Ozone and Chlorine Dioxide

Oxygen, Ozone & ClO2,
The Flexible Bleach Plant

TAPPI BLEACHING
June 13 2002

by
Gord Homer

Presented June 13 2002 by Gordon Homer
Ozone and Chlorine Dioxide

**ECF - Z Bleaching is the future**

- Ozone is no longer restricted to TCF Pulps
- ECF pulps treated with Ozone will soon be standard
- Mills are moving strongly to Ozone/Chlorine dioxide
  - E.B Eddy (DOMTAR): extremely good results on the HW line
  - Wisaforest: $O_3$ in 2 lines (SW & HW), 3 injection points
  - Votorantim: $O_3$ in 2 mills, already ordered $O_3$ on a new line. *This will be the third system for Votorantim*
  - Japanese pulp industry will soon switch to $O_3$ as it is best alternative to $ClO_2$ for replacing $Cl_2$. Two mills operating and a third ordered, four under discussion

Presented June 13 2002 by Gordon Homer
Ozone and Chlorine Dioxide

Ozone (O3) is becoming more and more part of ECF Evolution

ECF Pulp Production: 48 Mt/year

ECF - Z Pulp Production 2000: 3 Mt/year

ECF - Z Pulp Production in 2001: 3.5 Mt/year (+17%)

ECF - Z Pulp Production in 2002: up to 5 Mt/year

Source: AET / AL

Presented June 13 2002 by Gordon Homer
# Ozone Bleaching Installations

<table>
<thead>
<tr>
<th>Mill</th>
<th>Location</th>
<th>Size (kg/h)</th>
<th>Start-Up</th>
<th>Sequence</th>
<th>Pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>LENZING</td>
<td>Lenzing(AUS)</td>
<td>40*</td>
<td>1992</td>
<td>(EOP)ZP</td>
<td>MC Kvaerner</td>
</tr>
<tr>
<td>UNION CAMP</td>
<td>Franklin, VA(USA)</td>
<td>280</td>
<td>1992</td>
<td>OZEoD</td>
<td>HC Sunds</td>
</tr>
<tr>
<td>SODRA CELL</td>
<td>Monseraas(SWE)</td>
<td>210</td>
<td>1992</td>
<td>OQPZP</td>
<td>MC Kvaerner</td>
</tr>
<tr>
<td>STORA</td>
<td>Skoghall(SWE)</td>
<td>40*</td>
<td>1992</td>
<td>O A Z/D Eop DEpD</td>
<td>MC Kvaerner</td>
</tr>
<tr>
<td>MODO PAPER</td>
<td>Hussum(SWE)</td>
<td>200*</td>
<td>1993</td>
<td>O QP Z(PO) Q P Z/D</td>
<td>MC Ahlstrom</td>
</tr>
<tr>
<td>KYMENE</td>
<td>Pietersaari(FIN)</td>
<td>100/100*</td>
<td>1993/94</td>
<td>OA Z/D Eop Z/D EpD</td>
<td>MC Ahl/Kva</td>
</tr>
<tr>
<td>METSA-BOTNIA</td>
<td>Kaskinen(FIN)</td>
<td>300*</td>
<td>1994</td>
<td>OOO Z P D, OO Z P</td>
<td>MC Ahlstrom</td>
</tr>
<tr>
<td>PETERSON</td>
<td>Saffle(SWE)</td>
<td>30*</td>
<td>1995</td>
<td>ZEP</td>
<td>MC</td>
</tr>
<tr>
<td>SCA</td>
<td>Ostrand(SWE)</td>
<td>&gt;&gt;100*</td>
<td>1995</td>
<td>Q Op Z (PO)</td>
<td>HC Sunds</td>
</tr>
<tr>
<td>SAPPI</td>
<td>Ngodwana(SAF)</td>
<td>270*</td>
<td>1995</td>
<td>O Z/D E D</td>
<td>HC Sunds</td>
</tr>
<tr>
<td>PONDEROSA</td>
<td>Memphis,(USA)</td>
<td>70*</td>
<td>1995</td>
<td>Propr. Rec Pulp</td>
<td>MC Ahlstrom</td>
</tr>
<tr>
<td>BACEL</td>
<td>Caamcarai(BRA)</td>
<td>70*</td>
<td>1995</td>
<td>TCF</td>
<td></td>
</tr>
<tr>
<td>METSA-RAUMA</td>
<td>Rauma(FIN)</td>
<td>420*</td>
<td>1996</td>
<td>TCF</td>
<td>MC</td>
</tr>
</tbody>
</table>

