THE USE OF HYDROGEN PEROXIDE IN THE BLEACHING OF CHEMICAL PULP

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Southeastern TAPPI and TAPPI Bleaching Committee

Joint Meeting

St. Augustine, FL - June 13, 2002
Agenda

• Introduction
• Safety and Handling
• Chemistry
• Process Control
• Bleaching Applications
• New Developments
Agenda

• Introduction
• Safety and Handling
• Chemistry
• Process Control
• Bleaching Applications
• New Developments
Overcoming Bleach Plant Limitations

- short sequences
- eliminate hypochlorite
- prevent dioxin formation
- extend ClO$_2$ capacity to more pulp prod’n
- ECF
  - decrease cost
  - increase brightness
  - increase pulp production
- TCF
Evolution in Hydrogen Peroxide Use

- Add to existing bleaching stages
- Intensify process conditions to get more effect
- Add pretreatment to get more focused effect
- Add specialized process stages and equipment
- Modify chemistry to get different effect
Hydrogen Peroxide Manufacture
Anthraquinone Process

Circulating work solution

H$_2$, O$_2$, H$_2$O$_2$
• clear, colorless liquid
• low vapor pressure
• sp.gr. (50% solution) = 1.19 at 4°C
• freezes at -52°C (50% solution)
• boils at 114°C (50% solution)
• pH 0.5 - 3.5
Freezing Point of Hydrogen Peroxide

Temperature, °C

H$_2$O$_2$ concentration, wt%
Storage System for Hydrogen Peroxide

- **H20** Cooling Water
- **H2O2-STORAGE TANK**: MIN 60 M³
- UNLOADING STATION
- REMOTE SETPOINT FROM PROCESS
- Dosing Tank: 2-4 M³
- **H2O2 TO DILUTION**
- **P1**
- **P2**
- **P3**
- **FIC**

**Point A**
• Introduction
• Safety and Handling
• Chemistry
• Process Control
• Bleaching Applications
• New Developments
Hazards

- Oxidizer
- Corrosive
- Dangerously Reactive
Personal Protective Equipment

- Splash-proof goggles (and face shield)
- Rubber gloves and boots
- Acid suit
Hazard of Combustion

- Peroxide, itself, does not burn
- Decomposition reaction is exothermic
  - produces heat and oxygen
- Remove combustible materials
- Water removes heat and decreases reactivity
Hazard of Pressurization

- Decomposition in pump
- Decomposition in storage tank
- Non-pulp & paper: Submarine Kursk
Hazard of Pressurization

- Decomposes continuously at slow rate
- Pressure increase in “closed” systems
  - storage tank vents
  - piping PRVs
  - ball valves drilled on upstream side
- Design systems to limit potential for contamination
- Use approved materials only
- Passivate process contact surfaces
Volume of Oxygen Released at Decomposition of H$_2$O$_2$
Stainless Steel Ball Valves

Vent hole is required to prevent entrapment in the cavity of the valve body.
Pumps for Hydrogen Peroxide

CENTRIFUGAL

SS 316 or 304 wetted parts

Process flush single mechanical seals: only seals of silicon carbide with Kal-Rez “O” Rings.
  - Ease of operation and maintenance
  - Requires recirculation line for assured minimum flow
  - Greater range of control of flow with flow meter and flow control valve (most common in industry)
  - Allows multiple application from one header

METERING OR POSITIVE DISPLACEMENT

SS 316 or 304 Teflon® wetted components.

Can provide very small flow control.

Requires pulsation damper for uniform flow and pressure regulating device for proper operation.

Can achieve high pressure discharge.

Has a tendency to vapor lock if shut down.

