Rethink Paper – Lean and Green

Effective Paper Machine Slime Control and No Vapor Phase Corrosion

Jim Anderson
Guilherme Fernando Cortinovi
Bruno Bolduc
“Evolution” of Effective PM Slime Control
Alkaline Fine Paper (North America)

• The evolution of using oxidizing biocides
• What are the current issues/problems?
• A “new” technology to address the current and “old” issues
“Evolution” of Effective PM Slime Control
Alkaline Fine Paper (North America)

1980-1990
Non
Oxidizing
Biocide(s)

1985-2000
“Strong”
Oxidizers
w/ Biocide

1995-2005
“Mild”
Oxidizers
w/ Biocide

2000-Present
“Mild”
Oxidizers
w/o Biocide

Issues:
- Cost
- Performance

Issues:
- Ox Control
  - Interactions
  - Performance

Issues:
- Cost
- Performance

Issues:
- Cost
- Vapor phase corrosion
“Evolution” of Effective PM Slime Control Alkaline Fine Paper (North America)

1980-1990
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Issues:
- Cost
- Vapor phase corrosion
Eka Purate® ClO₂

- It is a blend of sodium chlorate (NaClO₃) & peroxide (H₂O₂)
- Patented ClO₂ method
  - Chemical generation reaction:
    \[
    (2\text{NaClO}_3 + \text{H}_2\text{O}_2) + \text{H}_2\text{SO}_4 \rightarrow 2\text{ClO}_2 + \text{O}_2 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}
    \]
    (Chlorate + peroxide) plus (acid) \(\rightarrow\) (chlorine dioxide)
- Lowest cost for small scale generation of ClO₂
- State of the art control
  - Generation of chlorine dioxide (efficiency and simplicity)
  - Application for disinfection & slime control
**ClO₂ Generation**

- **Chlorate/Peroxide Blend**
- **H₂SO₄**
- **Generator**
- **Fresh Water**
- **Process Water flow**

**Flow Details**:
- Fresh Water: 0.5-3.0 g/l
- Process Water flow
ClO$_2$ Generator

[Image of a ClO$_2$ Generator and Chemical Pumps]
The Benefits of Using ClO₂

- Widely used in Europe (Paper & Water) & North America (Water)
- Cost effective
- Improved runnability
  - Less web breaks
  - Better retention – filler, sizing agents
The Benefits of Using ClO₂

- Improved paper quality
  - Less holes and spots
  - Less biofilm in pipes and towers
- Increased ORP
- Reduced Odors (No H₂S smell)
- Increased pH/less dissolved Ca++ level
- Lower demand for wet end starch
- Reduced potential for vapor phase corrosion
Corrosion with Oxidizer Hypo, Chloramines, and ClO$_2$

- **Liquid phase**
  - SS is resistant
  - No issues reported
- **SS pitting due to chlorides**
  - Chloride levels are normally a problem
  - No issues reported
- **Vapor phase**
  - Corrosion in wet end mist area (cat walks, ceiling, frame, etc.)
  - Corrosion in dryer section (dryer can surface, dryer section ventilation, dryer felt carrying rolls, etc.)
Vapor Phase Corrosion Testing Hypo, Chloramines, and ClO₂

- Lab studies to simulate WW evaporation and condensation – measuring the condensed vapor components
- Lab studies to document the impact of the WW vapors have on corrosion coupons
- Paper Machine testing for the components in the condensed vapor from the first section of drying
Evaporation & Condensation Lab Apparatus
Evaporation & Condensation Lab Apparatus

![Diagram of evaporation and condensation process]

Condensed WW Vapors ~40 mls

<table>
<thead>
<tr>
<th>Untreated, Hypo, Chloramines (MCA or BAC), &amp; ClO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hypo, BAC, MCA, &amp; ClO₂ @ varying ppms</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>WW</td>
</tr>
<tr>
<td>WW after test</td>
</tr>
<tr>
<td>Condensed WW Vapors</td>
</tr>
</tbody>
</table>
Lab Study – Condensed Vapors

ORP Trend – Condensed Vapors – Mill A

Condensed Vapors ORP - mv

Dosage of Oxidizer - ppm

Hypo
AmBr - BAC
ClO2
Lab Study – Condensed Vapors

Total Cl₂ – Condensed Vapors – Mill A

![Graph showing the relationship between dosage of oxidizer and condensed total Cl₂ for different oxidizers (Hypo, AmBr - BAC, ClO₂)].

