Pulp and Paper Corrosion Symposium
Georgia Tech Renewable Bioproducts Institute
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Kraft Liquor Corrosion

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Federal Way, WA

Topics

• Brown Stock Corrosion
• Alkaline Liquor Corrosion
• Black Liquor Corrosion
  – Evaporators
  – Research
• High Solids Black Liquor Corrosion of Stainless Steel
• Material Selection Summary
Brown Stock Corrosion

• The pH may drop to levels that may make carbon steel unsuitable
• Pitting corrosion of carbon steel occurs in filtrate and seal tanks
  – Rather than spreading, pits tend to perforate the shell in isolated locations.
  – It can occur anywhere the metal is submerged, often areas that are aerated
  – Rust mounds or tubercles often cover the pits
  – Microbiological corrosion

Brown Stock Corrosion

• Corrosion control consists of
  – Organic coatings and linings to protect existing carbon steel tanks.
  – All stainless steel construction, 304L or duplex stainless steel
• Watch out for galvanic corrosion of carbon steel, if repairs are made with stainless steel.
Alkaline Liquor Corrosion

- Corrosion resistance of carbon steel depends on the ability to maintain a protective oxide film on the metal surface. As long as the passive layer remains intact, corrosion rates are low.
- Higher temperatures and flow rates result in higher corrosion rates. Increasing sulfidity increases corrosion however its impact is less predictable. There is no sulfidity number under which carbon steel corrosion will not occur.
- Stainless steel remains passive in white, green and black liquor. The exception for stainless steel is in high solids (70% or higher) black liquor.

Alkaline Liquor Corrosion continued

- White liquor is corrosive to carbon steel. Anywhere where the liquor is aerated, expect corrosion rates to increase due to the formation of thiosulfate. Increased sulfidity can augment this effect.
- Green liquor is less aggressive than white liquor though it can form thiosulfates at the air to liquid interface.
- Unlike green and white liquor, the formation of thiosulfate in black liquor does not increase carbon steel corrosion.
- Low silicon steel has improved resistance in less aggressive liquors. Because of low demand it is expensive and requires long lead times for delivery.
White Liquor Storage Tank Examination

Pitting at the liquid level. The average corrosion rate of the upper two courses exceeded 20 mils/yr over 12 years.

Side view of the WL Tank Samples

- The pitting tends to go to the same depth
- Side B has fewer pits but is thinner overall
- The weld stands proud even though it has higher silicon
The Sulfidity Question

- As sulfidity increases, the corrosion rate of carbon steel increases.
- The steel must be in the active state i.e. already corroding to see an effect.
  - If existing corrosion rates are low, an increase in sulfidity will not raise the corrosion rates high enough to require an upgrade in materials.
  - If existing corrosion rates are high, an increase in sulfidity will make the situation worse.

### Liquor Corrosion Data

**CORROSION RATES OF MATERIALS EXPOSED IN LOW (30%) AND HIGH (40%) SULFIDITY KRAFT LIQUORS (MPY).**

<table>
<thead>
<tr>
<th>Material</th>
<th>White Liquor</th>
<th>Green Liquor</th>
<th>15% Weak Black Liquor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>AS16-Grade 70</td>
<td>40</td>
<td>48</td>
<td>5.7</td>
</tr>
<tr>
<td>A285-Grade C</td>
<td>34</td>
<td>48</td>
<td>4.9</td>
</tr>
<tr>
<td>UNS S30403</td>
<td>0.04</td>
<td>0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>UNS S32304</td>
<td>0.04</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>UNS S31803</td>
<td>0.04</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>26% Solids Black Liquor</th>
<th>45% Solids Black Liquor</th>
<th>Flash Tank Liquor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>AS16-Grade 70</td>
<td>3.6</td>
<td>13.3</td>
<td>26</td>
</tr>
<tr>
<td>A285-Grade C</td>
<td>0.20</td>
<td>7.7</td>
<td>20</td>
</tr>
<tr>
<td>UNS S30403</td>
<td>0.08</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>UNS S32304</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>UNS S31803</td>
<td>0.03</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

## Affect of Sulfidity on Corrosion

<table>
<thead>
<tr>
<th>Existing Situation</th>
<th>After increasing sulfidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion rate &lt; 2 mils/yr, the metal is passive</td>
<td>No appreciable change in corrosion</td>
</tr>
<tr>
<td>Corrosion rate up to 10 mils/yr, carbon steel has acceptable resistance</td>
<td>Rates could increase so that carbon steel is marginal</td>
</tr>
<tr>
<td>Corrosion rate 10-20 mpy, carbon steel is marginal</td>
<td>Rates could further increase so that carbon steel is unsuitable</td>
</tr>
<tr>
<td>Corrosion rate &gt; 20 mils/yr, carbon steel is unsuitable</td>
<td>Rates will remain unacceptably high</td>
</tr>
</tbody>
</table>

