ANNUAL PROGRAM REVIEW

CHEMICAL RECOVERY

Slide Material

March 24-25, 1999
ANNUAL PROGRAM REVIEW

CHEMICAL RECOVERY AND CORROSION

Slide Material

March 24-25, 1999

Institute of Paper Science and Technology
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CHEMICAL RECOVERY & CORROSION
ANNUAL PROGRAM REVIEW
At the Institute Conference Center
575 14th Street N.W. Atlanta, GA
Auditorium
Wednesday, March 24, 1999

8:00  Coffee and Rolls
8:15  Welcome/IPST Issues  Baum
8:30  Introduction  Morency
8:40  Overview of Chemical Recovery and Corrosion Division Research Projects  Frederick
9:00  Recovery Boiler Capacity Improvements  Lien, Lisa
9:30  Control of Evaporator Fouling  Schmidl, DeMartini, Frederick
10:00 Break
10:30 VOC in Kraft Mills  Zhu
11:15 Fundamentals of Dregs Removal  Empie
11:35 Closed Mill Salt Recovery  Pfromm
12:15 Lunch
1:00 Black Liquor Gasification and Status of the Pressurized Gasifier  Isa, Sinquefield, Horenziak
2:00 Control of Non-Process Elements  Frederick, Schmidl, Werner
2:45 Break
3:00 Corrosion Projects  Singh
5:00 Adjourn
CHEMICAL RECOVERY PAC MEETING
At the Institute Conference Center
575 14th Street, N.W. Atlanta, GA
Auditorium
Thursday, March 25, 1999

8:00 Administrative Issues          Morency
8:15 Discussion of Current Projects Morency
9:30 Planning for FY00               Frederick
11:00 Summary and Report Preparation Morency
12:00 Adjourn                       Morency
Melting Temperature Calculations for Fume Deposits

Steven Lien
March 24, 1999

Introduction

- The melting temperature of the fume deposits has a major impact on the plugging and fouling behavior in the recovery boiler
- Above the melting point the corrosion rate increases dramatically and hard deposits can form
- Even below the melting point there can be a large impact on the sintering rate of the deposits
- As the melting point is approached the sintering rate will increase
Melting Temperatures

- For a single compound there is a single melting temperature
- For a mixture of compounds there is a range of melting temperatures
  - $T_0$ first melting temperature (FMT)
  - $T_{15}$ sticky temperature
  - $T_{70}$ flow temperature
  - $T_{100}$ complete melting temperature

Melting Curve - Dust E

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Determination of Melting Temperature

- An effort is being made to determine the melting temperatures of the sintering dusts
- Our first approach was to use ChemSage software package
  - Gibbs free energy minimizer
  - Using thermodynamic data file developed by Abo Akademi

ChemSage Results

- Predictions Vs. Experimental data
  - Literature values - single compounds and binary mixtures
  - University of Toronto data
    - Synthetic deposits
    - ESP dust samples
Good agreement was found between the calculated and literature values.

Overall the average values are within 1 C.

ChemSage was as much as 13.8 C high and 17.6 C low Vs. The reported values.

The average absolute error was 5 C.
The ChemSage FMT values average 33 C higher than the measured data.

The ChemSage values are a minimum of 6.2 C to a maximum of 54.3 C higher than the university of Toronto data.

The shape of the ChemSage curves are very similar to the UT data, shifted by 20 - 50 C.
ChemSage Predictions Vs. Data for ESP Dust Samples

- Experimental FMT ranged from 509 to 597°C with an average of 542.4°C
- Calculated FMT ranged from 541 to 608°C with an average value of 582.2°C
- Average difference between the calculated and measured FMTs was 40°C, for the 46 samples
- There is a distinct trend where the predictions parallel the measured values, and are about 40°C higher

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Conclusions

- ChemSage can accurately predict the first melting temperature (FMT) for single and binary compounds
- ChemSage is much less accurate with tertiary and more complex mixtures

Future Plans

- We are working with both the universities of Toronto and Abo Akademi to determine the cause of this discrepancy
- Use the existing FMT data to adjust the model parameters and improve accuracy
- Using DSC to determine the melting point of the dusts currently being used in the sintering study
The influence of composition of recovery boiler dust on the sintering process.

Josefina Lindblom, Chalmers University of Technology, Gothenburg, Sweden

Steve Lien and Jim Frederick, IPST

Measuring the specific surface area is one way of measuring sintering.
Influence of composition

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Sintering at 500 °C.

The importance of the microstructure.
F016-01

Recovery Boiler Capacity Improvements:
Liquor-to-Liquor Differences in Fume Formation

Kristiina lisa
Qun Jing

F016-01 Fume Formation

- Objective:
  - to determine liquor-to-liquor variation in fume formation and K and Cl enrichment
- Incentive:
  - improved recovery boiler capacity by reduction of boiler fouling and plugging, reduced corrosion
- FY 1999 goals
  - complete study
- Status:
  - experiments complete
  - chemical analyses 90% complete
**Laminar Entrained-Flow Reactor**

- Primary gas and particle feed
- Furnace
- Secondary gas
- Quench gas
- Gas to analyzers
- Particles < 3 μm
- Particles > 3 μm

**F016-01 Fume Formation - Liquor Compositions**

- 19 liquors from 15 mills
- 12 softwood, 5 hardwood, 2 mixed liquors
- Na: 14.0-18.3%
- K: 0.7 -2.7 %
- Cl: 0.12 -0.87 %

- Cl added to two liquors to make 1.5 and 2% Cl
- NaOH, Na₂CO₃, Na₂SO₄ additions to one liquor
No statistically significant correlation of Na vaporization with liquor Na content

Fume K content increased as liquor K content increased
Fraction of K vaporization independent of liquor K content

K in Black Liquor

K enrichment factor slightly decreased as liquor K content increased

K in Black Liquor
K enrichment factor slightly increased as liquor CI content increased

Cl enrichment factor independent of liquor Cl content
Effect of Na salt addition on Na vaporization

