ANNUAL RESEARCH REVIEW

SLIDE MATERIAL

CORROSION CONTROL

March 13, 1998
INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
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- to sustain an international position of leadership in dynamic scientific research which is participated in by both students and faculty and which is focused on areas of significance to the pulp and paper industry; and

- to contribute to the economic and technical well-being of the nation through innovative educational, informational, and technical services.

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Corrosion Control PAC Meeting

Agenda

March 13, 1998
8:00 am - 4:00 pm

1. Introduction

2. Review of 1997 Dues Funded Projects and Other Related Projects
   Singh
   Al-Hassan

   Coffee Break

3. Discussion of Projects/Future Directions
   Recent IPST Developments
   Frederick/Baum

   Lunch Break

4. Discussion and Development of Future Dues Funded Projects
   Singh/PAC

   Break

5. Further Discussions
   Corrosion Group/PAC

Adjournment
Member Dues Funded Projects

- F018 - Recovery Boiler Corrosion
- F019 - Corrosion Control in Closed-Cycle Mills

Other Corrosion Projects at IPST

- Recovery Boiler Related Projects
  - Corrosivity Monitoring in Kraft Recovery Boilers (DOE/AF&PA Funded)
  - Stress Corrosion Cracking of Composite Tube (ORNL Funded)
- Corrosion Fatigue of New Roll Materials
  (Externally Funded Project)
- Others - (Consulting Projects)
Long Term Kinetics Study

(F018)
Member-Dues Funded Project

Objectives

- Investigate Corrosion Kinetics
  - Carbon Steel in 1% H₂S
  - 10,000 Hours Test at 400°C
  - Effects of Scale Sapalling and Breakaway on Corrosion Kinetics
Tasks For 1997-98
(F018)

- Complete 10,000 hr. Test  (Done)
- Characterize Sulfide Film  (Done)
- Resolve Discrepancy Between Quartz Spring Data and Interrupted Tests  (Done)
- Schedule On-Line Gas Analysis by GC To Study Gas/Smelt Interactions (Done, Equipment by April-98.)
- Complete Database Design  (Done)

Quartz Spring Balance

Pyrex cap → Quartz spring → Platinum wire → Furnace → Pyrex tube → Thermocouple → Gas inlet → Test Coupon → Endcap → Gas outlet → Cathetometer
Used vs Unused Quartz Spring

Spring Comparison

- T = 25°C
- "New" spring
- "Old" spring

Old spring constant = 1.29 cm/g
New spring constant = 1.34 cm/g
Quoted value = 1.26 cm/g

Weight (g)

Delta Length (cm)

Long-Term Kinetics

Carbon Steel Coupon in 1% H2S Environment at 400°C

Weight Gain (mg/cm²)

Time (hr)
Long-Term Kinetics

Carbon Steel Coupon in 1% H₂S Environment at 400°C

Optical Microscopy
Sample Preparation For SEM/EDS

- Sample was Mounted in Cold-setting Epoxy
- Mounted Sample was Dry-cut into Half
- One Half was Dry-polished to 2000 Grit Finish
- Polished Sample was Dry-cleaned and Carbon Coated
Surface Observations

- There was a Very Thin, Loose, and Dark Outer Layer
- Inner Layer was Intact and Continuous
- Some Surface Cracks were Visible on the Inner Layer as well

Scanning Electron Microscopy
SEM Observations

- Even Surface Attack
- Corrosion Rate of ~35 mils/year
- Most of Scale/Metal Interface had Microcracks
- Sulfide Scale had Cracks Parallel to the Interface
- Outermost Thin Layer was Different From Rest of Scale

Film Characterization
EDS Results (B6)

X-RAY: 0 - 10 keU
Live: 50s Preset: 50s Remaining: 0s
Real: 66s 24% Dead

EDS Results (C6)

X-RAY: 0 - 10 keU
Live: 50s Preset: 50s Remaining: 0s
Real: 63s 21% Dead

MEM1:980004b Metal, 10um from gap
MEM1:980004c First Corrosion Band
EDS Results (6D)

X-RAY: 0 - 10 keV
Live: 50s Preset: 50s Remaining: 0s
Real: 68s 24% Dead

EDS Results (B7)

