Corrosion

• Corrosion is the destruction or deterioration of a material because of reactions with its environment
• Many fields are applied to understanding corrosion
  ➢ Thermodynamics
  ➢ Electrochemistry
  ➢ Metallurgy
  ➢ Physical chemistry

• Fortunately this can be summarized by the following:
  – Metals (except gold and platinum) are found in nature as oxides. So, there is a driving force for the metal to return to its natural state as a metal oxide
  – The way in which metals return to their natural state determines the type of corrosion
Factors Affecting Corrosion

- Temperature
- Conductivity
- pH
- Corrosive ionic species
  - Chloride
  - Thiosulfate
  - Sulfite
  - Sulfide
  - Hydrogen peroxide

Sources of Corrosive Ionic Species

- Chlorides
  - Bleaching chemicals
  - Biocides
  - Sea floating logs
- Sulfurous compounds
  - Brightening chemicals
  - Kraft pulping
  - Sulfur dioxide quenching
    - Of oxidizers
- Hydrogen peroxide
  - Bleaching chemicals
Corrosion Basics

Nine forms of corrosion typical to the paper industry

1. Uniform attack
2. Galvanic corrosion
3. Crevice corrosion
4. Pitting
5. Intergranular corrosion
6. Selective leaching (dezincification)
7. Erosion corrosion
8. Microbiologically influenced corrosion
9. Stress-corrosion cracking

Forms of Corrosion

1. Uniform attack
   - The most common form of corrosion
     - Rusting steel
   - Uniform attack or general corrosion is usually prevented or controlled by:
     - Coatings (paint)
     - Inhibitors
     - Cathodic protection
       - Zinc plating
       - Magnesium anode in hot water tanks
Forms of Corrosion

1. Uniform attack
   - Some comments about paints, coatings and cathodic protection
     - A paint system does not exist that will survive in paper making environments for 10 years or more. Paints are susceptible to water penetration and other types of degradation that limit their life
     - Thermal sprayed or electroplated coatings always have pores that can cause galvanic corrosion of the substrate they are meant to protect
     - Cathodic protection and galvanizing works well in situations like your steel hot water heater, where the environment is mild. Paper making environments are never mild.

Forms of Corrosion

2. Galvanic corrosion
   - A little bit of electrochemistry
   - Galvanic corrosion is the principle behind all batteries
   - There is a potential difference (voltage) between dissimilar materials immersed in a conductive solution
     - Alkaline batteries are copper and nickel in a caustic (alkaline) solution
     - Car (lead) batteries are lead and lead sulfate in an acid (sulfuric acid) solution
   - Published data called a galvanic series is available for a wide variety of metals in different solutions
Forms of Corrosion

2. Galvanic corrosion
   - When two metals are far apart on the galvanic series there is a greater potential (voltage) or driving force for the more active or anodic metal to corrode
   - For example, if you have passive stainless in contact with steel in paper machine whitewater, the steel will corrode much more rapidly than when there is no contact.
   - This is because the stainless steel is more cathodic or noble than the steel in whitewater environments. If you hooked up a voltmeter between the stainless steel and the mild steel, you could actually measure the driving force for the steel to corrode.
   - Not only is the potential difference important, but the actual exposed surface areas of the materials are important.
   - In the classic example you can use copper rivets to fasten steel plates, but you should never use steel rivets to fasten copper plates.
     - This is because copper is more cathodic than steel. With copper rivets, the area of copper is small compared to the steel, and the increased corrosion of the steel will be negligible. However, if steel rivets are used in copper plates the area of copper is very large compared to the steel and the rivets will corrode rapidly.

Forms of Corrosion

3. Crevice corrosion
   - Crevice corrosion is the intense localized corrosion that occurs in shielded areas on metal surfaces exposed to corrosives.
   - This type of attack usually occurs in small volumes of stagnant solution caused by holes, gasket surfaces, lap joints, surface deposits, and under bolt and rivet heads.
   - Crevice attack is common in stainless steels. Crevices can be formed by deposits or loose joints or can be man made.
   - Crevice corrosion can be auto-catalytic. In other words, once the corrosion starts, the environment in the crevice changes to increasing the corrosion.
3. Crevice corrosion
   - Environments containing chloride ion (Cl\(^-\)) are prone to auto-catalytic crevice corrosion. Cl\(^-\) ions are small and easily migrate into the crevice, to balance the charge created by the corrosion process. The combination of increased Cl\(^-\) with low pH creates hydrochloric acid, a strong corrosive
   - Examples:
     • Flanged stainless steel piping
     • Pulp deposits in suction roll holes
     • Pulp deposits on stainless steel framing

