Evaporator Fouling

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Outline

• Types of fouling
• Mechanisms of formation
• Operating strategies to avoid fouling
• Methods for cleaning evaporators
Locations of Evaporator Fouling

- Soluble Na scales
- Insoluble Ca scale
- Lignin precipitation
- Soap fouling

AQ (vapor side)

Alumosilicate

Fiber clumps

Fiber mats

1 2 3 4 5 6

Soluble Sodium (Na) Scales

- BL contains about 35% dissolved salts
- Salts can precipitate as scale in evaporators
- $\text{Na}^+$, $\text{SO}_4^{\text{-}}$, and $\text{CO}_3^{\text{=} \text{ cause scaling}}$
- Scale composition mostly $\text{Na}_2\text{SO}_4$ and $\text{Na}_2\text{CO}_3$
- Appear brown, grainy, dense, and hard
  - Deposit samples dissolve in hot water
- Can be removed by boiling out
Crystal and Scale Types
(for 12% Na$_2$CO$_3$+Na$_2$SO$_4$ in BLS)

Onset of Crystallization

- Below critical solids all Na salts are dissolved
- Critical solids typically ~ 50% and 55%
- Crystallization point 1-5% above critical solids
- First salt depends on CO$_3$/SO$_4$ ratio in BL
  - Low ratios: Burkeite (~2Na$_2$SO$_4$•Na$_2$CO$_3$)
  - High ratios: Dicarbonate (~2Na$_2$CO$_3$•Na$_2$SO$_4$)
- For BL > 110°C (230°F), slight inverse solubility of salts
Transition to Dicarbonate Crystallization

- Crystallization removes dissolved Na salts from BL
- If burkeite first, two Na$_2$SO$_4$ removed per Na$_2$CO$_3$
- When Na$_2$SO$_4$ depleted, burkeite can’t form
- Solids content at onset decreases with increasing CO$_3$/SO$_4$ ratio in black liquor

Reduce Na Scale in LTV Evaporators

- Reduce Na$_2$CO$_3$
  - White liquor from recaust contains Na$_2$CO$_3$
  - Improve causticizing efficiency, 80 - 82%
- Reduce Na$_2$SO$_4$
  - Increase RB reduction efficiency, > 90%
  - Add saltcake/spent acid after LTV bodies
- Reduce total Na in black liquor
  - Control AA-to-wood target at digester
  - Reduce NaCl deadload
- Operate about 2 - 3% below critical solids
Soluble Na Scale in FF Evaporators and Concentrators

- Falling film evaporators are not susceptible to burkeite scale
- Concentrators typically operate where dicarbonate fouling can occur
- All concentrators are crystallizers
  - Want crystallization on suspended solids, not heater surface
  - Dicarbonate crystallizes only on dicarbonate
- Tools being developed to determine where in concentrator dicarbonate crystals will form

Reducing Na Scale in FF Concentrators

- Operate with solids profile that avoids running any effect at the crystallization point of dicarbonate; preferable to operate above it.
- Start up with product liquor
- Use high liquor recirculation rates
- Long residence time in concentrator
- Distribute liquor uniformly on heater surfaces
- Operate to avoid upset conditions
  - Slow, ramped changes in operation
  - Minimize changes in black liquor composition
Evaporator Configuration Where Dicarbonate Fouling Will Occur in 1B, Why?

- No Crystals
- Burkeite
- Dicarbonate

% of Na$_2$CO$_3$ and Na$_2$SO$_4$ that remain in solution

Raising Product Solids Avoids Dicarbonate Fouling In 1B, Why? What about 1A?

- No Crystals
- Burkeite
- Dicarbonate

% of Na$_2$CO$_3$ and Na$_2$SO$_4$ that remain in solution
**Insoluble Calcium (Ca) Scale**

- Dissolved Ca precipitates as insoluble CaCO$_3$ or Pirssonite (Na$_2$CO$_3$•CaCO$_3$)
- White or tan scale with high (>20%) calcium
  - Deposit samples dissolve in acid
- CaCO$_3$ scale cannot be removed by boiling out
  - Hydroblasting required
  - Acid or chemical cleaning after
- Pirssonite is partially soluble due to its Na$_2$CO$_3$

**Dissolved Calcium in BL**

- Calcium in BL has very low solubility
  - Solubility product indicates ~ 50 ppb (μg/Kg)
- BL organics keep Ca in solution
  - Typical dissolved Ca in BL ~ 200 to 2000 ppm (mg/Kg on BLS)
  - Soluble Ca is from wood, not lime carryover
- Difficult to control Ca input to black liquor
  - Good debarking helps
Mechanism For Ca Precipitation

