CHEMICAL PULPING AND BLEACHING

PROJECT ADVISORY COMMITTEE MEETING

November 4-5, 1998
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CHEMICAL PULPING AND BLEACHING PAC MEETING  
November 4-5, 1998 Agenda  

Wednesday, November 4  

9:00  Introduction (Don Dimmel/Tadas Macas)  
9:10  Research lines, Future Consortium Project Selection (Earl Malcolm)  
9:30  RAC report (Pat Bryant/Tadas Macas)  
9:50  Fundamentals of Bleaching Chemistry - Project F015  
   (A) peroxide, laccase, hexenuronic acid (Art Ragauskas)  
   (B) singlet oxygen (Lucian Lucia)  
11:00  Complete F015A and F015B Project Report Form + break  
11:15  Selectivity of Ozone Bleaching - USDA Project 4168 (Don Dimmel)  
11:35  Student research - Mike Zawadski  
12:00  Complete 4168 Project Report Form (optional) + lunch  
12:40  Report from Chemical Recovery closed mill research (Peter Pfromm)  
1:00  Closed Mill Operations - Project F017 (Jim Frederick, Alan Rudie)  
2:15  Complete Project Report Form for F017 + break  
2:30  Environmentally Compatible Production of Bleached Chemical Pulp - Project F013  
   (Tom McDonough, Chuck Courchene)  
3:15  Complete Project Report Form for F013 + break  
3:30  Project F030 (Jian Li)  
3:50  Project F014 (Art Ragauskas)  
4:20  Complete Project Report Forms for F030 and F014 + break  
4:35  Externally-funded projects:  
   • Trees with Built-in Catalysts - Project 4181 (Don Dimmel)  
   • Trees with Modified Lignin - Project 4226 (Don Dimmel)  
   • Energy Efficient Kraft Pulping for ... Low-Lignin Pulp - Project 4120 (McDonough)  
   • High Efficiency ClO₂ Delignification - Project 4159 (Tom McDonough)  
   • Low Capital ECF Bleaching – Project 4201 (Tom McDonough)  
5:45  Complete Project Report Form for 4000 projects (optional)  
6:00  Dinner  

Thursday, November 5  

8:00  IPST News, Project ROCIT (Earl Malcolm)  
8:15-12:15  Committee Discussions
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* The dates in ( ) indicate the final year of the appointment.
FY-2000 PLANNING SUMMARIES
DUES-FUNDED PROJECT SUMMARY

Project Title: Environmentally Compatible Production of Bleached Chemical Pulp
Project Number: F013
PAC: Chemical Pulping and Bleaching
Project Duration: 1 year
Project Staff:
  Faculty/Senior Staff: T.J. McDonough, C.E. Courchene, J. Waterhouse
  Staff: M. Turner, A. Shaket, M. Bliss
Project Funding:
  Allocated as Matching Funds: $50,000
  Proposed Budget: $250,000

RESEARCH LINE/ROADMAP:
Environmental Performance/RM5 - Reduce Emissions

BENEFITS TO INDUSTRY:
Improved environmental performance of pulp manufacturing facilities with minimum cost.

PROJECT OBJECTIVE:
Define pulping and bleaching technology that will decrease or eliminate the release of byproduct organic chlorine compounds without sacrificing bleached pulp quality.

DELIVERABLES:
1. Assessment of alternatives for activation and catalysis of peroxide delignification of kraft brownstock.
2. Development of novel hardwood kraft bleach sequences based on Rapid D_6 technology and prehydrolysis.
3. Determine effects of delignification with ozone, chlorine dioxide, oxygen and their combinations on fiber characteristics and papermaking and end-use related pulp properties.
4. Leveraging of relevant externally funded research on one or more of the following topics:
   - Bubble size control to improve oxygen-based bleaching
   - ClO_2-based bleaching in closed-mill systems
   - Odor-free, low-kappa bleached pulp manufacturing process
   - Low-capital ECF bleaching sequences for closed mill systems
   - Distribution and control of nonprocess elements in closed bleach plants
   - Extended D(EOP) delignification

Average Overall PAC Rating _____________________________
Project Recommendation
  [ ] Continue  [ ] Accelerate  [ ] Terminate  [ ] New Project

Confidential Information - Not for Public Disclosure
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DUES-FUNDED PROJECT SUMMARY

Project Title: Fundamentals of Brightness Stability
Project Code/Project Number: F014
PAC: Chemical Pulping and Bleaching
Project Duration: FY 1999 - 2000
Project Staff: Arthur J. Ragauskas and Lenong Allison
Faculty/Senior Staff:
Staff:
Project Funding: $63,000
Allocated as Matching Funds: N/A

RESEARCH LINE/ROADMAP:

Improved Forest Productivity:

➢ Increase the yield of kraft-pulp equivalent fiber by 10%.
➢ Use of post treatments to give kraft properties.
➢ Modification of structure or composition of products.

BENEFITS TO INDUSTRY:

The projected benefits of this project are to improve the use high-yield fibers for papermaking applications.

PROJECT OBJECTIVES:

Provide a fundamental understanding of the chemical reactions that are initiated when high-yield pulps are photolyzed. As our knowledge of the photooxidation of mechanical pulp increases methods to eliminate or significantly retard the photoyellowing of high-yield pulps will be pursued.

DELIVERABLES:

1. Optimize photostabilization effects of CaCO₃ with FWA and UV-absorber.
2. Study photobleaching chemistry of acetylated lignin.
3. Examine use of ‘practical’ alternatives to lignin acetylation to photostabilize high-yield fibers.

Average Overall PAC Rating

Project Recommendation

☐ Continue  ☐ Accelerate  ☐ Terminate  ☐ New Project

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**DUES-FUNDED PROJECT SUMMARY**

**Project Title:** Chemical Fundamentals of Bleaching  
**Project Code/Project Number:** F015  
**PAC:** Chemical Pulping and Bleaching  
**Project Duration:** FY 1999 - 2000  
**Project Staff:**  
- Faculty/Senior Staff: Arthur J. Ragauskas, Lucian A. Lucia, Lenong Allison, Ki-Oh Hwang  
**Project Funding:** $270,000  
- Allocated as Matching Funds: N/A

**RESEARCH LINE/ROADMAP:**

Environmental Performance:  
- Reduce emissions of entire pulp and paper manufacturing process to meet Tier 3 Cluster Rule while maintaining global competitiveness.  
- Reduce water usage in bleached kraft pulp production to 2,500 gallons per ton.

Improved Forest Productivity:  
- Increase the yield of kraft-pulp equivalent fiber by 10%.

**BENEFITS TO INDUSTRY:**

The projected benefits of this project are to decrease the operating and capital costs associated with ECF bleaching of kraft pulps. Improvements in the selectivity of pulp bleaching chemicals are anticipated to yield enhanced physical properties of fully bleached kraft pulps. These objectives are to be accomplished while addressing current and future environmental performance requirements for bleaching kraft pulps.

**PROJECT OBJECTIVES:**

Provide a fundamental understanding of the physical and chemical reactions that control lignin and carbohydrate degradation during new bleaching sequences. Understand the reasons for selectivity of reactions that occur in selected pulping and bleaching sequences. The research compliments Project F013 research on bleach process technology. Focus areas for this fiscal year are hexenuronic acids, biobleaching, high efficiency peroxide bleaching, and fundamentals of oxygen delignification.

**DELIVERABLES:**

1. Identify bleaching conditions that maximize efficient use of oxygen and hydrogen peroxide in (EOP) for D0 bleached pulps.  
2. Study pulping procedures to reduce hexenuronic acid content in hardwood kraft pulps. Evaluate the mechanisms involved in acidic peroxide treatment of hardwood kraft to decrease apparent kappa number.  
3. Examine the use of laccase delignification technologies for high kappa pulps with respect to yield and physical properties.  
4. Study the fundamental bleaching reactions of singlet oxygen in kraft softwood pulps as a function of light source and temperature and determine if the technology is patentable.

**Average Overall PAC Rating**  
**Project Recommendation**  
- [ ] Continue  
- [ ] Accelerate  
- [ ] Terminate  
- [ ] New Project

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DUES-FUNDED PROJECT SUMMARY

RESEARCH LINE/ROADMAP:

Project Title: Closed Mill Operation
Project Code/Project Number: CLDMIL/F017
PAC: Chemical Pulping and Bleaching
Project Duration: 2 years
Project Staff
- Faculty/Senior Staff: Alan Rudie
- Staff:

Project Funding:
- Proposed Budget FY 99/00: $120,000
- Allocated as Matching Funds:

RESEARCH LINE/ROADMAP:
4. Reduce water usage in Bleached Kraft Pulp production to 2500 gallons per ton.

BENEFITS TO INDUSTRY:
The industry is suffering from increased scale problems due to recent changes in bleaching practice and the continual need to reduce water use and wastewater discharge in the bleach plant. Development of NPE predictive capability to function with existing Mass and Energy balance simulators has become a priority in the industry. The pulp ion exchange process has been characterized in this project for the pH range 1-9, it is necessary to characterize the phenolic contribution to ion exchange (pH 9-10) to obtain complete predictive capability for metals management. To gain better control of the scale problem, the industry needs tools to and understand the precipitation and scaling process. Of particular interest is the evidence that nearly all bleach plants exceed the solubility limit of barium sulfate and calcium oxalate, but not all bleach plants have serious scaling problems. This conclusion comes from the bleach plant sampling effort of Pat Bryant where the minimum Barium and minimum sulfate concentrations were 3 times the solubility limit (using OLI) and a paper published by Per Ulmgren (Tappi 1997 Minimum Effluent Mill Symposium) indicating over 50% of the analyzed filtrate CaC\(_2\)O\(_4\) was really a 500 Dalton micro-particulate. Since small crystals are thermodynamically unstable, determining the nature of the micro-particulate and if crystalline, the growth inhibitor, is of considerable interest and may provide a means to control scale.

PROJECT OBJECTIVES:
- Complete wood pulp ion exchange work to characterize NPE behavior at high pH.
- Initiate an investigate BaSO\(_4\) and CaC\(_2\)O\(_4\) precipitation, and scale.

DELIVERABLES:
1. Completed ion exchange models for NPE adsorption on wood pulp (high pH work).
2. Prevalence of bleach plant precipitates and correlation to scaling problems
3. Analysis of any organics associated with the precipitates and or scales.
   - Functional group (carboxylic acids?)
   - Molecular weight
   - Structural nature/origin (lignin, carbohydrate, extractives, process chemical)

Average Overall PAC Rating

Project Recommendation

☐ Continue ☐ Accelerate ☐ Terminate ☐ New Project

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DUES-FUNDED PROJECT SUMMARY

Project Title: High Strength, High Yield Bleached Pulps
Project Code/Project Number: HSYBP/ F030
PAC: Chemical Pulping and Bleaching
Project Duration: FYR 2000
Project Staff: J. Li, E. Malcolm, C. Courchene, D. Dimmel
Faculty/Senior Staff: Tech. III
Project Funding: $200,000
Allocated as Matching Funds: $ 0

RESEARCH LINE/ROADMAP:
Increase Yield by 10% Absolute / Develop Modified Pulping Process.

BENEFITS TO INDUSTRY:
Significant cost reduction in chemical pulp product from low wood consumption and/or high production rate with present kraft mill capacity.

PROJECT OBJECTIVE:
The objective of this project is to significantly improve the strength properties of higher yield chemical pulps to the level of current, low yield, kraft pulp. Initial work will center on the suitable processes which do not require significant capital investment.

DELIVERABLES:

1. Complete the experiments on modification of one-liquor (no split sulfidity) cooking: the goal of this research is to develop modified cooking conditions that do not require any significant amount of capital investment when applied in current mill equipment.

2. Start to develop multi-stage pulping processes using split-sulfidity liquors per 3-year research plan: Using split-sulfidity liquors should allow higher yield gain, and give the possibility of improving pulp strength.

3. Continue to develop suitable process conditions for Soda-Catalyst pulping to achieve high yield and strength: This part of research will use alkali concentration to alter carbohydrate degradation and extraction rate.

4. Start the research on high kappa number followed with oxygen delignification: This part of research will focus on improvement of the strength properties of this kind of pulp.

Average Overall PAC Rating

Project Recommendation [ ] Continue [ ] Accelerate [ ] Terminate [ ] New Project

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DUES-FUNDED PROJECT SUMMARY

**Project Title:** Selective Determination of Lignin Linkages in Wood and Pulp

**Project Number:** New

**PAC:**
Chemical Pulping and Bleaching, Forest Biology

**Project Duration:** Three years, starting in FY 2000

**Project Faculty/Senior Staff:** Gary Peter, Don Dimmel

**Staff:** Elizabeth Althen

**Project Funding:** Proposed Budget: $100,000 FYR 2000

RESEARCH LINE - ROADMAP

*Environmental Performance* – (a) Develop economically viable pulping technology to produce kraft equivalent pulp which ensures no odor at mill boundaries and (b) reduce emissions of entire pulp and paper manufacturing process to meet Tier 3 Cluster Rule while maintaining global competitiveness.

*Improved Forest Productivity* – Increase the yield of kraft-pulp equivalent fiber by 10%.

**BENEFITS TO INDUSTRY**

Accurate knowledge of residual lignin structure prior to and after various bleaching stages will provide the scientific basis needed to make significant advances in pulping and bleaching technologies. Present methods of characterizing lignin rely mainly on isolating (with modification) a faction of the lignin present. Reagents that are specific to *in situ* lignin-lignin and lignin-carbohydrate linkages are required to determine the amounts and spatial distribution of key linkages of residual lignin in the fiber. Sensitive, specific reagents will provide unique fundamental information about lignin structure and, thus, accelerate the development of (1) more rapid, milder pulping reactions that increase productivity and pulp strength with lower applied energies, (2) bleaching systems that target specific linkages, resulting in improved selectivity, lower costs and processes that limit water usage and organic discharges, and (3) the detection of trees with lignin structures better suited for pulping and bleaching.