*Air Liquide/Ozonia

Presented June 13 2002 by Gordon Homer
# Ozone Bleaching Installations (2)

<table>
<thead>
<tr>
<th>Mill</th>
<th>Location</th>
<th>O&lt;sub&gt;3&lt;/sub&gt; (kg/h)</th>
<th>Start-Up</th>
<th>Sequence</th>
<th>Pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONSOLIDATED</td>
<td>Wisc. Rap., (USA)</td>
<td></td>
<td>1996</td>
<td></td>
<td>HC Valmet</td>
</tr>
<tr>
<td>PONDEROSA FIBRES</td>
<td>North Hampton (NH)</td>
<td>135</td>
<td>1997</td>
<td>Propr. Rec. Pulp</td>
<td>MC Ahlstrom</td>
</tr>
<tr>
<td>VCP</td>
<td>Luis Antonio, (BRA)</td>
<td>180</td>
<td>1996</td>
<td>O Z/D Eo D</td>
<td>MC Ahlstrom</td>
</tr>
<tr>
<td>VCP Line A</td>
<td>Jacarei, (BRA)</td>
<td>180</td>
<td>1997</td>
<td>OOp Z/D, OOp Z (PO)</td>
<td>MC Kvaerner</td>
</tr>
<tr>
<td>KLABIN</td>
<td>Monte Alegre, (BRA)</td>
<td></td>
<td>1997</td>
<td>TCF</td>
<td></td>
</tr>
<tr>
<td>E.B. EDDY</td>
<td>Espanola, Ont (CAN)</td>
<td>135</td>
<td>1999</td>
<td>O Z/D E DnD</td>
<td>MC Ahlstrom</td>
</tr>
<tr>
<td>MATUSSIERE &amp; FORET</td>
<td>(FRA)</td>
<td>40</td>
<td>1999</td>
<td>Z P</td>
<td>HC Andritz</td>
</tr>
<tr>
<td>ROSENTHAL</td>
<td>(GER)</td>
<td>110</td>
<td>2000</td>
<td>Q(OP)(DQ) (ZPO)(PP)</td>
<td>HC Valmet</td>
</tr>
<tr>
<td>NIPPON PAPER</td>
<td>Yufutsu, (JAP)</td>
<td>120</td>
<td>2001</td>
<td>O Z/D Ep D</td>
<td>MC Ahlstrom</td>
</tr>
<tr>
<td>BURGO</td>
<td>Ardennes, (BEL)</td>
<td>280</td>
<td>2001</td>
<td>OO D (ZEo) (DD)</td>
<td>HC Metso</td>
</tr>
<tr>
<td>OJI</td>
<td>Nichinan, (JAP)</td>
<td>175</td>
<td>2001</td>
<td>O (Z/D) EoD</td>
<td>HC Metso</td>
</tr>
<tr>
<td>VCP New Line B</td>
<td>Jacarei, (BRA)</td>
<td></td>
<td>2002</td>
<td>O A Z D P</td>
<td>HC Metso</td>
</tr>
</tbody>
</table>

