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2017 Annual Executive Conference

Georgia Tech Renewable Bioproducts Institute
The Effect of Particles and Viscosity on the Erosion-Corrosion of Steels Exposed to Pulping Liquors

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Background-Examples

Erosion-corrosion the Pulp & Paper Industry

Erosion corrosion in cast iron weak black liquor line

Erosion corrosion in evaporator tube sheet inlet

Erosion corrosion in duplex stainless steel black liquor gun

Erosion corrosion of stainless steel flash tank inlet

Source: P.M. Singh & B.A. Baykal, TAPPI 2015
Background-Corrosion states

Corrosion states of an active-passive alloy
- Active corrosion
- Passivity
- Transpassivity

Erosion-corrosion is a synergy between electrochemical and mechanical effects that interferes with passivity to cause accelerated, localized corrosion.

Source: BP
Background-Flow and Viscosity

• Flow effects:
  – Enhanced transport rate
  – Erosive potential

• Flow parameters:
  – Reynolds number: $Re = \frac{\text{inertial forces}}{\text{viscous forces}} = \frac{\rho V D}{\mu}$
  – Wall shear stress: $\tau = \mu \frac{\partial u}{\partial y} |_{y=0}$, $u(y) = \frac{\Gamma}{2\pi(r_{RCE}+y)}$
  – Schmidt number: $Sc = \frac{\text{viscous diffusion rate}}{\text{molecular diffusion rate}} = \frac{\nu}{D}$
  – Sherwood number: $Sh = \frac{KL}{D} = f(Re, Sc)$

• All flow parameters are linked to viscosity!
### Experimental - Materials

#### Materials

- **Carbon steel C1018**
  - Evaporator tube sheets and storage tanks
- **Austenitic stainless steel 304L and 316L**
  - Pipes, fittings, valves, impellers, baffles
- **Duplex stainless steel 2205**
  - Black liquor streams, pipes and tanks

#### Compositions

<table>
<thead>
<tr>
<th>Element</th>
<th>C1018</th>
<th>304L</th>
<th>316L</th>
<th>2205</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.20</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>Mn</td>
<td>0.90</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>P</td>
<td>0.040</td>
<td>0.045</td>
<td>0.045</td>
<td>0.03</td>
</tr>
<tr>
<td>S</td>
<td>0.050</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>Si</td>
<td>0.90</td>
<td>0.75</td>
<td>0.75</td>
<td>1.00</td>
</tr>
<tr>
<td>Cr</td>
<td>-</td>
<td>18-20</td>
<td>16-18</td>
<td>22</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>8-12</td>
<td>10-14</td>
<td>6</td>
</tr>
<tr>
<td>Mo</td>
<td>-</td>
<td>-</td>
<td>2-3</td>
<td>3.10</td>
</tr>
<tr>
<td>N</td>
<td>n/a</td>
<td>0.10</td>
<td>0.045</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Sources: P.M. Singh, ICRC 2014; M. Gorog, RBI 2014. Compositions from AK Steel.
Experimental - Environment

Test solution: White liquor (pulping liquor)
- 150 g/L NaOH (3.75 M) + 153.8 g/L Na$_2$S.9H$_2$O (0.64 M) in water
- pH=14.7
- Viscosity: 2.85 cP at room temperature, adjustable up to 19000 cP with additives
- Density: 1.17-1.27 g/cm$^3$

Solution of interest: Black liquor (spent pulping liquor)
- Lower sulfidity and alkalinity
- Organics-Higher viscosity (1-1200 cP at 121$^\circ$C), shear thinning behavior
- Varying composition and solid content

Erodent: Alumina (Al$_2$O$_3$)
- Common erodent

Viscosity adjustment: Agar agar (vegan gelatin)
- Inert in neutral and alkali solution
- Causes shear thinning behavior just like black liquor
Experimental - Setup