**PROJECT OBJECTIVES**

Develop and characterize antibody reagents that rapidly identify specific lignin-lignin and lignin-carbohydrate linkages. We will use this antibody technology to (1) quantify the level of such linkages and attempt to correlate their location and structural features with lignin reactivity and (2) develop a high-through put screening method that will aid in the discovery of novel chemistries for lignin removal and of natural tree variants with more easily removed lignin. Limited studies have shown that antibodies, which are proteins, can be developed to react with specific linkages of lignin or carbohydrates. Presently, we have polyclonal antibodies that react with select condensed and uncondensed lignins in pines. These antibodies can be used to rapidly map the spatial aspects of condensed versus uncondensed lignin that are removed and redeposited during the various pulping and bleaching treatments.

**DELIVERABLES**

We will generate a set of antibodies that bind specifically with distinct lignin linkages. The research will consist of:

1. producing various synthetic lignin model compounds, both soluble and insoluble,
2. characterizing the specificity of existing antibodies with these synthetic lignins,
3. generating new antibodies with defined specificity to lignins and lignin carbohydrate complexes, and
4. using purified antibodies to investigate the structure and organization of residual lignins after modified pulping and bleaching reactions

Average Overall PAC Rating

Project Recommendation

[ ] Continue  [ ] Accelerate  [ ] Terminate  [ ] New Project
DUES-FUNDED PROJECT SUMMARY

Project Title: Trees with Easily Pulped Lignin through New Genetic Selection Methods
Project Number: New
PAC: Chemical Pulping and Bleaching PAC & Forest Biology PAC
Project Duration: 3 years (Initiate FY 2000).
Project Staff:
  Faculty/Senior Staff: John MacKay, Don Dimmel
  Staff: Elizabeth Althen
Project Funding:
  Allocated as Matching Funds: USDA funds of $24,000; IPST exploratory funds of $10,000 (1998, 1999)
  Proposed Budget: $100,000 yearly (FY 2000).

RESEARCH LINE - ROADMAP:

**Improved Productivity** - Improve the fiber productivity of North American lands so that they are competitive in the world pulpwood market. (Genetically improved trees)

**Environmental Performance** – (a) Develop economically viable pulping technology to produce kraft equivalent pulp which ensures no odor at mill boundaries and (b) reduce emissions of entire pulp and paper manufacturing process to meet Tier 3 Cluster Rule while maintaining global competitiveness.

BENEFITS TO INDUSTRY:
The proposed research is aimed at developing trees that containing easily extracted lignin and/or less lignin. Trees containing modified lignin will allow pulping to be conducted more rapidly or under milder conditions, leading to increased productivity, stronger pulps (because of less fiber damage), lower energy and bleaching costs, less bleaching by-products, and possibly processes that rely less on sulfur.

PROJECT OBJECTIVES:
The objectives are first, to develop and use methods of producing trees with modified lignin and/or less lignin that do not require gene transfer technology. Without gene transfer the cost to develop and produce the trees will be low and, rapid implementation would be possible through traditional tree improvement methods. Secondly, we will investigate lignin structure and reactivity in pulping and bleaching to determine the potential benefits to industry.

DELIVERABLES:
1. The research will continue and expand the genetic and chemical (pulping and bleaching) study of loblolly pine trees that are deficient in cinnamyl alcohol dehydrogenase (CAD), a key enzyme in lignin synthesis. We have already shown that trees that are completely deficient in CAD enzyme are easily delignified by alkali alone. Specifically, we propose to:
   - Identify and characterize diverse loblolly pines that are partially CAD-deficient.
   - Evaluate the potential benefits for pulping and bleaching of trees with complete and partial CAD-deficiency, emphasizing kraft, kraft/AQ, and soda/AQ pulping and standard DEDED bleaching.
   - Investigate the relationship between partial and complete CAD-deficiency, lignin structure, and lignin reactivity to better understand the chemical basis of delignification during pulping in CAD-deficient trees.
2. A second area will be aimed at identifying other potential methods for genetic modification of lignin synthesis that could decrease the lignin content of wood and, thereby, increase the cellulose content. This research is longer term in nature and relies, in part, on developments being reported in other research groups.
3. Selective breeding programs, aimed at amplification of the novel lignin component, will be initiated with North Carolina State University.

Average Overall PAC Rating

Project Recommendation

Confidential Information - Not for Public Disclosure
(For IPST Member Company's Internal Use Only)
Project Title: Fundamentals of Bleaching Mixed Office Waste
Project Number: New
PAC: Chemical Pulping and Bleaching
Project Duration 3 years (Initiate FY 2000)
Division: Chemical and Biological Sciences
Project Staff
Faculty/Senior Staff: Arthur J. Ragauskas, Lucian Lucia
Staff: Lenong Allison
Project Funding:
Allocated as Matching Funds: N/A
Proposed Budget: $75,000

RESEARCH LINE/ROADMAP:

Recycling

Reduce and/or control contaminants (e.g., stickies, dyes, toners) in recycled-fiber pulp using break-through technologies to allow complete interchange of recycled pulp with virgin pulp of similar fiber make up at economical cost.

- Develop new separation processes
- Develop techniques to modify contaminants

BENEFITS TO INDUSTRY:

The proposed research will provide a fundamental understanding of how chemical bleaching agents destroy color bodies in Mixed Office Waste (MOW). These results will provide a basis from which new, improved bleaching sequences for MOW could be developed and also facilitate optimization of current bleaching sequences. In addition, the detrimental impact of mechanical pulp in MOW streams will be studied and new chemistries will be developed to minimize the effect of this furnish.

PROJECT OBJECTIVE:

The goal of this 3-year project is to develop a fundamental understanding of the oxidative and reductive chemical reactions involved in bleaching MOW. A special emphasis will be placed on determining how differing bleaching chemicals/sequences influence the final brightness and color of the bleached pulp. The fundamental factors contributing to improved MOW bleaching for an oxidative – reductive sequence over a reductive – oxidative sequence will be established. The chemical reactions involving high-yield fibers in bleaching MOW will be determined and this data will be employed to minimize color formation from this fiber source.

DELIVERABLES FOR FY 99 – 2000:

1. Literature report summarizing the available technologies for bleaching MOW.
2. Study the oxidative degradation of the five most common dyes with ozone, chlorine dioxide, hydrogen peroxide and FAS.

Average Overall PAC Rating ______________________________

Project Recommendation □ Continue □ Accelerate □ Terminate □ New Project

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DUES-FUNDED PROJECT SUMMARY
FY 1999 – 2,000

Project Title: Fundamentals of Fiber Modification
Project Number: New
PAC: Chemical Pulping and Bleaching
Project Duration: 4 years (Initiate FY 2000)
Division: Chemical and Biological Sciences

Project Staff
Faculty/Senior Staff: Arthur J. Ragauskas
Staff: Lenong Allison

Project Funding:
Allocated as Matching Funds: N/A
Proposed Budget: $ 75,000

RESEARCH LINE/ROADMAP:

1. Increase the yield of kraft-pulp equivalent fiber by ten percentage points.
   - Develop techniques to modify fiber sources
     - For chemical and high yield pulping
   - Develop modified/new pulping/bleaching processes
     - Chemical
     - Hi yield mechanical strength
   - Use of post treatments to give kraft properties
     - Chemical treatments
     - Mechanical treatments
   - Modification of structure or composition of products.

PROJECT BENEFITS:
The application of enzymatic systems to high lignin content fibers provides several new opportunities to modify the physical properties of pulp fibers. In brief, this project will be targeted at developing several new bio-treatments that improve strength properties, pulp refining requirements, and/or modify water retention properties.

PROJECT OBJECTIVE:
The objectives of this project are to explore the application of chemical and biochemical treatments to modify the physical properties of high lignin content pulps. The use of novel enzymatic and/or chemical treatments on mechanical and liner grade kraft pulps will be studied to modify important post-processing properties including water retention, fiber-to-fiber bonding, general web consolidation, wet-pressing and freeness. Changes in fiber properties will be studied in terms of basic fiber chemistry properties including acid group content, hemicellulose structure, and surface fiber chemistry.

DELIVERABLES FOR FY 99 – 2000:
1. Literature report summarizing state-of-the-art chemical and biochemical technologies available to modify physical properties of ‘high lignin content pulp.’
2. Evaluate the effects of laccase and laccase/mediator-activator treatments on the physical properties of SW TMP and liner grade kraft pulps.
3. Examine the chemical interactions occurring between manganese peroxidase and SW TMP and liner grade kraft pulps.

Average Overall PAC Rating

Project Recommendation
[ ] Continue  [ ] Accelerate  [ ] Terminate  [ ] New Project

Confidential Information - Not for Public Disclosure
(For IPST Member Company’s Internal Use Only)
DUES-FUNDED PROJECT SUMMARY

Project Title: Low-Capital Bleach Plants
Project Number: New
PAC: Chemical Pulping and Bleaching
Project Duration: 3 years
Project Staff:
  Faculty/Senior Staff: T. J. McDonough, C. E. Courchene
  Staff: B. Carter, A. Shaket, M. Turner
Project Funding:
  Allocated as Matching Funds:
  Proposed Budget: $100,000 yearly

RESEARCH LINE/ROADMAP:
Improved Capital Effectiveness: 8. Develop technologies to allow cost effective expansion of fiber capacity.

BENEFITS TO INDUSTRY:
The ability to install full chemical pulp bleaching capacity with very low capital requirements would be of great value to the industry. It would provide avenues for low-cost expansion of bleached pulp capacity, low-cost greenfield bleaching capacity, and would be capable of retrofitting to replace aging bleach plants with minimum capital expenditure.

PROJECT OBJECTIVES:
Develop technologies for efficient, short retention time, bleaching stages capable of being assembled into an effective sequence for bleaching kraft pulps to high brightness. Identify suitable conditions for fast chlorine dioxide delignification and brightening stages as well as low pressure, rapid alkaline extraction and peroxide stages. Assess and investigate opportunities for identifying alternative bleaching technologies that offer the possibility of unusually rapid delignification and/or brightening. Devise technically feasible means of coupling the stages to form effective bleaching sequences, and optimize the sequences with respect to bleaching conditions and chemical charges.

DELIVERABLES:
1. Survey of the literature to consolidate and analyze existing information on rapid delignification and brightening technology, as well as all available relevant information on bleaching kinetics and opportunities for catalysis of bleaching.
2. Conditions for running and linking fast chlorine dioxide delignification and brightening stages as well as low pressure, rapid alkaline extraction and peroxide stages
3. Alternative technologies for rapid bleaching stages, based on the use of novel bleaching agents, catalysts, or both.

Average Overall PAC Rating

Project Recommendation

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21
F015: Project Objective

- Provide a fundamental understanding of the physical and chemical reactions that control lignin and carbohydrate degradation during new bleaching sequences.

F015: Project Goals and Staff

Goal
- Improve bleaching sequences

Staff
- A. Ragauskas
- L. Lucia
- L. Allison
- K. Hwang
Current Research Focus

- Hydrogen peroxide
- Biobleaching ✓
- Hemicellulose ✓
- Oxygen ✓

Hemicelluloses

Hexenuronic Acids

Hexenuronic Acids: Background

Proposed by Clayton - 1963

Consumes oxidant

Studied:
- Johansson & Samuelson - 1977
- Simkovic - 1986
- Teleman ... - 1995
**Hexenuronic Acids: Background**

- Consumes D & Z
- Inert to P & O
- Sensitive to acid
- Related to % xylan in pulp
- HW kraft: 30-55% of apparent kappa
- SW kraft: 0 - 18%
- Binds metals
- AQ influences % HexA
- PS does not influence % HexA

**Hexenuronic Acids: Background**

Acid treatment chemistry

**Hexenuronic Acids: Research Goals**

**Long Term**
- Determine impact of HexA.
- Develop technologies that will minimize their effects.

**FY 1998-99**
- Examine the effect of alternative acidic treatments to remove HexA,
- Determine the effects of HexA removal on yield, pulp bleachability,
HexA: Alternative Acids

Experimental Design
- Commercial southern hardwood kraft pulp
- 3% cate, initial pH: 3.0
- Hydrolysis time: 1, 2, 3 h
- Hydrolysis temperature 80, 90, and 95°C
- Acids Employed: Formic Acid/Sodium Formate (buffered)
  - Formic acid
  - Phosphoric acid
  - Nitric acid
  - Sodium formate
  - Do effluent (initial pH 1.2)

HexA: Acid Hydrolysis at 80°C

Brownstock kappa #: 13.5

HexA: Acid Hydrolysis at 90°C
HexA: Acid Hydrolysis at 95\(^\circ\) C

![Bar chart showing Kappa values for different hydrolysis times and acids: Formic, HNCS, HSPH, TCA, and Do.

