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

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Introduction

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

A sub-contract for remaining work on tasks A-2, C-1, C-2, D-1, and D-2 was submitted by IPST to OSU. The target date for beginning the subcontract was changed to May 1, 1997. Responsibility for all tasks is 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. In addition, IPST has provided adsorption isotherm data for several cations on wood pulps and will provide samples of dissolved organic matter that have been analyzed for functional group content by NMR. IPST has provided extensive non-process element balance data on three kraft pulp mills, and has underway computation of steady-state mass balances for these three mills.

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:

As reported earlier, bleach plant filtrate samples were obtained from the Louisiana Pacific Pulp Mill in Samoa, California. The total solids (suspended plus dissolved) contents were: P3 Filtrate 0.14%; EOP Filtrate 0.34%; PO2 Filtrate 1.43%; #1 Brownstock Filtrate 10.94%; Q Filtrate 0.33%. The ash content of the recovered solids (recovered by freeze-drying) were: P3 Filtrate solids 91.0%; EOP Filtrate solids 84.4%; PO2 Filtrate solids 70.6%; #1 Brownstock Filtrate solids 58.6%; Q Filtrate solids 74.7%. The Klason Lignin content (solids insoluble in 72% sulfuric acid) were determined in the recovered solids from the #1 Brownstock Filtrate (25.8% Klason lignin) and the recovered solids from the PO2 Filtrate (8.2% Klason lignin).

A-1.2 Separation of carbohydrates and lignin degradation products.

Scheduled completion date: 12/97

Current status: in progress

Progress during this quarter:

The recovered solids from the #1 Brownstock Filtrate were extracted with methanol (66.1% solubilized) and ethyl acetate (11.2% solubilized). The methanol and ethyl acetate solvents were used to dissolve the lignin products and extractives away from the carbohydrates. Evaluation of the dissolved material is in progress, but preliminary work indicates the presence of catechin, an orthohydroxyl-containing extractive.

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A-1.3 Analysis of functional groups.

Scheduled completion date: 6/98

Current status: in progress

Progress during this quarter:

TLC is being used to identify known compounds in organic extracts of the solids recovered from the #1 Brownstock Filtrate. To date, catechin has been identified and dihydroquercetin tentatively identified. These are extractives known to be in Douglas-fir wood (the raw material for the Brownstock Pulp) and contain orthohydroxyl groups.

A-1.4 Characterization of carbohydrate polymers.

Scheduled completion date: 12/98

Current status: in progress

Progress during this quarter:

Pulp samples have been hydrolyzed with 77% sulfuric acid.

A-2.1 Selection of model compounds.

Scheduled completion date: 6/97

Current status: in progress

Progress during this quarter:

The identification of catechin and possibly dihydroquercetin in the #1 Brownstock Filtrate is indicative. These two compounds are readily available and are to be considered as potential model compounds for further study. Lignin materials are now commercially available from Aldrich (Lignin, kraft, Cat.#37,096-7) that also represent potential model compounds.

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: in progress

Progress during this quarter:

LP-Samoa #2 brownstock samples have been analyzed for hemicellulose content. Hemicellulose sugars are qualitatively present by TLC analysis of the acid hydrolysates of pulp. Quantitative analysis of hemicellulose sugars by HPLC is being held up by HPLC equipment repairs.

B-2.1 Measure metal adsorption isotherms on wood pulp.

Scheduled completion date: 9/97

Current status: in progress

Progress during this quarter:

Isotherms for the adsorption of divalent alkaline earth metal ions on wood pulp (LP-Samoa #2 brownstock) were characterized. Specifically, adsorption isotherms for calcium ions on wood pulp at 25°C and 70°C for Ca concentrations ranging from 40 to 2000 mg/L were determined. The adsorption isotherm for barium ions (Ba) on wood pulp at 25 C for Ba concentrations ranging from 40 to 2000 mg/L was also determined. Statistical limits an the adsorption capacity were obtained. Freundlich and Langmuir adsorption isotherm parameters for both Ca and Ba were determined from data.

The results are:

Ca²⁺

Langmiur: $Q = Q_{\max} C_e (1 + K C_e)$

$Q_{\max} = 9.6 \text{ mg Ca/g dry pulp}$

$K = 1.6 \times 10^{-3} \text{ L/mg}$

Freundlich: $Q = K C_e^{1/n}$

C_e in mg/L, Q in mg metal/g-pulp

$n = 1.33, K = 0.03$

Ba²⁺

Langmuir:

$Q_{\max} = 4.7 \text{ mg Ba/g dry pulp}$

$K = 18.3 \text{ L/mg}$

Freundlich:

$n = 1.96, K = 0.32$

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 April 1, 1997 to June 30, 1997

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

- The experimental methodology is essentially complete. Additional filtrates will be obtained and the solids recovered as previously reported to ensure adequate solids are available for additional work.

A-1.2 Separation of carbohydrates and lignin degradation products.

- Identify by thin-layer chromatography (TLC) the hydroxyl-containing compounds in the methanol and ethyl acetate extracts. Precipitate lignin-like materials from #1 Brownstock Filtrate by the addition drop by drop of dilute (10 vol.%) sulfuric acid as commonly described in the literature.

A-1.3 Analysis of functional groups.

- Continue to identify known compounds by TLC. Initiate ¹³C-NMR experiments to obtain data on functional groups.

A-1.4 Characterization of carbohydrate polymers.

- Identify the monosaccharides in the 77% sulfuric acid hydrolyzates of the pulps.

A-2.1 Selection of model compounds

- Progress during this quarter: The identification of catechin and possibly dihydroquercetin in the #1 Brownstock Filtrate is indicative. These two compounds are readily available and are to be considered as potential model compounds for further study. Lignin materials are now commercially available from Aldrich (Lignin, kraft, Cat.#37,096-7) that also represent potential model compounds. Goals for the next quarter: Identify additional known compounds that are potential model compounds.

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

- Resolve HPLC analytical equipment problems and obtain quantitative analysis of hemicellulose sugars in acid-digested pulp samples. From the quantitative hemicellulose sugars profile, the residual hemicellulose content will be estimated.

B-2.1 Measure metal adsorption isotherms on wood pulp.

- Adsorption isotherms of divalent transition metals on wood pulp will be measured at 25 C. The first divalent transition metal ion to be characterized is Manganese (Mn).

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

- Adsorption isotherm parameters for Ca, Ba, and Mn will be correlated to carboxylic acid functional group content of the LP-Samoa #2 Brownstock, provided the functional group characterization measurements for the pulp under Task A-1 are completed.

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

- The adsorption kinetics of Ba, which is strongly adsorbed on wood pulp at concentrations exceeding 100 mg/L, will be determined.

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

- complete the search for free energy data and ion activity coefficient parameters for inorganic ions
- input these to the thermodynamics data bases