Crevice corrosion
Headbox

Back Pond Side: 9” from the front side at the bottom joint of the apron support.
Front Pond Side: 8” from the front side at the bottom joint of the Apron Support.
Forms of Corrosion

4. Pitting
- Pitting is another form of localized attack. It is one of the most destructive and insidious forms of attack resulting in equipment failure due to perforation with very little loss of metal
- Very similar to crevice corrosion
- Cl⁻ is a major contributor to pitting in stainless steels

5. Intergranular corrosion
- Intergranular corrosion is the localized attack at or adjacent to grain boundaries
- High carbon austenitic stainless steels such as 304, 316, 317, 904 CF8 and CF8M, are susceptible to this type of attack
- Attack occurs with improper heat treatment, or post heat treatment welding
- Other names are weld decay, knife line attack
- High strength aluminum alloys and some copper alloys are also susceptible
Forms of Corrosion

5. Intergranular corrosion
   - Intergranular corrosion can be compared to a brick structure where the mortar has been removed. There is complete loss of strength with very little visible evidence. Occasionally, grain popping can be seen
   - Sandusky suction roll alloy CF8M suffered several short term failures before being removed from production
   - Sandusky CF3M a low carbon equivalent to CF8M also experienced intergranular corrosion when improperly heat treated

Intergranular corrosion
Cracking in a CF8M suction roll
6. Selective leaching (dealloying)
   - Selective leaching is the removal of one element from a solid alloy by corrosion
   - The most common form, called dezincification, is the selective removal of zinc from brass
   - Again this is an insidious form of corrosion. There is loss of strength without visible metal deterioration
   - Kable-metal suction roll alloy, nickel aluminum bronze, (gc-cu-al9.5ni) experienced dealloying with short term failures in a variety of whitewaters
Dealloying in a Bronze Suction Roll

As polished cross wall sample 12.5 mm from OD surface

Dealloying in a Bronze Suction Roll

As polished land area between drilled holes
Forms of Corrosion

7. Erosion corrosion
   - Erosion corrosion is the accelerated or increased rate of attack due to relative movement between a corrosive fluid and the metal surface
   - Erosion corrosion is common in refiners, pumps and piping elbows
   - Erosion corrosion is common in alloys that require a passive film for corrosion protection. All stainless steel alloys have a chromium oxide film to prevent corrosion of the metal
   - Bronze suction roll alloys have exhibited erosion corrosion, primarily due to improper end deckle adjustment

8. Microbiologically influenced corrosion (MIC)
   - Corrosion caused or influenced by microbial activity
   - There are numerous types of microbes that can cause corrosion of metals
     - Sulfate reducing bacteria are anaerobic and reduce sulfate to corrosive sulfide ion
     - Bacteria, molds, and slime can cause crevice corrosion in piping and other process equipment
   - MIC is not usually a factor in paper making equipment because of controls to limit microbes that can cause holes and other defects in paper
Forms of Corrosion

9. Stress-corrosion cracking
   - Stress-corrosion cracking is caused by the presence of tensile stresses and a corrosive environment
   - Types of stress-corrosion cracking include ammonium embrittlement of copper alloys, caustic embrittlement of steels

<table>
<thead>
<tr>
<th>Environment</th>
<th>PAPER MAKING ENVIRONMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical Grade</td>
<td>ACID-ALUM with SULFUR</td>
</tr>
<tr>
<td>pH</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
</tr>
<tr>
<td></td>
<td>°F</td>
</tr>
<tr>
<td>Conductivity</td>
<td>micro-siemens</td>
</tr>
<tr>
<td>Chloride Ion</td>
<td>mg/L</td>
</tr>
<tr>
<td>Sulfate Ion</td>
<td>mg/L</td>
</tr>
<tr>
<td>Thiosulfate Ion</td>
<td>mg/L</td>
</tr>
<tr>
<td>Sulfite Ion</td>
<td>mg/L</td>
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</tbody>
</table>
## Typical Environment by Machine Section

