Managing Mineral Deposit in Pulp Mill
at
IPPTA Workshop & Seminar

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19th July 2019

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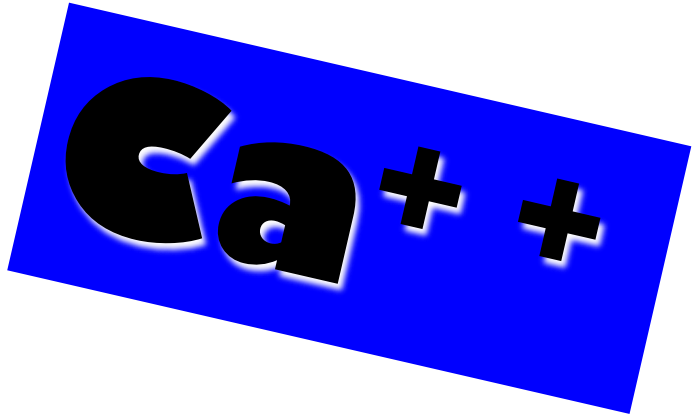
NPE in pulp raw materials

Particulars	Bagasse	Wheat Straw	Rice straw	Tropical hardwood
Ash	2.3	9.5	18	0.3
Silica	1.8	5.8	11	0.2
Potassium	0.2	1.8	2	<0.1
Calcium	0.23	0.12	0.18	0.15
Chlorides	<0.1	0.88	0.94	<0.1

expressed as % ovendry basis

Range,ppm	Non Process Elements in wood							
400-1000	K	Ca						
100-400	Mg	P						
10-100	F	Na	Si	S	Mn	Fe	Zn	Ba
upto 10	B	Al	Ti	Cu	Ge	Se	Rb	Sr
<1	Cr	Ni	Br	Rh	Ag	Sn	Cs	Ta



- In cooking: calcium scaling on the digester screens
- In bleaching:
  - Iron, manganese, copper detrimentally effect brightness
  - Calcium scales washing equipment, reducing the washing efficiency & productivity.
- In recovery: silica and calcium promote scale formation in evaps. effecting productivity

Why Does it Deposit /scale?

Necessary conditions for scaling

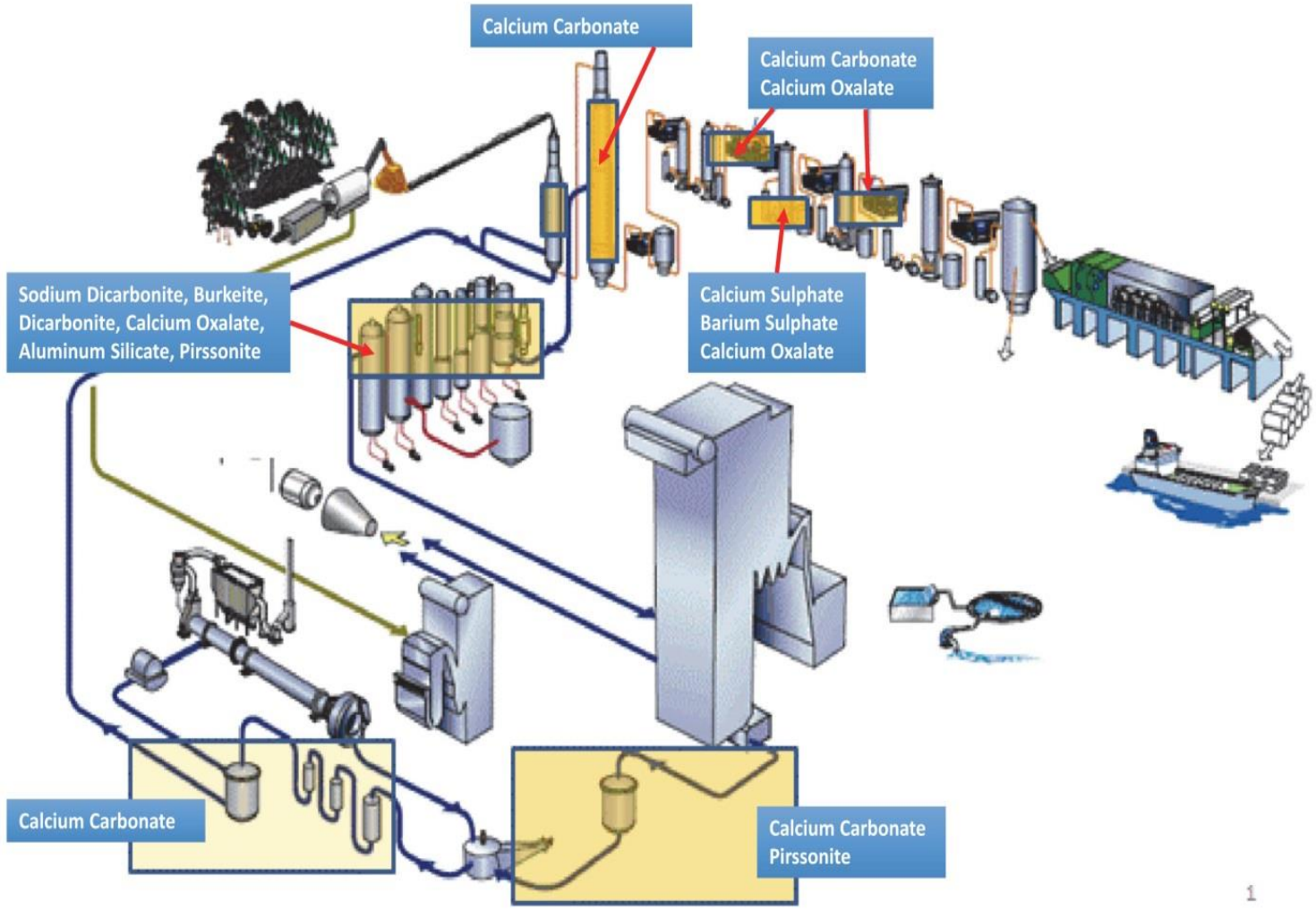
- **Supersaturation**: dissolved ions like Ca++, $CO3^{--}$,$C2O4^{--}$,Na+, Ba++ and $SO4^{--}$ increase in concentration to levels that exceed normal solubility limits

