Project: Control of the Accumulation of Non-Process Elements and Organic Compounds in Pulp Mills with Bleach Filtrate Reuse

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Introduction

During the second quarter of this project, progress was made in tasks A-1 and B-2. A summary of this progress is included in the following sections. Plans for the next quarter are also included.

W. J. Frederick, the project PI, left Oregon State University as of December 31, and joins the faculty of the Institute of Paper Science and Technology as of January 1, 1997. Oregon State University and IPST have agreed that the project will remain at Oregon State University, with W. J. Frederick as PI on contract to OSU. OSU will provide a subcontract to IPST for the work to be accomplished by W. J. Frederick at IPST. The target date for beginning the subcontract is April 1, 1997. Responsibility for all tasks will be as indicated in the original project proposal, except that Dr. Alan Rudie of the IPST faculty will be added to the IPST subcontract to take responsibility for A-2, Characterization of Complexing of Metal Ions with Dissolved Organic Matter.

Also, the project will be carried out cooperatively with an on-going similar project at IPST will provide samples of dissolved organic matter analyzed for functional group content by NMR, and adsorption isotherm data for several cations on wood pulps. IPST will also provides extensive non-process element balance data on three kraft pulp mills and the modeling capability for computing steady-state mass balances in pulp and paper mills.

Matching funds for the project will be provided by NCASI (\$10,500 to OSU), and by IPST through in-kind research.

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: in progress

Progress during this quarter: A portion of each filtrate sample obtained from the Louisiana Pacific pulp mill in Samoa, CA on August 15th and 16th, 1996 was freeze-dried and the resulting solids were analyzed for ash content. The ash contents on a dry-weight basis were: P3 Filtrate 91.0%; EOP Filtrate 84.4%; PO2 Filtrate 70.6%; #1 Brownstock Filtrate 58.6%; and Q Filtrate 74.7%. These results show that inorganics constitute at least 60% of all dissolved solids. Most significantly, over 90% of the dissolved solids in the P3 filtrate were inorganic. The organic constituents in these filtrate samples therefore may be less significant in transporting non-process elements than had been assumed earlier.

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

Scheduled completion date: 12/97

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Current status: in progress

Progress during this quarter: The freeze-dried solids from the PO2 Filtrate and the #1 Brownstock Filtrate were investigated for extractive-like compounds, particularly polyphenols. The PO2 solids were extracted with methanol and ethyl acetate. Thin-layer chromatography (TLC) of the solubles showed a spot that remained at the origin. Attempts to find a TLC solvent system that moves the compounds so that they can be identified and characterized are in progress. The #1 Brownstock solids were also extracted with methanol and ethyl acetate. The methanol-soluble materials migrated rapidly on TLC plates with methanol as solvent, indicative of polyphenolic materials. Traces of dihydroquercetin, a known polyphenolic compound, were found in the #1 Brownstock solids. Dihydroquercetin is an extractive known to be in Douglas-fir wood.

A-1.3. Analysis of functional groups.

Scheduled completion date: 6/98

Current status: in progress

Progress during this quarter: A method of measuring the functional group content in lignin degradation products from kraft pulping and bleaching was developed by Dr. A. Ragauskas at IPST. The functional group content of a number of lignin samples have been measured and will be available for sub-tasks A-2.2 and A-2.3.

A-1.4. Characterization of carbohydrate polymers.

Scheduled completion date: 12/98

Current status: not yet begun

A-2.1. Selection of model compounds.

Scheduled completion date: 6/97

Current status: not yet begun

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

Scheduled completion date: 12/97

Current status: not yet begun

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

Scheduled completion date: 6/98

Current status: not yet begun

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

Scheduled completion date: 12/98

Current status: not yet begun

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

Scheduled completion date: 9/96

Current status: completed

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

Scheduled completion date: 12/96

Current status: completed

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

Scheduled completion date: 12/96

Current status: completed

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

Scheduled completion date: 4/97

Current status: not yet begun

B-2.1 Measure metal adsorption isotherms on wood pulp.

Scheduled completion date: 9/97

Current status: in progress

Progress during this quarter: Adsorption experiments with calcium and barium were carried at 70°C in a temperature controlled incubator under continuous mixing in order to simulate the environment experienced by brownstock as it moves through the Q stage. In the calcium experiments, we found that it was difficult to accurately determine the calcium adsorbed on the pulp by measuring the depletion of calcium in the aqueous phase. Consequently, the technique was modified. In the modified technique, the calcium-adsorbed pulp is acid washed again to release the calcium. The calcium concentration in the washings is measured, and the calcium adsorbed on the pulp is estimated by material balance. Measurement of calcium adsorption on the brownstock pulp fibers from the L-P/Samoa mill have been obtained.

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

Scheduled completion date: 12/97

Current status: not yet begun

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

Scheduled completion date: 3/98

Current status: not yet begun

C-1.1. Development of a data base for inorganic ions.

Scheduled completion date: 6/97

Current status: in progress

C-1.2. Estimation of unavailable thermodynamic parameters.

Scheduled completion date: 12/97

Current status: not yet begun

C-1.3. Evaluation of the inorganic data base.

Scheduled completion date: 6/98

Current status: not yet begun

C-2.1. Develop an organometal equilibrium calculator.

Scheduled completion date: 12/98

Current status: not yet begun

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: not yet begun

D-2.1. Evaluation of the estimation procedure.

Scheduled completion date: 3/99

Current status: not yet begun

Goals For The Period January 1, 1997 to March 31, 1997

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

- Complete the work on this sub-task.

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

- Specific organic compounds in the bleach plant filtrates which are capable of chelating metal ions will be identified.
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B-1.4 Determine the residual hemicellulose content in the pulp samples.

- Analysis of the hemicellulose content of the pulps from the L-P/Samoa bleach plant will be completed.

B-2.1 Measure metal adsorption isotherms on wood pulp.

- Obtain the adsorption constants for calcium and barium and on wood pulp using the Langmiur and Freundlich adsorption isotherm models.
- Measure the adsorption constants of barium and manganese on the brownstock #2 from the L-P/Samoa plant.

- Measure the functional group content of the brownstock #2 from the L-P/Samoa plant.

For tasks A-2, C-1, C-2, D-1, and D-2, prepare a subcontract to IPST for these tasks.