Built in check valve can be a problem.
Most Common Materials Compatible with Hydrogen Peroxide in Concentrations of 70%, 50% and 5%

<table>
<thead>
<tr>
<th><strong>Compatible</strong></th>
<th><strong>Incompatible</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Storage Tanks</strong> - wetted parts only</td>
<td>Exterior Structural</td>
</tr>
<tr>
<td>Aluminum 5254</td>
<td>Aluminum 6061T</td>
</tr>
<tr>
<td>Stainless Steel 316L, 304L</td>
<td>High carbon content SS</td>
</tr>
<tr>
<td><strong>Piping</strong> Stainless Steel 316L, 304L</td>
<td>Carbon Steel</td>
</tr>
<tr>
<td><strong>Wetted Parts Pumps</strong> Valves ASTM A- 312 and Hoses</td>
<td>All other Metals</td>
</tr>
<tr>
<td>Stainless Steel 316, 304, 321, and Teflon®</td>
<td>Carbon Steel, Brass and most other materials</td>
</tr>
<tr>
<td><strong>Pump Seals</strong> - Silicon Carbide, Glass filled</td>
<td>Carbon and most other materials</td>
</tr>
<tr>
<td>Teflon® on 316SS</td>
<td>Asbestos Graphite and most other materials</td>
</tr>
<tr>
<td>Kal-Rez “O” Rings, Viton®</td>
<td>Brass</td>
</tr>
<tr>
<td><strong>Gaskets</strong> Teflon®, Gylon®, Tygon®, Teflon® envelope</td>
<td>Silicone, mineral oil and most other fluids</td>
</tr>
<tr>
<td><strong>Pressure Gauges</strong> 316 Stainless Steel</td>
<td>ABS, Brass, Copper, Lead, Mercury</td>
</tr>
<tr>
<td><strong>Liquid pressure gauges</strong> 316 Stainless Steel filled with Flurolube® or Krytox®</td>
<td></td>
</tr>
<tr>
<td><strong>Lab Supplies</strong> Glass, Stainless Steel 316, 304, Tygon®, Polyethylene, PVC, Teflon®</td>
<td></td>
</tr>
</tbody>
</table>
Materials of Construction

Acceptable:

• 316L (304,304L) stainless steel
• 5254 aluminum

Not Acceptable:

• carbon steel
• brass
• copper
• zinc
Materials of Construction

Titanium

- high “Handbook” corrosion rate
- significant corrosion potential at:
  - > 0.2% $\text{H}_2\text{O}_2$ in solution (≥ 2% on pulp @10% Cs)
  - > pH 11
  - > 90°C
- corrosion inhibited by Ca and Mg
- corrosion has not been an issue in refit TCF sequences
• Introduction
• Safety and Handling
• Chemistry
• Process Control
• Bleaching Applications
• New Developments
Chemistry
Perhydroxyl Anion

\[ \text{H}_2\text{O}_2 + \text{HO}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \]

\[ pKa = 11.6 \text{ at } 25^\circ\text{C} \]
Chemistry
Radicals

\[ \text{H}_2\text{O}_2 + \text{M}^{n+} \rightarrow \text{OH}^{-} + \text{M}^{(n+1)+} + \cdot\text{OH} \]

\[ \text{M}^{(n+1)+} + \text{OOH}^{-} \rightarrow \text{M}^{n+} + \cdot\text{O}_2^{-} + \text{H}^{+} \]
Assay Methods

Pure solution
  • Density

Process residual
  • KI-Thio titration

Differentiation from ClO₂
  • 2° titration with Ceric Sulphate
  • peroxide-specific Ti⁴⁺ indicator
  • Peroxidase analytical sticks
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Process Control

pH

Conditions: 8 kg H₂O₂/metric ton, 82°C, 12 min at 30 psig
60 min at atm. press.

(EOP) - stage brightness, % ISO

(EOP) - stage final pH
Process Control
Temperature and Time

H$_2$O$_2$ charge: 35 kg/metric ton
Consistency: 10-12%

Brightness, % ISO

Retention time, h
Process Control

Consistency

![Graph showing the relationship between Pulp consistency and Brightness (ISO)]

- **Brightness, % ISO**
  - 75
  - 76
  - 77
  - 78
  - 79
  - 80
  - 81
  - 82
  - 83
  - 84
  - 85

- **Pulp consistency, %**
  - 10
  - 15
  - 20
  - 25
  - 30
  - 35

- **Kappa number of oxygen-delignified pulp**: 9
- **(PO) stage**: 100°C, 2 h

- **H₂O₂ Change, kg/metric ton**
  - 40
  - 20
Process Control
Peroxide Charge

![Graph showing the relationship between hydrogen peroxide charge and brightness (ISO)]