Na vaporized/(liquor fixed C) as a function of liquor Na content
Conclusions

- Simple correlations do not adequately describe variation of fume composition with liquor composition
- Modeling required to obtain correlations:
  - NaCl/KCl vaporization
  - Reduction of alkali metal phenolate groups
  - Formation of HCl
**F016-02**

*Control of Evaporator Fouling*

*Status Report March 25, 1999*

By Wolfgang Schmidl
and Jim Frederick
IPST

---

**Soluble Scales are Mixtures of Burkeite* and Na₂CO₃**

<table>
<thead>
<tr>
<th></th>
<th>39</th>
<th>51</th>
<th>51</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄, wt-%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂CO₃, wt-%</td>
<td>51</td>
<td>39</td>
<td>26</td>
</tr>
<tr>
<td>Na₂SO₄/Na₂CO₃ mole ratio</td>
<td>0.6</td>
<td>1.0</td>
<td>1.5</td>
</tr>
</tbody>
</table>

**Other inorganic, wt-%**

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic, wt-%</td>
<td>9</td>
<td>9</td>
<td>21</td>
</tr>
</tbody>
</table>

*Nominally 2Na₂SO₄·Na₂CO₃, but ratio can range from 1.4 to 2.2*

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Critical Solids Points

Evaporator Operating Limits

- LTV (rising film) evaporators cannot operate above 1st Critical Solids without fouling
- Falling film evaporators can operate up to 2nd Critical Solids without fouling
- Forced circulation concentrators may foul above 2nd Critical Solids, but less than falling film units
Current Work

Objectives of Current Work

- Simulate solubility behavior of $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$ to predict critical solids points
  1. Solve fouling problem in the 1st effect of a falling film evaporator ("Mill A")
  2. Evaluate evaporator operating strategies for an evaporation train ("Mill B")
- Use NAELS, an advanced chemical equilibrium simulator for aqueous electrolyte solution chemistry

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**Equilibrium Predictor: NAELS**

- Nonideal Aqueous Electrolyte Simulator
- Gibbs free energy minimization subject to mass and charge balance constraints
- Species database contains temperature dependent chemical potentials
- Pitzer activity coefficient model accounts for 2-, 3-ion interactions
- Accounts for interaction of Na\(^+\) with organic electrolytes

**Mill A: Predicted Na\(_2\)CO\(_3\) + Na\(_2\)SO\(_4\) Solubility in Black Liquor**

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**Mill A: Incremental Salt Precipitation**

<table>
<thead>
<tr>
<th>Curve</th>
<th>Na</th>
<th>CO₃</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>21</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>B</td>
<td>20</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>C</td>
<td>18</td>
<td>6</td>
<td>3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Total Solids Content, wt. %</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>kg Salt Precipitated per kg Water Evaporated</td>
<td>C</td>
<td>B</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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---

**Mill A: Effect of Na₂SO₄ Addition on Sodium Salt Precipitation**

<table>
<thead>
<tr>
<th>Total Solids Content, wt. %</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>kg Salt Precipitated Per kg Water Evaporated</td>
<td>D</td>
<td>B</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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**Effect of Liquor Composition on Predicted Critical Solids**

<table>
<thead>
<tr>
<th>Liquor</th>
<th>Liquor composition</th>
<th>Critical Solids</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na</td>
<td>Na$_2$CO$_3$</td>
</tr>
<tr>
<td>Low Inorganic</td>
<td>18.0</td>
<td>10.6</td>
</tr>
<tr>
<td>Typical</td>
<td>20.0</td>
<td>14.1</td>
</tr>
<tr>
<td>Typical + Na$_2$SO$_4$</td>
<td>20.7</td>
<td>13.3</td>
</tr>
<tr>
<td>High Inorganic</td>
<td>21.0</td>
<td>17.7</td>
</tr>
</tbody>
</table>

Recommendations: keep inorganic out of liquor; add Na$_2$SO$_4$ particles to recirculating liquor in 1st effect

**Mill B**

- 6 effect tube falling film evaporator + forced circulation concentrator.

- Use solubility calculations to predict critical solids to evaluate operating plans:

  Case 1: 1st effect product = 65%

  Case 2: 1st effect prod. = 59%

  concentrator product = 65%

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### Mill B: Calculated Critical Solids

<table>
<thead>
<tr>
<th>Case</th>
<th>Current liquor composition</th>
<th>Critical Solids</th>
<th>Reduce Na₂CO₃ in liquor</th>
<th>Critical Solids</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>124</td>
<td>52, 54</td>
<td>111</td>
<td>53, 57</td>
</tr>
<tr>
<td>2a</td>
<td>111</td>
<td>53, 57</td>
<td>116</td>
<td>52, 56</td>
</tr>
<tr>
<td>2b</td>
<td>116</td>
<td>52, 56</td>
<td>111</td>
<td>64</td>
</tr>
<tr>
<td>3a</td>
<td>111</td>
<td>64</td>
<td>116</td>
<td>77</td>
</tr>
</tbody>
</table>

- **Current liquor composition**

<table>
<thead>
<tr>
<th>Case</th>
<th>Liquor Temperature, °C</th>
<th>Critical Solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>124</td>
<td>52, 54</td>
</tr>
<tr>
<td>2a</td>
<td>111</td>
<td>53, 57</td>
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<tr>
<td>2b</td>
<td>116</td>
<td>52, 56</td>
</tr>
<tr>
<td>3a</td>
<td>111</td>
<td>64</td>
</tr>
<tr>
<td>3b</td>
<td>116</td>
<td>77</td>
</tr>
</tbody>
</table>

**Mill B: Results and Recommendations**

- 1st effect would be operating past 2nd critical solids transition—PROBLEM!
- Must limit 1st effect product liquor to 53-55% liquor
- Implementing process changes to reduce total Na₂CO₃ load would permit desired product solids concentrations without major fouling problems

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### Conclusions

- The 2nd critical solids point correlates with soluble scale problems in falling film evaporators.
- Precipitation rate is higher above the 2nd critical solids point than below it.
- The 2nd critical solids point can be controlled by adjusting the Na$_2$CO$_3$ and/or Na$_2$SO$_4$ content of the liquor.

