Managing Mineral Deposit in Pulp Mill at IPPTA Workshop & Seminar

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• Non process elements in pulp raw materials/wood chips
• Why does it deposit?
• Different types of deposits in pulp mill
• Calcium balance around batch digester
• Calcium carbonate deposit and ways to minimize it
• Calcium oxalate deposit ways to reduce it
• Barium sulfate deposit and the ways to minimize it
• Pirssonite scaling in green liquor and ways to reduce it
• Types of Evaporator Scales
• Ways to reduce evaporator scaling/fouling
• Case histories
• Conclusion
NPE in pulp raw materials

- In bleaching:
  - Iron, manganese, copper detrimentally effect brightness
  - Calcium scales washing equipment, reducing the washing efficiency & productivity.

- In cooking: calcium scaling on the digester screens

- In recovery: silica and calcium promote scale formation in evaps. effecting productivity
Why Does it Deposit /scale?

Necessary conditions for scaling

- **Supersaturation**: dissolved ions like Ca++, CO3$$^\text{-2}$$, C2O4$$^\text{-2}$$, Na+, Ba++ and SO4$$^\text{-2}$$ increase in concentration to levels that exceed normal solubility limits

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Solubility at 18°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium carbonate</td>
<td>CaCO3</td>
<td>0.014</td>
</tr>
<tr>
<td>Calcium oxalate</td>
<td>CaC2O4</td>
<td>0.0074</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Na2CO3</td>
<td>75</td>
</tr>
<tr>
<td>Barium sulphate</td>
<td>BaSO4</td>
<td>0.0025</td>
</tr>
<tr>
<td>Calcium sulphate</td>
<td>CaSO4</td>
<td>2.4</td>
</tr>
<tr>
<td>Sodium sulphate</td>
<td>Na2SO4</td>
<td>50</td>
</tr>
</tbody>
</table>

- **Accelerated Kinetics**: temperature shock, intense mechanical, hydrodynamic shear force optimum pH

- **Optimum substrate**: Non uniform surface providing mechanical foothold for scale microcrystal to begin growing
Typical inorganic scale in fiber line

- Calcium (carbonate, oxalate, sulphate, silicate)
- Aluminum (silicates, hydroxides, phosphates)
- Barium, radium (sulphate)
- Magnesium (silicates)
- Sodium (burkeite, dicarbonate, pirssonite)
Scale Control in Fiber line
Calcium Balance in Cooking for 700 ADT/ D, with 0.4% bark

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>2.73 kg/ADT</td>
</tr>
<tr>
<td></td>
<td>1914 kg/day</td>
</tr>
<tr>
<td>Bark</td>
<td>0.11 kg/ADT</td>
</tr>
<tr>
<td></td>
<td>77 kg/day</td>
</tr>
<tr>
<td>WL</td>
<td>33.35 kg/day</td>
</tr>
<tr>
<td>BL to maintain L/W</td>
<td>84.375 kg/day</td>
</tr>
<tr>
<td>Brown pulp</td>
<td>290 kg/day</td>
</tr>
<tr>
<td>Liq. To Evap</td>
<td>962.5 kg/day</td>
</tr>
<tr>
<td>Total Ca In Dig/day</td>
<td>2108 kg/day</td>
</tr>
<tr>
<td>Total Ca out Dig/day</td>
<td>1252.5 kg/day</td>
</tr>
</tbody>
</table>

Ca remaining in Dig/tanks/liq is 0.856 Tons/day
Calcium Carbonate Scale

- Calcium is present as high as 2000ppm in wood.
- Most common scale in kraft pulping is calcium carbonate.
- Scale formation is extremely pH & Temperature dependent.
- More often than not, pitch-scale combination is frequent in bleach plant & often cause for dirt (quality) problems in pulp

- **Operating conditions to reduce Cal.carbonate scale**
  - Bark contaminations of less than 0.5%
  - Suspended solids in white liquor < 25ppm
  - Chemically treated shower water to tie up Ca++
  - Part of filtrate should be severed to remove Ca++ from loop.
  - Use of antiscalant chemical

![pH equilibrium during bleaching](image)

![CaCO3 scale in a EOP pipeline](image)

![CaCO3 scale in a MC pump](image)

![Scale in white liquor heater tubes](image)
Calcium oxalate deposit

- Oxalic acid is found in the wood also formed as a result of oxidation of lignin
- When pH drops below 7, calcium dissolves, react with oxalic acid to form cal.oxalate

Operating conditions to reduce Cal.oxalate scale
- bark contaminations of less than 0.5%
- First acid stage vat below 2-2.8 pH
- Use of specific antiscalant
BaSO4 Scale

Barium sulphate is most difficult scale to remove & prevent. Barium enters along with wood.