- (PO): 110°C, 2h, 5 bar
- (PO): 100°C, 2h, 5 bar
- P: 90°C, 4h

Brightness, % ISO vs. Hydrogen peroxide charge, kg/metric ton.
Process Control

Metals Removal

P-stage: 25 kg H$_2$O$_2$/metric ton, 90°C, 4 h

EDTA in Q, % on pulp

- 1.2
- 0.6
- 0.2

OQP brightness, % ISO

Sodium hydroxide in P-stage, kg/metric ton

OP
Process Control

Metals Removal

![Graph showing the relationship between sodium hydroxide in the P-stage and OQP brightness.](image)

- **P-stage:** 25 kg H₂O₂/metric ton, 90°C, 4h
- **X-axis:** Sodium hydroxide in P-stage, kg/metric ton
- **Y-axis:** OQP brightness, % ISO
- **Points:**
  - 0.2% DTPA in P-stage
  - No DTPA in P-stage
Process Control
Magnesium

![Graph showing the relationship between hydrogen peroxide consumption and brightness, with curves for QZQP, QZQP*, and QZP, and conditions for Z-stage, P-stage, and P*-stage.]

- Z-stage: 0.5% O₃, pH 2
- P-stage: 90°C
- P*-stage: 90°C, includes Mg addition
• Introduction
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Effectiveness of Applications

- Consumption in non-bleaching reactions
  - chemical carryover
  - organic carryover
  - metals

- Optimized process conditions

- Mixing
Peroxide-Reinforced Oxygen Delignification

![Graph showing viscosity and kappa number relationship](image-url)
Peroxyde-Reinforced Oxygen Delignification
Peroxide-Reinforced Brownstock Eop

![Graph showing the relationship between percent ClO₂ substitution in C-stage and AOX* (kg/air-dry metric ton bleached pulp)]
Peroxide-Reinforced E1-Stage

- Decrease colour
- Eliminate dioxin in $C_D$
- Decrease AOX in $D_C$
- Decrease cost and increase brightness in $D_E$
Peroxide-Reinforced E1-Stage

![Graph showing DE vs. Kappa Factor with DE₀ and DE₊ lines.]

Northem Softwood Kraft
Kappa No. 30

- DE₀
- DE₊
Peroxide-Reinforced E1-Stage
Peroxide-Reinforced E1-Stage
Peroxide-Reinforced E2-Stage

- higher ClO$_2$ replacement ratio (>2:1)
- limited H$_2$O$_2$ consumption (<2 kg/tp)
- lower pH target than for Eop-stage
Peroxide in Bleached Pulp Storage

- improved brightness stability
- complicated process control
- decreased bleach plant operating flexibility
Peroxide in Bleached Pulp Storage

![Graph showing the brightness of bleached pulp with different peroxide concentrations over time. The x-axis represents retention time in hours, and the y-axis represents brightness in % Elrepho. Three lines represent different peroxide concentrations: 0.1% H₂O₂, 0.2% H₂O₂, and 0.3% H₂O₂. All bleaching is at 49 degrees Celsius.]

- 0.1% H₂O₂
- 0.2% H₂O₂
- 0.3% H₂O₂
Final Peroxide Brightening Stage

(EOP)-Q-P Bleaching
1.2% EDTA in Q
2.5% H₂O₂ in P

P-stage
4 h, 90°C
2 h, 90°C
4 h, 70°C
2 h, 70°C

(EOP)-P
Control
2 h, 70°C

ISO Brightness after (EOP)-Q-P, %

NaOH added in P, % on pulp (dry basis)
Final Peroxide Brightening Stage

- high pressure, high temperature
- low metals content
- Mg/Mn > 100
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Final Peroxide Brightening Stage
PO Stage in a TCF Bleach Plant
TCF Bleaching

