Capital Equipment Preservation
-Corrosion Control

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Pulp and Paper Industry

• Capital Intensive Industry
  – New State of the Art **Pulp Mill** Costs ~$1.5 Billion
• More Than $2 Billion with Paper Machines
• Equipment is Used Beyond its Design Life
Reasons for Equipment Failure

• Flaws in an Existing Equipment may be:
  – From Manufacturing Processes (Pre-Service Flaws)
    • Material production flaws
    • Welding related flaws
    • Fabrication related flaws
    • Heat treatment related flaw
  – Induced During Service (In-Service Deterioration)
    • General and Localized Corrosion (Pitting, Crevice etc.)
    • Environment Sensitive Fracture (Stress Corrosion Cracking, Corrosion Fatigue)
    • Hydrogen Embrittlement
    • Mechanical Failures (Overloading, Fatigue, Erosion or Wear)
    • Metallurgical Changes

• In-Service Failure Modes are Affected by the Pre-Service Flaws
Total Cost of Corrosion in the United States Per Year is ~$276 Billion Dollars or 3.1% of GDP

2002 Study (FHWA-RD-01-156) Mandated by the U.S. Congress in 1999

Total Corrosion Cost Includes:
- Lost Capital due to Corrosion Deterioration
- Loss of Productivity /Reliability
- Loss of Revenue Due to Disruption in Supply of Product
- Labor for Corrosion Management Activities
- Cost of Expensive Materials Used to Prevent Corrosion
- Equipment Required for Corrosion-Related Activities
Cost of Corrosion in the Pulp and Paper Industry

Between 1.2% and 6.0% of the Sales

- Depending on the product and process
- Cost for the pulp industry alone - ~$808.5 million per year

50% or More of Corrosion Costs can be Avoided by Applying Existing Scientific Knowledge and Focused Research
Corrosion Management Approaches

• Corrosion Control Philosophies in the P&P Industry Include
  – “Do Nothing” Approach
    • Machinery is used until it fails
    • Once failed, equipment needs to be completely replaced
      – Results in high capital costs
      – Loss of production due to downtime
      – Lower quality products
      – Even catastrophic failure in the worst case scenario
  – Not a Cost-Effective Solution in the Long Run

  – “Do Everything” Approach
    • Includes Monitoring Corrosion
    • Using Protective Techniques (cathodic protection, inhibitors, and protective coatings)
    • May Not be Cost or Time Effective
Corrosion Management Approaches

- “Do What It Takes” Approach
  - Need Qualified Person to Direct this
  - Risk Based Inspection and Maintenance
  - Fundamental Knowledge of Possible Corrosion and Failure Mechanisms in Every Process Stream or Equipment
    - Relevant to the Metallurgy Used in a Given Mill
  - Focused Research to Fill Gaps in Knowledge-Base
Some Changes in the Pulp and Paper Industry and Equipment Reliability

• Reduced Water Usage - Closed-Loop System Processes
  – Increase in corrosion-related problems due to increased temperatures and concentrations of chemicals in the closed-loop process streams

• Reduce Emissions and Increase Efficiency of Recovery Boilers
  – Corrosion in Mid and Upper Furnace
  – Superheater Corrosion (Molten Salt Corrosion)
  – New Corrosion Problems with Composite Tubes

• New Pulping Processes
  – Increased Alkalinity and Sulfidity
  – Other modifications
Some Changes in the Pulp and Paper Industry and Equipment Reliability

• Older Mills Converted for New Processes
  – New Corrosion Problems Observed - Not Observed Before
  – Biorefineries!
    • New Corrosion Issues with Extraction Processes, Storage, Fuel Transportation

• Use of Recycled Paper
  – Bio-Corrosion in Some Cases
Examples of Changes in Environment
Mill Closure and Wastewater Discharge

- Progressive Reduction in Fresh Water Usage
- Reduction of Process Water Discharge Volume
- Process Water Recycling
Example of Possible Changes in a Closed White Water System

- Increased Non-Process Chemical Concentration
- Increased Temperature (Increase)
- Changes in pH
- Other Factors (e.g., Scale Formation, Hard Precipitates, etc.)
White-Water Closure and Corroison

- Higher Conc. of Cl\(^-\), SO\(_4\)\(^{-2}\), etc.
- Increase in Temperature
- Increased Scaling
- Higher Soluble Organics
- Increased Micro-Organism Activity
  - Higher Microbial Corrosion
  - More Slime
  - More Odor

On-Going Changes in Recovery Boilers

• Changes in Air Distribution and Increases in %BL Solids to Increase Boiler Efficiency and Reduce TRS, NOₓ, and CO Emissions
  – Increased Corrosion in Mid-Furnace and Upper Furnace