---

### Conclusions

- Chemical equilibrium predictions can be used to
  - identify evaporator operating regions susceptible to scaling, and
  - develop alternatives for reducing scaling
- This tool is ready for use in solving evaporator and concentrator fouling in member company pulp mills
Plan for FY00

A. Implement Evaporator/Concentrator Analysis Tool

- Identify member mills with soluble scale fouling problems in falling film evaporators and high solids concentrators

- Provide consulting service to evaluate problems, recommend solutions, and evaluate outcome of changes made

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B. Experimental Scaling Studies

- Complete the solubility measurements for Na salts in black liquor
- Obtain on-line crystal size distribution measurement equipment.
- Conduct pilot-scale evap tests for impact of evaporation rate, liquor recirculation rate, and suspended particle concentration and size distribution on soluble scale deposition rate
- Define operating bounds for minimal fouling in falling film evaporators

C. Modeling of Sodium Salt Solubility in Black Liquor

- Collect liquor composition data from mills with soluble scale problems in FFE's
- Calculate the 2nd critical solids point to check correlation with soluble scaling experience
- Evaluate the NAELS model with the solubility data. Update the Na-organic interaction parameters in the model as needed.
- Issue the final report from the Survey of Evaporator Fouling
VOC CONTROL IN KRAFT MILLS

Presented to the Chemical Recovery PAC

Dr. J.Y. Zhu
Dr. X.S. Chai
Dr. P.H. Liu
Dr. Sung Hoon Yoon
Garry Heedick
Jeremy Thomas (MS Student)

Institute of Paper Science and Technology

March 24, 1999

Research Line/Roadmap

Environmental Performance:

5. Reduce emissions of the entire pulp and paper manufacturing process to meet Tier 3 Cluster Rule criteria while maintaining global competitiveness.
# BUDGET

- **BUDGETING PERIOD:** 7/98-6/99
- **SALARY BUDGETED:** $18,087
- **STAFF:**

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<td>Zhu</td>
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<td>Chai</td>
<td>50%</td>
<td>50%</td>
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<tr>
<td>Liu</td>
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<td>Heedick</td>
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<tr>
<td>Yoon</td>
<td></td>
<td></td>
<td></td>
<td>100%</td>
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## OVERVIEW OF THE PROGRAM

### Task A
- Predictive Model
  - IPST (Zhu)
  - UI (Edwards)
  - GT (Teja)
  - NCSU (Kirkman)
  - NCASI (Southeastern)
  - MILL X

### Task B
- Separation Tech.
  - IPST (Pfromm)
  - GT (Rezac)

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Previous Accomplishments on Vapor Liquor Equilibrium Member Company Report I, II, and III


Progress in This Period

- Completed Methanol, MEK, and Aceton Henry's Constants in Black Liquors
- Developed Empirical Correlations

Previous Accomplishments on Methanol Formation
Member Company Report IV

- Methanol Formation in Laboratory Pulping: Pine and Birch, Bleached Grade
- Methanol Formation in Black Liquor Storaged Tanks: Simulation Study Using Lignin + Hydroxide
- Methanol Formation during Black Liquor Evaporation: Laboratory Batch Study
Progress in This Period

- Further Study on Methanol in Pulping
  - Understanding of Reaction Pathway Fundamental
  - Effect of Kappa Number on Methanol Formation
  - Effect of Wood Species on Methanol Formation (on going)
- Methanol Formation in Storage: Using Black Liquors

Other MAJOR MILESTONES

- Presentation at NCASI CCA Meeting at GP
- Coordinating Meeting for Mill Sampling at Boise Cascade - Southern Operation, LA
VLE of Methanol in Black Liquors

Previous Study Found That

\[ \ln(H) = \frac{A}{T} + B \cdot S + C \]

\[ H = m \exp\left(\frac{A}{T} + B \cdot S\right) \]
EFFECT OF TOTAL SOLIDS CONTENTS

CORRELATIONS

\[ H = m \left[ \exp\left(-\frac{A}{T}\right) + B \cdot S \right] \]

A = 6000
B = 1.5
m = 1.1902 \times 10^{13}
H in Pascal
MEASURED vs PREDICTED

Methanol Formation in Pulping

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EFFECT of Kappa NUMBER

EFFECT of Kappa NUMBER

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EFFECT of H-Factor

**Graph 1: MeOH Concentration vs. H Factor**
- MeOH Concentration (mg/L) on the y-axis
- H Factor on the x-axis
- Data points for Conventional Pulping
- AA = 18%, Sulfdity = 30%

**Graph 2: Methanol (kg/ODT Pulp) vs. H Factor**
- Methanol (kg/ODT Pulp) on the y-axis
- H Factor on the x-axis
- Data points for a different process or condition

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EFFECT of PULPING PROCESS

Methanol (kg/ODT Pulp)

- Conventional Kraft AA = 18% S = 30%
- Conventional Kraft S = 15% Without Aq
- Conventional Kraft S = 15% With Aq
- Polysulfide 1.45% S = 15% Without Aq
- Polysulfide 1.45% S = 15% With Aq
- Polysulfide 0.21% S = 30% Without Aq
- Multistage

H Factor

METHANOL FORMATION FUNDAMENTAL

1. Hydrolysis of Hemicellulose Methyl-D-Glucuronoxylan

\[
\begin{align*}
\text{CO}_2H & \quad + \text{OH}^- \quad \rightarrow \quad \text{CO}_2H \\
\text{CH}_3O &
\end{align*}
\]

+ CH₃OH

2. Demethylation of Lignin

\[
\begin{align*}
\text{CH}_3OH & \quad + \text{OH}^- \quad \rightarrow \quad \text{CH}_3OH \\
\text{OCH}_3 &
\end{align*}
\]

+ CH₃OH
Correlation between Methanol and HUA

Correlation between Methanol and HUA

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Summary

- 80% of the Methanol Formed in Pulping is due to Rapid Hydrolysis of Methoxyl Groups on Xylan
- The Effect of Kappa Number on Methanol Formation Can Be Explained as the on Going Hydrolysis Reaction of the Methoxyl Groups on Xylan.
- Xylan Hydrolysis Reaction Is Completed Right at the Cooking Temperature Reaches the Final Temperature (or H=400)
- Cooking Process Itself does not Significantly Affect the Overall Methanol Formation.