Hardwood

EDTA  0.8 - 1.3 kg/t
H₂O₂  5 kg/t
NaOH  10 kg/t
MgSO₄ 1 kg/t

PAA  4-5 kg/t

EDTA  1.3 kg/t
H₂O₂  19 kg/t
NaOH  11 kg/t

Final pH: 5
H₂O₂ residual: 1 kg/t

Final pH: 5.8
H₂O₂ residual: 5.2 kg/t

Final pH: 9.8
TCF Bleaching

O₂ Stage

- Brightness: 59.3 %ISO
  Kappa: 9
  Viscosity: 1025 dm3/kg

- Brightness: 76.3 %ISO
  Kappa: 7.4
  Viscosity: 976 dm3/kg

- Brightness: 79.4 %ISO
  Kappa: 5.8
  Viscosity: 954 dm3/kg

- Brightness: 88.7 %ISO
  Kappa: 4.8
  Viscosity: 818 dm3/kg

Hardwood
Modify Peroxide Chemistry

- Peroxide Bleaching Enhancers
- Peracids
  - *in situ* formation
  - distilled Peracetic Acid, PAA
- Metal Catalysis, mP
## Oxidation Potentials of Bleaching Chemicals

<table>
<thead>
<tr>
<th>Oxidation Reaction</th>
<th>Oxidation Potential, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{O}_2 + \text{H}_2\text{O}$</td>
<td>2.07</td>
</tr>
<tr>
<td>$\text{HClO}_2 + 3\text{H}^+ + 4\text{e}^- \rightarrow \text{Cl}^- + 2\text{H}_2\text{O}$</td>
<td>1.56</td>
</tr>
<tr>
<td>$\text{HOCl} + \text{H}^+ + 2\text{e}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O}$</td>
<td>1.49</td>
</tr>
<tr>
<td>$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$</td>
<td>1.36</td>
</tr>
<tr>
<td>$\text{ClO}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{HClO}_2$</td>
<td>1.15</td>
</tr>
<tr>
<td><strong>$\text{CH}_3\text{CO}_3\text{H} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O}$</strong></td>
<td><strong>1.06</strong></td>
</tr>
<tr>
<td>$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Cl}^- + 2\text{OH}^-$</td>
<td>0.90</td>
</tr>
<tr>
<td>$\text{HOO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 3\text{OH}^-$</td>
<td>0.87</td>
</tr>
<tr>
<td>$\text{ClO}_2^- + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow \text{Cl}^- + 4\text{OH}^-$</td>
<td>0.78</td>
</tr>
<tr>
<td>$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$</td>
<td>0.40</td>
</tr>
</tbody>
</table>
Production of Peracetic Acid

\[
\text{H}_3\text{C} = \text{C} - \text{O} + \text{H}_2\text{O}_2 \rightarrow \text{H}_3\text{C} = \text{C} - \text{O} - \text{OH} + \text{H}_2\text{O}
\]

acetic acid + hydrogen peroxide → peracetic acid + water

catalyst
Production of Distilled Peracetic Acid

Hydrogen peroxide

Acetic acid

Catalyst

Stabilizer

ePAA Product storage

dPAA Product storage

Water
Generation of Caro’s Acid

Effect of Molar Ratio and Concentration of Feed Chemicals

[Graph showing the effect of molar ratio and concentration of feed chemicals on peroxide conversion. The graph includes lines for 65% Oleum, 70% H₂O₂, and 50% H₂O₂. The x-axis represents the molar ratio of 98% H₂SO₄/H₂O₂, and the y-axis represents peroxide conversion in percentages.]
# Chemical Impact of Peracid Addition

## Need of neutralisation & side products

<table>
<thead>
<tr>
<th></th>
<th>dPAA</th>
<th>ePAA</th>
<th>PFA</th>
<th>Caro's acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peracid, kg/tp *</td>
<td>10</td>
<td>10</td>
<td>7.9</td>
<td>15</td>
</tr>
<tr>
<td>NaOH Demand, kg/tp **</td>
<td>1</td>
<td>4</td>
<td>26</td>
<td>20</td>
</tr>
<tr>
<td>By-Product</td>
<td>acetic acid</td>
<td>CH₃COONa</td>
<td>HCOONa</td>
<td>Na₂SO₄</td>
</tr>
<tr>
<td>Na, kg/tp</td>
<td>negligible</td>
<td>4.6</td>
<td>29.9</td>
<td>23</td>
</tr>
<tr>
<td>S, kg/tp</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>9.9</td>
</tr>
</tbody>
</table>