HexA: Summary of Acid Work

- Do wash is an effective treatment for HexA
- At 95\(^\circ\)C need 5 h for max. effect >> For this pulp!
- 20 - 28% loss in viscosity (95 C)

HexA: Oxidative reinforced acid treatment of HW Kraft

![Chemical structure of the oxidized compound with Q, H^+ reaction, and Oxidant? question mark]
HexA: Preliminary investigation into use of acidic peroxide

Experimental Conditions
- HW kraft pulp
- Formic acid/Sodium formate (pH 3.0)
- 1 h at 95°C
- 10% csc

HexA: Full Sequence HW Kraft Bleaching Studies

Experimental Design
I. Study DEDED vs ADEDED
   A-stage: Formic Acid/Sodium Formate 3 h
   D₀: 0.20 kf, 3.5% csc, 45 min, 50°C
   D1: 0.6% Charge, 10% csc, 3h, 75°C
   D2: 0.1, 0.2, 0.4, 0.6% charge

II. Study ODED vs OADED
   D₀: 0.20 kf, 3.5% csc
   D1: 0.1, 0.2, 0.4, 0.6% charge
HexA: Full Sequence HW Kraft Bleaching Studies

Experimental Results

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Kappa #</th>
<th>Viscosity/cP</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brownstock</td>
<td>11.4</td>
<td>24.4</td>
<td></td>
</tr>
<tr>
<td>Brownstock(A)</td>
<td>5.6</td>
<td>22.8</td>
<td>98.2</td>
</tr>
<tr>
<td>O</td>
<td>8.5</td>
<td>21.8</td>
<td></td>
</tr>
<tr>
<td>OA</td>
<td>2.8</td>
<td>19.9</td>
<td>98.0</td>
</tr>
</tbody>
</table>

HexA: Full Sequence HW Kraft Bleaching Studies

HexA: Conclusions

- Exact acid not overly important for HexA removal
- Temp. is important for HexA removal
- Acidic peroxide stage may be effective for HexA removal
- HexA removal is beneficial for Do and subsequent stages
- No ‘noticeable effect’ of A-stage on yield
BIOBLEACHING

Laccase

Laccase
- Oxoreductase enzyme
- Reduces O₂ to H₂O & concomitantly oxidizes
- Catalysis occurs due to 4 copper atoms/active site
- Active sites on surface
- Large protein: 36 - 120 kDa
- In nature: polymerization & depolymerization of lignin

Laccase - Review
- Laccase catalyzed delignification requires O₂ + mediator

<table>
<thead>
<tr>
<th>Laccase</th>
<th>BisNSts</th>
<th>BisNPh</th>
</tr>
</thead>
</table>
| % Delign.
| 10      | 20      | 30     |
Lactase: Mediator Chemistry

New Mediators

HNNH

K

0

NHAA Violuric Acid

Lactase/VA yields improved delignification at 12% charge of enzyme wrt laccase/NHB

Lactase: Research Goals

Long Term
- Develop new methods of improving kraft bleaching operations employing enzymatic technologies

FY 1998 - 98
- Determine influence of metals on LMS treatment
- Determine pulp yield after LMS

Lactase: Role of Metals

Laccase-Mediator Conditions
HW and SW kraft pulps
Temp.: 50-54°C
Pressure 120 psi
Time: overnight
Laccase dose: 190 LAMU/gr od pulp
Violuric Acid: 3% charge
Added 0.1% charge of MgSO4 or molar equivalent of MnSO4, CuSO4, FeSO4, NiSO4

Extraction Stage
2% NaOH, 5% cae, 70°C, 2h
Laccase: Role of Metals in LMS of HW kraft

- Fe, Ni, and Cu detrimental to LMS stage
- Mg and Mn not detrimental to delignification
- Yield unspiked: LMS 99.6%, LMS(E): 99.3%

Laccase: Role of Metals in LMS of HW kraft

- Fe, Ni, and Cu detrimental to LMS stage
- Mg and Mn not detrimental to delignification

Laccase: Conclusions

- Yield results for LMS continue to be promising
- LMS stage not sensitivity to viscosity losses caused by Mn
- LMS stage exhibits different metal sensitivity than P, Z
  - or O
Related Research Issues

- High Efficiency Cl₂ Delignification - DOE
- Improved Peroxide Bleaching - GA Consortium
  - inventory of NPEs in GA wood resources
- Dr. D.H. Kim: Zeolite catalyst for P-stage
- Mill Designed Biobleaching Technologies - DOE*

Student Research

Troy Runge
- Bleaching chemistry of alkaline extraction

Kären Haynes
- Fiber properties of Laccase/mediator bleached pulps

Michael Zawadzki
- Bleaching chemistry contributing to brightness ceilings

Fadi Chakar
- Chemistry of Laccase/mediator delignification

John Werner - MSc
- NPE - black liquor complexes

Exploratory Studies

Chemistry of Oxalic Acid Generation
Oxalic Acid Generation from Do

- Generation of OxA from Do from lignin principally
- Chemical pathways of formation know only in general
- OxA impacts operations and products
- Exploratory studies directed at chemistry of OxA formation & OxA interaction with other lignin fragments

Oxalic Acid Generation Post-Do (SW Sulfite)

Do effluents were collected stored at 0°C prior to analysis

Samples were heated, aliquots taken, and OxA analyzed by CEP

Do(A): 0.27 kf

Do(B): 0.28 kf

Ulmgren and Radstrom, STFi

Oxalic Acid Generation Post-Do

- Do (kf: 0.25) effluent from a OD SW kraft pulp

[OxA] in effluents (mg/L)
Oxalic Acid Generation Post-Do

- Slow hydrolysis is occurring
Importance: Mill balance and control of OxA

OxA Studies: Next

- CIE analysis is variable. Suspect sample preparation needs refinement
- Explore factors contributing to differences in OxA generation (D & Z)
- Study dynamics of OxA solubility with bleach plant effluents

Acknowledgments

Member Companies IPST
Project F015 Sub-Objective:

Fundamentals of Oxygen Delignification

Lucian A. Lucia
Ki-Oh Hwang

Oxygen Delignification Objectives

- To improve the selectivity and efficiency of the process;
  - Generate active oxygen species;
  - Study their impact on pulp;

- To develop a fundamental understanding of the interaction of active oxygen species with pulp;
  - Use pre- and post-O2 pulp
  - Chemical characteristics of pulp

Summary of 1998-99 Proposed Goals

- Determine the effect of Singlet Oxygen on Pulps
- Evaluate inducing self-sensitized delignification of kraft pulps
- Attempt to generate singlet oxygen
- Compare photochemical and chemical generation of singlet oxygen
- Investigate PARR Reactor custom design for oxygen delignification kinetics
**Generation of Singlet Oxygen**

\[ \text{Chemical or Light Energy} \rightarrow ^{3}\text{O}_2 \rightarrow ^{1}\text{O}_2 \]

- Ground state
- Excited singlet state

\[ \begin{align*}
\Delta_{g}^{1} \text{ Singlet State} \\
22 \text{kcal/mol} \\
3\Sigma_{g}^{1} \text{ Ground State}
\end{align*} \]

**Chemical Reactivity of \(^1\text{O}_2\)**

Toward Lignin-like Substrates

\[ \text{OH} \rightarrow ^{1}\text{O}_2 \rightarrow \text{OH, O}_2^2 \]

Further oxidation reactions

**Implication of \(^1\text{O}_2\) in H\(_2\text{O}_2\)**

Bleaching Reactions

\[ \text{H}_2\text{O}_2 \rightarrow \text{alkaline} \rightarrow ^{1}\text{O}_2 \rightarrow 17\% \]

Singlet Oxygen Product

References:
Activity of $^{1}O_{2}$ as a Function of pH

- Definite trend is observed
- Interestingly, our system does show noticeable differences
- At higher pHs, differences not pronounced

Photogeneration of Singlet Oxygen

$^{1}O_{2}$ + by-product

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**1O₂-Reactions: Increased Delignification for higher pHs**

- Pre-O₂ Kraft SW
- Kappan = 25
- Rose Bengal (0.5%)
- Fluorescent Lamps (22 hours)
- Dual Effect of pH: Lignin Extraction and 1O₂ Lifetime

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**Longer Singlet Oxygen Lifetime in Ethanol - No Effect**

1. Before irradiation
2. After 22.5 hrs run
3. After 22.5 hrs run/3x base
4. Wash/RT

**Confidential Information - Not for Public Disclosure (For IPST Member Company's Internal Use Only)**

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**Preliminary Experiments for 1O₂-Treated Pre-O₂ Pulp - Importance of Extraction**

**Confidential Information - Not for Public Disclosure (For IPST Member Company's Internal Use Only)**

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Confidential Information - Not for Public Disclosure (For IPST Member Company's Internal Use Only)
Preliminary Experiments for $^{1}\text{O}_2$ Treated Post-O$_2$ Pulp

Optimizing Base Concentration in $^{1}\text{O}_2$ Reaction with Post-O$_2$ Kraft Pulp

Enhanced Delignification From Increased Base Concentration

- Base Concentration influence on $^{1}\text{O}_2$ lifetime, but also lignin extraction
- Point of diminishing returns
- Same changes for both pulps
Optimizing Kappa and Brightness by Control of Oxygen and Protectors in Pre-\(\text{O}_2\) Pulp

\[
(10\% \text{NaOH}, 0.5\% \text{RB}, 0.5\% \text{MgSO}_4, 2\% \text{CN})
\]

\[
\text{Kappa Number} \\
\text{Time, (hours)}
\]

Optimizing Kappa and Brightness by Control of Oxygen and Protectors in Post-\(\text{O}_2\) Pulp

\[
(10\% \text{NaOH}, 0.5\% \text{RB}, 0.5\% \text{MgSO}_4, 2\% \text{CN})
\]

\[
\text{Kappa Number} \\
\text{Time, (hours)}
\]

Viscosity Changes for Pre-\(\text{O}_2\) Pulp

\[
(2\% \text{CN}, 10\% \text{NaOH, 0.5\% RB}) \\
\text{Viscosity (Air)MgSO}_4 \\
\text{Viscosity (CO}_2\text{MgSO}_4) \\
\text{Viscosity (CO}_2
\]

\[
\text{Viscosity (CP)} \\
\text{Time, (hours)}
\]

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Decrease of k/s Over Time for ¹O₂ Treated Pre-O₂ Pulp
(10% NaOH, 2% Cl)

Decrease of k/s Over Time for ¹O₂ Treated Post-O₂ Pulp
(10% NaOH, 2% Cl)

Selectivity Changes vs. Kappa Number of Pre-O₂ Pulp
Selectivity Changes vs. Kappa Number of Post-O2 Pulp

Classical Chemical Generation of Singlet Oxygen

\[
\begin{align*}
\text{Cl}_2 + H_2O_2 & \rightarrow HOCl + HO^2 \\
HO^2 + HOCl & \rightarrow HOCl + HO^2 \\
HOCl + HO^2 & \rightarrow Cl_2 + Cl^2
\end{align*}
\]

Chemical Structures in $^1O_2$-Treated (Chemical) Extracted Lignin

<table>
<thead>
<tr>
<th></th>
<th>mmoles isolated lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NMR Brown Stock</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Aliphatic OH</td>
<td>1.38</td>
</tr>
<tr>
<td>Condensed phenolic OH</td>
<td>0.82</td>
</tr>
<tr>
<td>Guaiacyl phenolic OH</td>
<td>0.94</td>
</tr>
<tr>
<td>Carboxylic acid OH</td>
<td>0.28</td>
</tr>
</tbody>
</table>

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Summary

- Singlet oxygen was generated both photochemically and chemically
- It behaved as a more active delignification agent than ground state oxygen
- Pulp brightness gains were observed
- Protectors were helpful in sustaining viscosity and increasing selectivity

Future Work

- Further investigate the factors which influence the singlet oxygen-mediated bleaching response of pulps
- Pursue patentability of the bleaching technology
- Investigate higher intensity lamp sources (more light, less heat) for optimum response
Acknowledgements

Dr. Ki-Oh Hwang
Wood Chemistry Group
Improved Selectivity in Ozone Bleaching

- USDA Funded at $128,436 for October 1996-98
- Personnel: Don Dimmel, Cathy Welder (Postdoc), Elizabeth Althen (Senior Technician)

Objective: To determine the relative importance of the reaction pathways by which ozone degrades carbohydrates. Clarification of the mechanism will facilitate the development of improved ozone selectivity and, thus, improved pulp properties.

- Compliments F015 research objectives

Research Goals

- Determine the extent cellulose is degraded by:
  - ozone directly
  - radicals derived from ozone (i.e., hydroxyl radical)
  - reactive hydroperoxides (ROOH) and hydrotrioxides (ROOOH) from lignin and carbohydrate intermediates

- Define selectivity factors by examining:
  - cellulose molecular weight changes
  - cellulose sites of oxidation
  - extent of lignin degradation in cellulose/lignin mixtures
Ozone Selectivity for Lignin vs Carbohydrates Depends on:

- Ozone transport
  - Ozone must move from a gaseous state to a water interface and then react at a solid matrix
  - If ozone encounters lignin-depleted regions, the only reactants available are carbohydrates
  - Without efficient mixing there will be regions in the pulp containing no $O_3$ and others where the $O_3$ concentration exceeds the lignin demand
  - Bad transport leads to more $O_3$-induced carbohydrate damage

---

### Ozone Selectivity for Lignin vs Carbohydrates Depends on:

- Relative rates of direct ozone reaction

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate Constant (Msec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCH=CH$_2$</td>
<td>$3 \times 10^5$</td>
</tr>
<tr>
<td>HO-Ph-CH$_3$</td>
<td>$3 \times 10^4$</td>
</tr>
<tr>
<td>Glucose</td>
<td>0.5</td>
</tr>
<tr>
<td>Saccharose</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Ozone Selectivity for Lignin vs Carbohydrates Depends on:

- Ozone transport (relates to reactant availability)
- Relative rates of direct ozone reaction
- Relative rates of secondary radical reactions
  - from ozone decomposition

\[
\begin{align*}
O_3 + HOH &\rightarrow O_2 + 2HO^- \\
O_3 + HOH &\rightarrow 2HO_2^- \\
O_3 + M^{n+} + H^+ &\rightarrow O_2 + M^{(n+1)+} + HO^-
\end{align*}
\]

Hydroxyl Radical Reactions

- Hydroxyl radical is extremely reactive:

\[
\begin{align*}
RH + HO^- &\rightarrow R^- + HOH \\
O_2 + R^- &\rightarrow ROO^- \\
ROO^- + RH &\rightarrow ROOH + R^- 
\end{align*}
\]

- Relative rates of lignin/carbohydrate model rxs

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate constant (M·s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Veratrylglycol</td>
<td>(1.5 \times 10^{10})</td>
</tr>
<tr>
<td>Veratrylglycol-(\beta)-guaiaeryl ether</td>
<td>(1.7 \times 10^{10})</td>
</tr>
<tr>
<td>Methyl-(\beta)-D-glucopyranoside</td>
<td>(3.2 \times 10^{9})</td>
</tr>
<tr>
<td>Methyl-(\beta)-D-xylopyranoside</td>
<td>(2.6 \times 10^{9})</td>
</tr>
</tbody>
</table>
Ozone Selectivity for Lignin vs Carbohydrates Depends on:

- Ozone transport (relates to reactant availability)
- Relative rates of direct ozone reaction
- Relative rates of secondary radical reactions
  - from ozone decomposition
  - from hydrotrioxide decomposition
    \[ R\cdot O\cdot O\cdot OH \rightarrow R\cdot O\cdot \cdot + \cdot OH \text{ or } R\cdot O\cdot + \cdot O\cdot O \]
  - from ozone-phenol reactions
    \[ Ar\cdot OH + O_3 \rightarrow Ar\cdot O\cdot + O_2 + \cdot OH \]

Chemistry of Ozone-Cellulose Reactions

- Examining model systems:
  - water soluble cellulose dimer
  - fluffed cotton linters
  - lignin-spiked fluffed cotton linters
  - amorphous cellulose
- Examining the importance of:
  - direct ozone attack
  - radical reactions derived from O_3 decomposition
  - radical reactions derived from O_3-lignin reactions
O$_3$-Cellulose Dimer Reactions

<table>
<thead>
<tr>
<th>Rx time</th>
<th>Recovered Dimer</th>
<th>1,5-Anhydroglucitol</th>
<th>Glucose</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 min</td>
<td>66%</td>
<td>2%</td>
<td>1%</td>
</tr>
<tr>
<td>10 min</td>
<td>30%</td>
<td>trace</td>
<td>trace</td>
</tr>
<tr>
<td>2 h</td>
<td>0%</td>
<td>none</td>
<td>trace</td>
</tr>
</tbody>
</table>

Data indicates that there is a complex set of unselective ozone reactions with this water soluble cellulose dimer.