Simple steps to eliminate Barium Sulfate Scale:
• Reduced sulfate-ion carryover into the D0 stage is the most likely way for the elimination of this scale.
• Improve brownstock washing to reduce residual carryover of sulfate, sulfide & lignin bound sulfur.
• Avoid use of spent acid (sodium sesquisulfate) for pH control in the D0 stage.
• Acid stage vat pH below 2.0.
• Partly sewer the filtrate.
• Take chelant boil-out at regular intervals to keep wire open.
• Use of antiscalant.
Scale Control in Recovery
Evaporator Scaling & Fouling

- Kraft recovery cycle is a very effective & proven simple system
- However, scaling & fouling reduces the efficiency due to downtime
- Evaporator scaling can have serious implications on fiberline productivity if Evaporator capacity is limited

[Diagram showing the classification of evaporator scales: Hard Scale (Silica, Calcium, Calcium Carbonate, Calcium Oxalate, Pirssonite Scale) and Soft Scale (Burkeite (Sodium Sulphate/Sodium Carbonate), Dicarbonate (Sodium Carbonate/Sodium Sulphate), Precipitated lignin fragment).]
Pirssonite scale & Ways to reduce it

Pirssonite scaling occurs because of double salt $\text{Na}_2\text{CO}_3\cdot\text{CaCO}_3\cdot2\text{H}_2\text{O}$

- Improve the causticizing efficiency to 82%
  - For each 1% decrease in CE 5kgNa2CO3 enters the process
- Reduce (NPEs) dead load on the system
- Reduction in available calcium lesser will be CaCO3 and pirssonite scale
- Use scale control product with weak wash to keep the scrubber and green liquor lines clean

<table>
<thead>
<tr>
<th>%CE</th>
<th>Kg Na2CO3/ADT</th>
</tr>
</thead>
<tbody>
<tr>
<td>82</td>
<td>68</td>
</tr>
<tr>
<td>78</td>
<td>88</td>
</tr>
</tbody>
</table>

Pirssonite scale in green liq.line
Evaporator Fouling

**Sulphate Rich**
Burkeite: Double salt of 2 moles of Na$_2$SO$_4$ and one molecule of Na$_2$CO$_3$

**Carbonate Rich**
Dicarbonate: Double salt 2 moles of Na$_2$CO$_3$ and one molecule of Na$_2$SO$_4$

Either or both may crystallize simultaneously depending on ratio of carbonate to sulphate in black liquor
- Lower ratio: Burkeite
- Higher ratio: Dicarbonate
Scale types at different dry solids

At Na2SO4 / Na2CO3 crystallization solubility limit is called “Critical Solids Content”

- Reducing the content of each component to lower critical solids is key to reduce fouling.
Ways to reduce sodium scales in LTV

How to reduce Na Scale in LTV:

- Reduce Na$_2$CO$_3$
  - Improve causticization efficiency, 80-82%
  - Maintaining CE is critical to prevent both calcium carbonate scale and also soft sodium salt scales like Burkeite and dicarbonate scale.

- Reduce Na$_2$SO$_4$
  - Increase RB reduction efficiency >90%

- Add saltcake/spent acid after LTV

- Reduce total Na in black liquor
  - Control AA charge to digester
  - Reduce NaCl dead load

- Operate about 2-3% below critical solids
Ways to Reduce Fouling in concentrator

• Operate the solids profile above the crystallization point

• Encourage the sodium salts to crystallize on the suspended crystals instead of heat transfer surface

• Use high liquor circulation rates

• Maintain long residence time in concentrator

• Distribute liquor uniformly on heater surfaces

• Avoid upset conditions
  ❖ Minimize changes in black liquor composition
Calcium precipitation in Evaporator

- High Temp. break down organic near heat transfer surface
- Calcium is released and combines with carbonate
  - Deposit on the surface
  - Generally occurs at 120°C but sometimes even starts at 104°C
Ways to Reduce Calcium scaling in Evaporator

• Limit temperature
• Improve soap skimming &
• Minimize bark if possible
Ways to Reduce Silica Scaling in Evaporator

• Decrease bark and dirt in chips
• Decrease silica in make up lime
• Avoid white water in brown stock washing
• Minimize use of defoamers
• Increase silica purges with dregs and grits
Case Histories
Digester (Cal.carbonate) scale control of 750 tons continuous digester

Inspection after 6 months of operation.