- High temperatures break down organic
  - Occurs near heat transfer surfaces
  - Ca$^{2+}$ is released, combines with CO$_3^{2-}$
    $\rightarrow$ deposits on surfaces
- Typically occurs at $\sim$ 250°F (120°C)
  - Can occur at 220°F (104°C) in displacement batch pulping liquors

Mechanism of Ca Scale Deposition

~ 250°F

Ca-organic breaks down
CaCO$_3$ deposits form

Ca-organic stays together
Ca stays dissolved
Reducing Ca Scale in Evaporators

- Limit steam pressure to evaporators
  - Max pressure ~ 30 to 35 psig (capacity?)
- Improve soap skimming efficiency
  - Soap contains high soluble calcium
- Add tall oil spent brine (laden with calcium) after the evaporators
- Improve debarking
- Thermal deactivation

Aluminosilicate Scale

- Thin, glassy scale in mid-to-high solids effects
  - Deposit samples do not dissolve in most solvents
- Caused by dissolved Al and Si in BL
  - Al is 30 to 300 ppm (mg/Kg) of BLS
  - Si is 300 to 2000 ppm of BLS
- Concern when Al > 150 to 200 ppm of BLS
- Hydroblasting required
Control of Al-Si scales
Which may apply to your mill?

- Decrease bark and dirt in chips
- Decrease Al-Si in water and make-up lime
- Avoid white water in brown stock washing
- Minimize use of silicon-based defoamers
- Increase Al-Si purges in dregs and grits
  - Mg in GL can aid Al removal with dregs

Fouling Due to BL Soap

- Soap can be incorporated into other scales
  - Deposit samples have slippery appearance
- Contains high fiber content and soluble Ca
- Can increase fouling rates
- Controlled by controlling other scales
- Only remedy is better soap skimming
Fouling Due to Fiber Plugs

- Fiber can form mats in low-solids effects
  - Heavier than weak liquor
  - Concentrates in stagnant areas
- Calcium carbonate can deposit on fiber in mid-solids effects, forming clumps
- Dislodged mats and clumps can plug tubes
  - Fiber is obvious in magnified deposit samples

Fiber Fouling in Falling Film Units

- Clumps stick in distributor plate openings
- Causes poor liquor distribution
- Only remedy is fiber removal from liquor
- Install and maintain fiber filter
  - Target < 100 ppm fiber in BL streams to evaps
**Fouling Due to Lignin**

- Lignin precipitates at low liquor pH
  - Deposit samples are soft and gunky
- Maintain weak liquor pH > 12
- Control residual EA from digester
- Neutralize acidic inputs
  - ClO_2_ plant sesquisulfate
  - Tall oil plant brine
- Add caustic or white liquor

**Cleaning Evaporators**

- Boiling out
  - Dissolves Na scales
  - Removes hard scales by thermal shock
- Hydroblasting
- Chemical cleaning
  - Muriatic acid
  - Sulfamic acid
  - Phosphoric acid
  - Chemical / chelant wash
Boiling Out Evaporators

- Boil out procedures
  - Full
  - Front half (1st and 2nd effect)
  - Back half

- Wash liquid
  - Keys: dilution and time
  - Weak liquor (15% to 35%)
  - Condensate
  - Fresh water

Front Half Boil Out

Combined condensate

Feed liquor

To weak storage or spill tank
Boil Out Problems: Rapid Recovery

Rapid return of salt-rich liquor from storage

Rapid fouling and plugging

Boil Out Problems: Shortcut Boils

What is wrong with this picture?

Total Solids, wt. %

Solubility Limit
Boil Out Guidelines

- Transfer boil-out liquor back to evaporator feed as slowly as possible
- During boil must drop below solubility limit and hold long enough to dissolve crystals
- Controlled product liquor recirculation may restore crystal population after boils

Implications for Evaporator Operation

- Many potential causes for fouling
- Remedies often involve other areas of the mill
  - Recovery boiler for Na$_2$SO$_4$ input to BL
  - Recaust for Na$_2$CO$_3$ input to BL
  - Digester for total Na and residual EA
  - Brownstock washing / screening fiber input to BL
  - Wood room for bark (Ca) and dirt input to liquor
Implications for Evaporator Operation

• Some remedies involve evaporator operation
  – Handling boiler ash and Na/S waste streams
  – Limiting steam pressure
  – Soap skimming
  – Flow configuration, boil out procedures
  – Steady controlled operation, steady liquor transfers

Final Words

• Mitigating recurrent fouling can be counter-intuitive in some cases
  – Higher concentrator product solids
• Operating culture difficult to overcome
  – Hard piping or automating changes
    sometimes the only way to solve problems
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