Peroxide Bleaching of Eucalyptus CTMP Using Mg(OH)₂ as the Alkali Source

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Conventional Peroxide Bleaching of Mechanical Pulp

- Use NaOH as the alkali source
- High alkalinity, especially in the initial phase
- Peroxide decomposition and darkening reactions
- High COD load of the effluent
- High anionic trash production
- Decreased light scattering coefficient
- Decreased pulp yield
Mg(OH)$_2$: An Alternative Alkali for Peroxide Bleaching

- Mild alkalinity
- Gradual release of HO$^-$ due to low solubility
- One unit weight of Mg(OH)$_2$ equals to 1.4 NaOH in the capacity of accepting protons.
Mg(OH)$_2$ - $P_M$ Bleaching Process

MC #1

DTPA/Na$_2$S$_2$O$_4$

“$Q_Y$”

MC #2

Mg(OH)$_2$

H$_2$O$_2$

PM
\[ \text{P}_{\text{Mg(OH)}_2} \text{ Versus } \text{P}_{\text{NaOH}} \]

\begin{align*}
\text{P}_{\text{Mg(OH)}_2} & \quad \text{P}_{\text{NaOH}} \\
\text{Lower pH} & \quad \text{Higher pH} \\
\text{Silicate decreased or eliminated} & \quad \text{Silicate needed} \\
\text{Longer time required} & \quad \text{Less sensitive to time} \\
\text{Less dissolved organics} & \quad \text{More dissolved organics} \\
\text{Lower COD} & \quad \text{Higher COD} \\
\text{Less anionic trash} & \quad \text{More anionic trash}
\end{align*}
Objectives

• To compare the Mg(OH)$_2$-based and NaOH-based peroxide bleaching of a eucalyptus CTMP, in terms of
  – Pulp brightness
  – COD
  – Anionic trash
  – Pulp yield
Experimental

• Eucalyptus CTMP from a Brazilian mill
• Chelation: 0.2% DTPA (as 100%), 3% consistency, pH 6.0, 70°C, 30 minutes.
• Bleaching conditions:
  – 2.5%, 4.0%, 6.2% H₂O₂;
  – 1.5%-6.0% NaOH, or 0.5%-2.5% Mg(OH)₂;
  – 16% (MC), 30% (HC) pulp consistency;
  – 80-90 °C, 2-6 hours.
Medium-Consistency (MC) System
Effect of Peroxide and Alkali Charge on Brightness (MC System)

Other bleaching conditions: 2.6% silicate, 0.13% Epsom salt (NaOH-based process), 16% pulp consistency, 80°C, 3 hours
Eucalyptus CTMP vs. Maple CTMP: Mg(OH)$_2$-based Peroxide Bleaching

- The eucalyptus CTMP is less bleachable in the Mg(OH)$_2$-based process, compared with the maple CTMP.
Why Is the Eucalyptus CTMP Less Bleachable in the Mg(OH)$_2$-based Process?

- Wood properties
  - Extractives
  - Lignin
- Pulping process
  - Chemical pretreatment (alkali dosage)
Effect of Acetone Extraction

Without acetone extraction

With acetone extraction

Other bleaching conditions: 2.6% silicate, 0.13% Epsom salt (Na process), 16% pulp consistency, 80°C, 3 hours (6 hours for the Mg process).
## Alkaline Pre-treatment on Peroxide Bleaching of A TMP

<table>
<thead>
<tr>
<th>NaOH %</th>
<th>Mg(OH)$_2$ %</th>
<th>Silicate %</th>
<th>DTPA (40%) %</th>
<th>End pH</th>
<th>Residual H$_2$O$_2$, %</th>
<th>Bright. % ISO</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>Without alkali pre-treatment</td>
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<tr>
<td>1.85</td>
<td>0</td>
<td>2.0</td>
<td>0</td>
<td>7.97</td>
<td>1.24</td>
<td>71.5</td>
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<tr>
<td>1.85</td>
<td>0</td>
<td>0</td>
<td>0.4</td>
<td>7.65</td>
<td>1.24</td>
<td>71.6</td>
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<tr>
<td>0</td>
<td>1.0</td>
<td>0</td>
<td>0.4</td>
<td>7.81</td>
<td>1.70</td>
<td>71.2</td>
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<td>With alkali pre-treatment</td>
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<tr>
<td>1.0</td>
<td>0</td>
<td>2.0</td>
<td>0</td>
<td>9.20</td>
<td>1.43</td>
<td>67.6</td>
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<tr>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0.4</td>
<td>9.39</td>
<td>1.22</td>
<td>67.3</td>
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<tr>
<td>0</td>
<td>1.0</td>
<td>0</td>
<td>0.4</td>
<td>8.90</td>
<td>1.83</td>
<td>62.7</td>
</tr>
</tbody>
</table>
Conductivity of Bleach Filtrate (MC System)

Other bleaching conditions: 2.6% silicate, 0.13% Epsom salt (NaOH-based process), 16% pulp consistency, 80°C, 3 hours
Anionic Trash Formation (MC System)

Other bleaching conditions: 2.6% silicate, 0.13% Epsom salt (NaOH-based process), 16% pulp consistency, 80°C, 3 hours
Summary

• In the MC system
  – The Na process was effective
  – The Mg process gave ~ 5 units lower brightness than the Na process at the same peroxide dosage.
  – But the Mg process produced less anionic trash and conductivity
High-Consistency (HC) System
Effect of Temperature and Time on Brightness (HC System)

NaOH-based Process

- Other bleaching conditions: 2.6% silicate, 0.13% Epsom salt (NaOH-based process), 30% pulp consistency.

