A-2.3, Measurement of stability constants for wood organics with metal ions (scheduled completion date: 6/98), Task B-2.1, Measure metal adsorption isotherms on wood pulp (scheduled completion date: 9/97), and Task B-2.3, Measure metal ion adsorption kinetics for strongly adsorbing metal species (scheduled completion date: 3/98). The reasons and expected completion dates are discussed in the *Performance Variances and Open Items* section below. All other tasks are either completed, on, or ahead of schedule.

Performance Variances and Open Items

Task A-2.3, Measurement of stability constants for wood organics with metal ions (scheduled comp. date: 6/98). This task is behind schedule due to delays in starting this task as discussed in the Quarter 8 report, and due to the continuing experimental difficulties encountered in trying to select a suitable complexation indicator compound. Although some useful data has already been collected, work is still underway to identify a more suitable indicator. We anticipate completing this task within the next nine months.

Task B-2.1, Measure metal adsorption isotherms on wood pulp (scheduled completion date: 9/97), and Task B-2.3, Measure metal ion adsorption kinetics for strongly adsorbing metal species (sched. comp. date: 3/98). Both of these tasks are behind schedule because the experimental work has progressed more slowly than originally planned, and because of problems with analytical methods and instrumentation. A capillary ion electrophoresis system (CES) was initially used for the metals analysis, but it could not simultaneously profile all of the metals which was required for the planned multi-metal competitive adsorption isotherm experiments. Also, the CES was only on loan to the project and had to be returned to Dr. Kristiina Iisa of IPST. An ion chromatograph (IC) was selected to replace the CES, but it required significant upgrading. Finally, significant time has been invested in methods development for the CES and IC units. We anticipate completing both tasks within the next nine months.

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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:

The sample preparation procedure was established for NMR spectroscopy. It consists of (1) dialysis filtration of the raw mill samples followed by freeze-drying, and (2) acetylation of the organics with acetic anhydride, and with carbon-13 enriched acetyl chloride. Dialysis followed by freeze-drying isolates and concentrates the larger organic molecules that are of interest in this study by removing the large amounts of small molecular sized inorganics that interfere with NMR spectroscopy, and acetylation of the organics enables the various functional groups to be differentiated in the NMR spectra.

Additional filtrate samples from a totally chlorine free (TCF) bleaching run (labeled #1BS(a) and (b), #2BS, and CB) were received from the Louisiana-Pacific kraft pulp mill in Samoa, CA. The #1BS and #2BS filtrates were obtained from brown stock washing after kraft pulping, and the CB filtrate was obtained after oxygen bleaching. These samples were analyzed by carbon-13 NMR spectroscopy, and the results are presented in Table I.

Table I. Functional group concentrations in filtrate samples

Functional Group	Functional group content (as % of total carbons in spectrum)					
	#1BS(a)	#1BS(b)	#2BS	#1BS	#2BS	CB
Carbonyl carbon	1.00	1.45	1.45			
Aromatic carbon	3.55	3.66	0.91			
C-O carbon	-0.52	0.98	-0.53			
Methoxyl carbon	2.18	2.99	1.61			
Aliphatic carbon	3.17	3.17	4.19			
Primary-OH				0.27	0.33	0.64
Secondary-OH				0.08	0.09	0.23
Phenolic-OH				0.65	0.58	0.13

The lower phenolic-OH content in the CB filtrate suggests that the preferred reaction during oxygen bleaching is on the site of the phenolic-OH.

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:

Complexation indicators were used in a continuing effort to determine formation constants between black liquor and alkaline earth metals. For example, using the indicator Calcon, the formation constant at pH 10 between Mg and vanillin, and between Mg and black liquor, was estimated to be 10^5 , and 10^4 , respectively. Additionally, inherent problems of indicator purity and stability were investigated: several are unstable in air at high alkali contents, and none is commercially available in a pure state. Also, in most cases, the indicators have formation constants of $\sim 10^5$ - 10^6 , which are higher than ideal. Data analysis is easier if the formation constant for the indicator is slightly less than that for the black liquor. The current work has helped identify the ideal attributes for a complexation indicator for this analysis: (1) suitable for the pH range 10 to 13, (2) stable for 8-12 hours in alkaline pH, (3) a formation constant with Ca and Mg $\sim 10^4$, and (4) a visible absorption between 450 and 700 nm.