Compound	Formula	Solubility at 18°C
Calcium carbonate	CaCO3	0.014
Calcium oxalate	CaC2O4	0.0074
Sodium carbonate	Na2CO3	75
Barium sulphate	BaSO4	0.0025
Calcium sulphate	CaSO4	2.4
Sodium sulphate	Na2SO4	50

- **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)

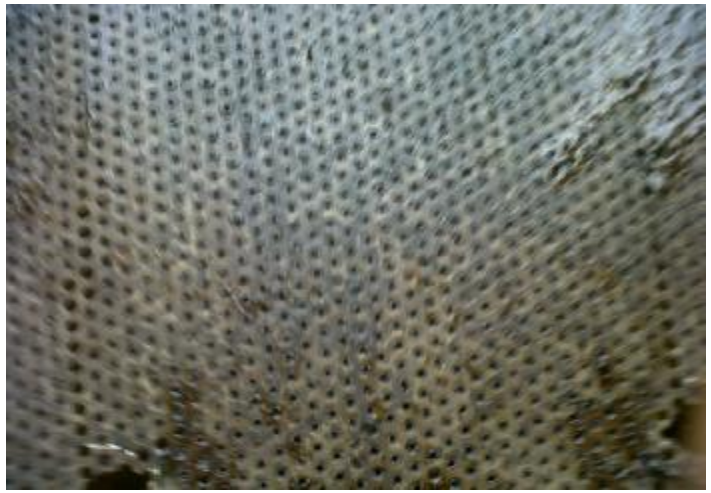
Scale Control in Fiber line

Calcium Balance in Cooking for 700 ADT/ D, with 0.4% bark

Wood	2.73kg/ADT 1914kg/day
Bark	0.11kg/ADT 77Kg/Day
WL	33.35kg/day
BL to maintain L/W	84.375kg/day
Total Ca In Dig/day	2108kg/day

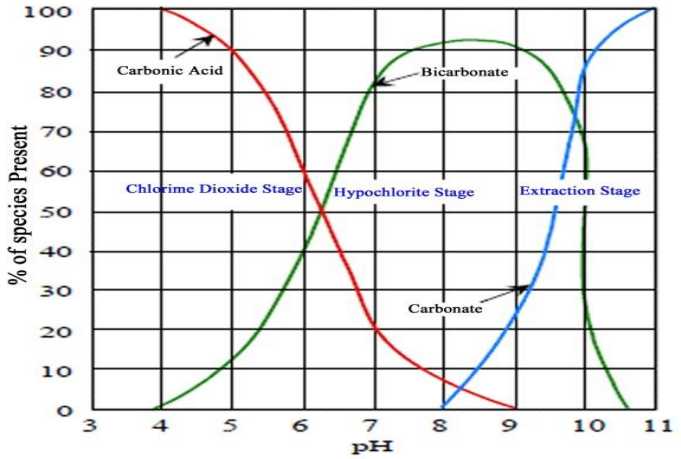
Brown pulp	290 kg/day
Liq. To Evap	962.5kg/day
Total Ca out Dig/day	1252.5kg/day

