Impact of Water Reuse on Corrosion of Paper Machines – Advancing Tomorrow’s Operations

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Corrosion in Pulp and Paper Mill Operations
Corrosion Research at GaTech Related to the Pulp and Paper Industry

- Material Performance in Pulping Liquors
- Corrosion in Recovery Boiler Superheaters
- Corrosion in Evaporators and Concentrators
- Corrosion in Bio-Fuels
- Stress Corrosion Cracking of Carbon steel in Bio-Ethanol
- Corrosion in Pyrolysis Oils

Paper Machine Corrosion
- Impact of Water Reuse
- Lean Duplex Stainless Steels for White Water

Effect of Water Reuse on Corrosion in Paper Machine

- General Corrosion
- Fatigue Corrosion
- Localized Corrosion (Pitting and Crevice Corrosion)
- Microbial Corrosion
Wastewater Discharge Over Years

- Progressive reduction in fresh water usage
- Reduction of process water discharge volume
- Process water recycling

From National Council for Air and Stream Improvement (NACASI) Report, 2009

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Chemicals in Closed White Water System

- From Fresh Water
- Chemical Additions
- Control
- Closed White Water
- Out with Fiber
- Waste Water Discharge
- Scale Deposits

With Pulp
### Chemical Changes in Closed White Water

<table>
<thead>
<tr>
<th></th>
<th>Clarified Water (Open)</th>
<th>Clarified Water (Closed)</th>
<th>Liner Water (Open)</th>
<th>Liner Water (Closed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.3</td>
<td>4.9 - 7.0</td>
<td>7.0</td>
<td>5.0 - 7.1</td>
</tr>
<tr>
<td>Cl(^{-}) ppm</td>
<td>76</td>
<td>50 - 180</td>
<td>86</td>
<td>76 - 205</td>
</tr>
<tr>
<td>SO(_4)(^{2-})</td>
<td>65</td>
<td>195 - 460</td>
<td>63</td>
<td>251 - 600</td>
</tr>
<tr>
<td>Conductivity mScm(^{-1})</td>
<td>597</td>
<td>1520 - 4270</td>
<td>703</td>
<td>1480 - 4460</td>
</tr>
<tr>
<td>Temp. °C</td>
<td>-</td>
<td>30 - 38</td>
<td>-</td>
<td>38 - 39</td>
</tr>
<tr>
<td>Total Solids</td>
<td>684</td>
<td>3375 - 5533</td>
<td>1026</td>
<td>3188 - 8010</td>
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<tr>
<td>Total Organic Solids</td>
<td>204</td>
<td>711 - 1617</td>
<td>286</td>
<td>696 - 1897</td>
</tr>
<tr>
<td>Acetic acid ppm</td>
<td>240</td>
<td>480 - 1120</td>
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</tr>
</tbody>
</table>


### Corrosion Issues in Paper Mills

- **Microbial Corrosion**
- **Suction Roll Cracking**
Accelerated Corrosion of Cast Iron Rolls
– Effect of Biocide Additions or Other Changes?

Effect of pH and Chlorides

Effect of Cl⁻ to SO₄²⁻ Ratio in White Water on Breakdown Potential of Stainless Steels

Wensley D. A., Material Performance, No. 11, pp68-71, 1989

Alloys Included in This Study
(Others may be included after discussions)