## Corrosion Control

- Anodic Protection
  - For white and green liquor
- Full or partial replacement
  - Carbon steel
  - Stainless steel
- Linings
  - Organic
  - Inorganic
  - Stainless steel
“Dry” side cracking of a 304L Liner

Intergranular Stress Corrosion Cracking of 304L
Stainless Steel Band is Too Narrow

Black Liquor Corrosion

- Carbon steel is suitable for weak black liquor
- The transition to marginal use is ~20% black liquor solids
- Carbon steel does not passivate in 45% and higher solids black liquor
- Corrosion chemistry is not well understood
- Sulfdity is not a good measure for black liquor though there appears to be some correlation with corrosion
- Anecdotally, the conversion from batch to continuous cooking has resulted in the more claims for increased black liquor corrosion
Evaporator Corrosion

- All carbon steel is affected to some degree
  - Liquor splashing causes erosion-corrosion
  - It has little resistance in effects 1, 2 and 3
  - Corrosion may be noticeable where liquor enters the evaporator train, often the fifth effect.
- 304L stainless steel and duplex stainless steels are resistant

Pitting Corrosion in the Vapor Dome
Case Study

- Severe carbon steel erosion-corrosion was detected in the fourth effect after it was switched to a position between the first and third effects.
  
  Original order 6,5,4,3,2,1
  
  New order 6,5,3,4,1 (no change in solids to 6,5,3)

- The entire vapor dome corroded with corrosion rates of 60 mils/year and pits 1/8 inch deep.

- The fourth effect vapor dome was rebuilt with 304L SS

Severe Carbon Steel Corrosion

Note the baffle is corroding away from vapor dome wall
Erosion Corrosion

Fine pitting of the vapor duct wall

Corrosion Control

- Weld overlay with 309L stainless steel
  - Time consuming to apply
- Thermal spray alloy 625
  - Works better in the lower solids effects
  - Estimated coating life is < 10 years
- Linings
  - Liquor gets between the lining and shell
- Section Replacement
Third Effect Arc Spray

Some blistering

Stainless Steel Lining Plug Welded to the Shell

3rd effect

1st effect
Corrosion Research

Carbon steel in laboratory generated liquors.

Notice the peak in corrosion around 50% BL solids

Stainless steel in laboratory generated liquors.

The corrosion rates are low, < 1 mil/yr

316 has the highest corrosion rate of the stainless steel

Preet Singh, et al, IPST, Georgia Institute of Technology
Corrosion Research

Corrosion of carbon steel in real black liquor under static conditions

Mill A supplied liquor, tested at 170ºC

The corrosion rate peaks at around 50% BL solids

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Corrosion Research

Corrosion of stainless steel in real black liquor under static conditions

Mill A supplied liquor, tested at 170ºC

There is a peak just below 50% BL solids, however the rates are low.
Corrosion Research

Mill B supplied liquor, tested at 170°C

There is a peak around 50% BL solids, however the rates are low.

Duplex stainless steels have lower corrosion rates than 304 or 309.

Erosion Effect

Mill B supplied liquor, tested at 170°C

Tensile samples simulate loss of passivity and effects of flow

Little difference is seen with carbon steel, however the corrosion rate increases significantly with stainless steel.
Note the peak around 50% BL solids. Rates are more typical of actual carbon steel corrosion.

Failures of 316L have occurred in 72% liquor

High Solids Corrosion of Stainless Steel

- Stainless steel corrosion occurs in black liquor with as low as 70% solids
- Failures may be rapid, on the order of weeks or months, and catastrophic
- The failure mechanism is flow assisted corrosion
- Black liquor chemical analysis reveals a correlation between NaOH concentration
- Sulfide tends to be higher. Chloride and thiosulfate are variable with little correlation to corrosion
- Stress Corrosion Cracking is also an issue
High Solids Corrosion of Stainless Steel

- At least 18% chromium is required for corrosion resistance.
- With 16% chromium, 316L is not recommended for this service. The molybdenum in 316L offers no benefit.
- 304L is sufficient for most applications.
- Duplex stainless steels are more resistant though not immune to corrosion in high flow conditions.
- Reducing stresses and deposition will improve resistance to stress corrosion cracking.