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



pH equilibrium during bleaching

CaCO3 scale in a EOP pipeline

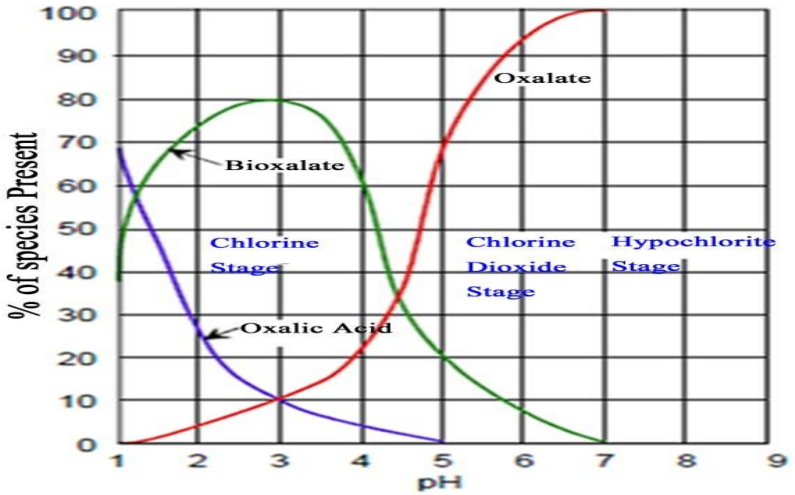
CaCO3 scale in a MC pump

- **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

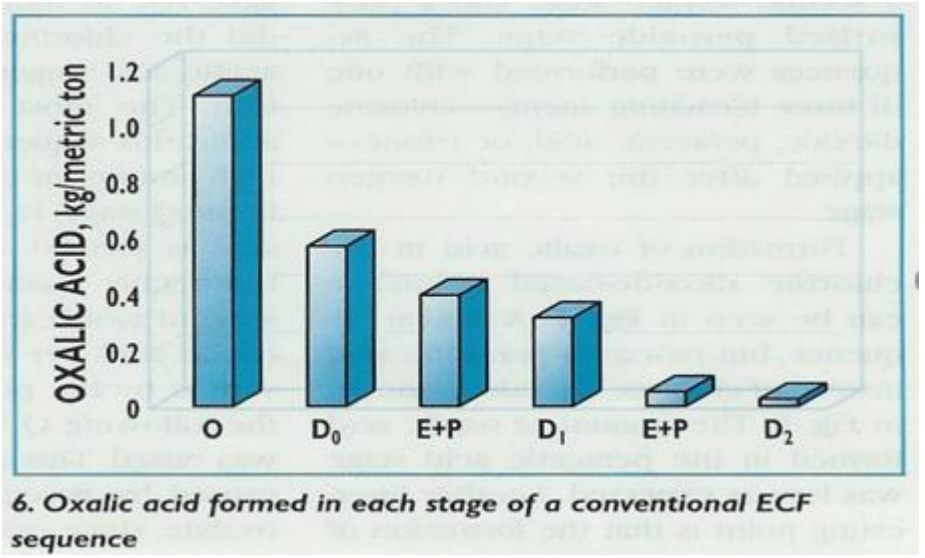
Scale in white liquor heater tubes

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



pH equilibrium during bleaching



6. Oxalic acid formed in each stage of a conventional ECF sequence

- **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 :

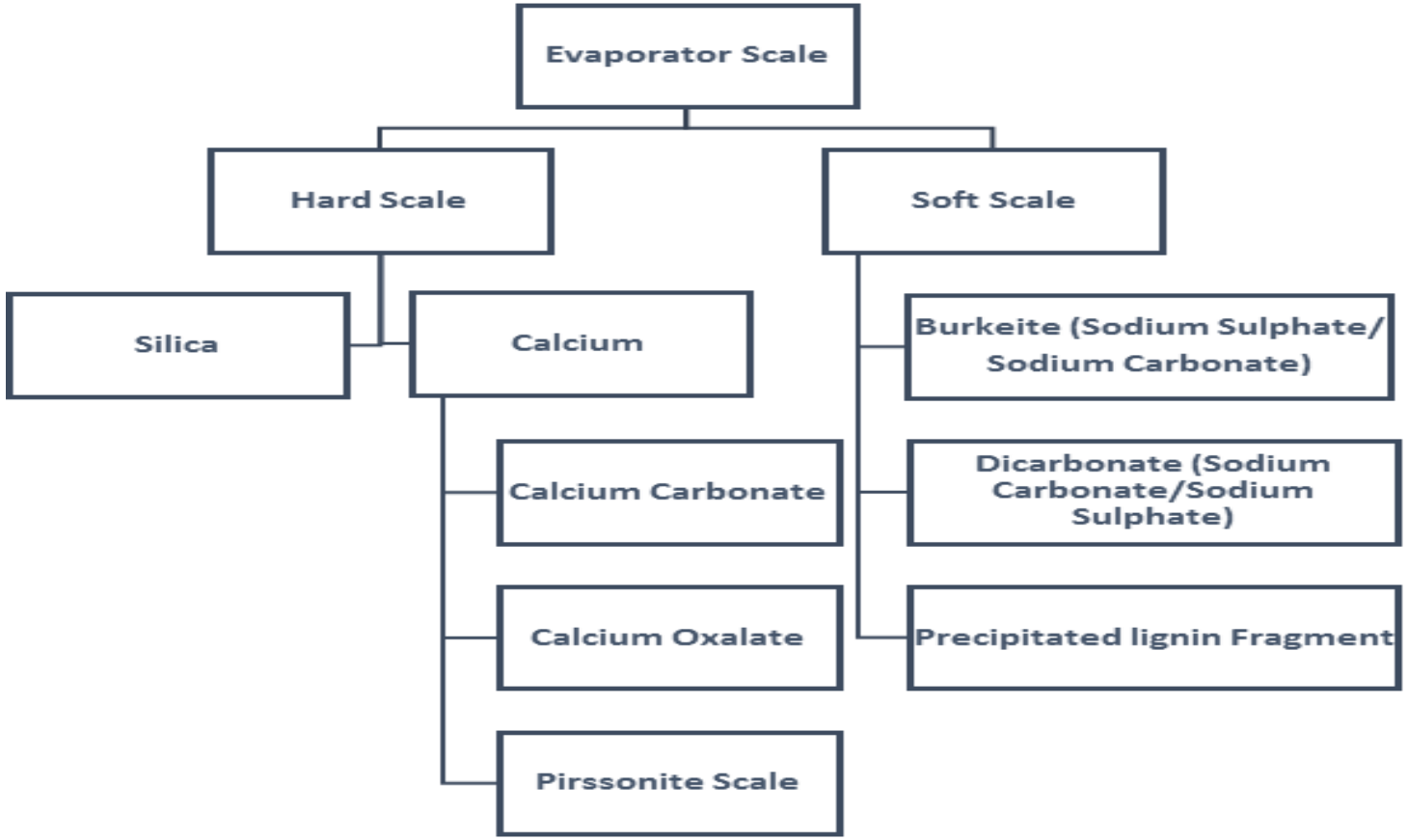
- Reduced sulfate-ion carryover into the D0 stage is the most likely way for the elimination of this scale.
- Improve brownstock washing to reduce residual carryover of sulfate,sulfide & lignin bound sulfur
- Avoid use of spent acid (sodium sesquisulfate) for pH control in the D0 stage
- Acid stage vat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