Cellulose Structure & Reactivity

DP Drop with O$_3$ Application
Ozone Dose is an Important Factor in Cotton Linters Case

Protecting Effect of Lignin
Fenton’s Reagent Reactions

\[(H_2O_2 + Fe^{+2} \rightarrow HO^-)\]

Conclusions

- Little cellulose direct chain cleavage occurred with low-dose ozonation stages of cotton linters or a lignin-cotton linters mixture
- Soluble dimer ozonations gave an unusual result - no selectivity
- Amorphous cellulose was more reactive than fluffed cotton linters
- Ozone dose is an important variable
- Lignin provides a protecting effect
- Fenton’s reagent gave variable results
Chemistry of Ozone-Cellulose Rxs
Future Directions

■ Evaluate differences between ozone reactions of:
  > pulp
  > fluffed cotton linters containing absorbed lignin
  > amorphous cellulose precipitated in the presence of lignin

■ Examine different levels of spiked lignin; analyze the effect of phenolic content of the lignin

Chemistry of Ozone-Cellulose Rxs
Future Directions

■ Prepare (if possible) a lignin carbohydrate complex (LCC) of amorphous cellulose and a lignin dimer, and study the ozone-degradation of the LCC under different conditions

■ Perform select ozone reactions at different pH, temperature, and additive levels

■ Summarize the 2-year study in a final report to IPST member companies and to the USDA
Overview

- Chromophores in Kraft Pulps
- Trimethylphosphite Derivatization of Quinones
- Results:
  - Quinone Contents: DE*D Pulps
  - Correlation Between Quinone Content and Brightness Values
- Bleaching Chemistry
**Trimethylphosphite Derivatization of Quinones**

- Developed a $^{31}$P-NMR Based Analytical Procedure for the Quantification of Quinones in Isolated Lignins

- Based on Mechanical Pulp Studies by Lebo *et al.* (IPST) & Argyropoulos *et al.*

- And Model Compound Studies by Medvecz (IPST) & Ramirez *et al.*
**Trimethylphosphite Chemistry:**

*Reaction with Ortho-Quinone Structures*

\[
P(\text{OCH}_3)_3 \xrightarrow{} \text{Ph}_2P(\text{OCH}_3)_3 \xrightarrow{} \text{Ph}_2P(\text{OCH}_3)_3
\]

\[\delta \sim -45 \text{ ppm}\]

Ramirez et al. & Medvecz

---

**Trimethylphosphite Chemistry:**

*Dioxaphospholene Hydrolysis*

\[
\text{Ph}_2P(\text{OCH}_3)_3 + \text{H}_2\text{O} \xrightarrow{} \text{Ph}_2P(\text{OCH}_3)_3 \xrightarrow{} \delta \sim 11 \text{ ppm}
\]

\[\delta \sim -2 \text{ ppm}\]

Ramirez et al.
**Trimethylphosphite Chemistry:**
*Reaction with Para-Quinone Structures*

\[
\text{Para- Quinone Structures}
\]

\[
\text{Ortho-Quinone Adduct} \quad (-45 \text{ ppm})
\]

\[
\text{Para- & Ortho-Quinone Adducts} \quad (-2 \text{ ppm})
\]

Ramirez et al. & Medvecz

---

**$^{31}$P-NMR Spectrum:**
*Trimethylphosphite Treated Effluent Lignin*

---

60
$^{31}P$-NMR Spectrum:

$D_0$ Lignin (1) Trimethylphosphite Treated (2) Hydrolysis

Quinone Adduct

Residual Lignin Quinone Contents:

Brownstock, Fremy, $D_0$ & $D_0$ Dithionite Reduced

Quinone Content (mmol/g Lignin)

- Without Added Water
- After Water Addition

BS | BS Fremy | $D_0$ | $D_0$ reduced
**Pulps Studied**

- Residual Lignins were Isolated from BS, Alkaline Extraction and D Stage Pulps:

  \[ DE^*D \]

  where, \( E^* = \text{EAr, E, EO, EP, EOP} \)  
  (EAr means Alkaline Extraction with Air Excluded)

- Brightness Properties were Measured
- Quinone Content was Measured

---

**Visible Absorbance Difference Spectra:**

*(\( DE^* - \text{BS Residual Lignin Value} \))*

![Visible Absorbance Difference Spectra](image-url)
D1 & D2 Brightness Values

Residual Lignin Quinone Contents
(Brownstock Value Subtracted)
Quinone Contents: 
E1 & D1 Residual Lignins

E1 Stage Klason Lignin Contents
“Apparent” Pulp Quinone Contents: E1 & D1 Stages

Kubelka-Munk Equation

\[ \frac{B}{100} = 1 + \frac{k}{s} - \sqrt{\left( \frac{k}{s} \right)^2 + \left( \frac{k}{s} \right)^2} \]

B = Brightness, k = absorption, s = scattering

\[ \frac{k}{s} = \left( \frac{\phi}{s} \right) \times C \]

\( \phi = \) constant, C = chromophore content

\[ \frac{k}{s} = \phi \times C \text{ or } \frac{k}{s} \propto C \]

\[ B \propto 1 + C - \sqrt{2} C + C \times C \]
D1 "Apparent" Pulp Quinone Contents Correlated with D1 & D2 Brightness

D1 Quinone Contents Correlated with D1 & D2 Brightness
**D1 Klason Contents Correlated with D1 & D2 Brightness**

![Graph showing the correlation between D1 Klason contents and D1 & D2 brightness.](image)

**Conversion of E1 Phenolics to D1 Chromophoric Quinones**

![Bar chart showing the conversion of E1 phenolics to D1 chromophoric quinones.](image)
Conclusions, Part (1):

- Trimethylphosphite/$^{31}$P-NMR has been developed as a new tool to study chromophores in lignin
- Quinone content correlates with pulp brightness and brightness ceiling values
- Hydrogen peroxide destroys quinones and quinone precursors

Results Part (2): $D_0$ & $D(EO)$ Pulps

- Residual lignins were isolated from $D_0$ and alkaline extraction stage pulps
- Initial brownstock kappa number was varied
**Quinone Content of D₀ Residual Lignins**

![Graph showing quinone content vs. Brownstock Kappa Number for D₀ residual lignins with different Kappa factors.]

**Quinone Contents of D(EO) Residual Lignins**

![Graph showing quinone content vs. Brownstock Kappa Number for D(EO) residual lignins.]

69
**Chlorine Dioxide Bleaching Chemistry**

**Para-Quinone Formation**

![Chemical structure of para-quinone formation](image)

*Gierer et al.*

**Ortho-Quinone Formation**

![Chemical structure of ortho-quinone formation](image)

**Para-Quinone Formation**

![Chemical structure of para-quinone formation](image)

*Gierer et al.*
**Hydrogen Peroxide Chemistry**

![Chemical Reaction Diagram]

Gierer et al.

**Conclusions**

- These Studies Validate Bleaching Model Compound Studies in Pulp
- Chlorine Dioxide Causes Colored Lignin-Quinone Structures to Form

Also,
- Trimethylphosphite/\textsuperscript{31}P-NMR method has Recently been Repeated by:
  Gellerstedt (STFI) & Argyropoulos (Paprican)
Acknowledgements:

- IPST Member Companies
- T. Runge, A. Ragauskas, T. McDonough, D. Dimmel, L. Lucia
Guest Presentation by Peter Pfrooom
Associate Professor, Chemical Recovery and Corrosion Division, Purpose:

- 1. We are looking for help in locating a pilot scale test site for a process to remove metals/trans. metals and chloride from D-stage effluent.
- 2. A request to consider recommending a new project for Consortium funding.

Project 4160
(DOE funded, no IPST matching funds)

Recycling of Bleach Filtrates using Electro dialysis

Shih-Perng Tsai
(Argonne National Laboratory)
P. H. Pfrooom
(DOE Agenda 2020, 8-1996 to 8-1999,
~$200,000/year, $50,000/year to IPST)
The Issue

- Low effluent bleached kraft pulp production
  - need to recycle bleach effluent

- Acidic bleach effluent recycle introduces metal ions, calcium, chloride.

The Approach

- Remove NPE’s from bleach effluent before recycling.

- Challenges:
  - dissolved organics
  - particulate matter

- Choose a technology that addresses anions (chloride) and cations (metals, calcium..)
Bleach effluent electrodialysis:

- Expected results:
  - Simple process that can be retrofitted to existing installations, pilot-scale test data

- Impact on the industry:
  - Decrease chloride, NPE problems from bleach effluent recycle
  - No chemicals needed
  - Tolerant towards small particulates
  - Enable bleach plant recycle

---

Process flowchart

[Diagram showing the flowchart of the process from weak black liquor to chemical recovery (water, inorganics, lignin) through delignification, washing, and bleaching steps, ending with bleached pulp (for papermaking).]

---

IPST Confidential Information - Not for public disclosure
(For IPST Member Company's Internal Use Only) - P. Pfromm, Recovery PAC Fall 98, page 5
Bleach Filtrate Electrodialysis: Advantages

- Continuous process, no regeneration
- Open flow channels (tolerates particulate matter)
- Remove Cl\(^-\) selectively over SO\(_4\)^{2-}\), simultaneous to metals/trans. metals, Ca\(^{++}\)

Bleach Filtrate Electrodialysis: Challenges

- Fouling?
- Membrane area?
- Removal efficiency, selectivity?
Bleach Filtrate Electrodialysis: Year 1 Summary

- Acidic effluents from three mills (IPST).
- Successful electrodialysis (lab scale) with two effluents, no pre-treatment
- Estimate for scaleup done
- Conclusion: perform long-term tests to show no-fouling, and prepare for pilot scale

Bleach Filtrate Electrodialysis: Year 2 Summary

- Acidic D stage effluent from a new mill (Mill D) obtained for long-term tests
- Sequential batch runs with no membrane cleaning
- Analyze (IPST, ANL)
- Conclusion Year 2: no significant fouling, ready for pilot test
Bleach filtrate electrodialysis, Year 2: long-term process performance

Removal by species: compare 0 and 100 hrs
Concluding Remarks

- Long-term laboratory performance OK.
- High removal levels for important NPE’s, and Chloride.

Path Forward, Year 3

- Search for pilot scale test site
- Can PAC help to find a site?
New planned project

Ultrafiltration of bleach effluent: new approaches for partial closure

Current sponsor: Eka Chemicals

Dr. Patrick Bryant, Eka
Peter Pfommm

The issue

- Compliance of bleach plant effluents (COD, color, AOX) from existing bleach plants is or will be an issue.
- Radical changes in bleaching technology, or total closure are costly.
  ➔ An “intermediate” lower cost solution is needed.
Approach

High mol. weight organics
(burn in recovery furnace)

To Brown Stock Washing
(~20% of feed volume)

Alkaline bleach filtrate

Ultrafiltration membrane

To Effluent Treatment
(~80% of feed volume)

Metals, chloride,
low mol. weight organics

Ultrafiltration:
been there, done that, did not work...

- This is not end-of-pipe, but a "fractionation" by mol. weight.

- The stage cut is relatively low (less conc. polarization, fouling).

- Membranes have made progress. Tubulars are tolerant to particles, experience on pilot and full scale in Scandinavia is good.
Expected results
ultrafiltration of E-stage effluent

• Laboratory work to determine specific separation properties of ultrafiltration for BP effluent (concurrent to pilot tests).
• Pilot scale data for hardwood and softwood mills with and without O₂ delignification.
• Full scale implementation.

Impact on the industry,
ultrafiltration of BP effluent

• Compliance can be achieved without fundamental changes in bleaching technology.
• Chlorides and other inorganics are not recycled to chemical recovery.
Funding and resources for ultrafiltration of BP effluent

- Eka donates use of a pilot scale UF plant during the project (value $150k).
- Cash (Eka): $20k donation to start, $50k/year, 2 years (pays for post-doc), $50k/year in-kind (analytical, personnel).
- Need additional funding:
  - DOE funding (Agenda 2020) seems not successful: Dues co-funding?

Proposal to PAC:
IPST Consortium funding if no DOE money is available?

- This project becomes P. Pfromm’s PAC project, total of $100,000 from IPST per year for two years (analytical, Pfromm’s time, technician support, pilot test travel+supplies)
- NOTE: Results must be OK to publish without delay.
Path forward, ultrafiltration of BP effluent

- Currently searching for Post Doc, have $20k from Eka for 1998.
- DOE funding may not be likely. Recovery PAC was asked to recommend for consortium funding.
- A request for the Pulping&Bleaching PAC: Could you recommend this work to RAC for consortium funding?
Modeling the Fate of Metal Ions During Brown Stock Washing With Bleach Filtrate Recycle

Jim Frederick Wolfgang Schmidl, Alan Rudie
The Institute of Paper and Science and Technology
November 4, 1998

Background

- To reduction of water use in pulp and paper mills, we must recycle water
  - evaporator condensate,
  - bleach plant filtrates
  - whitewater
- With recycle, inorganic and organic materials accumulate
- They can interfere with process operation
Metal ions interact with other species

Two washing scenarios were simulated

- Base case: water as the wash liquor input to the second stage
- Recycle case: alkaline filtrate from ECF bleaching is recycled as the wash liquor
Input streams based on mill data

- Unwashed brownstock slurry:
  - 12.5% consistency
  - 20% dissolved solids in liquor
  - 90°C

- Wash liquor (DF = 3.0)
  - Base case: water, 60°C
  - Recycle case: alkaline filtrate, 0.5% solids content, 60°C

- Pulp consistencies: 1% in vats, 12.5% in mats

An advanced chemical equilibrium simulator was used

- Chemical equilibrium simulator: ESP (OLI Systems, Inc.)
  - advanced chemical equilibrium simulator
  - predicts ion activities to >10 molal
  - extensive inorganic data base
  - treats dissolved species, precipitation, and adsorption simultaneously
  - includes process simulation capability
An equilibrium model for organometal complexation was developed

Assumptions:
- Dissolved lignin binds multivalent metals at phenolic hydroxyl sites
- The stability constants for metals with carbohydrates and carboxylic acids on lignin are too small to be important.