METHANOL FORMATION IN LIQUOR STORAGE - Previous Results

\[
\frac{dC_{MeOH}}{dt} = k \cdot [\text{Lig}]^a \cdot [\text{OH}^-]^b = \text{Cons}
\]

\[
k = Z \cdot \exp \left(-\frac{E}{RT}\right)
\]
METHANOL FORMATION IN LIQUOR STORAGE - Black Liquor

**Liquor:** AA = 18%, S = 15%, Pulp Kappa = 104
- T = 70°C
- T = 80°C

Time (min)

Methanol (mg/L)

METHANOL FORMATION IN LIQUOR STORAGE - Black Liquor

**AA = 15%, S = 15%**
- Kappa = 104
- Kappa = 59

Time (min)
Comparison: Lignin vs Black Liquor

![Graph showing methanol formation with time and temperature.]

**Summary**

- Methanol can be formed in black liquor storage even at temperature as low as 70°C.
- The total formation is about 10% of the amount in the fresh liquor.
- The formation process is completed within the 10 hours.
- The effect of evaporation of the stored liquor needs to be studied.
FUTURE WORK

- Data analysis (sulfur compounds) of the existing pulping experiments.
- Complete the study on methanol formation in storage tanks using black liquor.
- Conduct methanol during evaporation on a pilot scale evaporator.
- Study wood species on methanol formation
- Measure methanol Henry’s constants in fiber-suspension solutions (DOE Mandate)
- Data analysis of Henry’s constants of MEK and DMS in black liquors
- Summarize the Study in Reports

THANK YOU
Fundamentals of Dregs Removal

Jeff Empie
Maribeth Amundsen
Murray Ellis (PAPRO)

Recovery PAC Committee
March 24, 1999

Project Objective

Determine effect of elevated levels of NPE's on composition and settling/filtration rates of green liquor dregs to facilitate closed cycle operation
Objectives for Current Period

• Complete formation of synthetic smelts with one NPE added per run
• Determine dregs settling/filtration rates at 80°C and compare with base case
• Subject smelt sample from a kraft mill to laboratory procedures and compare dregs properties with those from a raw green liquor sample from the same mill
• Obtain physical/chemical analyses of dregs and green liquors
• Write final report

Accomplishments in Current Period

• Smelt formation runs successfully completed for each NPE addback run, plus one duplicate Mg run
• Settling/filtration rates determined at 80°C
• Mill smelt and green liquor samples obtained and settling/filtration rates determined for comparison purposes
• Draft final report completed
### Baseline Starting Composition

<table>
<thead>
<tr>
<th>Smelt Component</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂CO₃</td>
<td>74</td>
</tr>
<tr>
<td>Na₂S</td>
<td>20</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>2</td>
</tr>
<tr>
<td>NaCl</td>
<td>2</td>
</tr>
<tr>
<td>Dregs</td>
<td>2</td>
</tr>
</tbody>
</table>

### Baseline Starting Composition

<table>
<thead>
<tr>
<th>Dregs Component</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>65</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.5</td>
</tr>
<tr>
<td>Mg(OH)₃</td>
<td>12.5</td>
</tr>
<tr>
<td>MnO₂</td>
<td>6</td>
</tr>
<tr>
<td>SiO₂</td>
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Laboratory Smelt Reactor

Sedimentation/Permeability Apparatus
### NPE's in Clarified Green Liquor (mg/kg)

<table>
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<th>Metal</th>
<th>Run 040</th>
<th>Run 045</th>
<th>Run 049</th>
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<th>Run 092</th>
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<th>Mill dissolv</th>
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### NPE's in Dregs Produced (wt.%, dry basis)

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<th>Elimnt</th>
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<th>Run 083</th>
<th>Run 090</th>
<th>Run 092</th>
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</tr>
</tbody>
</table>

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NPE's in Dregs Produced

- NPE concentrations in dregs from mill smelt are essentially the same, whether or not smelt was heated in lab reactor. Deficiency in organic carbon resulting from lab smelting procedure most likely due to combination of gasification and sulfate reduction.
- Dregs from mill green liquor, with or without addition of polymer during clarification, are essentially the same as dregs from mill smelt.
- High organic carbon value for dregs resulting from dissolution of solid mill smelt in lab, relative to mill green liquors (where molten smelt is dissolved), is consistent with this in that there could be some carbon gasification of the molten mill smelt as it contacts water in the dissolving tank.
- High Mg runs (049, 092) represent only case of gauging reproducibility in green liquors formed. Agreement is fair.
- Each NPE addback lab run showed elevated level of the respective NPE in dregs for that run. It should be noted with high Ca run (090), that concentrations of other NPE's are all significantly lower than other runs.

NPE's in Mill Dregs

- Literature data from 14 mills (5 Swedish, 4 Canadian, 4 U.S., 1 Wisc.) show considerable variation.
- Comparison of lab data shows fair agreement with some notable exceptions:
  - Organic carbon below lit. avg. (which has large std. dev.)
  - Fe and Mn for Al and Si addbacks and mill derived dregs > 2σ above lit. avg.
  - Mg for Al addback and mill derived dregs > 2σ above lit. avg.
  - Al for mill derived dregs > 2σ above lit. avg.
## Partition Coefficients (M in Dregs, M in GL)

<table>
<thead>
<tr>
<th>Run</th>
<th>Addback</th>
<th>Ca</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
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</thead>
<tbody>
<tr>
<td>040</td>
<td>Base</td>
<td>4.83</td>
<td>0.006</td>
<td>94.3</td>
<td>29.4</td>
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<td>Mg 10</td>
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<td>0.003</td>
<td>95.8</td>
<td>27.0</td>
<td>0.007</td>
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<td>11.9</td>
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<td>Mill GL</td>
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<td>92.7</td>
<td>11.9</td>
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## Wt.% of Input NPE in Clarified Green Liquor