Air Liquide/Ozonia

Presented June 13 2002 by Gordon Homer
Ozone and Chlorine Dioxide

Ozone Supply Capacity

O3 Kg/h

- New
- Existing

Presented June 13 2002 by Gordon Homer
## D/Z for Pulp Bleaching

**Mill Systems Using D/Z, Z/D**

<table>
<thead>
<tr>
<th>ZD Mills</th>
<th>Location</th>
<th>Sequence</th>
<th>Pulp</th>
<th>Mill</th>
<th>R.Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nippon</td>
<td>Yufutsu (JAP)</td>
<td>O (Z/D) EoD</td>
<td>HWK</td>
<td>MC</td>
<td></td>
</tr>
<tr>
<td>Votorantim</td>
<td>Jacarei-Line B (BRA)</td>
<td>O A Z D P</td>
<td>EUK</td>
<td>MC</td>
<td></td>
</tr>
<tr>
<td>OJI</td>
<td>Nichinan (JAP)</td>
<td>O Z/D Eo D</td>
<td>HWK</td>
<td>HC</td>
<td></td>
</tr>
<tr>
<td>Burgo</td>
<td>Ardennes (BEL)</td>
<td>OO D (ZEo) (DD)</td>
<td>HWK</td>
<td>HC</td>
<td></td>
</tr>
<tr>
<td>Eddy</td>
<td>Espanola (CAN)</td>
<td>O Z/D E DnD</td>
<td>HWK</td>
<td>MC</td>
<td></td>
</tr>
<tr>
<td>Votorantim</td>
<td>Luis Antonio (BRA)</td>
<td>OO (Z/D) EoD</td>
<td>EUK</td>
<td>MC</td>
<td>1.7</td>
</tr>
<tr>
<td>Votorantim</td>
<td>Jacarei (BRA)</td>
<td>OO Z D PO</td>
<td>EUK</td>
<td>MC</td>
<td>1.7</td>
</tr>
<tr>
<td>Wisaforest</td>
<td>Pietersaari (FIN)</td>
<td>OO Z/D EoO Z/D E D</td>
<td>HWK</td>
<td>MC</td>
<td>2.5</td>
</tr>
<tr>
<td>Wisaforest</td>
<td>Pietersaari (FIN)</td>
<td>OO Z/D OEo D P</td>
<td>SWK</td>
<td>MC</td>
<td>2.8</td>
</tr>
<tr>
<td>Sappi</td>
<td>Ngodwana (SAF)</td>
<td>O A Z/D E D</td>
<td>HWK</td>
<td>HC</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Trends is toward D/Z or Z/D, last 5 are mainly Z/D systems... Accepted technology now
EB EDDY REPORTED CONCLUSIONS

• Reduced bleaching cost by 8% and increased brightness by 0.5% ISO on a hard to bleach pulp.
• No impact on viscosity or mechanical strength
• Reduced DCM extractives by 30 to 50%
• Reduced TOX pulp content by 50 to 70%
• Reduced hardwood bleach plant AOX by 65%
• Reduced hardwood bleach plant effluent COD by 18%
• Reduce overall mill color (2 lines) by 27%. This assumes over a 50% reduction in the ozonated hardwood line.

Fred Munro, IPBC, Halifax, June, 26, 00
Ozone and Chlorine Dioxide

Domtar, E. B. Eddy Specialties

O-A-Z/D-Ep-Dn - D

Ozone consumption 5.0 kg/ADT

Final AOX 0.18 kg/ADMT  Color reduction 27% of total Mill Color

AOX Reduction 60% from hardwood  COD reduction 18%

Final Brightness >90.5 % ISO  TOX, (Birch) 40 ppm (160 in ECF)

DCM reduction 50 %  Cost 10% reduction

Replacement Ratio 2.2 to 3.5 plus  Raw wood species Aspen, Maple, & Birch

Presented June 13 2002 by Gordon Homer
Ozone and Chlorine Dioxide

E Stage Effluent Colour - ECF vs. Z ECF

Presented June 13 2002 by Gordon Homer

Courtesy Of FRED MUNRO
E B Eddy
Ozone and Chlorine Dioxide

DOMTAR BLEACHING SEQUENCE

Hardwood

D/C E H D E D  (60% sub)
D Ep D E D
D Ep Dn D
Z/D E Dn D
A Z/D E Dn D  (Current)
A Z E D  (Future)
Round Robin Objectives

➡ To equivocate our lab results to produce consistent results for all labs.

➡ To find a common lab procedure that will give us those results. If a common procedure cannot be found then a correlateable procedure is the goal.