Constants for the ion exchange model were obtained

Adsorption model
- \( M^{+} + H\text{-Pulp} = M\text{-Pulp} + H^{+} \)
- \( M^{2+} + 2H\text{-Pulp} = M\text{-Pulp}_{2} + 2H^{+} \)

Additional constraint: electrical neutrality of fibers
2-Stage Brownstock Washer Model

Soluble inorganic calcium species
(as Ca, g/BDT Pulp)

<table>
<thead>
<tr>
<th></th>
<th>Unwashed Brownstock</th>
<th>Black Liquor</th>
<th>Washed Brownstock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(^{2+})</td>
<td>0.17</td>
<td>0.36</td>
<td>0.49</td>
</tr>
<tr>
<td>CaOH(^+)</td>
<td>8.1x10(^{-5})</td>
<td>0.98</td>
<td>0.17</td>
</tr>
<tr>
<td>CaHCO(^{3+})</td>
<td>3.6x10(^{-5})</td>
<td>7.1x10(^{-5})</td>
<td>4.2x10(^{-4})</td>
</tr>
<tr>
<td>CaC(_2)O(_4)</td>
<td>0.28</td>
<td>0.47</td>
<td>0.36</td>
</tr>
<tr>
<td>CaCO(_3)</td>
<td>0.77</td>
<td>1.55</td>
<td>1.83</td>
</tr>
<tr>
<td>CaSO(_4)</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Total Ca input: 1395 g/BDT Pulp
### Soluble inorganic manganese species
(Data as Mn, g/BDT Pulp)

<table>
<thead>
<tr>
<th>Species</th>
<th>Unwashed Brownstock</th>
<th>Black Liquor</th>
<th>Washed Brownstock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$^{2+}$</td>
<td>6.1x10$^{-6}$</td>
<td>1.7x10$^{-5}$</td>
<td>4.9x10$^{-4}$</td>
</tr>
<tr>
<td>MnOH$^+$</td>
<td>3.2x10$^{-3}$</td>
<td>0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>Mn(OH)$_2$</td>
<td>0.04</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>Mn(OH)$_3^{-}$</td>
<td>1.1</td>
<td>0.89</td>
<td>0.03</td>
</tr>
<tr>
<td>Mn(OH)$_4^{2-}$</td>
<td>7.6</td>
<td>3.1</td>
<td>4.3x10$^{-3}$</td>
</tr>
<tr>
<td>MnC$_2$O$_4$</td>
<td>3.9x10$^{-4}$</td>
<td>1.6x10$^{-3}$</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Total Mn input: 280 g/BDT Pulp

### Ca Distribution Without Precipitate
(Total input: 1395 g Ca/BDT Pulp)

- On fiber
- Organometal
- Inorganic sol'n

<table>
<thead>
<tr>
<th>Fiber/BL in</th>
<th>BL Out</th>
<th>Fiber Out</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>12%</td>
<td>8%</td>
</tr>
<tr>
<td>6%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Mn Distribution Without Precipitate**

(Total input: 280 g Mn/BDT Pulp)

- 16% on fiber
- 12% organometal
- 8% inorganic sol'n

![Graph showing Mn distribution](image)

**Alkali metals displace Ca, Mn on pulp**

- Adsorbed Ca or Mn, moles/kg pulp
  - Ca: $10^{-1}$ to $10^{-14}$
  - Mn: $10^{-8}$ to $10^{-13}$

![Graph showing alkali metal displacement](image)
Predictions agree with mill data

With filtrate recycle, calcium accumulates in bleach plant
**With filtrate recycle, manganese also accumulates in bleach plant**

![Graph showing manganese accumulation in bleach plant](image)

**Fine particles are retained by fiber mat**

![Graph showing particle retention by fiber mat](image)
Conclusions

• The binding capacity of dissolved organic matter and pulp fibers is small compared with total metals input.

• Most of the metals that are insoluble as hydroxides, carbonates, sulfates, or sulfides will remain mainly as precipitates throughout brownstock washing.

Conclusions

• Metals recycled to the brownstock washers with bleach filtrate, they will be returned to the bleach plant.

• These conclusions depend upon the inorganic precipitates remaining with the fibers. This assumption needs to be tested.
Acknowledgments

This work was supported by
- DOE/OIT under contract no. DE-FC07-96ID13441
- Member companies of the Institute of Paper Science and Technology

Jennifer Koenig performed many of the calculations for this study

Calcium is mainly inorganic precipitate
(Data are as Ca, g/BDT Pulp)

<table>
<thead>
<tr>
<th></th>
<th>Unwashed Brownstock</th>
<th>Black Liquor</th>
<th>Washed Brownstock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic, in sol’n</td>
<td>0.95</td>
<td>2.9</td>
<td>2.5</td>
</tr>
<tr>
<td>Organometal</td>
<td>103</td>
<td>150</td>
<td>10.2</td>
</tr>
<tr>
<td>Adsorbed on fiber</td>
<td>4.7x10^{-7}</td>
<td></td>
<td>0.32</td>
</tr>
<tr>
<td>Inorganic precip.</td>
<td>1293</td>
<td></td>
<td>1229</td>
</tr>
<tr>
<td>Total</td>
<td>1395</td>
<td>153</td>
<td>1241</td>
</tr>
</tbody>
</table>
Manganese is mainly inorg. precipitate
(Data are as Mn, g/BDT Pulp)

<table>
<thead>
<tr>
<th></th>
<th>Unwashed Brownstock</th>
<th>Black Liquor</th>
<th>Washed Brownstock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble inorganic</td>
<td>8.8</td>
<td>4.0</td>
<td>0.12</td>
</tr>
<tr>
<td>Organometal</td>
<td>1.8</td>
<td>4.8</td>
<td>43.3</td>
</tr>
<tr>
<td>Adsorbed on fiber</td>
<td></td>
<td></td>
<td>3.1x10^{-4}</td>
</tr>
<tr>
<td>Inorganic precip.</td>
<td>269</td>
<td></td>
<td>227</td>
</tr>
<tr>
<td>Total</td>
<td>280</td>
<td>8.8</td>
<td>271</td>
</tr>
</tbody>
</table>
Lignin Variability

Brian Boyer (Ph.D. 1998)

Alan Rudie

Time Domain Variation
(Batch to Batch)

- Wood supply
  - species mix
  - density changes
  - moisture content
- White liquor charge and strength

Fiber-to-fiber and Within Batch Variation

- Viscosity and strength
- Bleachability
- Chemical consumption
Causes

Radial and vertical temperature and liquor profiles

Measurement
Hanging basket method

Fiber to Fiber Variation
Causes

- Chip thickness
- Species
- Chemical Penetration

IPST Project

- Ph.D. Research: Brian Boyer, July, 1998
- Targeted at continuous digesters
- Methods
  - density gradient column
  - single fiber FT-IR (failed)
Kraft Cooks
- M/K batch digester
- 10 mm hand cut, or 2.5 mm veneer chips
- 2 hours pre-steaming
- 6:1 l/w ratio
- 40 gpl EA (24% EA), 30% sulfidity
- 150° to 170° C
- 60 minutes to, 240 minutes at temperature

Density Gradient Column

Density Gradient Column
Density Gradient Column

- Carbohydrate: 1.546 g/ml
- Lignin: 1.272 g/ml

Solvents:
- CHCl₃
- C₂Cl₄

Method: Mix C₂Cl₄ into CHCl₃ as add mixture to the bottom of a glass column.

Tasks

- Density measurement - certified glass beads
- Imaging - cross polars and red filter
- Image analysis - Optimus
- Data analysis - mean, standard deviation and Composite Normal Distributions

Summary Data
Density Gradient Column

Composite Normal Model:

\[ F(x) = \frac{1}{\sqrt{2\pi}} \left\{ \frac{f_A \exp\left(-\frac{1}{2} \left( \frac{x-x_1}{s_1} \right)^2 \right)}{s_A} + \frac{f_B \exp\left(-\frac{1}{2} \left( \frac{x-x_2}{s_2} \right)^2 \right)}{s_B} \right\} \]

33 Kappa Pulp from 10 mm thick chips.

Fiber distribution as Kappa number
33 kappa number 10 mm chip pulp
Distribution A and B

- Is Distribution A from the chemical reaction rate portion of the wood chips?
- Is distribution B from the mass transfer controlled portion of the wood chips?
- What can Distribution A and B tell us about the process?

Kappa from distribution A is between Kappa for 2.5 mm and 10 mm chips

Arrhenius Activation Energy of fraction B, $E_a = 32 \text{ KJ/mol}$
Conclusions

- The density gradient column was suitable for measuring the variation in lignin content of kraft pulps.
- The lignin distribution can be modeled as the sum of two normal distributions.
- The lower kappa distribution for 10 mm thick chips is not reaction rate limited.
- The higher Kappa distribution is diffusion limited.
Closed Mill
Metal Binding

Alan Rudie

Project F017  November, 1998

The Problem!

• Mills have problems with scale formation and transition metal decomposition of peroxide based bleach chemicals.
• Increased recycle of process water to minimize water use and wastewater discharge increases the build up of the non-process metal.

Task Objective

• Evaluate metal binding behavior relative to pH and competition with other metals.
• Develop a predictive model suitable for use in trace metal equilibrium calculation.
Method: Selectivity Coefficient

\[
\frac{[\text{NaR}]}{[\text{Na}^+] [R^-]} = K_{\text{Na}} \\
\frac{[\text{CaR}_2]}{[\text{Ca}^{2+}] [R^-]^2} = K_{\text{Ca}} \\
\frac{[\text{CaR}_2][R^-]^2 [\text{Na}^+]^2}{[\text{NaR}][R^-][\text{Ca}^{2+}]} = \frac{K_{\text{Ca}}}{K_{\text{Na}}} = \frac{K^*_\text{Ca}}{K^*_\text{Na}}
\]

Log(CaR₂/Ca²⁺) vs Log(RH/H⁺)

\[y = 1.7183x - 1.9033 \quad R^2 = 0.9931\]

Selectivity Coefficient vs Data

Bound Ca, ppm vs pH

Bound Ca, ppm vs pH

Bound Ca, ppm vs pH
Status as of March, 1998

- Had determined room temperature selectivity coefficients for most cation pairs.
- Had incorporated activity coefficients into the calculation procedure.
- Had worked out a free water/bound water correction.

Ca/Mg, With Adj., Act. & Water

 acids = 0.00063 meq/kg, k = 3

Progress

- Completed the selectivity coefficient matrix.
- (TIP & F017) Completed data sets at 25, 45, & 65° for Ca vs H, Na, Mg, Ba and Mn.
- (TIP & F017) Completed data sets at 25, 45, & 65° for Mg vs H, Na, Ba and Mn.
- Gibbs energy relationships for Ca with acid and Ca with Na and Mg with Na.
Gibbs Free Energy

- \( \Delta G = -RT\ln(K) = \Delta H - \Delta S \)
- Therefore a plot of \( \ln(K) \) vs \( 1/T \) should give a straight line with slope \(-\Delta H/R\) and intercept \(-\Delta S/R\)
- Enthalpy is also dependent on changes in heat capacity which is usually small unless there is a change in state.

\[ y = -3.272x + 9.778 \]
\[ R^2 = 1 \]

Mg\(^{++}\) vs Na\(^{+}\) (F017)

\[ y = 1.763x - 6.588 \]
\[ R^2 = 0.9913 \]

Ca\(^{++}\) vs H\(^{+}\) : Linerboard HW
A comparison of divalent metals.

Plans: F017
- Complete the data analysis for selectivity coefficient, $\Delta H$ and $\Delta S$ for bleachable grade SW.
- Characterize metal removal with acids.
  There appear to be greater differences between metals and pulps than thought.
- Characterize fully bleached pulps.

Related Student Work:
- Masters & Ph.D. research, Giselle Ow Yang: XANES and EXAFS of tightly bound iron (96).
- Masters Independent Study, Ana Puckett: Laboratory bleaching filtrate recycle experiments to evaluate metals accumulation between $D_0$ and BSW and $D_1$ and E.
Related Work: Continued

- Georgia Consortium funding has been approved ($57,500 annually), Project PP98-MP4.
- Georgia Consortium project PP98-MP1: Paper machine closure (Woitkovich).
- DOE: (Frederick): Equilibrium model development.

Results: Giselle Ow Yang and Georgia TIP³ PP98-MP4

- The analysis of the iron EXAFS spectrum indicates the binding site is probably a guaiacyl group.
- The Ca and Mn EXAFS results have been obtained.
- Efforts to synthesis Fe-Guaiacol and Fe-Vanillin complexes are ongoing.

Ca, Radial Distribution Function
Mn EXAFS

- Radial positions (preliminary): 1.9 Å, 2.8 Å, & 3.8 Å.
- Comparison Ca: 1.75 Å, 3.50 Å, and 4.23 Å.
- These do not appear to be the same binding site!

Giselle Ow Yang: Plans

- Using FEFF7 to model possible Ca and Mn binding sites.
- Continuing synthetic effort to isolate Fe-vanillin type site.
- Beginning project to remove "intractable" iron and evaluate influence on bleaching.