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<th>Mg</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
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<tr>
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Comparison of Laboratory and Mill Clarified Green Liquors

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<th>Mn</th>
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</table>

NPE Partitioning Summary

- Green liquor from heat treated mill smelt shows a high NPE partition coefficient for Mg and low values for Fe and Mn, relative to mill green liquor and green liquor made from solidified mill smelt. $K_{\text{add}}$, values for mill green liquor and green liquor from solidified smelt are essentially the same.
- Ca, Fe, Mg, and Mn stay predominantly with the dregs. Partition coefficients for addback runs are higher than for mill samples.
- Singularly high $K_{\text{add}}$ values for Ca, Mg and Mn addback runs show these metals will be removed effectively by dregs, even if their concentrations in liquor cycle increase.
- Partition coefficients for Si are low in all cases, implying removal from liquor cycle must be by some method other than by dregs.
- Al partitions fairly evenly between dregs and CGL, even with Al addback case. Hence, high Al input to liquor cycle will not be controlled by dregs removal.
### Mill Settling Rates

![Graph showing mill settling rates](image)

### Calculated Dregs Settling Times for Continuous Clarifier

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Type</th>
<th>Time (min.)</th>
<th>Effect</th>
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</thead>
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<tr>
<td>046</td>
<td>Mg x 10</td>
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<td>Na x 10</td>
<td>315, 392</td>
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</tr>
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<td>055</td>
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<td>520</td>
<td>high</td>
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<tr>
<td>062</td>
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<tr>
<td>003</td>
<td>Mill, washed</td>
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<td>Mill Gl w Poly</td>
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<tr>
<td>004A</td>
<td>Mill Gl, w Poly</td>
<td>365</td>
<td></td>
</tr>
</tbody>
</table>

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Implications for Continuous Clarifier

- Based upon hypothetical time for continuous GILC to reach 10% solids in the underflow:
  - Fe gives higher clarification time at 98% confidence level.
  - Particle size showed greater fraction of small particles ($< 20 \text{ \mu m}$).
  - Mn higher time at 88% confidence.
  - Ca lower time at 79% confidence. Had greater fraction of larger particles ($> 20 \text{ \mu m}$).
  - AI also gives higher settling time.
- Addition of polymer settling aid to raw mill green liquor lowered calculated settling time by 24%.

Filter Cake Permeability

From the differential form of Darc's Law, the cake permeability can be calculated as:

$$K = \frac{\pi\eta}{P} \ln\left|h_c - \frac{P_0}{P}\right|$$

where:

- $K$ = permeability for clarified green liquor (GIL)
- $\eta$ = density for GIL
- $h_c$ and $h$ = GIL heights in the settling column at time $t$ and $t$ respectively
- $P$ = cake thickness
- $P_0$ = degree of vacuum

The three constants on front of the logarithm combined as follows:

$$a \cdot K = \frac{\pi\eta}{P} \ln\left|h_c - \frac{P_0}{P}\right|$$

The parameter $L$, is pressure dependent due to expected compaction at higher pressures.
**Dregs Filter Cake Permeability Coefficients (K)**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Type</th>
<th>$\alpha K_s$</th>
<th>$\alpha K_{is} $</th>
</tr>
</thead>
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</tr>
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<td>0.0010</td>
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<td>n.a.</td>
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<tr>
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<td>Mn x 10</td>
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<td>0.0058</td>
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<tr>
<td>90</td>
<td>Ca x 10</td>
<td>0.0081</td>
<td>0.0155</td>
</tr>
<tr>
<td>92</td>
<td>Mg x 10</td>
<td>0.0039</td>
<td>0.0074</td>
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<tr>
<td>93</td>
<td>Mill, smelted</td>
<td>0.0027</td>
<td>0.0067</td>
</tr>
<tr>
<td>98</td>
<td>Mill, dissolved</td>
<td>0.0018</td>
<td>0.0040</td>
</tr>
<tr>
<td>100 A</td>
<td>Mill Cl w Poly</td>
<td>0.0009</td>
<td>0.0009</td>
</tr>
<tr>
<td>100 B</td>
<td>Mill Cl + as</td>
<td>0.0016</td>
<td>0.0016</td>
</tr>
</tbody>
</table>

**Conclusions on NP1 Composition**

1. Each NP1 additive laboratory run showed an elevated level of the NP1 added in the dregs for that run. The high Mg runs represent the only case for judging experimental reproducibility in the green liquor dregs-forming agreement was generally within a factor of two.

2. Starting with mill smelt, heat treated or not, NP1 concentrations in dregs and the clarified green liquors were essentially the same, respectively. The only exception was organic carbon in the dregs which heat treatment resulted in a lower value, probably due to gasification and or reduction reactions. NP1 concentrations in clarified green liquors from mill smelt and from mill green liquor are nearly identical.

3. NP1 concentrations in laboratory green liquors are within a factor of two vs. mill green liquors. Aluminum concentrations in laboratory green liquors are generally higher than in mill green liquors.

4. Partition coefficient results showed that Ca, Fe, Mg, and Mn would be removed effectively by the dregs— even if their concentrations in the liquor cycle increased. Partition coefficients for Si were uniformly low while Al partitions evenly between dregs and green liquor; hence removal of Si and Al from a closed liquor cycle must be by some method other than dregs removal.
Settling/Filtration Rate Summary

1. Settling rate curves showed fair reproducibility within the four conditions where duplicates were run. The Fe and Al additives exhibited poor settling characteristics, while Mg and Ca gave the highest settling rates.

2. Statistical comparison of three additive NPFE runs with the base case was made using hypothetical time to reach 10% solids underflow concentration in a continuous green liquor clarifier. Higher clarification times were given by Fe and Mn while Ca gave a lower time. Qualitatively, Al also gave a higher settling time. Microscopic particle size analysis showed the Fe additive to have a greater fraction of small particles (<29μm), which would explain a lower settling rate. It also showed Ca to have a greater fraction of large particles (>29μm), resulting in a higher settling rate.