BaSO4 scale choking washer wire holes

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



Pirssonite scale & Ways to reduce it

Pirssonite scaling occurs because of double salt $Na_2CO_3.CaCO_3.2H_2O$

- 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

%CE	Kg Na2CO3/ADT
82	68
78	88

Pirssonite scale in green liq.line

Evaporator Fouling

Sulphate Rich

Burkeite: Double salt of 2 moles of Na_2SO_4 and one molecule of Na_2CO_3

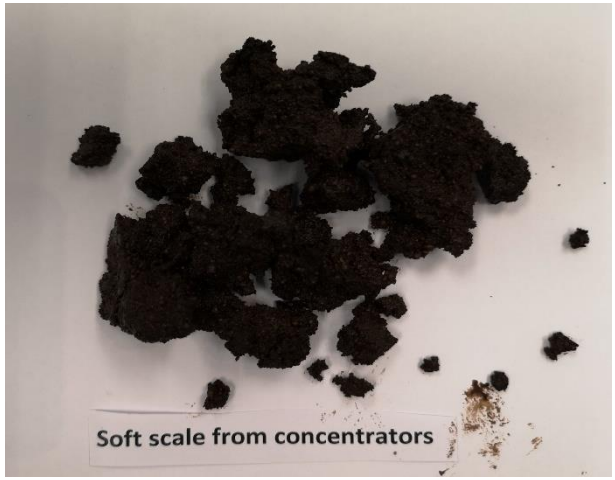
Carbonate Rich

Dicarbonate: Double salt 2 moles of Na_2CO_3 and one molecule of Na_2SO_4

Either or both may crystallize simultaneously depending on ratio of carbonate to sulphate in black liquor

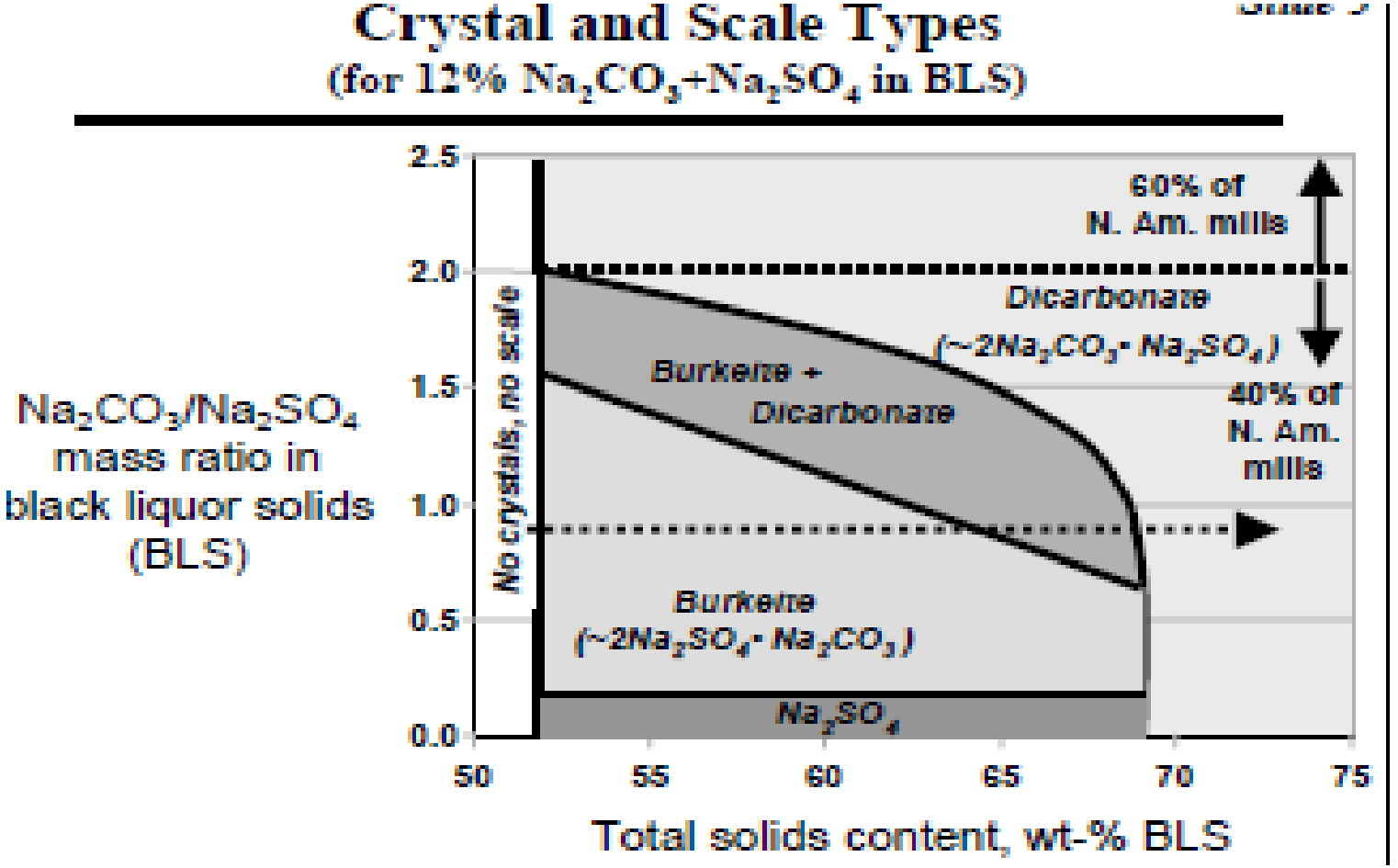
Lower ratio: Burkeite

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:

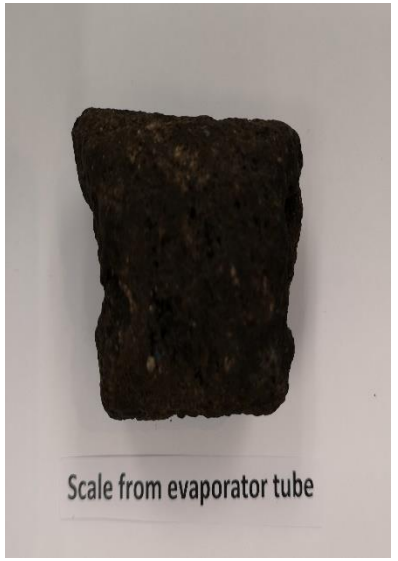
- Reduce Na_2CO_3
  - Improve causticization efficiency, 80 -82%
  - Maintaining CE is critical to prevent both calcium carbonate scale and also soft sodium salt scales like Burkeite and dicarbonate scale .

- Reduce Na_2SO_4
  - Increase RB reduction efficiency >90%

- Add saltcake /spent acid after LTV

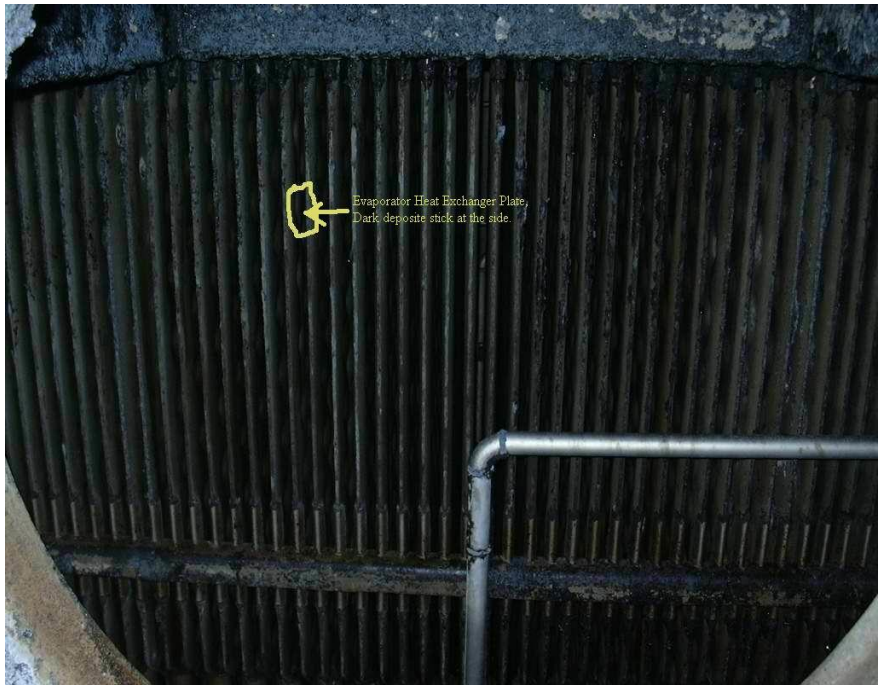
- Reduce total Na in black liquor
  - Control AA charge to digester
  - Reduce NaCl dead load