X-RAY: 0 - 10 keV
Live: 50s Preset: 50s Remaining: 0s
Real: 64s 22% Dead

Confidential Information - Not for Public Disclosure (For IPST Member Company's Internal Use Only)
EDS Results (E7)

**EDS Results (Outermost Thin Layer)**

Confidential Information - Not for Public Disclosure (For IPST Member Company's Internal Use Only)
EDS Results *(Globular Areas in Outermost Thin Layer)*

**Summary of Results (F018)**

- No Internal Sulfidation
- Chemical Composition of Innermost Layer and Outer Layers was Similar in Attached Areas and Detached Areas
- Scale Near Metal/Scale Interface was Mixed Oxide/Sulfide Scale
- Outer Scale Was Sulfide (Fe-S)
- Outermost Thin Dark Layer was Si/SiO₂
Composite Tube Cracking

ORN L Sponsored Project

Objective

- To Identify Wash Water Composition and Other Environmental Conditions That May Cause Stress Corrosion Cracking of 304-L Stainless Steel During Shut Down Condition
Composite Tube Cracking

- Stress Corrosion Cracking of Composite Tubes During Recovery Boiler Shut Down
  - Wash Water Solution
  - Local Environments During Shut Down
    » Concentrated Smelt Constituents
    » Different Chemical Compositions of Smelt in Different Boilers as well as Different Areas of The Same Boiler

Stress Corrosion Cracking

Diagram:

- Susceptible Material
- Corrosive Environment
- Tensile Stress
- SCC (Stress Corrosion Cracking)
Conditions for SCC

- Susceptible Alloy
  - Microstructure
- Liquid Environment
  - Chemical Composition
  - Temperature
  - Potential
- Stress
  - Residual
  - Applied

Environments That Are Known to Cause SCC In 304-L

- Smelt Related Non Aqueous (PPRIC/ORNL)
  - Na$_2$S . 9 H$_2$O > 170°C
  - NaOH @ > 350°C
  - NaOH + Na$_2$S - 170-350°C
- Aqueous Solutions
  - NaOH > 90°C
  - NaCl (Water System) - 260-300°C
  - Na$_2$S$_2$O$_3$ - Ambient Temp/Sensitized
  - H$_2$S
  - Polythionic Acids
Typical Wash Water (?)

- Local Chemical Differences
  - Firing Practices
  - Different Smelt Layers in Same Area
- Different Concentrations
  - Amount of Water
  - Improper Washing

Wash Water Composition

<table>
<thead>
<tr>
<th>Chemical Species (g/l)</th>
<th>Pohjanne (A)</th>
<th>Pohjanne (B)</th>
<th>Singbeil (Start)</th>
<th>Singbeil (Finish)</th>
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</thead>
<tbody>
<tr>
<td>Cl</td>
<td>0.66</td>
<td>1.65</td>
<td>16.3</td>
<td>1.0</td>
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<td>SO₄²⁻</td>
<td>15</td>
<td>24</td>
<td>200</td>
<td>30</td>
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<tr>
<td>S²⁻</td>
<td>8.4</td>
<td>7.1</td>
<td>1.2</td>
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<tr>
<td>CO₃²⁻</td>
<td>35</td>
<td>57</td>
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<td>-</td>
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<tr>
<td>Na⁺</td>
<td>69</td>
<td>64</td>
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<td>-</td>
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<td>K⁺</td>
<td>5.7</td>
<td>4.1</td>
<td>-</td>
<td>-</td>
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<td>12.5</td>
<td>13</td>
<td>12.8</td>
<td>12</td>
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</table>
Wash Water Compositions Tested

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Artificial WW#1</th>
<th>Artificial WW#2</th>
<th>Artificial WW#3</th>
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</thead>
<tbody>
<tr>
<td>Sodium Carbonate</td>
<td>65%</td>
<td>60.50%</td>
<td>33.333%</td>
</tr>
<tr>
<td>Sodium Sulfate</td>
<td>17%</td>
<td>14%</td>
<td></td>
</tr>
<tr>
<td>Sodium Sulfide</td>
<td>15%</td>
<td>15%</td>
<td>33.333%</td>
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<tr>
<td>Sodium Thiosulfate</td>
<td>2%</td>
<td>5%</td>
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<tr>
<td>Sodium Chloride</td>
<td>0.50%</td>
<td>5.00%</td>
<td></td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>0.50%</td>
<td>0.50%</td>
<td>33.333%</td>
</tr>
</tbody>
</table>