➡ To equate lab procedures to that of industrial applications – Domtar (E.B. Eddy).
# Ozone and Chlorine Dioxide

## Round Robin 1 & 2

<table>
<thead>
<tr>
<th>Participants</th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Liquide</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Ahlstrom</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Champion</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>IPST</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Nexfor</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>Paprican</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Quantum</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Weyerhaeuser</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>
Hemlock kraft fibers exposed to ozone at 0.5 kPa pressure

Ozonation time : 20 s

Ozonation time : 30 s

Pictures show sharp reaction front
O$_3$-Lignin front moves inwards with time

Adriaan Van Heinigen
Ozone and Chlorine Dioxide
Power Required to Fluidized Pulp

Presented June 13 2002 by Gordon Homer

\[
Ef = (4.5 \times 10^4) \cdot C^2.5
\]
where \( C \) is pulp consistency (\%), and \( Ef \) is power dissipation per unit volume (W/m³)

Gullichsen and Harkonen (1981)

Wahren (1980)

Chad Bennington, Tappi Journal, Vol. 79, No. 2, p. 258

Gullichsen and Harkonen (1981)

Wahren (1980)

Chad Bennington, Tappi Journal, Vol. 79, No. 2, p. 258

Gullichsen and Harkonen (1981)

Wahren (1980)

Chad Bennington, Tappi Journal, Vol. 79, No. 2, p. 258

Gullichsen and Harkonen (1981)

Wahren (1980)
Round Robin 2000: Low Consistency
O3 Partial Pressure at O3 Uptake

Ozone Partial Pressure (ps)

O3 Consumed (% on pulp)

Mill Operation

Laboratory Upper Limit

Low Consistency

Softwood Kraft
Longview Douglas Fir

Presented June 13 2002 by Gordon Homer
Ozone and Chlorine Dioxide

**Round Robin 2000: Medium Consistency**

O3 Partial Pressure at O3 Uptake

---

**Mill Operation**

**Laboratory Upper Limit**

- Softwood Kraft
- Longview Douglas Fir

---

**Ozone Partial Pressure (ps)**

**O3 Consumed (% on pulp)**

Presented June 13 2002 by Gordon Homer
Ozone and Chlorine Dioxide

Why does ZD work?

⇒ A washing step can be avoided

⇒ Both Z & D are acidic

⇒ The chemistry of ClO$_2$ & O$_3$ on residual lignin complement each other

⇒ ZD selectivity far superior than Z

Presented June 13 2002 by Gordon Homer
Ozone and Chlorine Dioxide

Chemistry
Main Reactions Sites

Lignin cleavage
Aromatic ring → Cl₂ → Phenolics group
→ O₃ → Carboxyl group

Free Phenolic group → ClO₂ and O₂ → Carboxyl group

Carbonyl group → NaOCl and H₂O₂ → Carboxyl group

Unbleached pulp is high in phenolics, alcohol and methoxyl group

Lachenal & al. SPCI, Stockholm (SWE)-1991
Ozone and Chlorine Dioxide

ClO₂ Scan Results

- Low Intensity Ozone Mixing
  - 6.0 kg/ton ozone
  - Low (2.5%) Consistency first stage
  - Initial Kappa = 23.3

ClO₂ savings

Kappa Number

ClO₂ Charge (% on pulp)

Presented June 13 2002 by Gordon Homer
Ozone and Chlorine Dioxide

D/Z or Z/D location?

D

E₀

D

E

D

High KF
×0.3% O₃

Low KF
×0.3% O₃

Brightness
Boost

Presented June 13 2002 by Gordon Homer
Ozone and Chlorine Dioxide

Ozone as a Final Stage,
Effect on Strength - Burst Index versus Tensile Index

- Z (0.0), 90.3 ISO
- Z(0.08), 91.1 ISO
- Z(0.14), 91.3 ISO

Burst Index

Tensile Index

Presented June 13 2002 by Gordon Homer
Ozone as a Final Stage, Effect on Strength - Freeness at PFI Revolutions

Ozone and Chlorine Dioxide

Presented June 13 2002 by Gordon Homer
Mixing technology

⇒ H.C from Sunds/Metso
  - Need a press...expensive...
  - No need for O₃ compression
  - If press is already present, low investment retrofit

⇒ M.C from Kvaerner or Ahlstrom
  - Most popular one so far
  - Installed and performing well
  - Need O₃ high concentration ozone compressed to 150 psig