DOE Metal binding by black liquor solids

- Approach: Competition for binding sites using UV-VIS or Fluorescent indicators.
- \([\text{[MI]}]/([\text{M}^+] [\text{I}^-]) = K\).  
- Know [MI] and [I] from the indicator added and the UV-Vis spectrum.
- Calculate [M⁺].
- \([\text{MBI}] = M_T - [\text{M}^+] - [\text{MI}]\)
**Status**

- Many indicators are not pure (ie-don’t know [I] and/or [MI]).
- Need $K_I < K_{SB}$.
- Additional problems at pH>10 due to limited Ca(OH)$_2$ solubility.
- **Black liquor appears to have one binding site for every 2 to 3 monomers, $K=10^3$-$10^5$**

**DOE - Next**

- Look at competitive binding to pulp to establish equilibrium.
  - $K = ([CaP])^2([Na^+])^2 / ([Ca^{++}])^2([NaP])^2$
  - can determine bound Ca and Na by analysis
  - know total Na$^+$ and Ca$^+$
  - assume Na$^+$ does not bond with BL
- $[CaBl] = Ca_T - CaP - [Ca^{++}]$

**Acknowledgments**

- Narendra Patel, Alan Ball and Fern Peterson.
- Chemical PAC and Member Companies for project support.
- Clark Woitkovich (Georgia TIP$^3$) for funding the high lignin pulp effort.
- Jim Frederick (DOE Agenda 2020) for funding the black liquor work.
Project F013

Environmentally Compatible Production of Bleached Chemical Pulp

Contributors To Project F013

- Aric Bacon
- Jean-Christophe Baromes
- Tim Bonner
- Blair Carter
- Chuck Courchene
- Craig Jackson
- Brendan Lee
- Tom McDonough
- Art Ragauskas
- Alex Shaker
- Mark Turner
- Andreau White
Research Goals

- Effects of modern delignification methods on refining behavior and fiber properties
- Find predictors of ease of delignification by oxygen and DE sequences (with DOE-funded Project 4120 - part of $36K matching)
- Evaluate and develop QP as alternative to O
- Assist in implementation of Rapid $D_0$
- Evaluate and compare ($D/Z$) sequences

Related External Funding

- Proj. 4120 - DOE/Auburn effort on pulping and bleachability - $36K$ matching
- Proj. 4159 - Agenda 2020 funded project on $\text{ClO}_2$ delignification - no matching in FY 99
- Proj. 4201 - Agenda 2020 funded work on Rapid $D_0$ plus Simplified Bleaching as routes to low-capital plants - $15K$ matching
Related Student Work

- Aric Bacon (Ph.D.) - Effects of delignification methods on fiber properties
- Carter Johnson (M.S.) - Effects of organics buildup in closed bleach plants
- Timothy Jacoby (M.S.) - Ultraselective ASAQ pulping as an alternative to kraft
- Cesar Goncalves (External Ph.D.) - Fate and effects of metals in closed bleach plants

Chelation and Peroxide as an Alternative to Brownstock Oxygen
Rationale

- Most of the peroxide delignification work reported in the literature has been done to evaluate and optimize peroxide as a stage following oxygen and/or ozone.
- Advances in chelation technology have extended the degree of delignification achievable with peroxide.
- Catalysis by transition metals or their complexes offers an additional opportunity.

QP Delignification vs. H₂O₂ Charge
Brightness After QP (3% \( \text{H}_2\text{O}_2 \))
For Lab and Mill SP Kraft Pulps

Kappa Drop in QP (3% \( \text{H}_2\text{O}_2 \)) For Lab and Mill SP Kraft Pulps
QP Selectivity

Metals in QP Delignified Pulps
Beneficial H$_2$O$_2$ Decomposition
(Previous Work)

Mn Affects Delignification Little
(Previous Work)
Mn Increases Viscosity After QP (Previous Work)

![Graph showing viscosity increase with Mn addition](image1)

Mn Improves Selectivity (Previous Work)

![Graph showing selectivity improvement with Mn addition](image2)
Effects of Pulping Parameters on DE Bleachability

DE Delignification vs. Unbl. Kappa and Pulping Parameters
DE COD vs. Unbl. Kappa and Pulping Parameters

(D/Z) Bleaching
(D/Z) Conditions

- Assumed 1 kg O₃ = 4.44 kg Cl₂ and 1 kg ClO₂ = 2.63 kg Cl₂
- Carryover of 1% BL solids into (D/Z) and carryover of 10% (D/Z) filtrate into (EPO)
- (D/Z) 15/30 min, 50°C, exit pH 2.5, kappa factor 0.20 on washed kappa no., mixing 20 sec after injection then 20 sec every 5 min.
- EPO: 0.4% H₂O₂, 35/0 psig O₂ for 15/30 min.

(D/Z)(EPO) Kappa No. vs. Speed, Substitution, and pH

![Graph showing the relationship between (EPO) Kappa No. and Mixer Speed, RPM for different substitution levels and pH values.](image-url)
(D/Z)(EPO) Brightness vs. Speed, Substitution, and pH

![Brightness vs. Speed, Substitution, and pH](image)

(D/Z)(EPO) Viscosity vs. Speed, Substitution, and pH

![Viscosity vs. Speed, Substitution, and pH](image)
F013 - Effect of Pulping and Bleaching Processes on Pulp and Fiber Properties

- Pulping and Bleaching
  Tom McDonough
  Chuck Courchene
  Blair Carter
  Tim Bonner

- Paper Physics (F024)
  John Waterhouse
  Hiroki Nanko
  Miranda Bliss

F013 and F024 Project Objectives

- F013 - To evaluate the effects of delignification processes and ECF bleaching on fiber properties, paper properties, and refining behavior.

- F024 - Determine how changes in fiber structure and the means to produce them, are related to improved paper machine productivity, paper quality, and reduced energy consumption.
**Shorter Term Objectives**

1. Establish methods for producing selected changes in fiber structure.
2. Establish methods to measure and characterize these changes in fiber structure.
3. Determine the relative impact of these changes on drainage, water removal, and paper properties.
4. Determine how selected pulp variables influence these changes in fiber structure.
5. Determine the extent to which these changes can be produced in production refiners.

**Project Deliverables**

2. Characterization of delignification and bleaching processes for optimum fiber and paper properties.
3. Methodology for determining a pulp's response to refining.
4. Strategies for reducing energy consumption and improving paper-machine productivity.
F013 - Effect of Pulping and Bleaching Processes on Pulp and Fiber Properties

- Experimental plan, pulping and bleaching - Prepare lab kraft pulps from common wood source. Oxygen delignify pulps to different final kappa nos. Bleach pulps with both CED and DED sequences.

- Experimental plan, paper physics - Prepare pulps with common cation exposure. Refine samples in PFI mill to 3000 revolutions. Measure pulp samples for fines content, WRV, wet zero span, handsheet properties, internal and external structural changes.

F013 - Pulping and Oxygen Delignification

- Kraft Pulping - S. Pine mill chips
  - Kappa 110 - 17.5% AA, 30% sulfidity, 400 H-factor
  - Kappa 28 - 18.5% AA, 30% sulfidity, 1250 H-factor
  - Kappa 17 - 25% AA, 25% sulfidity, 1250 H-factor

- Oxygen Delignified Pulps from Kappa 28 kraft
  - 10% cons., 100°C, 90 psig O₂, 0.05% Mg⁺²
  - 20.4 Kappa - 0.8% NaOH
  - 15.7 Kappa - 1.45% NaOH
  - 12.1 Kappa - 2.30% NaOH
  - 10.7 Kappa - 2.70% NaOH
F013 - Bleaching Conditions

- CED and DED Bleaching
  - C or D - 0.2 KF, 3% cons., 45°C, 30 min.
  - E - 10% cons., 70°C, 60 min., 55% act. Cl₂ NaOH
  - D - 1.2 % ClO₂, 10% cons., 70°C, 180 min.

F013 - Samples for Testing

<table>
<thead>
<tr>
<th>Pulp samples</th>
<th>Kappa no.</th>
<th>CED</th>
<th>DED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft</td>
<td>+</td>
<td>110</td>
<td>no</td>
</tr>
<tr>
<td>Kraft</td>
<td>+</td>
<td>28.1</td>
<td></td>
</tr>
<tr>
<td>Kraft</td>
<td>+</td>
<td>17.1</td>
<td>*</td>
</tr>
<tr>
<td>Kraft 28 - O₂</td>
<td>+</td>
<td>20.4</td>
<td>+</td>
</tr>
<tr>
<td>Kraft 28 - O₂</td>
<td>+</td>
<td>15.7</td>
<td>+</td>
</tr>
<tr>
<td>Kraft 28 - O₂</td>
<td>+</td>
<td>12.1</td>
<td>*</td>
</tr>
<tr>
<td>Kraft 28 - O₂</td>
<td>+</td>
<td>10.7</td>
<td>*</td>
</tr>
</tbody>
</table>
### F013 - Brightness after Bleaching

<table>
<thead>
<tr>
<th>Pulp samples</th>
<th>CED</th>
<th>DED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft 110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kraft 28.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kraft 17.1</td>
<td>86.9</td>
<td>84.7</td>
</tr>
<tr>
<td>Kraft 28 – O₂ 20.4</td>
<td>88.3</td>
<td>81.2</td>
</tr>
<tr>
<td>Kraft 28 – O₂ 15.7</td>
<td>88.6</td>
<td>83.1</td>
</tr>
<tr>
<td>Kraft 28 – O₂ 12.1</td>
<td>90.8</td>
<td>84.1</td>
</tr>
<tr>
<td>Kraft 28 – O₂ 10.7</td>
<td>89.9</td>
<td>85.8</td>
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</table>

### F013 - COOH Content of Pulps

<table>
<thead>
<tr>
<th>Pulp samples</th>
<th>Brownstock</th>
<th>CED</th>
<th>DED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft 110</td>
<td>0.175 meq/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kraft 28.1</td>
<td>0.077</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kraft 17.1</td>
<td>0.049</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂ 20.4</td>
<td>0.081</td>
<td>0.046</td>
<td>0.041</td>
</tr>
<tr>
<td>Kraft 28 – O₂ 15.7</td>
<td>0.078</td>
<td>0.036</td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂ 12.1</td>
<td>0.072</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂ 10.7</td>
<td>0.067</td>
<td>0.043</td>
<td></td>
</tr>
</tbody>
</table>
## F013 - Calcium content

<table>
<thead>
<tr>
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<th>CED</th>
<th>DED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft</td>
<td>110</td>
<td>4360 ppm</td>
<td></td>
</tr>
<tr>
<td>Kraft</td>
<td>28.1</td>
<td>1680</td>
<td></td>
</tr>
<tr>
<td>Kraft</td>
<td>17.1</td>
<td>903</td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>20.4</td>
<td>1720</td>
<td>663</td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>15.7</td>
<td>1610</td>
<td>613</td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>12.1</td>
<td>1425</td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>10.7</td>
<td>1420</td>
<td></td>
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</table>

## F013 - PFI Refining - CSF 0 revs/3000revs

<table>
<thead>
<tr>
<th>Pulp samples</th>
<th>Brownstock</th>
<th>CED</th>
<th>DED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft</td>
<td>110</td>
<td>751/669</td>
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<tr>
<td>Kraft</td>
<td>28.1</td>
<td>743/400</td>
<td></td>
</tr>
<tr>
<td>Kraft</td>
<td>17.1</td>
<td>727/342</td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>20.4</td>
<td>753/364</td>
<td>728/341</td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>15.7</td>
<td>740/338</td>
<td>733/320</td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>12.1</td>
<td>732/296</td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>10.7</td>
<td>755/347</td>
<td></td>
</tr>
</tbody>
</table>
### F013 - WRV - 0 revs/3000 revs

<table>
<thead>
<tr>
<th>Pulp samples</th>
<th>Brownstock</th>
<th>CED</th>
<th>DED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft</td>
<td>110</td>
<td>1.70/2.17</td>
<td></td>
</tr>
<tr>
<td>Kraft</td>
<td>28.1</td>
<td>1.83/2.41</td>
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</tr>
<tr>
<td>Kraft</td>
<td>17.1</td>
<td>1.87/2.33</td>
<td></td>
</tr>
<tr>
<td>Kraft - O₂</td>
<td>20.4</td>
<td>1.53/2.31</td>
<td>1.60/2.27 1.64/2.32</td>
</tr>
<tr>
<td>Kraft - O₂</td>
<td>15.7</td>
<td>1.55/2.32</td>
<td>1.60/2.30</td>
</tr>
<tr>
<td>Kraft - O₂</td>
<td>12.1</td>
<td>1.59/2.37</td>
<td></td>
</tr>
<tr>
<td>Kraft - O₂</td>
<td>10.7</td>
<td>1.55/2.27</td>
<td>1.63/2.32</td>
</tr>
</tbody>
</table>

---

### Variation of WRV with KAPPA No.

![Variation of WRV with KAPPA No.](image)

---

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### F013 - Wet (never-dried) Zero Span Tensile Index - 0 revs/3000 revs

<table>
<thead>
<tr>
<th>Pulp samples</th>
<th>Brownstock</th>
<th>CED</th>
<th>DED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft</td>
<td>110</td>
<td>102/116</td>
<td></td>
</tr>
<tr>
<td>Kraft</td>
<td>28.1</td>
<td>124/119</td>
<td></td>
</tr>
<tr>
<td>Kraft</td>
<td>17.1</td>
<td>110/109</td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>20.4</td>
<td>85.9/106</td>
<td>101/103</td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>15.7</td>
<td>/105</td>
<td>98.0</td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>12.1</td>
<td>/92.2</td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>10.7</td>
<td>70.7/91.8</td>
<td>80.4</td>
</tr>
</tbody>
</table>

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### F013 - Dry Zero Span Tensile Index - 0 revs/3000 revs

<table>
<thead>
<tr>
<th>Pulp samples</th>
<th>Brownstock</th>
<th>CED</th>
<th>DED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft</td>
<td>110</td>
<td>112/121</td>
<td></td>
</tr>
<tr>
<td>Kraft</td>
<td>28.1</td>
<td>133/132</td>
<td></td>
</tr>
<tr>
<td>Kraft</td>
<td>17.1</td>
<td>132/137</td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>20.4</td>
<td>89.8/131</td>
<td>126/116</td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>15.7</td>
<td>/124</td>
<td>120</td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>12.1</td>
<td>/114</td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>10.7</td>
<td>85.5/120</td>
<td>111</td>
</tr>
</tbody>
</table>

**IPST Confidential Information - Not for Public Disclosure (for IPST Member Company Use Only)**
### F013 - Tear Index 0 revs/3000 revs

<table>
<thead>
<tr>
<th>Pulp samples</th>
<th>Brownstock</th>
<th>CED</th>
<th>DED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft</td>
<td>110</td>
<td>18.1/12.2</td>
<td></td>
</tr>
<tr>
<td>Kraft</td>
<td>28.1</td>
<td>23.0/12.8</td>
<td></td>
</tr>
<tr>
<td>Kraft</td>
<td>17.1</td>
<td>19.2/11.1</td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>20.4</td>
<td>15.3/13.1</td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>15.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>12.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>10.7</td>
<td>15.1/12.0</td>
<td></td>
</tr>
</tbody>
</table>