- **Condensed Vapors Total Cl₂ - ppm**
  - Y-axis range: 0.0 to 0.5
  - X-axis range: 0.0 to 5.0 ppm

- Different lines represent:
  - Hypo
  - AmBr - BAC
  - ClO₂

- The graph demonstrates a linear increase in condensed total Cl₂ with increased dosage of oxidizer for all three types of oxidizers.
Lab Study – Condensed Vapors

ORP Trend – Condensed Vapors – Mill B

<table>
<thead>
<tr>
<th>Oxidizer</th>
<th>Dosage - ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hypo</td>
<td></td>
</tr>
<tr>
<td>AmBr - BAC</td>
<td></td>
</tr>
<tr>
<td>ClO2</td>
<td></td>
</tr>
<tr>
<td>AmSO4-MCA</td>
<td></td>
</tr>
</tbody>
</table>

0.0 1.0 2.0 3.0 4.0 5.0

Condensed Vapors ORP - mv

150 200 250 300 350 400

Dosage of Oxidizer - ppm
Lab Study – Condensed Vapors

Total Cl₂ – Condensed Vapors – Mill B

- Hypo
- AmBr - BAC
- ClO₂
- AmSO₄-MCA

Dosage of Oxidizer - ppm

Condensed Vapors Total Cl₂ - ppm

0.0 1.0 2.0 3.0 4.0 5.0
Mill Study – Condensed Vapors

Dryer Section

Ice Chest

Hose to collect vapors from above the paper web

Vacuum Pump
Mill Study– Condensed Vapors

Mill Data – Total Chlorine in Vapors
Alkaline Fine Paper

Total Chlorine (ppm) HACH DPD

AmSO4 (MCA)  1.25
AmBr (BAC)    0.85
ClO2 PM1      0.56
ClO2 PM2      0.89
ClO2 PM4      0.22

- Headbox
- Condensed Vapors
Mill Study– Condensed Vapors
Increased ClO$_2$

Mill Data – Total Chlorine in Vapors
Alkaline Fine Paper

<table>
<thead>
<tr>
<th>Total Chlorine (ppm) HACH DPD</th>
<th>ClO$_2$ Normal Dose</th>
<th>ClO$_2$ 2X Normal Dose</th>
<th>ClO$_2$ 4X Normal Dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Headbox</td>
<td>0.00</td>
<td>0.41</td>
<td>0.71</td>
</tr>
<tr>
<td>Condensed Vapors</td>
<td>0.22</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Mill Study– Condensed Vapors Varying Operations and BAC Dose

Mill Data – Total Chlorine in Vapors
Alkaline Fine Paper - 1st Dryer Section

<table>
<thead>
<tr>
<th>Date</th>
<th>Headbox (ppm)</th>
<th>Condensed Vapors (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 1</td>
<td>1.60</td>
<td>0.61</td>
</tr>
<tr>
<td>July 22</td>
<td>1.30</td>
<td>0.55</td>
</tr>
<tr>
<td>Aug 16</td>
<td>1.20</td>
<td>0.49</td>
</tr>
<tr>
<td>Sept 9</td>
<td>0.40</td>
<td>0.03</td>
</tr>
</tbody>
</table>

July 1: normal operation
July 22: normal operation
Aug 16: baled pulp
Sept 9: BAC stopped for 6 hrs
Vapor Phase Testing – Coupons

2 Coupons suspended in the Heated Vapors (30 hrs)

To refill with HB stock

Max Min
Vapor Phase Testing – Coupons

- ClO$_2$
  - Front & Back
- AmSO$_4$
  - Front & Back
- AmBr
  - Front & Back
Vapor Phase Testing – Coupons

Corrosion Rate Result
Mild Steel Coupons Suspended in Vapors 30 hrs

<table>
<thead>
<tr>
<th>Compound</th>
<th>Corrosion Rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO2</td>
<td>23.4</td>
</tr>
<tr>
<td>ClO2</td>
<td>25.7</td>
</tr>
<tr>
<td>MCA</td>
<td>34.4</td>
</tr>
<tr>
<td>MCA</td>
<td>33.3</td>
</tr>
<tr>
<td>BAC</td>
<td>41.3</td>
</tr>
<tr>
<td>BAC</td>
<td>52.0</td>
</tr>
</tbody>
</table>
Vapor Phase Testing – Coupons

Corrosion Rate Result
Mild Steel Coupons Suspended in Vapors 30 hrs

- Blank: 15.3 mpy
- Blank: 16.1 mpy
- ClO2: 18.8 mpy
- ClO2: 16.4 mpy
- MCA: 24.6 mpy
- MCA: 23.2 mpy
- BAC: 27.6 mpy
- BAC: 34.5 mpy
Summary – Condensed Vapor Studies

- Lab Studies – Heating WW and Condensing Vapors
  - AmBr (BAC) – always detected Total Cl₂ in condensed vapors, varying amount & increased with BAC dose
  - AmSO₄ (MAC) – always detected Total Cl₂ in condensed vapors, varying amount & increased with MCA dose
  - ClO₂ – zero to trace amounts of Total Cl₂ in vapors, increased to trace amounts with increased dose of ClO₂
- Mill Condensed Vapor Studies – agreed with Lab Studies
- Corrosion Coupons in the Vapor Phase – the trend agreed with condensed vapor studies
- All agreed with what we see in the “real world
Effective Paper Machine Slime Control and No Vapor Phase Corrosion

- $\text{ClO}_2$
- Improved small scale generation of $\text{ClO}_2$
- Improved control with PLC
- A “new” technology to address
  - The current issues (vapor phase corrosion) and
  - “Old” issues (control and application)