Experimental Program

Initial Screening Tests

- **304-L Stainless Steel**
  - Microstructure Effects

- **Slow Strain Rate Tests in Individual Constituents of Wash Water**

- **Slow Strain Rate Tests in Typical Wash-Water and Doped Wash Water**

- **U-Bend Tests in Selected Environments Identified by Slow Strain Rate Tests**
**Slow Strain Rate Test Setup**

- Continuous Extension at Initial Strain Rate
- Load on Specimen is Monitored

- Environmental Cell
- Tensile Specimen

**Electrochemical Testing**

- **Potentiodynamic Polarization Tests**
  - Different Wash Water Compositions
  - Individual Chemical Constituents
  - Different Test Temperatures (<150°C)
  - Different Microstructure
### Electrochemical Tests

Log Current, A/cm^2

### Possible SCC Zones

Table IV. Results from 304L specimen tested in different environments using slow strain rate of 2x10^-6/in

<table>
<thead>
<tr>
<th>SP#</th>
<th>Test Solution</th>
<th>Temp. °C</th>
<th>E. mv (SCE)</th>
<th>Remarks</th>
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<tbody>
<tr>
<td>3</td>
<td>(IN)Na2S 9H2O</td>
<td>90</td>
<td>OCP</td>
<td>No Crack</td>
</tr>
<tr>
<td>4</td>
<td>(IN)Na2S 9H2O</td>
<td>90</td>
<td>OCP</td>
<td>No Crack</td>
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<tr>
<td>5</td>
<td>(IN)Na2S 9H2O +Na2CO3</td>
<td>90</td>
<td>OCP</td>
<td>No Crack</td>
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<td>6</td>
<td>(IN)Na2S 9H2O +Na2CO3</td>
<td>90</td>
<td>OCP</td>
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<tr>
<td>7</td>
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<td>90</td>
<td>OCP</td>
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<td>(IN)Na2S 9H2O</td>
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<tr>
<td>9</td>
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<td>30</td>
<td>Artificial WW # 1</td>
<td>90</td>
<td>OCP</td>
<td>No Crack</td>
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</tbody>
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Corrosivity Monitoring in Kraft Recovery Boilers

DOE/AF&PA

Corrosivity Monitoring in Kraft Recovery Boilers

◆ 4 year Project - DOE Funded
  – Cost Share by AF&PA
  – Cost Share by IPST (F018)
  – PPRIC and Battelle were Subcontractors in Phase I & II

◆ Third Phase Started on October 1, 1997

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Program Goals

- Task 1: Corrosion Monitoring in Recovery Boilers (Real-Time)
  - Direct Measurements
  - Indirect Measurements (Predictions)
  - Link to Corrosion Kinetics Database

- Task 2: Corrosion Kinetics Database for Recovery Boiler Environments

Phase I & II Summary

- Database Design is Complete
- Over 10,000 Data are Already in Database
- Survey of Corrosion Monitoring Technologies Done by PPRIC
- Electrical Resistance Probes Were Tested at IPST and Results are Very Promising
- Experimental Efforts to Understand
  - Isothermal Corrosion at Short Time Intervals
  - Thermal Excursion Effects
  - Smelt/Gas Interaction and Effect on Corrosion

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Phase III
Activities Planned

- Testing and Optimization of Corrosion Probe - ER Probe
- Design and Test a Prototype ER Probe
- Field Testing to Determine Environments (Gas Composition, Temp., Smelt) in Corrosive and Non-Corrosive Areas of Recovery Boilers
- Laboratory Tests to Understand Smelt/Gas Reactions - GC, XRD of Smelts

Tests to Understand Corrosivity of Recovery Boiler Environments

- Effects of Smelt on Gaseous Corrosion
  - Smelt Composition
  - Initial Gas Composition
    » Final Gas Composition at Metal/Smelt Interface
Effect of Smelt/Gas Interaction on SA-210 Carbon Steel Corrosion

Safaa Al-Hassan
IPST

For PAC/98
Gas Composition:

- 1% H₂S + Nitrogen
## Smelt Chemical Composition:

- Smelt #1  
  80% Na₂CO₃, 12% Na₂SO₄, 8% Na₂S

- Smelt #2  
  65% Na₂CO₃, 15% Na₂SO₄, 20% Na₂S

- Smelt #3  
  65% Na₂CO₃, 27% Na₂SO₄, 8% Na₂S

## Chemical Reactions-
Free Energy:

- \[ \text{H}_2\text{S} + \text{Na}_2\text{CO}_3 = \text{Na}_2\text{S} + \text{H}_2\text{O} + \text{CO}_2 \]
  \[ \Delta G = 15 - 4 \text{ kcal/mol at } 300-600^\circ\text{C} \]

- \[ 4\text{H}_2\text{S} + 3\text{Na}_2\text{SO}_4 = 3\text{Na}_2\text{S} + 4\text{H}_2\text{O} + 4\text{SO}_2 \]
  \[ \Delta G = 44 - 28 \text{ kcal/mol at } 300-600^\circ\text{C} \]
Weight Loss Using Smelt #1

![Graph showing weight loss over time for different conditions using Smelt #1.](image)

- W/O Sm
- W/25 Sm#1
- W/50 Sm#1
- 2x25 Sm#1

Weight Loss Using Smelt #2&3

![Graph showing weight loss over time for different conditions using Smelt #2 and #3.](image)

- W/O Sm
- Sm#2
- Sm#3

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## Smelt Chemical Composition:

<table>
<thead>
<tr>
<th>Smelt</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>#4</td>
<td>Smelt #2 + 2% NaCl</td>
</tr>
<tr>
<td>#5</td>
<td>Smelt #3 + 2% NaCl</td>
</tr>
<tr>
<td>#6</td>
<td>Smelt #3 + 4% NaCl</td>
</tr>
</tbody>
</table>

## Chemical Reactions - Free Energy:

\[ H_2S + NaCl = Na_2S + 2HCl \]

\[ \Delta G = 53 - 44 \text{ kcal/mol at 300-600}^\circ\text{C} \]
Weight Loss Using Smelt # 4&5,

Gas Composition:

- 1 % $\text{H}_2\text{S} + 1 % \text{O}_2 + \text{Nitrogen}$
Effect Of Oxygen:

- O₂ + 2H₂S = 2H₂O + S₂

ΔG = -74 - 73 kcal/mol at 300-600°C
Smelt Chemical Composition:

- Smelt #7 100% NaCl

Chemical Reactions - Free Energy:

- $2O_2 + 2NaCl + H_2S = 2HCl + Na_2SO_4$
  $\Delta G = -142 - -127 \text{ kcal/mol at } 300 - 600^\circ C$

- $1.5O_2 + 2NaCl + 2H_2S = 2HCl + Na_2SO_3$
  $\Delta G = -85 - -75 \text{ kcal/mol at } 300 - 600^\circ C$
Effect of NaCl-in 1% H$_2$S + 1% O$_2$:

Conclusions:

- The presence of smelt increased the weight loss by 25% in the case of smelt #1 (80% Na$_2$CO$_3$, 12% Na$_2$SO$_4$, 8% Na$_2$S).
- It decreased the weight loss by 9% in the presence of smelt #2 (65% Na$_2$CO$_3$, 15% Na$_2$SO$_4$, 20% Na$_2$S) in 24-hour tests.
- The smelt developed a crust with yellow color.
Conclusions:

- The presence of O₂ by 1% in the gas mixture increased the weight loss by 170% in the 24-hour test.

Conclusions:

- The addition of NaCl to smelt by percentage (2 to 4% in smelt), did not change the weight loss significantly when the tests were done with 1% H₂S as well as 1% H₂S + 1% O₂ gas mixture.
- The smelt developed a strong crust with orange color.
Conclusions:

- Testing NaCl only (without smelt) increased the weight loss of SA-210 in 1% H₂S + 1% O₂ gas mixture by 217% when compared to test results without salt.
Corrosion Control in Closed-Cycle Mills

(F019)
Member-Dues Funded Project

Corrosion Control in Closed-Cycle Mills

- Objectives: Identify Key Corrosion and Materials Issues Which may Impact the Successful Implementation of Various Closed Mill Scenarios and Provide Support to Maximize the Potential of these New Technologies
Corrosion Control in Closed-Cycle Mills