- Operate about 2 -3% below critical solids

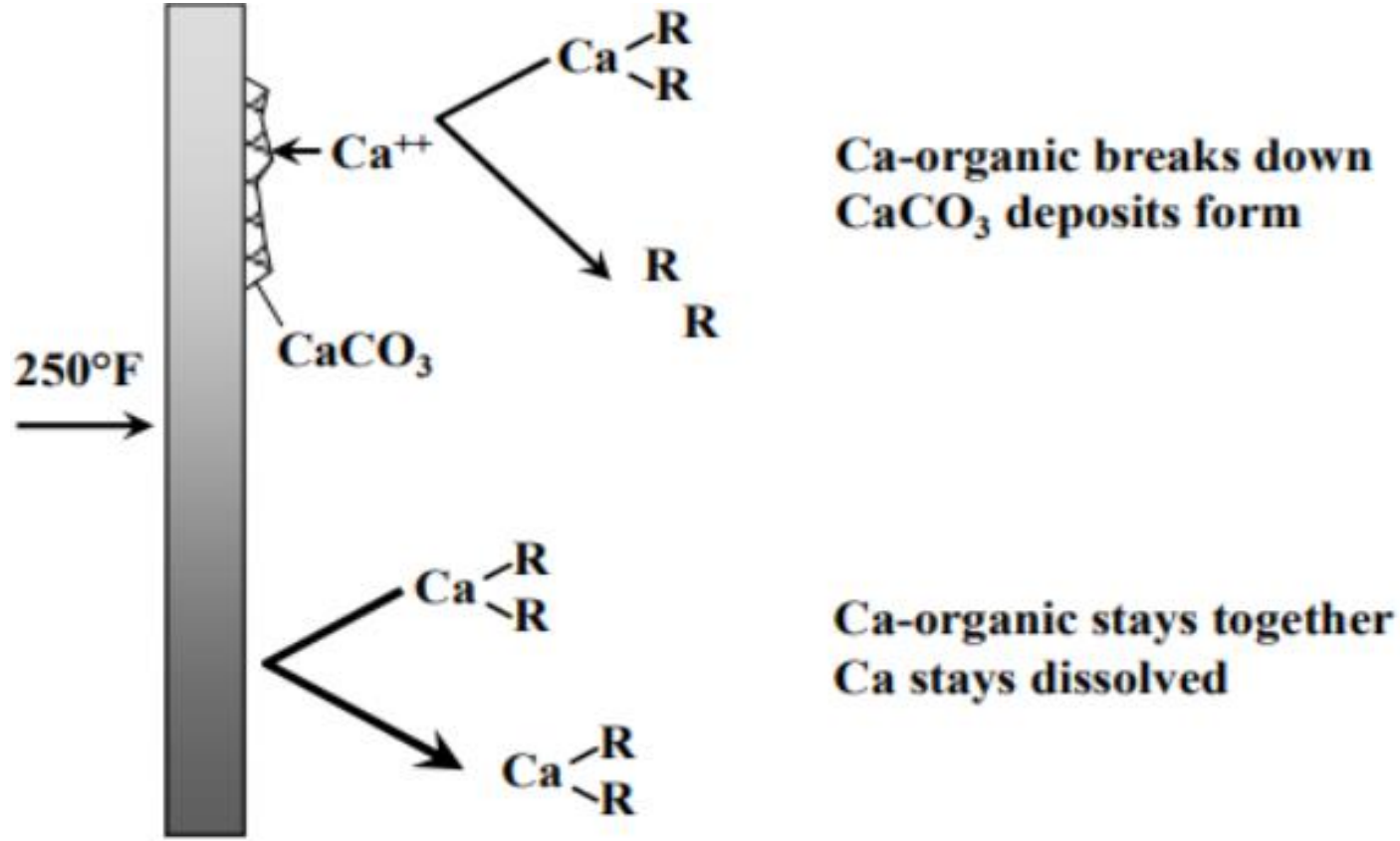

Scale from evaporator tube

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
  - Genarally occurs at 120C but sometimes even starts at 104C

Ways to Reduce Calcium scaling in Evaporator

- Limit temperature
- Improve soap skimming &
- Minimize bark if possible

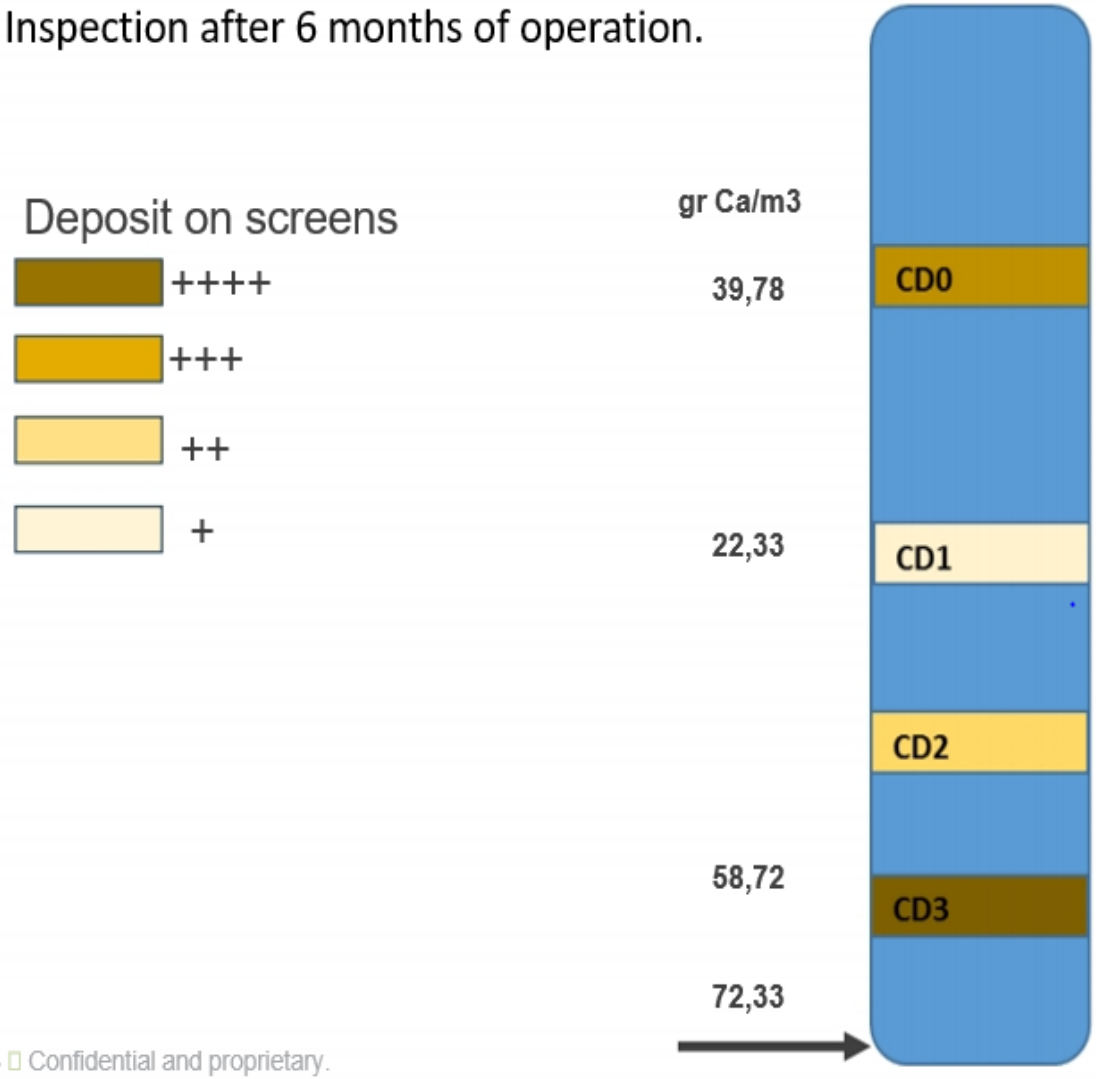
Ways to Reduce Silica Scaling in Evaporator