<table>
<thead>
<tr>
<th>Steel Grade</th>
<th>EN-Code</th>
<th>ASTM</th>
<th>Cr% (min)</th>
<th>Ni% (min)</th>
<th>Mo% (min)</th>
<th>C% (max)</th>
<th>Mn% (min)</th>
<th>N% (min)</th>
<th>S (max)</th>
<th>Si (max)</th>
<th>Fe</th>
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<tbody>
<tr>
<td>516 Gr-70</td>
<td></td>
<td></td>
<td>0.020</td>
<td>0.01</td>
<td>0.004</td>
<td>0.230</td>
<td>1.11</td>
<td>0.003</td>
<td>0.01</td>
<td>0.26</td>
<td>Bal</td>
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<tr>
<td>304</td>
<td>1.4301</td>
<td>304</td>
<td>17.5</td>
<td>8</td>
<td>0.07</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Bal</td>
</tr>
<tr>
<td>316L</td>
<td>1.4404</td>
<td>316L</td>
<td>16.5</td>
<td>10</td>
<td>2</td>
<td>0.03</td>
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<td>-</td>
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<td>Bal</td>
</tr>
<tr>
<td>317L</td>
<td>1.4438</td>
<td>S31703</td>
<td>18.0</td>
<td>11.0</td>
<td>3.0</td>
<td>0.035</td>
<td>2.0</td>
<td>-</td>
<td>0.03</td>
<td>0.75</td>
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<td>2304</td>
<td>1.4362</td>
<td>S32304</td>
<td>22</td>
<td>3.5</td>
<td>0.1</td>
<td>0.03</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>Bal</td>
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<tr>
<td>2205</td>
<td>1.4462</td>
<td>S32205</td>
<td>21</td>
<td>4.5</td>
<td>2.5</td>
<td>0.03</td>
<td>-</td>
<td>0.10</td>
<td>-</td>
<td>-</td>
<td>Bal</td>
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<tr>
<td>2507</td>
<td>1.4410</td>
<td>S32750</td>
<td>24</td>
<td>6</td>
<td>3.0</td>
<td>0.03</td>
<td>-</td>
<td>0.24</td>
<td>-</td>
<td>-</td>
<td>Bal</td>
</tr>
<tr>
<td>LDX 2101</td>
<td>1.4162</td>
<td>S32101</td>
<td>21</td>
<td>1.35</td>
<td>0.1</td>
<td>0.04</td>
<td>4.0</td>
<td>0.20</td>
<td>-</td>
<td>-</td>
<td>Bal</td>
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<tr>
<td>2404</td>
<td>1.4662</td>
<td>S32441</td>
<td>24</td>
<td>3.6</td>
<td>1.6</td>
<td>0.02</td>
<td>3.0</td>
<td>0.27</td>
<td>-</td>
<td>-</td>
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<tr>
<td>2012 (NSSC)</td>
<td>-</td>
<td>S82122</td>
<td>20.5</td>
<td>1.5</td>
<td>0.6</td>
<td>0.03</td>
<td>2.0</td>
<td>0.15</td>
<td>0.02</td>
<td>0.75</td>
<td>Bal</td>
</tr>
<tr>
<td>AL 2003</td>
<td>-</td>
<td>S32003</td>
<td>21.5</td>
<td>3.5</td>
<td>1.8</td>
<td>0.03</td>
<td>-</td>
<td>0.16</td>
<td>-</td>
<td>-</td>
<td>Bal</td>
</tr>
</tbody>
</table>
How Different Stainless Steels Grades are Different?

- **Austenitic stainless steel**
- **Martensitic stainless steel**
- **Ferritic stainless steel**
- **Duplex stainless steel**

![Schaffler Constitution Diagram](https://www.bssa.org.uk/topics)

**SCC of DSS in Chloride Containing Environments**

- Crack initiation occurred by pitting within ferrite grains or at austenite/ferrite grain boundaries in white water.
- In the absence of a sensitized microstructure, SCC nucleates at slip steps and propagates in a transgranular mode.
- Hydrogen influences the mechanism at cathodic potentials in NaCl.

SCC of DSS in Caustic Environments

- DSS are susceptible to SCC in synthetic white liquors (NaOH 150gm/L + Na₂S 50gm/L)
- Austenite phase is susceptible to TGSCC in caustic solutions at the open circuit potential (OCP)

Grade (a) 2101 and (b) 2205 DSS tested in synthetic white liquor at 170 °C.


Selective Corrosion in Duplex Stainless Steels

2M H₂SO₄ + 0.5 M HCl solution at 25°C

Aerated 50 wt% CaCl₂ solution at 100°C with pH = 6.5 to 7.0

Selective Attack of ferrite (Powder metallurgy DSSs)

DSS 2205 thin film after potentiostatic etching for 10 h, (a) ferrite network, -245 mV; and (b) austenite rod, -320 mV.