⇒ L.C from An Industrial Test At E B Eddy
  - 2/3 of mills are L.C at 3.5% in Do
  - Lower O₃ pressure can be used
Ozone and Chlorine Dioxide

Ozone Plant for LC Pulp Bleaching
Once Through with Oxygen
Purge & Reuse

VSA
Oxygen
93% Purity
by volume

29.4 tpdO₂

2 x 150 lbsO₃/h
12%O₃ by weight

Ozone

Pulp in

C

LC

VOD

SR

RT

Pulp out

By-pass

C = Compressor
B = Blower
SR = Scrubber
SP = Stand pipe
O₂ = Oxygen
O₃ = Ozone
Vent gas

VOD = Vent Ozone Destructor
LC = LC-Mixer
RT = Retention Tube

Air Liquide Supply
Mixer Supply

Presented June 13 2002 by Gordon Homer
Ozone and Chlorine Dioxide

Equipment Set-Up

Presented June 13 2002 by Gordon Homer
The secret to Ozone implementation in North America is Low consistency application of Z/D
Ozone and Chlorine Dioxide

TAPPI BLEACHING

O$_3$ Solubility vs Consistency
50 C, 12.0% wt [O3], pH 2.5

Presented June 13 2002 by Gordon Homer
Ozone and Chlorine Dioxide

Process Flow Sheet

Presented June 13 2002 by Gordon Homer
Operating Conditions

- Consistency
  - L.C = 4.5 - 4.85% Cs, M.C = 11.0% Cs

- Temperature
  - 135 °F

- Pressure
  - 135 psig for M.C, 135 psig for 2 L.C, 50 psig for 1 L.C

- pH
  - 2.5 to 3.5

- Pulp Dilution
  - Fresh water

- Ozone
  - $[O_3]$ of 5, 6, 8, 11, 12%
### Results: 1 vs 2 mixers, Low vs Medium

<table>
<thead>
<tr>
<th></th>
<th>Kappa after Z</th>
<th>Viscosity (mPas)</th>
<th>O$_3$ (% on pulp)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>M.C 2 mixers</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>“</td>
<td>5.1</td>
<td>11.7</td>
<td>0.45</td>
</tr>
<tr>
<td>“</td>
<td>4.4</td>
<td>11.5</td>
<td>0.46</td>
</tr>
<tr>
<td>“</td>
<td>4.1</td>
<td>10.2</td>
<td>0.50</td>
</tr>
<tr>
<td><strong>L.C 2 Mixers</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>“</td>
<td>5.2</td>
<td>12.4</td>
<td>0.23</td>
</tr>
<tr>
<td>“</td>
<td>5.2</td>
<td>12.6</td>
<td>0.24</td>
</tr>
<tr>
<td>“</td>
<td>3.5</td>
<td>9.9</td>
<td>0.46</td>
</tr>
<tr>
<td>“</td>
<td>3.4</td>
<td>9.2</td>
<td>0.48</td>
</tr>
<tr>
<td>“</td>
<td>3.4</td>
<td>9.9</td>
<td>0.56</td>
</tr>
<tr>
<td>“</td>
<td>3.3</td>
<td>10</td>
<td>0.58</td>
</tr>
<tr>
<td><strong>L.C 1 Mixer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>“</td>
<td>5.4</td>
<td>13.1</td>
<td>0.29</td>
</tr>
<tr>
<td>“</td>
<td>5.2</td>
<td>13.2</td>
<td>0.30</td>
</tr>
<tr>
<td>“</td>
<td>4.0</td>
<td>11.3</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>11.3</td>
<td>0.55</td>
</tr>
</tbody>
</table>

*O$_3$ charge 30% lower*
With 1 LC mixer & same kappa reduction:
- Kappa/kg $O_3$ equal
- Kappa/kg $O_3$ follow ISO trend
- $O_3$ consumed equal
  - 96-98%
- 25% less Power per ton pulp
- ~20% less COD
- Equal or slightly better viscosity

With 2 LC Mixers:
- 1.0 kappa/kg $O_3$ vs 0.8 for MC
- $O_3$ consumed > than MC
  - 99 vs 96%
- 50% more power per ton pulp
- 30% less COD
- For a 4 point kappa drop in Z alone:
  - Need 0.50% $O_3$ at M.C vs 0.40% $O_3$ with 2 L.C mixers
  - A 20% $O_3$ charge reduction

