Oxalic Acid Process Chemistry
ECF Bleaching - Generation

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Oxalic Acid: Introduction

Oxalic Acid (Oxa) impacts operations and products

- Ca:OxA scale formation impacts performance of bleaching equipment
- Influences reduced water usage practices
- Ca:OxA deposits have been noted on paper machine
## Oxalic Acid: Source

<table>
<thead>
<tr>
<th>Wood:</th>
<th>Bark/ (kg/ton)</th>
<th>Wood (kg/ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HW</td>
<td>9 –15</td>
<td>0.1 – 0.3</td>
</tr>
<tr>
<td>SW</td>
<td>4 -10</td>
<td>0.1 – 0.4</td>
</tr>
</tbody>
</table>

### Pulp

- **Lignin**: Oxidative Bleaching Agent
  - Oxidative Agent
  - Slow Hydrolysis
  - OxA
  - OxA
OxA Accomplishments

- Developed CIE analysis method to analyze OxA in bleach effluents
- Demonstrated that [OxA] in bleach effluents can be increased upon heat treatment
  - OxA formation occurs under acidic and basic conditions
- Commercial HW D₀ effluents contained approx. 20 mg OxA/L
- Heat treatment of HW D₀ effluents increased [OxA] by 5 - 30%
**Oxalic Acid Generation Post-Do**

- Do (kf:0.25) effluent from an OD SW kraft pulp

<table>
<thead>
<tr>
<th>Reaction Time/h</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>5</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Initial pH 2.6 (70°C)</th>
<th>27</th>
<th>47</th>
<th>54</th>
<th>55</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Initial pH 11.5 (70°C)</th>
<th>27</th>
<th>33</th>
<th>34</th>
<th>61</th>
</tr>
</thead>
</table>

| Initial pH 2.6 (90°C) | 27 | 59 | -- | 61 |

[OxA] in effluents (mg/L)
Oxalic Acid Research Goals

• Measure the amounts of oxalic acid in commercial SW $D_0$-stage effluents.
• Determine the effect of temperature on post bleaching formation of oxalic acid.
• Evaluate the effect of pulp kappa number on oxalic acid formation from a $D_0$-stage.
Experimental Protocol

- Commercial samples acquired.
- Bleach effluent samples were heated to 70°C for extended time period.
- Aliquots were removed and analyzed for oxalic acid content.
Oxalic Acid Results: Commercial D$_{o}$ Effluents

Increase in OxA is in the range of 10 - 30%.
Oxalic Acid Results: Laboratory Studies

Goal: Determine the influence of pulping and bleaching conditions on OxA formation.
Oxalic Acid Results: Laboratory Studies

Experimental Protocol

Bleach series of SW kraft pulps with
0.1, 0.15, 0.20 kf ClO$_2$.

Pulps Employed

<table>
<thead>
<tr>
<th>Conventional</th>
<th>Extended Modified Continuous</th>
</tr>
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<tbody>
<tr>
<td>31.9, 25.1, 22.4</td>
<td>29.1, 23.2, 19.4, 17.0</td>
</tr>
</tbody>
</table>

-all from the same tree
Oxalic Acid Results:

\([\text{OxA}] \text{ in } D_0 \text{ Effluents from SW Conventional Kraft Pulp}\]

2-fold increase in D-charge increases OxA by ca 2.8
Oxalic Acid Results:
[OxA] in D₀ Effluents from Extended Modified SW Kraft Pulp

2-fold increase in D-charge increases OxA by ca 2.7
Oxalic Acid Results: Heat Treatment of CK31.9 D₀ Effluent

Heat treatment of CK 31.9 D₀ effluent at 70°C
Oxalic Acid Results:
Heat Treatment of CK $D_0$ Effluents

Results from heat treatment of $D_0$ (0.20 kf) effluent from SW CK 31.9, 25.1, and 22.4.
Oxalic Acid Results:
Heat Treatment of EK $D_0$ Effluents

Results from heat treatment of $D_0$ (0.20 kf) effluent from SW EK 29.1, 23.2, 19.4, and 17.0
Results from heat treating $D_0$ (0.15 kf) effluent from SW EK 29.1, 23.2, 19.4, and 17.0.
Oxalic Acid Conclusion

• Factors contributing to OxA
  – OxA generation is sensitive to $D_0$ kf
  – OxA generation is sensitive to starting pulp kappa #

• Heat generation of OxA
  – higher pulp kappa # and $D_0$ kf favors oxalic acid generation
**OxA Research:**

- Any mill modeling of OxA-scale formation needs to take into account direct and indirect OxA formation chemistry
- Bench marked OxA in several member mills

**Value & Direction**

- Generation of OxA through bleaching mill
- Affinity of OxA for fibers
- Control of OxA in bleached fiber line
  - develop new chemistry to control OxA

>>Yield process and product improvements