CHLORINE DIOXIDE BLEACHING

Presented by:

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PURPOSE OF CHEMICAL BLEACHING

- Selectively Remove Lignin
- Brighten Pulp
- Remove Contaminants
- Remove Extractives
MAJOR WOOD COMPONENTS AT DIFFERENT STAGES OF DELIGNIFICATION

MacLeod, M., PAPRICAN, TAPPI Kraft Pulping
BLEACHING OF PULP

• **Sequence Development - Chemical Pulps**
  
  • Pre-bleaching to remove residual lignin
    – Fragmentation from the cellulose portion in an oxidation/substitution step
    – Solution of fragments for removal in washing
  
  • Final bleaching or brightening by oxidation of coloring material
    – Chemical selectivity important because of low lignin to cellulose ratio
## BLEACHING AGENTS

<table>
<thead>
<tr>
<th></th>
<th>Chlorine</th>
<th>Sodium Hypochlorite</th>
<th>Chlorine Dioxide</th>
<th>Oxygen</th>
<th>Hydrogen Peroxide</th>
<th>Ozone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage Design.</td>
<td>C</td>
<td>H</td>
<td>D</td>
<td>O</td>
<td>P</td>
<td>Z</td>
</tr>
<tr>
<td>Chem. Form.</td>
<td>Cl₂</td>
<td>NaOCl</td>
<td>ClO₂</td>
<td>O₂</td>
<td>H₂O₂</td>
<td>O₃</td>
</tr>
<tr>
<td>Delig. Eff.</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>P/F</td>
<td>F</td>
<td>G</td>
</tr>
<tr>
<td>Bright. Eff.</td>
<td>P</td>
<td>E</td>
<td>E</td>
<td>P</td>
<td>E</td>
<td>G</td>
</tr>
<tr>
<td>Selectivity</td>
<td>G</td>
<td>F/P</td>
<td>E</td>
<td>F</td>
<td>E</td>
<td>P</td>
</tr>
<tr>
<td>Shive Reduct.</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>F</td>
<td>F</td>
<td>P</td>
</tr>
<tr>
<td>Envir. Impact</td>
<td>P</td>
<td>P</td>
<td>G/E</td>
<td>G/E</td>
<td>G/E</td>
<td>G/E</td>
</tr>
<tr>
<td>Total Cost</td>
<td>I</td>
<td>I</td>
<td>Ex</td>
<td>I</td>
<td>M/Ex</td>
<td>VE</td>
</tr>
</tbody>
</table>

E = Excellent       G = Good       F = Fair       P = Poor
I = Inexpensive      M = Moderate      Ex = Expensive      VE = Very Expensive

Developed from TAPPI: Pulp Bleaching, Principles and Practice
COMMON BLEACHING TERMS

- Kappa number (Kp#) measure of lignin content
  - Lignin~(Kp#)*0.15
- Permanganate number (K#) measure of lignin content
  - K# ~ (Kp#)*0.67
- Active chlorine (aCl) term used to relate chlorine based bleaching compounds
  - aCl = (2.63* ClO₂) + Cl₂
- Kappa Factor = (aCl as % on pulp)/ (kappa number)
- Oxidative Equivalents (OXE) term used to convert bleaching compounds.
  - OXE is the quantity of substance that receives one mole of electrons when a substance is reduced.
## OXE FOR BLEACHING CHEMICALS

<table>
<thead>
<tr>
<th>Chemical</th>
<th>OXE/kg</th>
<th>aCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂</td>
<td>28.20</td>
<td>1.0</td>
</tr>
<tr>
<td>ClO₂</td>
<td>74.12</td>
<td>2.63</td>
</tr>
<tr>
<td>O₂</td>
<td>125.00</td>
<td>4.43</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>58.79</td>
<td>2.09</td>
</tr>
<tr>
<td>O₃</td>
<td>125.00</td>
<td>4.43</td>
</tr>
</tbody>
</table>
FACTORS EFFECTING ClO₂ PERFORMANCE

- Active Chlorine Distribution
- pH
- Charge
- Retention Time / Temperature
- Chemical Variants
  - mixing, lignin, carryover, consistency
MULTI-STAGE BLEACHING