• Rotating Cylinder Electrode (RCE) setup – hydrodynamically similar to pipe flow

\[ u_{cyl} = 0.1185 \left( \frac{\mu}{\rho} \right)^{-0.25} \left( \frac{3}{5} \frac{d_{cyl}^{7}}{d_{pipe}^{28}} \right) Sc^{-0.0857} u_{pipe}^{5} \]

D. Silverman, 2004

• Linear Polarization Resistance (LPR) – in situ electrochemical test for instantaneous corrosion rate
Results

Effect of particle size and content on corrosion rate of C1018 CS (90°C)

Effect of particle presence in White liquor for SS and DSS, 12.6 cP, 60°C
Results

Erosion-Corrosion Synergism for 316L SS

- **Agar & Al2O3**
- **Agar only**
- **Al2O3 only**
Results

Erosion-Corrosion Synergism for 2205 DSS

- Agar & Al2O3
- Agar only
- Al2O3 only
Results

Profilometry

2205 DSS in white liquor, 1 g/L alumina, 1% agar agar, 5 h exposure

Directional damage, about 1 micron deep after around 5 h exposure
Conclusions

- Presence of particles increases corrosion rate increases corrosion rate for all tested steels when flow is present
  - Increase is proportional to flow velocity
- Particle size and content does not make a significant and consistent difference in tested conditions
- Viscosity is a major factor in erosion-corrosion that has been overlooked in previous studies
  - Synergizes with erosive particles to increase erosion-corrosion rate
  - More effective than particles alone
  - Lowers threshold flow velocity for activation of erosion-corrosion mechanism
- Damage from erosion-corrosion is observable after even short exposure to white liquor with increased viscosity.
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• Most experiments using RCEs were performed using white liquor spiked with hard particles; much less viscous than real-world environments that were simulated.
• Important problems: Inaccurate Re, Sc and Ta
• Agar (vegan gelatin) is inert in neutral and alkaline environments and increases the viscosity of solutions
## Experimental – Viscosity Adjustment

<table>
<thead>
<tr>
<th>Agar content (wt. %)</th>
<th>Viscosity Method</th>
<th>Density (g/cm^3)</th>
<th>Density method</th>
<th>Dyn. Viscosity (cP)</th>
<th>Kin. Viscosity (cSt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Cannon-Fenske</td>
<td>1.17</td>
<td>Relative meas.</td>
<td>2.85</td>
<td>2.43</td>
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<tr>
<td>0.5</td>
<td>Rotary Viscometer</td>
<td>1.18</td>
<td>Calculated</td>
<td>6.20</td>
<td>5.25</td>
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<tr>
<td>1</td>
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<td>1.19</td>
<td>Calculated</td>
<td>12.58</td>
<td>10.57</td>
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<tr>
<td>2</td>
<td>Rotary Viscometer</td>
<td>1.21</td>
<td>Calculated</td>
<td>14.67</td>
<td>12.12</td>
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<tr>
<td>2.5</td>
<td>Rotary Viscometer</td>
<td>1.22</td>
<td>Calculated</td>
<td>361.1</td>
<td>295.98</td>
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<tr>
<td>3</td>
<td>Rotary Viscometer</td>
<td>1.23</td>
<td>Calculated</td>
<td>805.00</td>
<td>654.47</td>
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<tr>
<td>4</td>
<td>Rotary Viscometer</td>
<td>1.25</td>
<td>Calculated</td>
<td>3,820.00</td>
<td>3056.00</td>
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<tr>
<td>5</td>
<td>Rotary Viscometer (30 rpm)</td>
<td>1.27</td>
<td>Calculated</td>
<td>18,865.00</td>
<td>14854.33</td>
</tr>
</tbody>
</table>

**Variation of viscosity in agar-containing white liquor**

![Graph showing the variation of viscosity in agar-containing white liquor](image)
Results

- High viscosity (15000 cP) shows an increased corrosion rate at a lower threshold rotational speed.
Results

Prepared surface

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Unit</th>
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</thead>
<tbody>
<tr>
<td>Length</td>
<td>1000.000</td>
<td>μm</td>
</tr>
</tbody>
</table>

Before

After