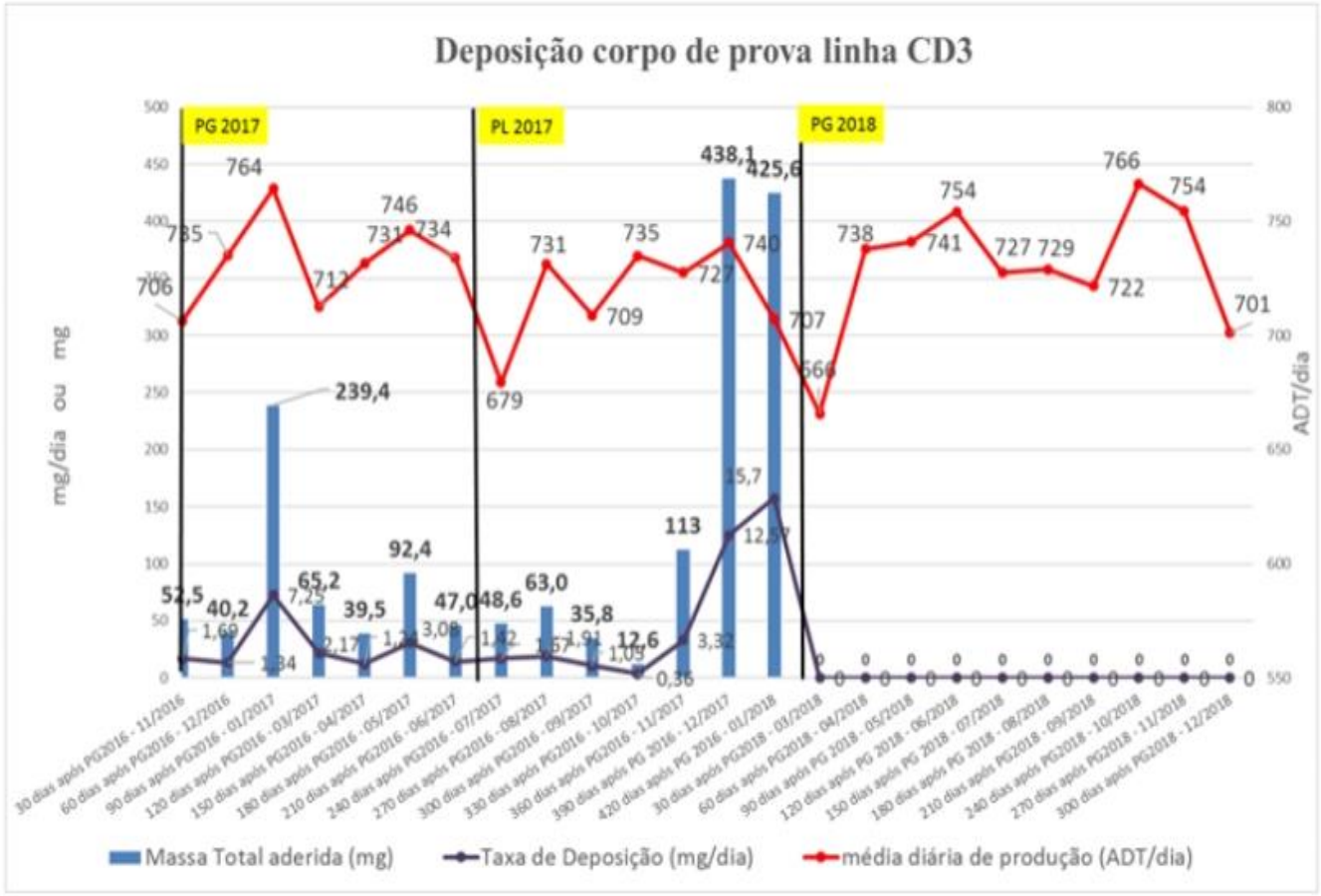
- Decrease bark and dirt in chips
- Decrease silica in make up lime
- Avoid white water in brown stock washing
- Minimize use of defoamers
- Increase silica purges with dregs and grits

Case Histories

Digester (Cal.carbonate) scale control of 750 tons continuous digester

Inspection after 6 months of operation.





Customer benefit:

- Outage time improved by 133%
- No scale control used in 1st washer

Case History: Bleach Scale Control

✓ **Mills Description**

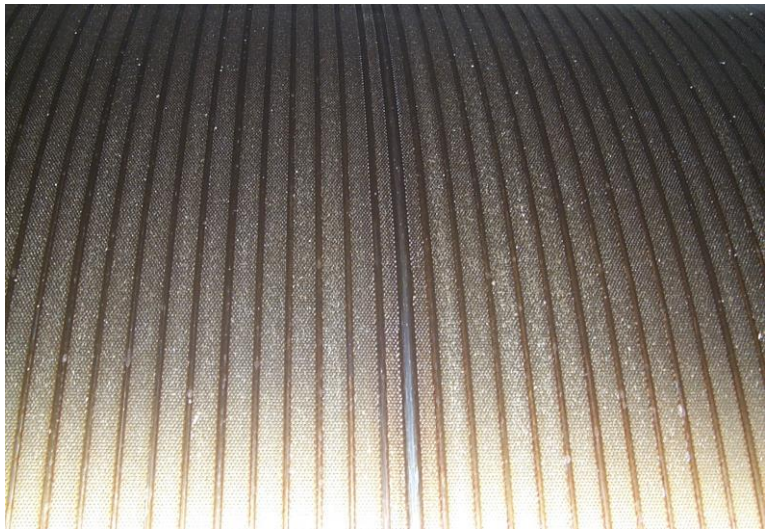
- Capacity: 800T/D ,BKP
- Furnish : Hardwood