Graph showing the relationship between chlorine dioxide concentration and brightness. The graph includes three lines:
- Purple line labeled Do-Eo
- Blue line labeled D1
- Red line labeled D2

The x-axis represents chlorine dioxide concentration (%), ranging from 0.2 to 1.8. The y-axis represents brightness (%ISO), ranging from 72 to 96. The graph illustrates how each line's brightness changes as the chlorine dioxide concentration increases.
ClO$_2$ DISTRIBUTION EFFECT ON TOTAL USAGE

Sequence: D (EO) D, 14 Kappa (9.4 K#)
Reference: EC bleaching model
D$_1$ VERSUS D$_1$+ D$_2$ ClO$_2$ DEMAND FOR BRIGHTENING

Reference: Axegard, et al., “E2 Stage Improves the Reactivity of Pulp Towards Chlorine Dioxide”
D₀ STAGE OPERATIONS
EFFECT OF pH IN $D_0$ STAGE (SW)

DELIGNIFICATION EFFICIENCY

![Graph showing delignification efficiency with Kappa Factor on the x-axis and Eop Kappa # on the y-axis. The graph compares SW and HW with two lines: red for SW and blue for HW.](image-url)
KAPPA NUMBER VS TIME

Kappa = 31, $K_f = 0.20$, $T = 45^\circ C$

Source: A Mathematical Model for Chlorine Dioxide Delignification; Savoie, Martin and Tessier, Patrick, TAPPI Journal June 1997
EFFECT OF COD CARRYOVER
(SW - O₂ Delig.)

![Graph showing the effect of COD carryover with SW-O₂ Delig.](image-url)
BLEACH PLANT OPERATIONS
$D_0$ STAGE SUMMARY

- $D_0$ Stage pH optimum at 2.5 - 3.2
- Temperature 120 - 130 F, depending on time
- Allow for COD carryover in charge
- $D_0$ Kappa Factor 0.18 - 0.22 for Economic & Environmental
- Residual not necessary
- Charge approx. 50 - 60 % of total active chlorine for $D_0$
- Brightness / Kappa relationship difference for Hardwood
EFFECT OF TERMINAL pH ON D1 STAGE

- Brightness at End of D1
- Chlorate + Chlorite
- Chlorite
- Chlorate

pH at End of D1

%Active Chlorine

Brightness at End of D1
EFFECT OF pH AND ClO₂ CHARGE ON D₁ STAGE BRIGHTNESS

O₂ - Delignified ECF Softwood Kraft, Kappa # 18 (K# 11.3)
Proceedings of 1991 Appita Annual General Conference
EFFECT OF END pH IN D₁ STAGE ON SHIVES IN PULP AFTER THE D₁ STAGE

Reference: *Pulp Bleaching - Principles and Practice*; C. Dence & D. Reeve
BLEACH PLANT OPERATIONS
D₁ STAGE SUMMARY

• Maintain residual 0.02-0.05 gpl for brightness

• Operate pH 3.5-4.5

• Lower pH leads to improved shive bleaching but also strength and viscosity loss

• Temperature range 160-175° F

• Charge approx 30-40% of total active chlorine
EFFECT OF RESIDUAL AND TEMPERATURE ON BRIGHTNESS

- Residual ClO₂
- No residual

Brightness, % ISO

- 40 lb/T ClO₂
- 30 lb/T ClO₂
- 20 lb/T ClO₂

Time (min)
D₁ EFFECT ON D₂ BRIGHTNESS CEILING

![Graph showing the effect of D₁ Chlorine Dioxide on D₂ Brightness.]

- D₁ Chlorine Dioxide, % on Pulp
- Brightness, %GE

Rapson, W.H., “Bleaching of Pulp”. Tappi Monograph
BLEACH PLANT OPERATIONS
D₂ STAGE SUMMARY

- Operate pH 3.5 - 5.0
- Temperature range 155 - 175 ºF
- Maintain residual at 0.02 - 0.05 gpl
- Residual important for brightness stability
- Important to stay away from brightness ceiling
QUESTIONS?