80% Recirculation Line
Step at the Butt Weld

Intergranular Corrosion

<table>
<thead>
<tr>
<th>% Element</th>
<th>Ruptured</th>
<th>Weld</th>
<th>Thicker</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>17.84</td>
<td>18.87</td>
<td>19.37</td>
</tr>
<tr>
<td>Nickel</td>
<td>10.09</td>
<td>11.13</td>
<td>7.93</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>1.84</td>
<td>1.63</td>
<td>0.53</td>
</tr>
</tbody>
</table>
70% Recirculation Line

316L Intergranular Corrosion

<table>
<thead>
<tr>
<th>% Element</th>
<th>Thicker</th>
<th>Weld</th>
<th>Ruptured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>18.30</td>
<td>19.61</td>
<td>17.10</td>
</tr>
<tr>
<td>Nickel</td>
<td>12.65</td>
<td>11.22</td>
<td>9.67</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>2.22</td>
<td>2.31</td>
<td>1.97</td>
</tr>
</tbody>
</table>
70%, Concentrator Tube Corrosion and Cracking

316L Enhancer, 304L Tube

Concentrator Tube Thinning
The metal under the bar is protected from corrosion.

Spiral Tube Cracking
74% Black Liquor Storage Tank

Cracking in the Heated Area
Widespread Crack Indications

Intergranular Attack – Grains are Popping Out
70% Flash Tank

Intergranular Corrosion

Original Shell  Wear Plate
### Equipment Failures

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Failure Mode</th>
<th>Metal</th>
<th>Fix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product liquor flash tank</td>
<td>Corrosion</td>
<td>304L</td>
<td>2205</td>
</tr>
<tr>
<td>BL heater pipe reducer</td>
<td>Corrosion/Cracking</td>
<td>316L</td>
<td>304L</td>
</tr>
<tr>
<td>Ring header piping</td>
<td>Corrosion</td>
<td>316L</td>
<td>2205</td>
</tr>
<tr>
<td>HSC tubes</td>
<td>Corrosion/Cracking</td>
<td>304L</td>
<td>304L/2205</td>
</tr>
<tr>
<td>HSC spiral enhancers</td>
<td>Cracking</td>
<td>316L</td>
<td>Removed</td>
</tr>
<tr>
<td>Tubel concentrator tubes</td>
<td>Corrosion</td>
<td>304L</td>
<td>2205</td>
</tr>
<tr>
<td>Liquor Heater Nozzle</td>
<td>Corrosion</td>
<td>316L/304L</td>
<td>304L/design</td>
</tr>
<tr>
<td>HSC valves (cast)</td>
<td>Corrosion</td>
<td>CF3M</td>
<td>CF3M</td>
</tr>
<tr>
<td>HSC piping</td>
<td>Corrosion/Cracking</td>
<td>316L/304L</td>
<td>304L</td>
</tr>
<tr>
<td>Liquor Solids Meter</td>
<td>Corrosion</td>
<td>316L</td>
<td>Alloy 20</td>
</tr>
<tr>
<td>74% storage tank</td>
<td>Corrosion/Cracking</td>
<td>304L</td>
<td>2304</td>
</tr>
</tbody>
</table>

%Solids 70 – 80; Temperature > 230 °F; All flow related
Material Selection Summary

<table>
<thead>
<tr>
<th>Corrosion Rate (mpy)</th>
<th>Severity</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;20</td>
<td>High</td>
<td>304L</td>
</tr>
<tr>
<td>10 – 20</td>
<td>Moderate</td>
<td>Prefer 304L</td>
</tr>
<tr>
<td>&lt; 10</td>
<td>Low</td>
<td>Carbon Steel</td>
</tr>
</tbody>
</table>

- Guideline Based on Carbon Steel Corrosion Rate
- Corrosion rates cannot be predicted by knowing liquor composition or sulfidity
- Both carbon and stainless steel can fail by erosion

Material Selection - Service

- White liquor  ▶  304L stainless steel
- H,S,I black liquor  ▶  304L stainless steel
- Green liquor  ▶  304L preferred
- Weak black liquor or less than 20% solids  ▶  Carbon steel
- Other choices  ▶  Lean Duplex stainless steel
  ▶  A weldable 12% Cr stainless steel for mildly corrosive liquors

2. Bennett, D. "Corrosion damage mechanisms and their prevention in tanks containing Alkaline pulping liquors", 2002 TAPPI Engineering Conference