3. Mill smell heat treated in lab gave green liquor drags which settled slower than same mill smell just dissolved in synthetic weak wash. Addition of polymer settling aid to raw mill green liquor lowered the calculated settling time, as expected.

Settling Filtration Rate Summary

4. Filter cake permeability coefficients for the Mn, Mg, and Ca additives and heat treated mill smell were the same as for the base case: Al was higher while Fe, Si, Mill Smell (Dissolved), and the Mill Green Liquors were lower. Microscopic analysis of the filter cakes showed the Fe, Si, Mill Smell (Dissolved), and Mill Green Liquors to have a greater fraction of small particles (<29μm), which should result in increased the permeability coefficients due to relatively high specific surface areas.

5. Permeability coefficients increased at higher vacuum (i.e., higher VP), contrary to expectation. Removal of cake fines at higher vacuum resulting in a reduced surface area per unit volume is a plausible explanation.

6. Mill closed cycle operation must anticipate problems with buildup of Si, Al, and Fe in the liquor cycle due to unfavorable partition coefficients and or settling rates in the green liquor clarifier or filter.
Project F01706 (Dues funded)

Remove Chloride and Potassium from Kraft
ESP Catch using Membranes

P. H. Pfromm, D. Taylor

The issue:
Cl and K enrichment due to low-effluent kraft pulping and bleaching

• Tight liquor cycles and bleach plant recycle cause increased Cl and K concentrations
• Decreased production, increased maintenance
  ➔ Recovery boiler plugging
  ➔ Corrosion
  ➔ Deadload

Electro-membrane processing for Cl and K removal:
relation to IPST Research Lines

• Research line Environmental Performance

  ➔ 4. Reduce water usage in Bleached Kraft Pulp production to 2500 gallons per ton.
Cl and K removal from the kraft recovery cycle: approach

- Treat ESP dust, remove Cl with K, Na.
- Electro-membrane processing, electrodialysis:
  - Removal of the unwanted ions from dissolved ESP dust, not separation of the majority of ions (as in crystallization)
  - No liquid/solid, adjustable removal, simple startup/shutdown, all organics are recycled

Process Overview

Selectiv Cl and K purge using electro-membrane processing:

- Expected results:
  - Simple process that can be retrofitted, pilot-scale test data
- Impact on the industry:
  - Decrease boiler plugging, increase production
  - Avoid saltcake & organic load in effluent treatment
  - Save makeup saltcake
  - Enable bleach plant recycle
Electro-membrane processing: project history

- Objective: selective removal of Cl and K from Kraft RB ESP catch, start: Fall 94'
- Pilot test performed in 1997.
- This report period: 9-98 to 3-99
- Budget: FY 99, $166,276
- Project will terminate with FY99
- Staff: P. Pfrohm, D. Taylor

Objectives for FY 99

- A: Technology transfer, electrodialysis of ESP dust
- B: K/Na selective membrane separation
- C: Ion exchange for chloride/potassium removal from green liquor.
- D: ESP dust electrodialysis, increase solids in feed to 25%, use more advantageous water sources

FY 99 Progress vs. objectives to date

- A: Technology transfer
  - One member mill agreed to use a DOE funded pilot test (Spring 99, electrodialysis of bleach effluent) to become comfortable with the technology. This mill has a need for chloride purge.
  - Capital investment availability is currently very low in the industry.
FY 99 Progress vs. objectives to date

• A: Technology transfer
  ➔ US Filter/HPD would engineer/implement the electrodialysis, but no warranty on membrane life (per Gerald Delaney).
  ➔ IPST IP Attorney reviewed possible infringement of a PAPRICAN patent. Conclusion: very likely no infringement problems.

FY 99 Progress vs. objectives to date

• B: K/Na selective membrane separation
  ➔ see evaluation of high solids experiment

• C: Ion exchange for chloride/potassium removal from green liquor.
  ➔ No new MS candidate found. Cl removal experiments planned for remainder of FY 99.

Progress vs. objectives to date

• D: ESP dust electrodialysis, increase solids in feed to 25%, use more advantageous water sources
  ➔ Extended continuous feed-and-bleed laboratory scale run with actual dust (no pre-treatment) was performed.
  ➔ Cl selectivity is still very good, despite the high ionic concentration.
  ➔ Detailed report follows.
Why use higher dust concentrations?

- Less water to evaporate from the dechlorinated recycle stream.
- Higher per-volume chloride concentration will possibly allow higher electrical current density (this means lower membrane area = lower capital investment).

Batch electrodialysis at 25 weight% ESP dust concentration

- Previous laboratory runs:
  - Pilot test: 170-190 grams/liter
  - Now: 311 grams dust/liter (25 wt%)
- Membranes are the same as in the pilot test, 40°C, 7.1 mA/cm² current density
- Dry dust contained 1.3 wt% chloride

Feed-and-bleed electrodialysis

- Diss. Dust 1.36 l/h
- NaCl 0.064 l/h
- Tap water
- Purge 35 g Cl/l
- Dissolved dust
- Bleed, 2.8 g Cl/l (recycle to recovery)
Why was only about 40% chloride removed in the feed-and-bleed test?

- An erroneous dust analysis initially indicated a lower chloride content than was later determined to be actually present.
- Based on the erroneous solids analysis, the electrical current density was set to remove ~70% of chloride at steady state operation.
- More chloride was in the feed than anticipated, so the % chloride removed was relatively low.

Feed-and-bleed run at 25wt% dust, 40°C

Sodium/Potassium

- Feed: 0.064 mol K/(mol K+mol Na)
- Purge: 0.100 mol K/(mol K+mol Na)
- Example: if 1000 kg chloride are purged per day then 143 kg potassium are purged per day (ideally, a crystallizer might purge 1100 kg potassium per day 1000 kg of chloride)
New mass balance, based on 25wt% solution

- 1000 kg C1 to be purged per day, ESP dust has 1.3 wt% C1, remove 80%.
- 96 tons of dust dissolved/day, 56 GPM to be evaporated from the recycle.
- ~375 m² membrane area.
- Op. cost savings $2MM/year vs. discarding dust and purchasing saltcake at market price.
  (taking in account: energy for electrodialysis (pumping + separation), steam for evaporation, membrane replacement.
  Excluded: energy for dissolving dust, maintenance)
- Cap. cost <$1MM for the electrodialysis system.