Deposit on screens
- +++++
- +++
- ++
- +

<table>
<thead>
<tr>
<th>Layer</th>
<th>gr Ca/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD0</td>
<td>39.78</td>
</tr>
<tr>
<td>CD1</td>
<td>22.33</td>
</tr>
<tr>
<td>CD2</td>
<td>58.72</td>
</tr>
<tr>
<td>CD3</td>
<td>72.33</td>
</tr>
</tbody>
</table>

Customer benefit:
- Outage time improved by 133%
- No scale control used in 1st washer
Case History: Bleach Scale Control

✓ Mills Description
  - Capacity: 800T/D, BKP
  - Furnish: Hardwood

✓ Customers’ overview:
  - Scale formation on wash press holes reduces the washing efficiency and consistencies drastically
  - Increased the bleach consumption
  - Reduces the production capacity

✓ Benefits:
  - Scale control when fed with pulp to inlet of wash press after boil out controlled the scale and interval of boil out was increased from 15 days to +120 days
  - Consistencies obtained with Infinity program was +28%
  - Increased and maintained the production
Case History: Pirssononite scale control

✓ Mills Description
  - Capacity: 1200T/D, BKP

✓ Customers’ overview:
  - +2 inches scale in green liquor lines
    High and fluctuating suspended solids in green liquor
  - Required manpower and long boil out hours for cleaning pipes

✓ Benefits:
  - Scale control when fed to the suction side of the Weak Wash Pump(s) providing dilution to the Recovery Boiler Dissolving Tank
  - Completely eliminated the need to acid clean or hydro-blast the Green Liquor lines, reducing costs and minimizing safety hazards to mill personnel
  - Improves the cleanliness of the Dissolving Tank itself, reducing time and money spent during outages to clean it out.
  - Reduced green liquor inlet velocity to the Green Liquor Clarifier helps the settling of dregs, improving green liquor quality
  - Maintained the cleanliness of the Green Liquor density meter on the outlet of the Dissolving Tank
  - Improved green liquor strength variability & TSS.
Case study of mineral deposits in causticizing area

Process
- 6 digesters batch with direct steam heating.
- cooking capacity – 250 ADT/day of unbleached pulp
- one line green liquor causticizing
- capacity white liquor – 40 000 m³/Month or 55 m³/h

Target
- Provide prevent mineral deposits on causticizing line.
- Provide capacity of the white liquor - 60 m³/h
- Increasing the time between cleanings line from 2 to 6 months.

Results achieved
- Ensuring a stable flow rate of the reaction blend resulting of increased capacity of white liquor from 55 to 61 m³/h ⇔ 44 000 m³/month
- NO Cleaning equipment during the period chemical was fed on dirty equipment
- Annual savings calculated = €185 000
Case History: Evaporator Scale Control

Problem Statement:

- Evaporator fouling impacting WBL throughput
- Hyrdoblasting 1st & 2nd effects every 6 months at a cost of roughly $35K per event

Solution

- Started scale control program
- Performance improvement and cost reduction
- Installed new feed equipment and implemented automated control through DCS
- Optimized dosage and changed feed ratio between 1st & 2nd effects when in single steam configuration (more to 1st effect – hotter effect)

RECORDED BENEFITS

- Hydroblasting events:
  - #2 Evaporator extended to 2.6 years and counting (last cleaning was Aug 2016)
  - #1 Evaporator extended to 1.5 years
- Documented ROI to mill, of $210K based on historical steam usage, hydroblasting cost and chemical cost reduction
- Maintaining Steam Economy and WBL throughput
- Continue to work on program improvements
Case History - Evaporator Scale

Mills Description
- Capacity: 2,450,000 t/a, BKP, Market pulp
- Furnish: Plantation hardwood

Customer overview:
- Mill experienced increased frequency of water wash and mechanical wash of evaporator
- Burkeite & Cal oxalate was found in scale
- Level of WBL tanks remained high and evaporator became a limitation for increasing the production

Benefits:
- Scale control product when dosed with weak black liquor increased the evaporator availability (running hours) by 23%
- Solids out from evaporator increased by 1.5% (average 70% to 71.5%) at higher flows
- Even at higher total pulp production by 6.1% Weak black liquor tank level was decreased by 7.5%.
- With Scale inhibitor evaporator was no longer a limitation for increasing the production rate of fiber line
Conclusion

• Scaling is an unavoidable phenomenon, caused by the presence of trace metals, coming into the system primarily with wood.

• Low bark content, good raw material preparation, efficient dregs and NPE removal from system are ways to minimize scaling.

• Boiler ash handling, good %CE & %RE steady controlled operation are the key to reduce scaling and fouling in evaporators.
Conclusion

• Seldom, the process requirements and conditions favoring a “low scaling” environment are contradictory. In these situations, usage of scale control chemicals work best to minimize scaling.

• Indian Pulp mill conditions where hardwood availability is limited, high bark contamination cannot be avoided, non wood is a raw material source where non process elements are high, use of antiscalants is the way to minimize or live with scales
Thank You