Presented June 13 2002 by Gordon Homer
Ozone and Chlorine Dioxide

UGA Pilot WV-HW Bleaching
Ahlstrom Mixer - 3600 RPM, Starting Kappa = 12.5

Feb 2002

Ozone Charge (kg/odt pulp)

<table>
<thead>
<tr>
<th>O3 Charge</th>
<th>Z Kappa</th>
<th>ZE Kappa</th>
<th>Z Eop</th>
<th>Kappa Drop</th>
<th>Kappa Drop/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>12.5</td>
<td>12.5</td>
<td>12.5</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>0.55</td>
<td>8.15</td>
<td>6.2</td>
<td>5.28</td>
<td>7.2</td>
<td>1.3</td>
</tr>
<tr>
<td>0.87</td>
<td>5.6</td>
<td>4.25</td>
<td>3.49</td>
<td>9.0</td>
<td>1.0</td>
</tr>
<tr>
<td>0.91</td>
<td>5.63</td>
<td>4.25</td>
<td>3.44</td>
<td>9.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Presented June 13 2002 by Gordon Homer
Ozone and Chlorine Dioxide

Total Gas Management Concept

93% Oxygen

Bleach Plant Eop Stage

O2 Delignification

~85% O2 Vent Gas

Polysulfides Generation

White Liquor Oxidation

Lime Kiln

Ozone Generation

Waste Water Treatment

Bleach Plant Ozone Stage

10-13% O3

On-Site Ozone

On-Site Oxygen

Presented June 13 2002 by Gordon Homer
Ozone and Chlorine Dioxide

Oxygen Purity After Z-Stage: VSA Supply

ASSUMPTIONS:
- Ozone at 10% (W/W) & 4 kg/t on pulp
- VSA (93% O2 V/V): 92.4% O2 (W/W)
- Air entering with pulp in the reactor - 10% (V/Vpulp)

VSA → O3 → Z → VOD with SCRUBBER → O2 Delig & Eo

92.4% O2
83% O2
10% O3
7% N2 + Ar

87.4% O2
0.5% O3
7.2% N2 + Ar
4.3% CO2

92.0% O2
0% O3
7.8% N2 + Ar

Numbers are expressed on dry gas

Presented June 13 2002 by Gordon Homer
## Ozone and Chlorine Dioxide

### O3 Plants Reuse of Vent Gas

<table>
<thead>
<tr>
<th>O2 Source at O3 Bleaching Start Up</th>
<th>O2 Source at O3 Bleaching Today</th>
<th>Configuration</th>
<th>Off Gas Reuse</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lenzing</td>
<td>LOX</td>
<td>ONCE THROUGH</td>
<td>-</td>
<td>YES</td>
</tr>
<tr>
<td>Union Camp</td>
<td>LOX</td>
<td>LOOP</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td>Södra</td>
<td>LOX</td>
<td>ONCE THROUGH</td>
<td>-</td>
<td>Vented</td>
</tr>
<tr>
<td>MODO</td>
<td>LOX</td>
<td>ONCE THROUGH</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td>UPM Wisaforest</td>
<td>LOX</td>
<td>LOOP WITH VSA</td>
<td>YES</td>
<td>Yes</td>
</tr>
<tr>
<td>Metsa Botnia Kaskinen</td>
<td>LOX</td>
<td>ONCE THROUGH</td>
<td>YES</td>
<td>?</td>
</tr>
<tr>
<td>Peterson</td>
<td>LOX</td>
<td>ONCE THROUGH</td>
<td>NO REUSE OF OXYGEN</td>
<td>YES</td>
</tr>
<tr>
<td>SCA</td>
<td>LOX</td>
<td>ONCE THROUGH</td>
<td>NO</td>
<td>YES</td>
</tr>
<tr>
<td>Sappi</td>
<td>VSA</td>
<td>ONCE THROUGH</td>
<td>YES (HC)</td>
<td>YES</td>
</tr>
<tr>
<td>Ponderosa</td>
<td>VSA</td>
<td>ONCE THROUGH</td>
<td>NO REUSE OF OXYGEN</td>
<td>YES</td>
</tr>
<tr>
<td>Bacle</td>
<td>VSA</td>
<td>ONCE THROUGH</td>
<td>YES</td>
<td>-</td>
</tr>
<tr>
<td>Metsa Rauma</td>
<td>LOX</td>
<td>ONCE THROUGH</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td>Consolidated</td>
<td>LOX</td>
<td>LOOP</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td>VCP Celpav</td>
<td>LOX</td>
<td>ONCE THROUGH</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td>VCP Jacarei</td>
<td>LOX</td>
<td>ONCE THROUGH</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td>Klabin</td>
<td>VSA</td>
<td>ONCE THROUGH</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ponderosa</td>
<td>VSA</td>
<td>ONCE THROUGH</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rosenthal</td>
<td>VSA + LOX</td>
<td>ONCE THROUGH</td>
<td>NO</td>
<td>YES</td>
</tr>
<tr>
<td>Eb Eddy</td>
<td>VSA</td>
<td>ONCE THROUGH</td>
<td>NO REUSE OF OXYGEN</td>
<td>Polysulfide</td>
</tr>
<tr>
<td>Matussiere &amp; Forest</td>
<td>LOX</td>
<td>ONCE THROUGH</td>
<td>NO REUSE OF OXYGEN</td>
<td></td>
</tr>
<tr>
<td>Burgo</td>
<td>LOX</td>
<td>ONCE THROUGH</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td>Nippon Yufutsu</td>
<td>VSA</td>
<td>ONCE THROUGH</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>
Ozone and Chlorine Dioxide