<table>
<thead>
<tr>
<th>Machine Section</th>
<th>Temperature</th>
<th>Environment</th>
<th>Other Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stock Approach</td>
<td>75 to 120°F</td>
<td>high humidity</td>
<td>Stock deposits</td>
</tr>
<tr>
<td>Headbox</td>
<td></td>
<td>high humidity</td>
<td>Stock deposits</td>
</tr>
<tr>
<td>Apron / slice lip</td>
<td></td>
<td>Traces of residual oxidants from bleaching stages.</td>
<td>Wet / dry concentration of corrosive salts</td>
</tr>
<tr>
<td>Former</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Press</td>
<td>75 to 120°F</td>
<td>high humidity</td>
<td>Deposits</td>
</tr>
<tr>
<td>Dryer</td>
<td>75 to 250°F</td>
<td>High humidity</td>
<td>paper dust</td>
</tr>
<tr>
<td>Coater / Size Press</td>
<td>75 to 250°F</td>
<td>75% RH Cleaning chemical</td>
<td>Deposits</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>High salt concentrations</td>
</tr>
<tr>
<td>Calender</td>
<td>75 to 150°F</td>
<td>75% RH Cleaning chemical</td>
<td>paper dust</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reel</td>
<td>70 to 100°F</td>
<td>75% RH</td>
<td>paper dust</td>
</tr>
</tbody>
</table>

## Typical Materials

<table>
<thead>
<tr>
<th>Machine Section</th>
<th>Less Corrosion Resistance</th>
<th>Typical Material</th>
<th>More Corrosion Resistant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stock Approach</td>
<td>S30403 304L</td>
<td>S31603 316L</td>
<td>S31703 or higher 317L</td>
</tr>
<tr>
<td>Headbox</td>
<td>Stainless steel clad mild steel</td>
<td>S31603</td>
<td>S31703</td>
</tr>
<tr>
<td>Apron / slice lip</td>
<td>S31603</td>
<td>S31703</td>
<td>6% molybdenum alloys</td>
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<tr>
<td>Former</td>
<td>S30403</td>
<td>S31603</td>
<td>S31703</td>
</tr>
<tr>
<td>Press</td>
<td>Painted mild steel</td>
<td>Stainless steel clad mild Steel</td>
<td>S31603</td>
</tr>
<tr>
<td>Dryer</td>
<td>Painted mild steel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coater / Size Press</td>
<td>Painted mild steel</td>
<td>S30403</td>
<td>S31603</td>
</tr>
<tr>
<td>Calender</td>
<td>Painted mild steel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reel</td>
<td>Painted mild steel</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Refiner Section Leading to Headbox Approach Piping

Corrosion of Machine Screen
Three Ply Linerboard

Materials specified S30403. Actual construction was S30403 and S31603. Corrosion occurred on S30403 parts.
Fourdrinier Wet-end Showing Headbox

Secondary Headbox
Corrosion of S30403 components
Forming Section
Deposition and Corrosion of S31603 Components
Forming Section
Mild Steel Contamination of S31603 Components
No passivation prior to startup

Typical Press Section
Press Section
Clad weld dilution S31603 Components

Typical Press Section to Dryer Section

Paul E. DiCaprieto
Effect of Felt Wash Chemicals

<table>
<thead>
<tr>
<th>Paper Machine</th>
<th>Sample</th>
<th>Conductivity microsiemens</th>
<th>pH</th>
<th>Chloride ion mg/L</th>
<th>Thiosulfate ion Mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1st press Uhle box bottom felt</td>
<td>1700</td>
<td>7.1</td>
<td>80.2</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>Seal pit flat box Fourdrinier</td>
<td>1900</td>
<td>6.8</td>
<td>140.0</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>1st press Uhle box bottom felt</td>
<td>1500</td>
<td>7.0</td>
<td>119.0</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
<td>Vacuum box</td>
<td>1400</td>
<td>6.8</td>
<td>156.0</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>Felt Wash 5% solution (manufacturers recommendation)</td>
<td>N.A.</td>
<td></td>
<td>13.7</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

Effect of Caustic on Painted surfaces

Atlas cell exposure 3 weeks
Dryer Section

High humidity 70°C (158°F) dew point

Dryer Section

Nickel Molybdenum Alloy thermal spray applied to 3 new shells
Dryer Section
Spray Coating after 2.5 years operation

Thank You