Chemical Additives to Optimize Black Liquor Recovery Throughput and Increase Campaign Life

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Agenda

• Deposit formation in black liquor recovery boilers
  – Fate of black liquor droplets
  – Composition of carryover and deposits
  – Deposition mechanism

• Chemical additives
  – What are they?
  – Targeted application
  – Operation mechanism

• Case study
  – Twenty years of continuous operation
    ○ Supporting mechanical upgrades with chemical additives
Fate of Black Liquor Droplets

Recovery Boiler Fouling Causes

More Particles
- Firing load
- Particle size
- Particle density
- Gas velocity

Stickier Particles
- Chloride content
- Potassium content
- Sulfide content
- Temperature

Poor Sootblowing Efficiency
- Jet PIP (force)
- Deposit strength
- Blowing frequency

Load is the most important variable affecting fouling!

Reference: Tran, H. 2015 TAPPI Kraft Black Liquor Recovery Course Lecture Notes
Melting Characteristics of Deposits

- Melting temperature between 825 °C (1517 °F) and 885 °C (1625 °F)
  - NaCl and KCl depress the melting point (e.g. fluxing agent) to 626 °C (1159 °F), plasticizing agents
- Partially molten (i.e. “sticky”) inorganic salts condense on cooler heat transfer surfaces
  - As deposit grows, leading edge approaches surrounding gas temperature
  - Leading edge can be “sticky,” adhering additional particles and carryover
- Deposits sinter into dense masses at $T > 450 ^\circ C$
Deposit Removal

• Motive force is critical to deposit removal
  − Sootblowers, sonic horns, impulse cleaners, etc.

• Sootblowers are often ineffective when:
  − Deposits sinter into dense masses
  − Deposits are above their fluid or plastic temperatures

• Chemical additives alter deposit physical characteristics
  − Microscopic: pore structure, local melting temperature
  − Macroscopic: pore structure, compression strength
Modification of Deposit Physical Properties

- Addition of Mg(OH)₂ modifies deposit pore structure
  - Untreated deposits contain numerous small pores with thick walls
  - Treated deposits contain larger pores with thinner walls in between adjacent pores
Modification of Deposit Physical Properties

• Microscopic-scale phenomena impact bulk properties
  − Force required to break sintered pellet decreases with increasing additive dose

Simulated Deposit
$\text{Na}_2\text{CO}_3$-$\text{Na}_2\text{SO}_4$ pellet
Sintered at 775 °C, 2 hrs
Targeted Application
Targeted Program Application

Gas Flow Dynamics

Prediction of Problem Areas

Targeted Mg(OH)$_2$ Application
Chemical Coverage in Problem Areas

Coverage Entering Generating Bank – Dosage: 0.9 lb/ton
Fuel Case: Softwood
Solids Firing: 4.1MMlb/D

6 injector array
8 injector array
Optimized array
RECOVERY-CHEM® Recovery Boiler Technology

Program Application:

- The chemical program is injected into the fireside of the boiler at specific locations based on Fuel Tech’s CFD model of the boiler.
Chemical Injection Technology

• Tunable droplet size characteristics
  − Fine mist for rapid evaporation and activation of Mg(OH)$_2$ particles
Case Study
Baseline Data (1995) – Without RECOVERY-CHEM

Average dry solids = 3.2 million lbs/day
Treatment Extends Campaign Life

Baseline (no additive)  Additive Injection

7 days to shutdown  24 days to shutdown

= thermal shed
Run 3

Generating Bank dp (in. water gauge)

- 7 days to shutdown
- 24 days to shutdown

Average dry solids = 3.2 million lbs/day
Dosage Optimization Trials: Fine Tuning

Graph showing Gen. Bank dP (in. H₂O gauge) over time, with different dosage levels indicated:
- 1.5 lbs/ton
- 0.75 lbs/ton
- 50% of "NORMAL"
- "NORMAL"
Dosage Optimization Trials: Fine Tuning
Dosage Optimization Trials: Reversal

- dP increase can be reversed with increased chemical injection
• 11 month run completed with 4.07 MM lbs/day of BL dry solids firing
Summary

• Sodium salts in the recovery unit deposit on heat transfer surfaces and sinter at $T > 450 \, ^\circ \text{C}$ (842 °F)

• Sootblowers lose efficiency as deposits continue to grow and sinter

• Mg(OH)$_2$ injection reduces deposit strength
  - Sootblowers are more effective

• Mechanical upgrades to increase throughput greatly benefit from deposit control programs
  - Mechanical upgrades increase throughput
  - Chemical additives maintain a clean boiler to sustain increased throughput

• Twenty years of operating experience
  - Have increased campaign life from 60 days to 330 days
  - Decreased “chill and blow” frequency by 50%-75%