W.T. Tsai, J.R. Chen, Corrosion Science 49 (2007) 3659-3668

Water Reuse Impacts on Corrosion in Paper Machines - Project Objectives

• To Understand the Reason for Recent Accelerated Corrosion in Paper Machines
  • Accelerated Corrosion of Cast Iron Rolls
  • Localized Corrosion in Stainless Steel in Headbox and other Areas
• Evaluate Corrosion Performance and Limitations of New Cost Effective Duplex Stainless Steels in White Waters
  • Determine Role of New Biocides on White Water Corrosivity
  • Determine Environmental Limits of Commonly Used Alloys in a Range of White Water Compositions
• Develop Corrosion Mitigation Strategies for New Paper Machine Environments

Cyclic Potentiodynamic Polarizations
**Effect of Thiosulfate ions**

![Graph showing the effect of thiosulfate ions on the potential vs. current density for different SS 304L conditions with various concentrations of Cl⁻ and SO₄²⁻.]

**Effect of Thiosulfates on Pitting – Cyclic Polarization – 300ppm Cl⁻ with thiosulfate ions**

<table>
<thead>
<tr>
<th>Alloy Name</th>
<th>304L</th>
<th>316L</th>
<th>2101</th>
<th>2205</th>
<th>2304</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNS Number</td>
<td>S30403</td>
<td>S31603</td>
<td>S32101</td>
<td>S31803</td>
<td>S32304</td>
</tr>
<tr>
<td>0ppm S₂O₃²⁻</td>
<td>Pitting</td>
<td>Pitting</td>
<td>Pitting</td>
<td>No pitting</td>
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<tr>
<td>58ppm S₂O₃²⁻</td>
<td>Pitting</td>
<td>Pitting</td>
<td>Pitting</td>
<td>No pitting</td>
<td>Pitting</td>
</tr>
<tr>
<td>115ppm S₂O₃²⁻</td>
<td>Pitting</td>
<td>No pitting</td>
<td>Pitting</td>
<td>No pitting</td>
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</tr>
</tbody>
</table>
Polarization Test Results
– 300ppm Cl\textsuperscript{−} 600ppm SO\textsubscript{4}\textsuperscript{2−}with thiosulfate anions

<table>
<thead>
<tr>
<th>Alloy Name</th>
<th>304L</th>
<th>316L</th>
<th>2101</th>
<th>2205</th>
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</tr>
</thead>
<tbody>
<tr>
<td>UNS Number</td>
<td>S30403</td>
<td>S31603</td>
<td>S32101</td>
<td>S31803</td>
<td>S32304</td>
</tr>
<tr>
<td>0ppm S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−}</td>
<td>Pitting</td>
<td>No pitting</td>
<td>No pitting</td>
<td>No pitting</td>
<td>No pitting</td>
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<tr>
<td>50ppm S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−}</td>
<td>Pitting</td>
<td>No pitting</td>
<td>Pitting*</td>
<td>No pitting</td>
<td>No pitting</td>
</tr>
<tr>
<td>100ppm S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−}</td>
<td>Pitting*</td>
<td>No pitting</td>
<td>No pitting</td>
<td>No pitting</td>
<td>No pitting</td>
</tr>
<tr>
<td>200ppm S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−}</td>
<td>Pitting*</td>
<td>No pitting</td>
<td>No pitting</td>
<td>No pitting</td>
<td>No pitting</td>
</tr>
</tbody>
</table>

* Pitting not observed on all tested samples.

Repassivation Behavior of New Steels

- **WW Simulated Solution** (5g/L Cl\textsuperscript{−}, 10g/L SO\textsubscript{4}\textsuperscript{2−}, 1.5g/L S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−}) at 50°C
Repassivation Test Results – DSS 2205

$5g \text{Cl}^{-}, 10g \text{SO}_4^{2-}, 1.5g \text{S}_2\text{O}_3^{2-}$

Repassivation Test Results – DSS 2304

$5g \text{Cl}^{-}, 10g \text{SO}_4^{2-}, 1.5g \text{S}_2\text{O}_3^{2-}$
Repassivation Test Results – 2304

Microscopy images of scratches in S32304 in solution at (a) 0mV (b) -100mV (c) -200mV (d) -300mV vs. SCE.

Expected Deliverables

- Environmental Limits of New and Existing Alloys in Paper Machines
- Performance of New Cost Effective Alloys –
  - Limitations of New Alloys in White Waters
- Effect of Recent White Water Changes on Corrosivity Towards Existing Metallurgy
- Corrosion Mitigation in New Corrosive White Water Compositions
- Provide Data to Make Decisions to Control Corrosion in Paper Machine Areas
Thanks!

Questions?