* amount needed for delignification of 3 kappa units
** amount of NaOH needed for adjusting the pH to 5
PAA in Final D-Stage
Softwood

Effect of ClO₂ Dosage

Brightness, %ISO

ClO₂, kg/tp (act. Cl)

ClO₂ + 2 kg Paa/tp
ClO₂ alone
PAA Post-Bleaching
Process Conditions

- Temperature: 40 - 70°C
- pH: 4 - 7
- PAA charge: < 3 kg/tp
- Fast reaction...even at low consistency
PAA Post-Bleaching
Benefits at Pulp Mill

• Decreased usage of ClO₂
  • decreased AOX
  • extra pulp production if ClO₂ capacity is a bottleneck

• Improved pulp quality
  • higher and less variable brightness
  • improved brightness stability (less yellowing)
  • less variable pH

• No brightness reversion

• Easy to install and use
PAA in Bleached Pulp Storage Tower

White water

D₂-washer

Pulp from pulp plant

PAA

Bleached pulp

Storage tower

pH 5-6
T: 55 °C

Effluent tank

Pulp to papermachine

pulp out

1 - 2 kg/tp PAA ≈ + 2 %ISO
Effect of PAA Charge on Brightness

softwood kraft pulp, initial Br. 89.8%ISO, kappa 0.4, viscosity 834 dm³/kg
PAA in Bleached Pulp Storage Tower

Effect of Time and Consistency on Brightness

Softwood kraft pulp, initial Br. 89.8%ISO, PAA @ 1.5 kg/tp
PAA in Bleached Pulp Storage Tower

Effect on Yellowness

PAA @ 2 kg/tp, final pH 5, 50°C, 60 min, Cs 10%

b* - yellow/blue axis

δE* - calculated difference in L,a*,b* space...corresponds to a visually perceived colour difference
PAA in Bleached Pulp Storage Tower
Mill Trial

Stora Enso - Veitsiluoto Pulp Mill, Kemi

PAA @ 2.5 kg/tp

avg. Br gain = 1.9 pts, std.dev. decreased by 30%

Softwood
# Brightening with Peracetic Acid

## Veitsiluoto Pulp Mill Trial

<table>
<thead>
<tr>
<th></th>
<th>Reference</th>
<th>PAA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tensile index, Nm/g</strong></td>
<td>SR 20</td>
<td>82.4</td>
</tr>
<tr>
<td></td>
<td>SR 30</td>
<td>94.6</td>
</tr>
<tr>
<td><strong>Tear index, mNm²/g</strong></td>
<td>SR 20</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>SR 30</td>
<td>7.9</td>
</tr>
<tr>
<td><strong>Viscosity, dm³/kg</strong></td>
<td></td>
<td>718</td>
</tr>
</tbody>
</table>
PAA: Effect on Microbial Growth

PAA added to ECF kraft bleached pulp storage chest

- Total microbes, 100,000/ml

**Reference period**

**Test period:**
- PAA in storage chest

**After PAA trial**
PAA: Effect on Optical Brighteners

Improved light emission at 457 nm

Graph showing the effect of PAA on OBA:
- Blue line: PAA 0 kg
- Red line: PAA 1 kg

Conditions:
- Pine:birch:euca=20:60:20
- 8% consistency
- 30 min.
- 40°C
- pH 7-7.5
- Pulp dewatered prior to OBA addition
PAA Post-Bleaching
Benefits at Fine Paper Machine

- Decreased demand for optical brighteners
- Stabilized surface charge on fibres
- Improved AKD/ASA size retention
  - size retention from 60-70% to 90-95%
  - decreased AKD content in white water
  - cleaner press section (fewer breaks, holes, and dirty spots)
  - decreased hydrolysis of AKD
    - decreased formation of ketones
      - copy machines run more cleanly
- Biocide-free paper production