Mg(OH)_2-based process
Comparison of the Bleaching Performance at Optimized Conditions (HC)

<table>
<thead>
<tr>
<th>Process</th>
<th>NaOH-based (2.6% silicate, 0.13% Epsom salt, 80 °C, 3 hrs)</th>
<th>Mg(OH)(_2)-based (2.6% silicate, 90 °C, 6 hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{O}_2), %</td>
<td>2.5 4.0 6.2 8.0</td>
<td>2.5 4.0 6.2 8.0</td>
</tr>
<tr>
<td>NaOH, %</td>
<td>2.0 2.5 4.0 4.0</td>
<td>0 0 0 0</td>
</tr>
<tr>
<td>Mg(OH)(_2), %</td>
<td>0 0 0 0</td>
<td>0.75 1.0 1.5 2.0</td>
</tr>
<tr>
<td>Resid. (\text{H}_2\text{O}_2), %</td>
<td>0.60 1.08 1.53 2.30</td>
<td>0.67 1.53 2.05 2.97</td>
</tr>
<tr>
<td>Bright., % ISO</td>
<td>78.5 82.9 85.8 86.9</td>
<td>76.9 80.8 83.2 85.0</td>
</tr>
</tbody>
</table>
For a very high-brightness CTMP

- Peroxide bleaching first
- Followed by the addition of OBA/FWA
Addition of Fluorescent Whitening Agent to Pulps from the Mg(OH)$_2$-based Process

<table>
<thead>
<tr>
<th>FWA (Tinopal UP), %</th>
<th>0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.8</th>
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<tbody>
<tr>
<td>Brightness, % ISO</td>
<td>83.2</td>
<td>85.5</td>
<td>87.2</td>
<td>87.8</td>
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<tr>
<td>Flu. comp., % ISO</td>
<td>0</td>
<td>2.76</td>
<td>4.00</td>
<td>5.17</td>
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<tr>
<td>CIE whiteness, %</td>
<td>59.0</td>
<td>66.9</td>
<td>71.5</td>
<td>72.9</td>
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<tr>
<td>L*</td>
<td>97.1</td>
<td>97.2</td>
<td>97.3</td>
<td>97.3</td>
</tr>
<tr>
<td>a*</td>
<td>-2.12</td>
<td>-1.51</td>
<td>-1.21</td>
<td>-1.04</td>
</tr>
<tr>
<td>b*</td>
<td>7.41</td>
<td>5.71</td>
<td>4.77</td>
<td>4.46</td>
</tr>
</tbody>
</table>

Other bleaching conditions: 6.2 % H$_2$O$_2$, 2.6% silicate, 30% pulp consistency, 90°C, 6 hours.
Total Anionic Trash Formation in the HC System

Cationic demand of filtrate measured at pH 7.0
Sources of Anionic Trash

• Polygalacturonic acids (pectic acids): polymer with uronic type of carboxylic groups (pKa= ~3.4).
• Oxidized lignin: macromolecule with lignin-bound carboxylic groups (pKa= ~5.4).
• Colloidal particles of extractive: aliphatic type of carboxylic groups (pKa= ~5.5-6.4).
De-methylation and Dissolution of Pectins

Pectin

De-esterification

Pectic acids

pKₐ = ~3.4

Dissolution

Anionic trash
Lignin Oxidation and Dissolution

\[ \text{CH}_3\text{O} \longrightarrow \text{Lignin} \]

Oxidation

\[ \text{CH}_3\text{O} \longrightarrow \text{Lignin} \quad \xrightarrow{\text{Oxidation}} \quad \text{CH}_2\text{O} \longrightarrow \text{Lignin} \]

Dissolution

\[ \text{COD} \]

\[ pK_a = \sim 5.4 \]

&

Anionic Trash
Extractives

- Dissolved and dispersed extractives
  - Example: resin acids, fatty acids

Resin acids
pKa = ~5.5-6.4
• The measured amount of anionic trash is pH-dependent.
• But the cationic demand of pectic acids is pH-independent from 4.5 to 7.
The increase of cationic demand with pH is due to:

- Extractives
- Oxidized lignin
Hemicellulose Type of Anionic Trash in Peroxide Bleaching of the Eucalyptus CTMP

Measured as the cationic demand of filtrate measured at pH 4.5
Lignin and Extractives Types of Anionic Trash in Peroxide Bleaching of the Eucalyptus CTMP

Difference of filtrate cationic demand measured between pH 7.0 and 4.5
Comparison of Pulp Yield Loss at Various Brightness Levels

- Lower yield loss for the Mg-based process.
Correlation of Pulp Yield Loss and COD

• The same correlation for both the NaOH-based and Mg(OH)$_2$-based processes
Dissolved Solid (HC system)

![Graph showing dissolved solid in filtrate (g/L) for Na-Based and Mg-based systems at different peroxide concentrations.]

- 2.5% peroxide
- 4.0% peroxide
- 6.2% peroxide

The graph compares the dissolved solid in filtrate (g/L) for Na-Based and Mg-based systems at varying peroxide concentrations.
Filtrate Conductivity (HC System)
Summary

• Under the optimized conditions, the Mg process in the HC system gives 1-2 units lower brightness than the Na process at the same peroxide dosages.

• The Mg process requires higher temperature and longer retention time to reach the brightness targets.

• At a similar brightness, the Mg process has
  – 50-80% less anionic trash
  – 40-50% less COD,
  – 20-30% less loss of pulp yield
  – 50-60% less dissolved solid
  – 50-60% less conductivity
Conclusions

• The Mg(OH)$_2$-based process has been successfully implemented in a number of mills in N.A.

• In comparison with the NaOH-based process, the Mg(OH)$_2$-based process offers:
  – Lower bleaching cost
  – Similar or slightly lower brightness
  – Higher light scattering coefficient
  – Higher pulp yield
  – Lower COD
  – Less anionic trash
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