Path forward

- Write final report.
- Write quick reference paper (mill level) on chloride and chloride control.
- Attempt chloride removal from model green liquor by ion exchange.

Project 4160
(DOE funded, no IPST matching funds)

Recycling of Bleach Filtrates using Electrodialysis
Shih-Pereng Tsai
(Argonne National Laboratory)
P. H. Pfommm
(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
Bleach Filtrate Electrodiagnosis: Advantages

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

Bleach Filtrate Electrodiagnosis: Challenges

- Fouling?
- Membrane area? (solutions are dilute)
- Removal efficiency, selectivity?
**Bleach Filtrate Electrodialysis:**

**Year 1 Summary**
- Acidic effluents from three mills (IPST):
- Electrodialysis (lab scale, ANL) with two effluents, no pre-treatment
- Analyze (IPST, ANL)
- 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

---

**Concluding Remarks, Year 1+2**
- Long-term laboratory performance OK.
- High removal levels for important NPE’s, and Chloride.
Year 3

- Pilot scale test site identified, mill visit was positive
- Address residual chlorine dioxide issue in bleach effluent, membrane stability?
- Address issue of entrained fibers
- Perform pilot scale test at the mill

Project F034

Elimination of the Calcium Cycle: Direct Electrolytic Causticizing of Kraft Smelt
J. Winnick (GIT Chem. E.), P. H. Pfroom

DOE Agenda 2020
Energy Performance Task Group
Proposal for FY 2000 pending

Electrolytical

Wood
Pulping

Washing
Organics
Inorganics

CO₂

“Black Liqueur”

CO₂, O₂

Carbon
Anode

Electrolysis cell

“White Liqueur”
NaOH, Na₂S
solution

Water

Electricity

Pulp to bleaching
1000 tons/day

Inorganic sodium: 400 tons/day 70wt% Na₂CO₃, Na₂S
### Motivation for Electrolytical Causticizing

- Incremental capacity is needed in many mills, it can not be done with traditional technology (lime kiln).
- Process control
- Avoid multiple separation/reaction steps
- Remove chemical equilibrium limit to causticizing

### Economics

- Estimate for a 1000 ton of pulp per day production:
  - $42\%$ savings in energy for electrolysis
  - Marginal savings in operating cost (since electricity is currently more expensive than fuel oil for the kiln)
  - No credit taken for production increase through lower deadload (increased causticizing level)

### Funding situation

- End of one-year DOE project was in October 1998. Since then, bootleg funding from GIT for PhD student, IPST for supplies.
- RAC approved (?) $100k for FY00 for GIT PhD student, supplies, PI time.
Funding situation outlook case A:
no DOE funding

- Use $100k from RAC for:
- GIT PhD student and very limited PI time
  (how to get the money there? Double overhead?). PhD student: $22k/year, add
  GIT overhead and IPST overhead.
- IPST supplies, and limited PI time.

Funding situation outlook case B:
DOE funding

- 3 years, GIT PhD student, post doc, equipment improvements.
- Use about $40,000/year from RAC as matching funds (Pfromm's time).

New Dues co-funded project F033-04

Ultrafiltration of bleach effluent:
new approaches for partial closure

Current sponsor: Eka Chemicals
Additional Sponsorship:
Georgia Consortium proposal pending

Dr. Patrick Bryant, Eka
Peter Pfromm
The issue

- Compliance of bleach plant effluents (COD, color, AOX) from existing bleach plants is or will be an issue.
- Compliance by radical changes in bleaching technology or total closure may be costly.
  - An "intermediate" lower cost solution is needed.

Approach

- Ultrafilter extraction stage effluent of a fully substituted bleach plant (with or without O₂ delig.), split into:
  - Low volume/high concentration stream with high molecular weight organics, color, AOX to brown stock washing.
  - A high volume/low concentration stream with easily treated low mol. weight organics, and inorganics (chloride) to effluent treatment.

Expected results

ultrafiltration of BP 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 of bleach effluents can be achieved without fundamental changes in bleaching technology.
- Chlorides and other inorganics are not recycled to chemical recovery.

Ultrafiltration of BP effluent

Case A (unlikely):
no Georgia Consortium funding

- RAC approved $50k co-funding for FY00
- Eka will give 50k, in addition to 20k donation.
- Post doc identified.
- Pilot unit will be moved to IPST.

Ultrafiltration of BP effluent

Case B (likely):
Georgia Consortium funding

- No IPST money needed.
- 3 year project, post doc, extensive pilot and laboratory work.
- Status: a cautious OK for this proposal
F028
Black Liquor Gasification

Kristiina lisa
Qun Jing
Scott Sinquefield

- Objective:
  ➔ to determine kinetics of inorganics (Na, K, Cl) transformations during black liquor gasification (FY98-99)

- Incentive:
  ➔ improved gasifier performance by optimization of conditions for liquor production
F028 Black Liquor Gasification

- FY 1999 goals:
  → complete atmospheric gasification experiments:
    - CO₂, H₂O
  → first pressurized experiments
    - feasibility of feeding black liquor
    - reproducibility, material balance closure
- Status:
  → atmospheric study of impact of CO₂ complete
  → 40% of atmospheric experiments of impact of H₂O complete
  → pressurized gasifier testing on-going

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F028 Black Liquor Gasification - Related DOE project

- "Fundamental Study of Black Liquor Gasification Kinetics Using A Pressurized Entrained-Flow Reactor"
  → with Air Products and NREL
  → emphasis on conditions of oxygen-blown gasification (900-1200°C)
  → gaseous trace compounds (tars, S compounds, N species)