• Changes in BL Spray and Firing
  – Local Reduced Sulfur Gases at Water Walls – High Corrosion

• Use of Composite Tubes in Floor and Lower Furnace
  – Provides Excellent Protection Against General Corrosion in Boilers
  – Stainless Layer Cracking and Balding - Related to Shutdown

• Increase in Superheater Temperature to Increase Efficiency
  – Molten Salt Corrosion in Superheaters
Recovery Boiler

Corrosion Problems on Fireside as well as on Waterside

To stack

Electrostatic precipitator

Boiler

Superheater

Economizer

Screen Tubes

Air delivery:

Tertiary

Secondary

Primary

Black liquor

Smelt
H$_2$S (100 ppm) Iso-Surface in a Recovery Boiler Under Different Air Split

Case 6
Primary Air = 29.4%
Secondary Air = 49.1%
Tertiary Air = 21.5%

Case 7
Primary Air = 29.4%
Secondary Air = 40.6%
Tertiary Air = 30.0%
(5X4 Ports)
Phase Stability of Fe-O-S System at 320°C – Based on Gas Samples From RB Mid-Furnace

Fe-O -S Phase Stability Diagram at 320.000 C

-5  -10  -15  -20  -25  -30  -35  -40  -45

log pO2(g)

0  -5  -10  -15  -20  -25  -30  -35  -40  -45

log pS2(g)

FeS2  FeS  Fe2S3  FeS  FeSO4  Fe3O4  Fe2(SO4)3

Port 1 – 3/9/04 - BS
Port 3 – 3/9/04 - BS
Port 4 – 3/9/04 - BS
Port 6 – 3/9/04 - BS
Port 7 – 3/9/04 - BS
Port 8 – 3/9/04 - BS
C-Steel, SA-210 at 320°C and 400°C in High Corrosion Area Gases

C-Steel, SA-210 @ 320 and 400°C in High-RB#1 Gases

- High - RB#1-400C
- High - RB#1-320C

Wt. Gain, mg/cm²

Time, days
Residual ClO$_2$ in Filtrate and Redox Potential

**Graph:**

- **Y-axis:** Redox potential vs. SCE (mV)
- **X-axis:** ClO$_2$ Concentration (mg/L)

The graph shows the relationship between residual ClO$_2$ concentration in the filtrate and the redox potential, with a spike in redox potential occurring around 1.0E+00 mg/L ClO$_2$ concentration.
Effect of Environment on Crevice Corrosion Susceptibility of Different Stainless Steels in ClO$_2$ Filtrates Environments
New Materials - New Issues
Duplex Stainless Steels in Pulping Liquors

• Duplex stainless steels superior corrosion and stress corrosion cracking resistance as compared with austenitic grades in many environments

• However, Presence of Chlorides in Pulping Liquors can Cause Accelerated Corrosion of Austenite Phase (Selective Corrosion) and Stress Corrosion Cracking

• Oxide films formed in alkaline sulfide solution are defective due to adsorbed sulfides and polysulfides
Capital Equipment Preservation by Corrosion Control

• Systematic Proactive Approach Towards Capital Equipment Design and Maintenance can Save Money and Time

• Need to Implement Risk Based Inspection and Maintenance Programs in the Pulp and Paper Industry

• Risk Assessment should be Based on the Fundamental Knowledge of Possible Corrosion Mechanisms in Given Process Streams

• 50% or More of Corrosion Costs can be Avoided by Applying Existing Scientific Knowledge and Focused (Proactive) Research
Corrosion Group at Georgia Tech

- Preet M. Singh  
  Professor and Principal Investigator
- Jamshad Mahmood  
  Research Engineer

**Graduate Students**

- **Di Yang** – Effect of Low Frequency Stress Fluctuations on SCC of Duplex Stainless Steels in Caustic Solutions
- **Kevin Chasse** – Mechanism of Stress Corrosion Cracking of Duplex Stainless Steels in Caustic solutions
- **Lindsey Goodman** – Stress corrosion cracking susceptibility of pipeline steels in fuel grade bio-ethanol
- **Xiaoyuan Lou** – Corrosion and Stress Corrosion Cracking of Carbon Steels in Fuel Grade Ethanol - Mechanisms
- **Stephani Gulbrandsen** – Corrosion and Stress Corrosion Cracking of Stainless Steels in Organic Solvents
- **Robert Moser** – Reinforcement Materials for Pre-strained Concrete Structures
- **Joseph Meyer** – Materials to Control Corrosion of Recovery Boiler Superheaters

**Undergraduate Student**

- **Sam Raji** – SCC of Pipeline Steels in Fuel Grade Ethanol
- **Tarun Sikri** – Localized Corrosion of Stainless Steels
- **Mark Braswell** – SCC in Biofuels