Oxidant Enhancement of a Kraft Mill

- Z/D adds a new dimension to the bleach plant
- $O_3$ can be applied at Low, Medium or High consistency
- Z/D will reduce Color
- Z/D will reduce COD
- Z/D will reduce AOX
- Z/D will reduce TOCL
- Z/D is cost effective
- Z/D is an easy installation
- Z/D is color effective
- O Z/D is more color effective

Presented June 13 2002 by Gordon Homer
Ozone and Chlorine Dioxide

Oxidant Enhancement of a Kraft Mill

- Oxygen Delignification is more Selective than cooking
- Oxygen can be used as Mini (EO), O or OO
- Z/D adds a new dimension to the bleach plant
  - $O_3$ can be applied at Low, Medium or High consistency
- Ozone vent gas can be reused in other applications like Eop, O Delignification, Oxidized white Liquor, Polysulphide
- Oxidized Liquors can be used for Yield Enhancement
- Recovery boilers can be Oxygen Enriched (OEA) to improve

Presented June 13 2002 by Gordon Homer
Ozone and Chlorine Dioxide

OXIDANT Solutions in a Kraft Mill

Wood

Chips Cooking & Washing

O

Eop

ClO₂ Bleaching

Pulp

Chemical Recovery

BLOX

LIME KILN

OWL

Z/D

Secondary Treatment

Presented June 13 2002 by Gordon Homer
Increase Cooking Kappa Yield
Heat/Solids Loading

<table>
<thead>
<tr>
<th>Kappa</th>
<th>Heat Load Chg</th>
<th>Solids Load Chg</th>
<th>Yield Incr.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>26</td>
<td>Base</td>
<td>Base</td>
<td>Base</td>
</tr>
<tr>
<td>28</td>
<td>-1.6</td>
<td>-1.7</td>
<td>+0.4</td>
</tr>
<tr>
<td>30</td>
<td>-3.1</td>
<td>-3.3</td>
<td>+0.7</td>
</tr>
<tr>
<td>32</td>
<td>-4.6</td>
<td>-4.9</td>
<td>+1.1</td>
</tr>
<tr>
<td>34</td>
<td>-6.0</td>
<td>-6.5</td>
<td>+1.5</td>
</tr>
</tbody>
</table>
Yield Improvement at either Constant Wood or Heat

1,000 TPD PULP @
43 % is 2,318 TPD
Chips

At constant chips
43% is 1,000 tpd
46% is 1,069 tpd
an increase of
69 tpd of pulp

At constant heat the
Increase is twice that
140 plus tons