Indicator purity is a particularly vexing problem, and the approach that was taken was to use the change in the visible absorption spectrum with addition of metal to determine the metal concentration at which 50% of the indicator had converted from the free form to the complexed form. Using this method on the Calmagite data, the purity was determined to be 39%, the extinction coefficient was calculated to be 19,000 compared to the literature value of 19,780, and the calculated equilibrium constant for the formation of the magnesium complex was $\log(K) = 5.5$ compared to a literature value of 5.69. These errors are on the order of 4%.

Experiments with competition between black liquor and Calmagite were evaluated using this method.

Unfortunately, the $\log K$ of 5.5 was higher than the formation constant between Mg and black liquor estimated at 10^4 which made it difficult to determine the total number of binding sites provided by the black liquor. It is theoretically possible to compensate by increasing the concentration of the black liquor, but at the higher concentrations the light absorption from black liquor begins to interfere with the indicator.

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: **in progress.**

Progress during the quarter:

Additional pulp samples from the Pope & Talbot pulp mill in Halsey, Oregon (brownstock washer, bleach plant HOCL #1, bleach plant EOP, bleach plant HOCL #2, and bleach plant high-pressure peroxide) were sent to IPST for carboxylic acid group and phenolic hydroxyl group functional analyses. Results have not yet been submitted.

The DIONEX DX-300 ion chromatograph (IC) in Rorrer's laboratory was upgraded and can now quantitatively profile five metal ions simultaneously: K, Na, Ca, Mg, and Ba. The rationale for this upgrade was discussed in the June 1998 report, and consisted of the installation of a new separator column, and a new conductivity detector retrofitted with a background ion suppression module. The IC was calibrated, and Strontium was chosen as an internal standard for future quantitative analyses, as it is not an NPE that is associated with wood pulp. Optimum operating conditions, e.g. eluent concentration and flowrate, and sample injection volume, must still be determined.

Multiple stage adsorption/desorption experiments were performed using calcium exchanged LP-Samoa brownstock pulp. Adsorbed calcium was gradually displaced by the series addition of small doses of dilute acid solution. From three separate runs, the total hydrogen ion adsorption capacities were 0.024, 0.033 and 0.033 mmol H⁺/g dry pulp. However, the calcium material balance showed that the calcium ion content in calcium-exchanged pulp was 0.068 mmol Ca²⁺/g dry pulp whereas the concentration of calcium ions displaced by hydrogen ions was only 0.023 mmol Ca²⁺/g dry pulp. A comparison of the concentration of adsorbed hydrogen ions to the concentration of binding sites (0.09 meq COOH/g dry pulp) implies that calcium ions are still bound to these sites.

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: **in progress.**

Progress during the quarter:

Dr. Greg Rorrer completed a journal paper discussing the nature of metal/pulp binding interactions, and the results from the Ni/Ca isotherm and adsorption kinetics experiments on brownstock and bleached pulp. This paper will also serve as the basis for the 1997-98 yearly progress report. A model to calculate mass transfer coefficients for metal ions on pulp was developed based on the assumption of ion-exchange processes for the Ca-Ni system. The model appears sound and will be evaluated with the available data in the next quarter.