### F013 - Tensile Index - 0 revs/3000 revs

<table>
<thead>
<tr>
<th>Pulp samples</th>
<th>Brownstock</th>
<th>CED</th>
<th>DED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft</td>
<td>110</td>
<td>29.4/65.8</td>
<td></td>
</tr>
<tr>
<td>Kraft</td>
<td>28.1</td>
<td>36.0/84.0</td>
<td></td>
</tr>
<tr>
<td>Kraft</td>
<td>17.1</td>
<td>44.8/83.1</td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>20.4</td>
<td>16.5/74.2</td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>15.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>12.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>10.7</td>
<td>16.3/71.5</td>
<td></td>
</tr>
</tbody>
</table>
Tear vs. Tensile Index

F013 - Palladium and Iron Colloid Staining - 0 revs/3000 revs

<table>
<thead>
<tr>
<th>Pulp samples</th>
<th>Pd, µg/g</th>
<th>Fe, µg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft</td>
<td>110</td>
<td>313/694</td>
</tr>
<tr>
<td>Kraft</td>
<td>28.1</td>
<td>229/1180</td>
</tr>
<tr>
<td>Kraft</td>
<td>17.1</td>
<td>128/612</td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>20.4</td>
<td>272/1370</td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>15.7</td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>12.1</td>
<td></td>
</tr>
<tr>
<td>Kraft 28 – O₂</td>
<td>10.7</td>
<td>367/1660</td>
</tr>
</tbody>
</table>
Future Work

- Finish analysis of all samples.
- Define meaningful characterizations of pulp properties.
- Identify additional delignification and bleaching processes to evaluate.
High Strength, High Yield Bleached Pulps

Dues-Funded Project - F030
(November 4, 1998)

Jian Li
Chemical Pulping and Bleaching Group

Institute of Paper Science and Technology

THE PLAN WAS
GOALS AND DELIVERABLES (July 1, 98 - July 1, 99)

- Complete digester modification -
  - capable of simulating commercial processes:
    RDH, SuperBatch, MCC, EMCC, ITC, Lo-Solids
  - investigating new processes leading to higher yield and
    strength, better bleachability (collaborate with F013), etc.

- Complete reference cooks
  - conventional kraft, “AQs” and polysulfide cooks

- Initial modification of no split-sulfidity cooking
  - How to use PS and “AQs” in RDH, Lo-Solids
  - (Batch version of Lo-Solids cooking of hardwood)
THE PLAN AFTER RAC REDIRECTION
GOALS AND DELIVERABLES (July 1, 98 - July 1, 99)

- Complete digester modification
- Complete reference cooks
- Initial modification of no split-sulfidity cooking

- A review on yield - strength relationship
  - Define theoretical background on what the yield gain limits are, based on its effects on physical properties.

- A three year research plan
  - Define scientifically sound and technically feasible research approaches in the proposed research area.

PROGRESS IN BUILDING DIGESTERS

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HIGH LIGHTS OF THE REPORT

Higher Yield $\approx$ Higher Hemicellulose

Fiber dimensions, Bonding potential, Fiber strength

Tearing, Tensile, Drainage, Finishing

HIGH LIGHTS - Fiber Dimensions

![Graphs showing fiber dimensions versus pulping yield.]

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Yield increase leads to:

a) no change on length,

b) transverse dimensions increase,

c) coarseness increases, e.g. 25% at 10% yield gain.

Bonding potential may be enhanced due to:

a) more bondings from hemicellulose,

b) higher swelling,

c) higher coarseness.
HIGH LIGHTS - Fiber Strength

As yield increases, the weight-based fiber strength will be lower for pulps without severe cellulose degradation.

Effect of Hemicellulose Content on Fiber Strength. (Scots pine)

<table>
<thead>
<tr>
<th>Scenarios</th>
<th>Yield gain, %</th>
<th>Cellulose &amp; Hemi % on wood</th>
<th>Cellulose % on pulp</th>
<th>% of orig. zero-span</th>
<th>Total yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original; Low yield kraft</td>
<td>0</td>
<td>35, 9</td>
<td>80</td>
<td>100</td>
<td>44</td>
</tr>
<tr>
<td>All gain from hemicellulose</td>
<td>10</td>
<td>35, 19</td>
<td>65</td>
<td>81</td>
<td>54</td>
</tr>
<tr>
<td>No cellulose loss</td>
<td>10</td>
<td>39, 15</td>
<td>72</td>
<td>90</td>
<td>54</td>
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<tr>
<td>Max gain without strength loss</td>
<td>5</td>
<td>39, 10</td>
<td>80</td>
<td>100</td>
<td>49</td>
</tr>
</tbody>
</table>

10% yield gain would reduce fiber strength by 10-20%; max. yield gain without strength loss is about 5%.
HIGH LIGHTS - Tearing Strength

Table IV. Effect of Starch Addition to Beaten Pulp

<table>
<thead>
<tr>
<th>Time beaten:</th>
<th>0 min</th>
<th>2 min</th>
<th>5 min</th>
<th>10 min</th>
<th>20 min</th>
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<tbody>
<tr>
<td>Without Starch</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Breaking length, m</td>
<td>2630</td>
<td>3350</td>
<td>4250</td>
<td>6010</td>
<td>7490</td>
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<tr>
<td>Tear factor</td>
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<td>287</td>
<td>233</td>
<td>176</td>
</tr>
<tr>
<td>Bulk, cm³/g</td>
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<td>1.74</td>
<td>1.66</td>
<td>1.55</td>
<td>1.49</td>
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<tr>
<td>Scott bond, ft-lb × 1000</td>
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<td>44</td>
<td>55</td>
<td>79</td>
<td>117</td>
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<tr>
<td>With 0.5% Starch</td>
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<tr>
<td>Breaking length, m</td>
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<td>4450</td>
<td>5790</td>
<td>6720</td>
<td>8520</td>
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<tr>
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<td>1.68</td>
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<td>1.50</td>
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<td>Scott bond, ft-lb × 1000</td>
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<td>With 2.0% Starch</td>
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<td>Bulk, cm³/g</td>
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<td>1.61</td>
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<td>1.43</td>
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<tr>
<td>Scott bond, ft-lb × 1000</td>
<td>91</td>
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<td>142</td>
<td>184</td>
<td>235</td>
</tr>
</tbody>
</table>

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HIGH LIGHTS - Tearing Strength

Tearing strength = \( k \) (zero span tensile)\(^n\)
\((n = 1 - 3)\)

Tear could be severely reduced at 10% yield gain because of higher bonding, lower zero-span.

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HIGH LIGHTS - Other Properties

- Tensile strength may not be strongly affected since lower fiber strength may be compensated by better fiber-fiber bonding.

- Drainage may be affected, but may be easily controlled.

- Optical property and flexibility may be affected, but could be easily corrected.

POSSIBLE APPROACHES TO IMPROVE TEARING STRENGTH

- Preserve intrinsic fiber strength by avoiding any cellulose degradation

- Reduce bonding potential by reducing the amount of hemicellulose available on fiber surface: a) obtain maximum possible yield gain; b) sacrifice (=extract) the low molecular weight hemicellulose; c) better control of beating operation, i.e. no over beating.
WHY MINIMIZE VISCOSITY LOSS

Strength loss of the pulp from high kappa + oxygen delignification is likely due to severe cellulose degradation.

MODEL FOR CELLULOSE DEGRADATION

Pulp Viscosity = f (T, t, [OH⁻])

In “G” factor Model, [OH⁻] is kept as constant:

\[
\frac{1}{\eta_t} - \frac{1}{\eta_0} = a \cdot G = a \cdot \int_0^t k_r dt = a \cdot \int_0^t e^{-\left(\frac{E}{RT} - \frac{1}{T}\right)} dt
\]
MODIFIED "G' FACTOR MODEL

\[
\frac{1}{\eta_i} - \frac{1}{\eta_0} = a' \int_0^t [OH^-](t, x) \cdot e^{\left( \frac{E}{R} \frac{1}{373} \frac{1}{T} \right)} \, dt = a'G([OH^-])
\]

[OH\textsuperscript{-}] is a function of time and position in chips.

HOW TO CALCULATE G(OH\textsuperscript{-})

\[
\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \left( D_i \frac{\partial C_i}{\partial x} \right) + R_i(x, t)
\]

C\textsubscript{i}: Concentration of Species i

D\textsubscript{i}: Diffusion Coefficient of Species i

R\textsubscript{i}(x, t): Reaction Rate of Species i
KINETIC RATE EQUATIONS \( R(X,T) \):

- Lignin: \( \frac{dL}{dt} = f([OH^-], [HS^-], T, L) \)
- Cellulose: \( \frac{dC}{dt} = f([OH^-], T, C) \)
- Hemicellulose: \( \frac{dH}{dt} = f([OH^-], T, H) \)
- Alkali: \( \frac{d[OH^-]}{dt} = f(\frac{dL}{dt}, \frac{dC}{dt}, \frac{dH}{dt}) \)
- Sulfide: \( \frac{d[HS^-]}{dt} = f(\frac{dL}{dt}) \)

AN EXAMPLE OF KINETIC EQUATIONS

Delignification:

Initial:

\[
\frac{dL}{dt} = 36.27 \times 10^{-5} \exp \left( \frac{-4807.69}{T} \right) L
\]

Bulk:

\[
\frac{dL}{dt} = \left[ \exp \left( 35.19 - \frac{17200}{T} \right) [OH] \right] + \exp \left( 29.33 - \frac{14400}{T} \right) [OH] \left[ HS \right] L
\]

Residual:

\[
\frac{dL}{dt} = \exp \left( 19.64 - \frac{10804}{T} \right) [OH] L
\]
MODEL OUTPUT:

Diffusing

Solid

Alkali

Sulfide

Dissolved Lignin

Cellulose

Hemicellulose

Lignin

Viscosity

ALKALI CONCENTRATION PROFILES

2 mm

8 mm

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G(OH-) - FACTOR RELATION TO VISCOSITY

Viscosity Factor Correlation: Table II

Viscosity: 3 MM THICK CHIPS

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VISCOSITY: 10 MM THICK CHIPS

Comparing 3 vs. 10 mm chips, the graph illustrates the predicted and measured viscosity levels across different thickness values. The predicted values show a clear distinction between the two thicknesses, indicating a significant difference in viscosity as the thickness increases.

Comparative analysis reveals that 10 mm chips exhibit higher viscosity levels compared to 3 mm chips, with the predicted values confirming this trend across the range of measured thicknesses.
GOALS TO BE COMPLETED IN REMAINING FY

• Complete digester modification
• Complete reference cooks
• Initial modification of no split-sulfidity cooking
• A review on yield - strength relationship.
• A three year research plan

GOALS PLANEFD FY 2000

• Complete the experiments on modification of no split sulfidity cooking
• Start to develop multi-stage pulping processes using split-sulfidity liquors per 3-year plan
• Continue to develop suitable process conditions for Soda-Catalyst pulping to achieve high yield and strength
• Start the research on high kappa number followed with oxygen delignification

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Fundamentals of Brightness
F014
Mid-Year Review
Art J. Ragauskas

F014: Project Objective
Research efforts are directed at investigating the fundamental chemical reactions that are initiated when high-yield pulps are photolyzed. As our knowledge of brightness reversion increases, methods to eliminate or retard photoyellowing will be pursued.

F014: Project Goals and Staff
Goal
- Increase the usefulness of high-yield fibers

Staff
- L. Allison
- A.J. Ragauskas

Budget
- $63,000
F014: Current Research Focus

- Photostabilization Additives
- Application Technologies
- Photoreversion chemistry of acetylated lignin

F014: FY 1998-99 Research Goals

- Study photoreversion of 75:25 SW Kraft - HW BCTMP handsheets with CaCO₃ and TiO₂.
- Examine role of FWA/co-additives with BCTMP to retard brightness reversion.
- Examine the photostabilization chemistry of acetylated BCTMP.
- Evaluate the effects of grafting acrylic acid onto BCTMP.

Previous Accomplishments
Lignin Acetylation

Experimental Procedure
BCTMP sheet → AcOH/Ac₂O → Acetylated Sheet
100°C
15 minutes

Previously employed with TMP, GSW shown to retard brightness reversion
enhance wet strength

Alternative Approach: Lignin Acetylation

Chemistry

Lignin Acetylation: BCTMP Reversion Results

Irradiated with 300-400 nm

Period Irradiation/h

Initial 0.08 0.33 0.72

- Control
- Acetylation 4.1%
- Acetylation 6.0%
- Acetylation 9.7%

DST Confidential Information - Not for public disclosure (For DST Member Company's Internal Use Only)
Summary of Lignin Acetylation: Summary
Acetylation causes significant drop in initial brightness
Acetylation reduces photoyellowing
Acetylation process works favorably with photostabilization additives:
- OBAs, UV-absorbers
- PEG, Polytetrahydrofuran
Equally effective for TMP SW and HW
Understanding fundamental chemistry could provide new opportunities
Performance of FWA Treated High - Yield Pulp

Prior Results

- FWA especially Tinopal & Phorwite UW enhance initial brightness
- Low charges of PEG improve performance of FWA
- Provide +80 brightness for ca. 20 days continuous irradiation
- Storage in dark or light/dark cycling does not influence FWA photostabilization effect
- FWA effect same for office light & sunlight

Prior FWA - Synergistic Effects
Prior FWA - Synergistic Effects

**FWA /co-additive Photostabilization Results**

**FY 1998-99 Goals**

- Study photostabilization effects of:
  - Tinopal
  - hydroxybenzophenone
  - hydroxybenzotriazole
BCTMP: FWA + UV Absorber Studies

25% HW BCTMP - 75% SW Kraft: CaCO₃ & TiO₂

- photoreversion studies employing 0.7 - 1.7% TiO₂ exhibited no photoreversion benefits

25% HW BCTMP - 75% SW Kraft: L* & b* values for CaCO₃
Conclusions

FWA and CaCO₃ provide readily available technologies to retard photoreversion of mechanical pulps.

Benzophenone derivatives extend the effect of FWAs for BCTMP.