- Task 1
  - Effects of White Water Closure on Corrosion of the Paper Machine

- Task 2
  - Effects of Bleach Plant Closure on Corrosion of the Existing Equipment

Tasks For 1997-98 (F019)

- Visit Paper Machine Builder for Information About Their Views on Closure (Done - Beloit)

- Visit One or Two Mills with Corrosion Problems Because of Closure (Need Help in Identifying Mills)

- Define (Worst) Case Conditions and Conduct Initial Tests on Four Materials (Done)

- Plan Crack Tip Opening Displacement Experiments for Closed White Water (Done)
Summary Of Beloit Visit

Meeting with Beloit Team:
- Paul Glogowski
- James E. Rippl
- M. Sundram Thiagrajan
- Bruce L. Lindstrand
- M. W. Beck (Mick)

Summary Of Beloit Visit (Cont.)

Concerns of Beloit Team on White Water Closure
- Mills Using Acid Alum may Have Large Effects Compared to Alkaline Alum or Alkaline Fine Paper Mills
- Corrosion Problems may Increase due to $\text{H}_2\text{O}_2$ Bleaching
- Surface Coating Erosion (*Due to Increased Solids*)
  - Ceramic Coatings
  - Granite
  - Uncoated Metallic Rolls
Summary Of Beloit Visit (Cont.)

- Test in Actual White Water Samples (From Mills) as well as in Simulated White Water (Fresh Water Source Differences etc.)
- Splash Zone and Mist Areas Do See Higher Corrosion (Both Closed and Open Mills) But Need Extra Care in Closed Mills
- Headbox Cleaners and Felt Cleaner Effluents Need to be Drained Effectively or They may End-up in Closed White Waters

Corrosion Control in Closed-Cycle Mills - Task 1

- Literature Review Continued
- Literature Classification
  - Different Closed Mill Designs
  - Affects on Process and Non-process Chemical Concentrations
  - Material Behavior
  - Monitoring Techniques
Possible Effects of White-Water Closure - From Literature

- Higher Concentration of Cl\(^{-}\), SO\(_4\)\(^{2-}\), etc.
- Increase in Temperature
- High levels of residual brightening agents, and higher microbial activity
- Increased Scaling
- Higher Soluble Organic Chemicals
- Increased Micro-Organism Activity
  - Higher Microbial Corrosion
  - More Slime
  - More Odor

Closure of 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-}) ppm</td>
<td>65</td>
<td>195 - 460</td>
<td>63</td>
<td>251 - 600</td>
</tr>
<tr>
<td>Conductivity (\mu)S/cm(^{-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>
</tr>
<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>
<td></td>
<td></td>
</tr>
</tbody>
</table>

White Water Closure

Possible Effects of White Water Closure on Corrosion

- White Water Closure
  - % Closure
  - Closure Design
  - Chemical Separation Techniques etc.
  - Chemical Changes
    - Concentration
    - Sealing
  - pH and Conductivity of White Water
  - Temperature Changes
  - Microbial Activity

Equipment Materials

- Localized Corrosion
  - Pitting
  - Crevice
  - Microbial Corrosion
- Environment Induced Fracture
  - Stress Corrosion Cracking
  - Corrosion Fatigue
  - Hydrogen Embrittlement
- General Corrosion

Effects of Mill Closure

- Main Questions About Mill Closure:
  - What are Local Environmental Changes?
  - How will a Given Material Behave in the Resultant Environment?
Environmental Changes

- General Trends are Known

- Magnitude of Chemical Changes are not Well Understood
  (Modeling Efforts Going-on at IPST and Other Organizations)

Corrosion Behavior of Specific Material

- Specific Environment Should be Known

- Corrosion Prediction for a Given Material
  
  - If Material Behavior in Existing Environments is Known
  
  - If Trends in the Environmental Changes are Known
  
  - Corrosion Behavior can Be Predicted
    
    » Through Published Information
    
    » Through Experimental Studies
Enrichment Factor for Non-substantive Chemical as a Function of % of Headbox Water Flow That is Returned to Headbox

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Chlorides (Cl⁻)
(From Literature)