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: **coupled with Task D-2.1.**

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:

The first generation improvements to the OLI Kraft database were implemented. Chemical equilibrium data were added to the species database that more accurately account for the formation of cation-dissolved organic species and cation-pulp species for both monovalent and divalent cations. Only primary metal-organic interactions were included: cation complexation with phenolic hydroxyl groups on dissolved organic species representative of lignin,

and cation binding to acid groups on a model pulp compound. Secondary metal-organic interactions have been ignored: (1) the complexation of Ca^{2+} and Mn^{2+} with carboxylic acid groups on dissolved organic species because the stability constants are much smaller than with phenolic hydroxyls, and (2) the formation of very weak complexes with hydroxyl groups on polysaccharides.

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:

Further simulations of metal ion solubilities in green and white liquors are on hold until (1) the OLI database is upgraded to include the appropriate insoluble aluminosilicate, aluminate, and silicate species that were identified in a recent study by Wannenmacher and Frederick, and (2) the green and white liquor sampling experiments (described below) have been completed. The experimental plan for sampling and analyzing mill green and white liquors consists of the following: (1) collect samples (three each) of raw green liquor, clear green liquor, raw white liquor, and clear white liquor; (2) for each liquor, filter one sample "hot" (i.e. immediately), and one sample "cold" (later at IPST) through a 0.45 μm pore size filter to remove suspended solids; (3) the third sample will remain unfiltered; and (4) submit all samples for metals and anion analyses at IPST. The concentrations of certain NPE cations and anions should differ significantly based on the type of filtration performed.

D-2.1. Evaluation of the estimation procedure.

Scheduled completion date: 8/99.

Current status: **in progress**.

Progress during the quarter:

A preliminary process model was developed for predicting the distribution of NPE's (principally Ca and Mn) between pulp and liquor streams in a two stage brownstock washer operating with water and recycled bleach plant alkaline filtrate as the wash liquor. Only equilibrium effects were considered. The kinetics of metal ion adsorption and diffusion limitations will be incorporated in modeling work to be conducted by Dr. Greg Rorrer in 1999.

This brownstock washer model was built using the OLI ESP software with the first generation of improvements to the database. It incorporates a multiphase chemical equilibrium model to account for ion exchange, aqueous speciation, precipitation, metal-pulp interactions, and complexation of metal ions with a dissolved organic compound, a model pulp compound, a model dissolved black liquor organic compound, and various inorganic salts. The primary objective was to demonstrate the validity of the modeling method, and to identify areas where equilibrium and adsorption data were lacking. For calculated Norden washer efficiency factors of approximately three, the computed Ca and Mn partitioning agreed reasonably well with mill data for non-recycled bleach filtrates.

Goals For The Period October 1 – December 31, 1998

Task A-1

Continue the NMR spectroscopic characterization of lignin fragments. Focus on determining the total number of phenylpropane groups and the composition of functional groups such as hydroxyls and carbonyls.

Task A-2

Continue the current efforts to identify a more suitable complexation indicator while obtaining as much useful information as possible with the existing indicators.

Task B-2

1. Optimize the operation of the IC.
2. Continue performing the multistage adsorption/desorption experiments and develop a model for the effect of pH on the adsorption isotherm. This model should be a simple one if the H^+ adsorption and Ca^{2+} release are stoichiometric.
3. Apply the adsorption model (incorporating ion-exchange) to the existing data to determine the mass transfer coefficient, K_{La} , and compare it to the K_{La} calculated from the previous model where an ion-exchange process was not assumed.

Task C

Upgrade the OLI database to include the insoluble aluminosilicate, aluminate, and silicate species that were identified in the recent study by Wannenmacher and Frederick, and include additional chemical equilibrium data for dissolved Ca and Mn complexed organic species, and Ca and Mn bound pulp species.

Task D

1. Conduct the experimental plan for sampling and analyzing mill green and white liquors, and profile the NPE composition.
2. Complete the preliminary simulation of the two stage brownstock washer, using both water and recycled bleach plant alkaline filtrate as the wash liquor, to evaluate calcium and manganese accumulation. Write a paper summarizing this modeling work, and present it at the 1998 TAPPI Pulping Conference on October 29th.