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F028 Black Liquor Gasification

- Related student project:
  MS project by Steve Horenziak:
  "Fate of Sulfur During Black Liquor Gasification"
  - split of S between gas and condensed phase
  - form of S in gas phase
  - atmospheric

Atmospheric Experiments of

- experiments in a laminar entrained-flow reactor
- effect of temperature: 700-1100°C
- effect of CO₂ concentration: 0-20%
- effect of H₂O concentration: 0-20%
- effect of residence time: 0.6-1.4 s
Laminar Entrained-Flow Reactor

Primary gas and particle feed

Furnace

Secondary gas Quench gas

Gas to analyzers

Particles < 3 μm

Particles > 3 μm

Composition of Black Liquor

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>33.24%</td>
</tr>
<tr>
<td>Na</td>
<td>19.00%</td>
</tr>
<tr>
<td>H</td>
<td>3.00%</td>
</tr>
<tr>
<td>K</td>
<td>1.71%</td>
</tr>
<tr>
<td>O</td>
<td>35.81%</td>
</tr>
<tr>
<td>S</td>
<td>4.40%</td>
</tr>
<tr>
<td>N</td>
<td>0.25%</td>
</tr>
<tr>
<td>Cl</td>
<td>0.43%</td>
</tr>
</tbody>
</table>

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Vaporization of Na strongly depends on temperature

- 0.6s
- 1.0 s
- 1.4s

Na Vaporized

Temperature, °C

500 700 900 1100 1300

40%
30%
20%
10%
0%
Vaporization of K also a strong function of temperature

K enrichment factor decreases with T in the range 900-1100°C
CO₂ suppresses Na and K volatilization

Cl in fume highest at 1000-1100°C
Conversion of NaCl/KCl to HCl important at long residence times

Cl Enrichment Factor decreases with T in the range 900-1100°C
CI Enrichment Factor increases with t at 900°C but decreases with t at 1000-1100°C

\[ \text{Cl enrichment factor} \]

Residence time, s

\[ \begin{align*}
\text{700°C} & : \bullet \\
\text{900°C} & : \square \\
\text{1000°C} & : \triangle \\
\text{1100°C} & : \diamond
\end{align*} \]

CO\textsubscript{2} affects Cl in fume but relationship complex

\[ \text{Cl in fume, % of liquor Cl} \]

\[ \text{CO}_2 \text{ concentration, %} \]

\[ \begin{align*}
\text{1.0 s} & : \diamond \\
\text{1.4 s} & : \square
\end{align*} \]
Cl enrichment factor usually increases with CO₂ content

H₂O Gasification

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Fume yield increases as residence time and temperature increased.

A maximum in fume yield as a function of $H_2O$ content.
CONCLUSIONS

- Na/K vaporization suppressed by CO₂
  - less fume during gasification than during combustion
- K enrichment factors higher than during combustion
  - fume better source of K removal in gasification than in combustion
- possible to concentrate all Cl into fume or gas phase
  - options for Cl purge.

F028 Black Liquor Gasification - Plan for March 99-September 99

- atmospheric
  - complete study of impact of H₂O on Na, K, Cl
  - fate of S during H₂O gasification
- pressurized
  - establish reproducibility, material balance closure
  - gas phase major (C,H) and minor species (S compounds, NOx, tars)
  - establish qualitative fume collection
Control of Non-Process Elements in Kraft Pulp Mills and Bleach Plants
Status Report March 25, 1999

By Wolfgang Schmidl
and Jim Frederick
IPST

Background

- To reduce the use of water 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

Current Work:
Evaluation of Prediction Capability for Solubility of Metals in Green and White Liquors
**Predicted Solubility Versus Mill Data**  
*(Green and White Liquors)*

<table>
<thead>
<tr>
<th>Column 1</th>
<th>Column 2</th>
<th>Column 3</th>
</tr>
</thead>
<tbody>
<tr>
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</table>

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**Current Work:**  
*Application to Brownstock Washing with Bleach Effluent Recycle*
**Two washing scenarios 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
- Examined two cations: Ca\(^{2+}\), Mn\(^{2+}\)

---

**Input streams based on mill data...**

**Unwashed brownstock slurry:**
- 12.5% consistency
- 20% dissolved solids in liquor
- 90\(^\circ\)C

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

**Pulp consistencies:** 1% in vats, 12.5% in mats
Used the OLI Systems Chemical Equilibrium Simulator...

- Inorganic solubility predictor
- Added equilibrium models for
  - Complexation of metal ions with dissolved organic matter
  - Adsorption of metal ions on wood pulp fibers
- Used the software’s process simulation capability

2-Stage Brownstock Washer Model

Brownstock Slurry From Digester → Weak Black Liquor

Stage 1
- MIX1 → SEP1 → MIX2 → SPLT1 → SPLT2

Stage 2
- MIX5 → SPLT3 → SPLT4 → MIX6

Wash Liquor In

Brownstock Slurry To Bleach Plant
### Soluble inorganic calcium species

*(as Ca, 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>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

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### 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

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Ca Distribution
(Total input: 1395 g Ca/BDT Pulp)

Mn Distribution Without Precipitate
(Total input: 280 g Mn/BDT Pulp)
Alkali metals displace Ca, Mn on pulp

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Predictions agree with mill data

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(For IPST Member Company's Internal Use Only)
With filtrate recycle, calcium accumulates in bleach plant...

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(For IPST Member Company's Internal Use Only)

With filtrate recycle, manganese also accumulates in bleach plant...

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**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 will be returned to the bleach plant.

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

Plan for FY00
**Improve Equilibrium Model**

- Improve prediction capability for green and white liquors
- Add thermodynamic and activity coefficient constants for aluminum and silicon to data base

**Mill Validation**

- Identify an industrial partner, whose brownstock washers and bleach plants will be the subject of this study, and industry experts
- Develop and validate steady-state mass and energy balance models for the mill's brownstock washers and bleach plant
- Implement the models to develop strategies for managing metals and oxalate
- Conduct mill trials to evaluate the strategies