- SCC of 304 SS in Cl-containing Media above 60°C.
- Localized Corrosion of Stainless Steels at High Cl⁻ Levels
- More Effect of Cl⁻ ion Conc. at Low pH or Around Neutral Conditions
- Mild Steel Corrosion Increases With Temp. and Cl⁻ Conc.
Corrosion of Mild Steel


Sulfates (SO$_4^{2-}$)
(From Literature)

- For 304 SS, SO$_4^{2-}$ makes pitting more difficult
- For the [SO$_4^{2-}$]/[Cl$^-$] $\sim$ 1, the breakdown potential rises with an increase in SO$_4^{2-}$ ion concentration
Anodic Polarization and Potential Decay Behavior of 304 SS in Simulated White waters


Effect of Cl⁻ & SO₄²⁻ Conc. in White Water on Breakdown Potential of 317L SS

Effect of %Mo in SS on Breakdown Potential in White Water


Effect of Cl- to SO4^2- Ratio in White Water on Breakdown Potential of Stainless Steels

Wensley D. A., Material Performance, No. 11, pp68-71, 1989
Role of Thiosulfate ($S_2O_3^{-2}$)
(From Literature)

- $S_2O_3^{-2}$ in White Water can Cause Pitting in 304 and CA15 Stainless Steels.
- Sensitized 304 can Undergo Pitting in the Range 3 to 75 ppm of $S_2O_3^{-2}$.
- Above 60°C, $S_2O_3^{-2}$ can Accelerate Pitting on 316 Stainless Steels.
- $S_2O_3^{-2}$ have No Effect Where the Cl⁻ Hannot Initiate Crevice.

Hydrogen Peroxide ($H_2O_2$)
(From Literature)

- Generally not present in white water
- Comes from Bleach plant if not removed by SO₂ souring.
- Major effect on copper alloy suction rolls.
  » Increased corrosion of CDA 360 brass,
  » De-alloying of NiAl bronze,
  » Higher corrosion rates of martensitic stainless steels compared to the 304 stainless steel
### Dissolved and Colloidal Material
*(From Literature)*

- Originate from wood, comprising lignin, carbohydrates, extractives, and ash.
- Do not participate directly in the corrosion but can enhance bacterial activity and slime formation.
- Corrosion of carbon steel decreased at > 10,000 ppm of (10 gL⁻¹) dissolved solids, due to a film (scale) buildup.

### Microbial Corrosion
*(From Literature)*

- Microbial activity may increase in closed white water
- Colonies of the sulfate reducing anaerobic bacteria on surface cause localized corrosion of carbon and stainless steel
- Temperatures above 60°C may help
- Continuous cleaning and sterilizing required
Suction Rolls
(From Literature)

- Increase in Thiosulfate and Other Reduced Sulfur Will Increase Corrosion of Bronze Rolls
- Duplex or Precipitation Hardened SS may not have Problems in Closed White Waters
- Alloy 75, VKA 171 may Undergo Thiosulfate-induced Pitting
- The Effects of Residual Peroxide not Known
- Corrosion Fatigue of Rolls may Become Problem Due to Increase in Chlorides

Carbon Steel and Cast Iron Structures (From Literature)

- Increased Temperature Increases Corrosion Rate
- Increased Chloride Ion Concentrations and Conductivity Increase Corrosion
- Higher Velocities will Increase Corrosion Rate - (changes not expected in velocity due to closure but other effects may get magnified)
Corrosion of Stainless Steels
(From Literature)

- High Corrosion Rates of Sensitized SS
- Cl-, SO$_4^{-2}$, and S$_2$O$_3^{-2}$, and Temp. Buildup will Increase Localized Corrosion of 304L SS depending upon ionic ratios.
- Residual Peroxides will Assist in Cl-induced Corrosion, but may reduce the effect of thiosulfate
- Pitting of 316L if the [SO$_4$-2]/[Cl-] Molar Ratio is < 1
- Increased Microbial Activity will Increase Localized Attack of SS

Wet-end Framework
(From Literature)

- Structural Framework is Either Constructed or Protected by 304 or 316 SS Layer.
- Pitting where ClO$_2$ is Carried Over From the Bleach Plants.
- Sensitized Austenitic Stainless Steels may Undergo Stress Corrosion Cracking.
- Corrosion Attacks Due to an Increase in Temperature and Chloride Ion Concentrations
Experimental Program