✓ **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 +120days
- Consistencies obtained with Infinity program was +28%
- Increased and maintained the production



Choked press roll hole

Treated press rolls

Case History: Pirssonite scale control

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

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

✓ **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

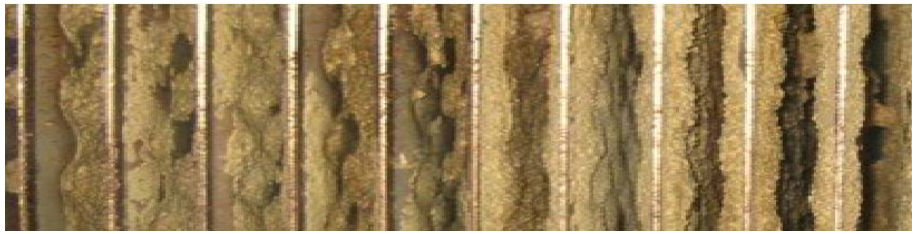
Solution

- 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

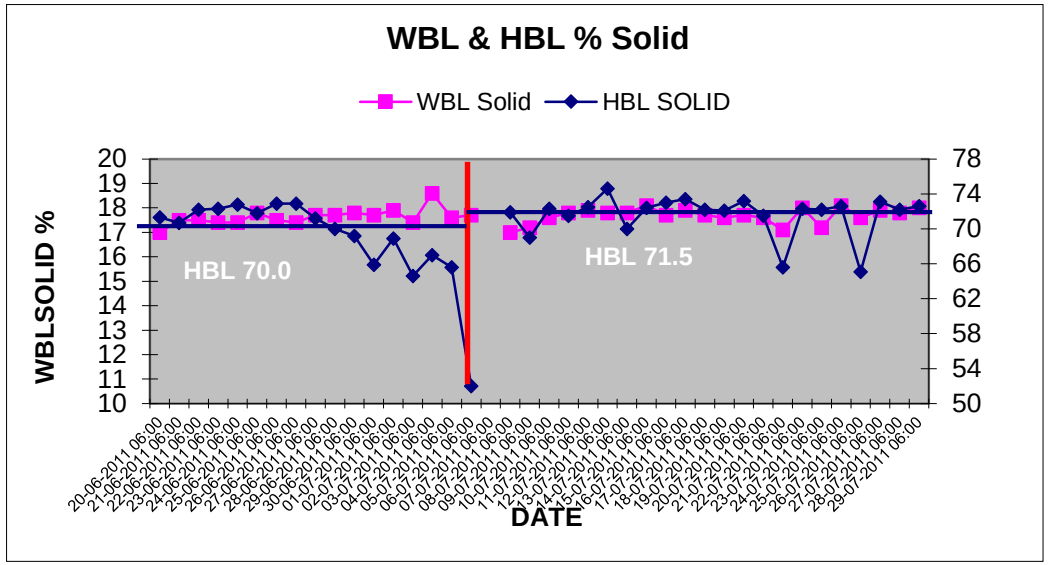
- Capacity: 2450000 t/a, BKP, Market pulp
- Furnish: Plantation hardwood

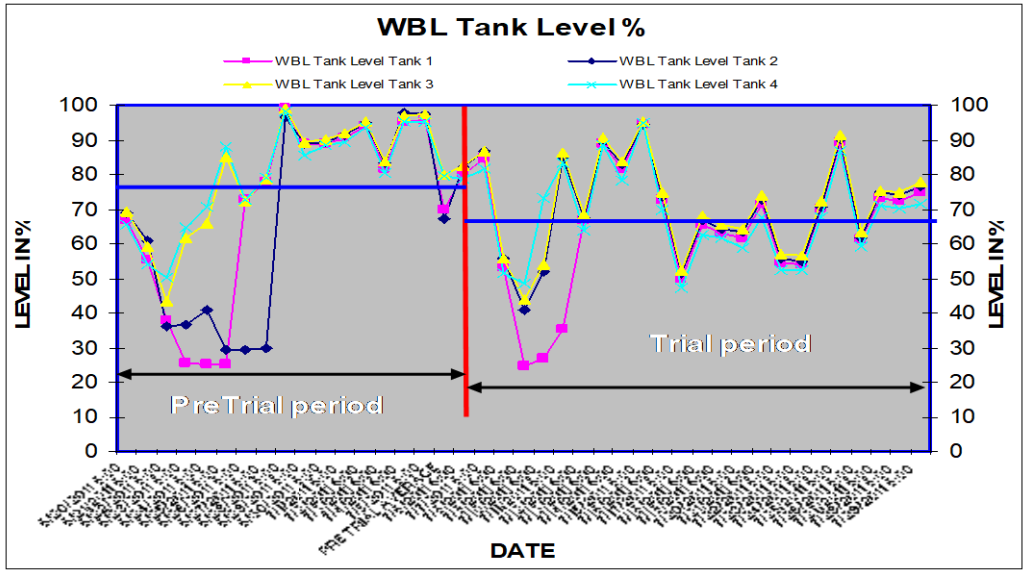
Customer overview:

- 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

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