Acetylation studies initiated and will be reported at spring PAC.
Acknowledgments

L. Allison, T. Runge, K. Haynes, M. Zawadzki, F. Chakar, J. Werner P. Argawal, C. Li

Member Companies IPST
**Tackling Environmental Problems**

- Add effluent treatment technologies ("end of the pipe cure")

- Change the process to one that produces less discharges; i.e., bleach with O$_3$ instead of Cl$_2$

- Change the starting material (wood) to a type that produces less discharges by having:
  - Trees produce their own pulping catalyst
  - Trees with easily removed lignin, greater amounts of cellulose

---

**Trees with Built-in Pulping Catalysts**

- **Funding:** DOE Agenda 2020 $337K for Aug '97-99

- **Personnel:** Don Dimmel, Jerry Pullman, Gary Peter, Huabin Meng (Postdoc), Elizabeth Althen (Sr Tech), Karen Crews (M.S. Student)

- **Objective:** To develop trees that contain anthraquinone of a type and in amounts that will catalyze their own pulping. Genetic engineering strategies will be employed to enhance endogenous AQ levels for the production of valuable tree varieties.
### AQs in Trees

<table>
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<tr>
<th>Tree</th>
<th>AQ types present</th>
<th>Percentage of AQ Components in Wood</th>
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<tbody>
<tr>
<td>Eastern Cottonwood</td>
<td>AQ</td>
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<tr>
<td></td>
<td>DMAQ</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>Mono-M AQ</td>
<td>0.035</td>
</tr>
<tr>
<td>Red Maple</td>
<td>AQ</td>
<td>0.011</td>
</tr>
<tr>
<td>Red Oak (wet)</td>
<td>AQ</td>
<td>0.020</td>
</tr>
<tr>
<td>Red Oak (Dry)</td>
<td>AQ</td>
<td>0.005</td>
</tr>
<tr>
<td>Walnut</td>
<td>AQ</td>
<td>0.010</td>
</tr>
<tr>
<td>Elm</td>
<td>AQ</td>
<td>0.007</td>
</tr>
<tr>
<td>Teak</td>
<td>Mono-M AQ</td>
<td>0.330</td>
</tr>
</tbody>
</table>
Further Cottonwood Extractions

- Have extracted two cottonwood varieties: stems, new shoots, and leaves.

- Used SIM GC/MS to aid in low level detection of various AQs.

- The leaves and new shoots from an AQ-containing (young) tree showed little (no) AQ components.

Removing AQs Before Pulping Decreases Delignification Rate

![Bar chart showing Kappa Number for Elm and Red Oak]

- Extracted
- Unextracted
Addition of Teak Chips to a Pine Cook Enhances the Delignification of Pine

![Graph](image)

**AQ in Hardwoods Conclusions**

- Six of ten hardwoods examined had AQ components; teak has the equivalent of 0.67% AQ.

- Cottonwood has AQ, methyl- and dimethyl-AQ in its heartwood, but none in its leaves and new shoots.

- Cottonwoods of different varieties contain significantly different levels of AQS.

- Pulping pine in the presence small amounts of teak is similar to adding AQ to a pine cook.
Studies on the Biological Side

- Want to isolate the genes that encode enzymes that catalyze AQ synthesis.
- Focus on isochorismate synthase - the first step in the biosynthesis of AQ in plants.
- Isochorismate synthase has been cloned from several prokaryotic organisms, but not from plants.

Anthraquinone Biosynthesis

Fig. 1. The competition of anthranilate synthase, chorismate mutase and isochorismate synthase on chorismic acid for the synthesis of aromatic acids and a number of secondary metabolites.
Results from the Biological Studies

+ Have isolated a full length isochorismate synthase cDNA (gene). The first AQ gene isolated from a plant.

+ A binary expression vector with isochorismate synthase gene has been constructed into *Agrobacteria tumefaciens*.

+ Currently progressing towards delivering isochorismate synthase gene into cottonwood via *Agrobacterium* infection.

Delivering AQ gene into trees

Superior trees
- more AQ
- less (?) lignin
Future Studies - I

- Determination of the AQ contents in:
  - turpentine condensates from mills not using AQ,
  - different cottonwood, softwood varieties, birch (which pulps easily), and western hemlock (turns red in air),
  - sections of wood from the same tree to learn the location of AQ in wood, and
  - juvenile vs mature wood varieties to establish production time for AQ in trees.

Future Studies - II

- Demonstrate a correlation between kappa drop and AQ content by pulping
  - cottonwoods containing different AQ levels and
  - extracted and unextracted cottonwoods that contain different AQ levels.
CAD-Deficient Trees

- **Funding:** USDA $50,000 for October 1997-99, in conjunction with NC State University
- **Personnel:** Elizabeth Althen (Sr Tech), Christy Parks (Summer Intern), Don Dimmel, John MacKay
- **Objective:** The ultimate goal is to develop trees that are easily delignified without using gene transfer technology. Our immediate goal is to understand the relationship between structure and reactivity of the lignin from CAD-deficient trees.

Multi-Laboratory Study

- **NC State:** Sederoff on tree genetics
- **IPST:** reactions of CAD-deficient wood
- **USDA, Madison, WI:** Ralph characterizing isolated CAD-lignin by NMR
- **France:** Lapierre characterizing CAD-wood by thioacidolysis
- **Netherlands:** Boon characterizing CAD-wood by pyrolysis GC-MS
Lignin Biosynthesis

phenylalanine

\[
\begin{align*}
\text{CO}_2\text{H} & \quad \text{CO}_2\text{H} & \quad \text{CO}_2\text{H} & \quad \text{CO}_2\text{H} \\
\text{CH}_2 & \quad \text{CH} & \quad \text{CH} & \quad \text{CH} \\
& \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{II} \quad \text{II} \quad \text{II} \quad \text{II} \\
\text{CH}_2 & \quad \text{CH} & \quad \text{CH} & \quad \text{CH} \\
& \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\end{align*}
\]

R₁ and R₂ = H and OCH₃

CAD = cinnamyl alcohol dehydrogenase

CAD-Deficient Trees

✦ Normal pine lignin biosynthesis:

\[
\begin{align*}
\text{CHO} & \quad \text{CHO} \\
\text{CH} & \quad \text{CH} \\
\text{CH} & \quad \text{CH} \\
\text{OCH}_3 & \quad \text{OCH}_3 \\
\text{OH} & \quad \text{OH} \\
\end{align*}
\]

CAD → polymerize → Normal Lignin

✦ CAD-deficient pine lignin biosynthesis:

\[
\begin{align*}
\text{CHO} & \quad \text{CHO} & \quad \text{CHO} \\
\text{CH} & \quad \text{CH} & \quad \text{CH} \\
\text{CH} & \quad \text{CH} & \quad \text{CH} \\
\text{OCH}_3 & \quad \text{OCH}_3 & \quad \text{OCH}_3 \\
\text{OH} & \quad \text{OH} & \quad \text{OH} \\
\end{align*}
\]

polymerize → Abnormal Lignin
Formation of C1-β Lignin Linkages

Lignin Linkage Types/Amounts

- β-O-4 (β-Aryl Ether)
  - Softwood: 43%
  - Hardwood: 26%
- α-O-4 (α-Aryl Ether)
  - Softwood: 19%
  - Hardwood: 18%
- p-H Phenylcoumaran
  - Softwood: 7%
  - Hardwood: 4%
- p-1,2-Diarylethane
  - Softwood: 2%
  - Hardwood: 1%
- S-8 Diaryl Ether
  - Softwood: 7%
  - Hardwood: 4%
- p-β Phenylcoumaran
  - Softwood: 2%
  - Hardwood: 3%
CAD-Deficient Lignin Structure

✦ Expect (and find) fewer $\beta$-O$_4$ linkages because of monomers having inactive/no C$_\beta$

✦ Expect (and find) more C$_5$ - C$_5$ and C$_5$ - O$_4$ linkages

✦ Expect CAD-deficient wood would be hard to delignify, unless the lignin:
  • Has a lower molecular weight
  • Is less branched
  • Contains more ionic groups (-CHO -> -COO$^-$)

Experimental Plan

✦ Five sets of soda cooks, varying:
  • Wood type (CAD- and two pine controls)
  • Severity (H-factor, %NaOH)
  • Presence of additives (NaSH and AQ)

✦ Analyzed for:
  • Kappa number and yield
  • Yield, purity and mol. wt. of dissolved lignins
  • Molecular weights of milled wood lignins from CAD- and control pines
Soda Pulping of CAD-Deficient and Normal Pine Wood Chips

Kappa Numbers of Soda Cooks
Liquor Precipitate - % of Wood

% Lignin Yield: Pulp + Liquor
Dissolved Lignin Molecular Weight as a Function of Soda Pulping Time

Pulp Yields from Soda Cooks
Molecular Weights of Mill Wood Lignins

Additional Results

- Dissolved lignin molecular weights from CAD- and control cooks are similar.

- Addition of NaSH or AQ to the soda cooks has little effect on the CAD- cooks, but a large effect on the control cooks.
Future Studies

✦ Determine the accuracy of CAD- kappa #s
✦ Finish analysis of cooks done with different additives and NaOH levels
✦ Prepare CAD- and control pulps with identical kappa numbers and determine:
  ● yield and dissolved lignin molecular weights
✦ Bleachability of CAD- pulps
✦ Sodium sulfite pulping of CAD- wood
✦ Characterize residual lignin in CAD- pulps?
"Energy Efficient Kraft Pulping for Highly Bleachable, Low Lignin Content Pulp"
(U.S.D.O.E. Project DE-FC36-95GO10091)

T. McDonough, N. Rawat and A.J. Bacon, IPST, and G. Krishnagopalan, Auburn University

Recent and Current IPST Research

- Bleachability of Auburn profiled pulps
- Analysis of residual lignin and Hex-A
- Systematic study of effects of pulping parameters on oxygen bleachability
- Search for bleachability indicator
- Conclusion of study of methods for on-line determination of AQ in pulping liquor
Effects of Pulping Conditions on Oxygen Bleachability

- M.S. research of Aric Bacon
- 21 kraft cooks of southern pine
- Pulping conditions systematically varied, according to a factorial experimental design
- Each pulp subsequently oxygen delignified
- Alkali charge in oxygen stage limited to 1.3% to increase likelihood of detecting differences between pulps

Experimental Design

<table>
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<tr>
<th>Run No.</th>
<th>X1</th>
<th>X2</th>
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<th>Solubility, %</th>
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178
### Oxygen Delignified Pulps

**Oxygen Bleachability Study: Unbleached Pulp Data**

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### Oxygen Delignified Pulps

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Regression Equation for Kappa No. After Oxygen

Kappa No. After Oxygen =
22.05 - 0.35(EA) - 0.30(S)
- 0.08(T) + 3.34(CK)
+ 0.48(EA)(S) + 0.54(EA)(T)

Alkali Charge and Sulfidity

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<td>16% S</td>
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<td>39% S</td>
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Oxygen bleachability is impaired when both alkali charge and sulfidity are low during the kraft cook.
Kappa No. After Oxygen

Alkali Charge and Temperature

Effects of Alkali Charge and Temperature on Kappa No. After O2 Delignification of 35 Kappa Pulp (L/W = 6, S = 28%)

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<td>T = 175 C</td>
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- Oxygen bleachability is impaired when both alkali charge and temperature are low during the kraft cook.
Viscosity After Oxygen

High Efficiency ClO₂ Delignification: ClO₂ Bleaching and Kinetics

D.O.E. Cooperative Agreement
DE-FC07-961D13442
T.J. McDonough, A.J. Ragauskas, A. Shaket and H. Tang
## Effects of Carrier, Temp. on Vapor Phase Bleaching

<table>
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<tr>
<th>Unbl. Kappa</th>
<th>Carrier Gas</th>
<th>Temp., °C</th>
<th>ΔK/ TAC</th>
<th>AOX, %</th>
<th>ClO₃⁻, %</th>
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## HexA Removal by D₀ Filtrate

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<th>Filtrate ΔK</th>
<th>Acid Δη, cp.</th>
<th>Filtrate Δη, cp.</th>
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Bleaching After Hydrolysis With Filtrate (Af Stage)

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<th>AfD(EO) Kappa</th>
<th>D(EO) Kappa</th>
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ClO$_2$ - Brownstock Kinetics

- HP 8453 UV-Vis system purchased by IPST
- Reactor system designed and implemented to allow continuous monitoring of UV-Vis spectrum during ClO$_2$ - pulp reaction
- Set of 28 runs completed to observe effects of pH, temperature and consistency
- Preliminary data analysis completed, assuming simple rate law
Fast Reaction Rate Constant
0.13% Cons'y., pH 2, 25°C
Kinetics - Next Steps

- Analyze existing data in terms of rate law incorporating stoichiometry and lignin concentration
- Design and run experimental series to test and refine rate law
- Develop second-generation rate law by separating reactions of ClO₂ and HOC1 after determining kinetics in presence of Cl trap
Some Conclusions

- Vapor phase bleaching much more efficient than conventional, producing less $\text{ClO}_3^-$, more AOX
- Greater efficiency not simply due to decomposition to $\text{Cl}_2$; efficiency better and AOX lower at lower temp.
- Rapid $D_0$ is effective on HW pulps and produces less AOX than conventional $D_0$

Some More Conclusions

- $D_0$ filtrate effectively removes HexA from hardwood pulps
- Bleaching after HexA removal by $D_0$ filtrate results in markedly improved delignification
- The system developed for studying $\text{ClO}_2$ bleaching kinetics is likely to enable useful $D_0$ stage rate laws to be defined
Bleach Plant Capital Reduction with Rapid D₀ Bleaching and Simplified (D/E/D) Stages

D.O.E. Cooperative Agreement
DE-FC07-971D13562
T.J. McDonough, C.E. Courchene and J.-C. Baromes

Rapid D₀ Residual vs. Time for Kappa 29 SW Pulp

![Graph showing % ClO₂ consumed vs. time in D₀ stage]
Rapid $D_0$ Complete in Less Than One Minute

**Graph:**

- **KF 0.10, 45 deg. C, DE**
- **KF 0.15, 70 deg. C, D(EPO)**
- **Unbleached**

**Axes:**
- **Y-axis:** Extracted Kappa No.
- **X-axis:** Time in $D_0$ Stage, sec

**Data Points:**
- Kappa values over time for different conditions.