- Commonly Used and New Materials
  » (C-Steel, 304-L, 316-L, 317-L, 254-SMO, 2205)
- Simulated White Water
  - Increased Conc. of Constituents/Temperature
    » Electrochemical Tests
    » Coupon Exposure Tests
    » Slow Strain Rate Tests for SCC
- White Water From Paper Machine
  - Changed Conc. of Constituents/Temperature
    » Coupon Exposure Tests
    » Electrochemical Tests
    » Slow Strain Rate Tests for SCC

White Water Composition
Test Matrix

Table V. Simulated White Water Solutions Compositions Used for Potentiodynamic Polarization Tests

<table>
<thead>
<tr>
<th>Environment</th>
<th>Cl ppm</th>
<th>SO₄²⁻ ppm</th>
<th>S₂O₃²⁻ ppm</th>
<th>pH</th>
<th>Temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Line (TAPPI-D)</td>
<td>200</td>
<td>500</td>
<td>50</td>
<td>4.0</td>
<td>50</td>
</tr>
<tr>
<td>High-Cl Solution</td>
<td>1000</td>
<td>500</td>
<td>50</td>
<td>4.0</td>
<td>50</td>
</tr>
<tr>
<td>High-Sulfate Solution</td>
<td>200</td>
<td>2500</td>
<td>50</td>
<td>4.0</td>
<td>50</td>
</tr>
<tr>
<td>Strong Solution</td>
<td>2000</td>
<td>5000</td>
<td>500</td>
<td>4.0</td>
<td>50</td>
</tr>
<tr>
<td>No-Thio Solution</td>
<td>200</td>
<td>500</td>
<td></td>
<td>4.0</td>
<td>50</td>
</tr>
</tbody>
</table>
Cyclic Polarization Results
(High Chloride Solution)

Log Current Density (A/cm²)

Potential (V) vs sce

Cyclic Polarization Results
(High Chloride Solution)

Log Current Density (A/cm²)

Potential (V) vs sce

Confidential Information - Not for Public Disclosure (For IPST Member Company’s Internal Use Only)
Cyclic Polarization Results
(Strong Solution)

Potential (V) vs see

Log Current Density (A/cm²)

Cyclic Polarization Results
(Strong Solution)

Potential (V) vs see

Log Current Density (A/cm²)
Cyclic Polarization Results
(High Sulfate Solution)

Confidential Information - Not for Public Disclosure (For IPST Member Company's Internal Use Only)
Test Summary

- Materials Tested
  - (C-Steel, 304-L, 316-L, 317-L, 254-SMO, 2205)
- 304-L, 316-L, 317-L, 254-SMO, and 2205 Do not Show Pitting Corrosion in Base Line Solution
- High Chlorides May Cause Pitting in 304L, 316L, and 317L
- Strong Solution May Cause Pitting of 304L and 316L - Areas with Concentrated Solutions May Have Localized Corrosion Attack

Projects For

FY 1998-99
Tasks For 1998-99  
(F018)

- To Study Gas/Smelt Interactions by On-line Analysis
- To Continue Studying Effects of Smelt/Gas Interactions on Corrosion of Carbon Steel
- To Study Effects of Smelt/Gas Interactions on Corrosion of 304L Stainless Steel

Tasks For 1997-98  
(F019)

- Visit Mills with Corrosion Problems Due of White Water Closure
- Continue With Electrochemical Tests in Simulated White Water
- Coupon Exposure Tests (Long Term and Short Term) on Selected Materials in Different White Water Scenarios
- Experiments to Study the Effects of White Water Closure on Corrosion Fatigue of Roll Materials (Crack Growth Rate, S-N Curves)
New Research Proposals (1997-98)

- Corrosion Process and Control in Kraft Digesters
  - Preet Singh & Safaa Al-Hassan
  - AF&PA (Agenda 2020)

- Objectives
  - Characterize Inorganic and Organic Components in Black Liquor Which Affect Corrosion
  - Correlate Black Liquor Compositions to Corrosion Rates of Different Materials
  - SCC Susceptibility of Different Materials as Function of Liquor Composition
  - New Materials: Thermal Spray Coatings, Weld Overlay, New Alloys For Digester Applications