D0 Stage Best Practices to Minimize Barium Sulphate and Calcium Oxalate Scale, Down Time and Cost

Michael Wang, *Ph. D*,

SOLENIS™

Agenda

- Ideal condition of the first stage in multiply bleaching sequence
- Effect of pH on ClO_2 delignification and scale formation
  - ✓ *Effect of pH on chlorite and chlorate formation*
  - ✓ *Best pH in terms of optimal efficiency for delignification and brightness*
  - ✓ *What happens when ClO_2 is operated under elevated pH?*
- Comparison of calcium carbonate and barium sulphate
- Impact of raising D0 pH on scale formation
- Minimize scale formation via process optimization
- Benefits to adopting a scale control program
- Present scale inhibitors used in the industry
  - ✓ *Comparison of various scale inhibitors at various pHs*
  - ✓ *Case studies with advanced scale control technology*
- Industry best practice

Ideal condition of the first stage in multiply bleaching sequence

Idea chlorination conditions

- ✓The pH of chlorination: <2
- ✓Pulp consistency: 3%
- ✓Retention time: ~ 30 min.
- ✓Temperature: <50 C
- ✓Impact on calcium solubility

Ideal D0 conditions

- ✓The pH of D0 stage: 2.5 ~ 4.5
- ✓Pulp consistency: 10%
- ✓Retention time: 30 ~ 80 min.
- ✓Temperature: 75 C
- ✓Impact on metal ions solubility

Effect of pH on ClO_2 Bleaching Reactions

ClO_2 + Pulp → ClO_2^- → Cl^- + ClO_3^- @ pH 3

→ Cl^- + ClO_2^- + ClO_3^- @ pH 5.8

→ ClO_2^- No reaction @ pH 7

$2ClO_2 + 2\ OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O$ pH > 7.5

$HClO + 2HClO_2 \rightarrow 2\ ClO_2 + Cl^- + H^+ + H_2O$

$8\ HClO_2 \rightarrow 6\ ClO_2 + HClO + HCl + 3H_2O$

$HClO + Cl^- + H_3O^+ \rightleftharpoons Cl_2 + 2H_2O$

$HClO + 2HClO_2 \rightarrow 2\ ClO_2 + Cl^- + H^+ + H_2O$

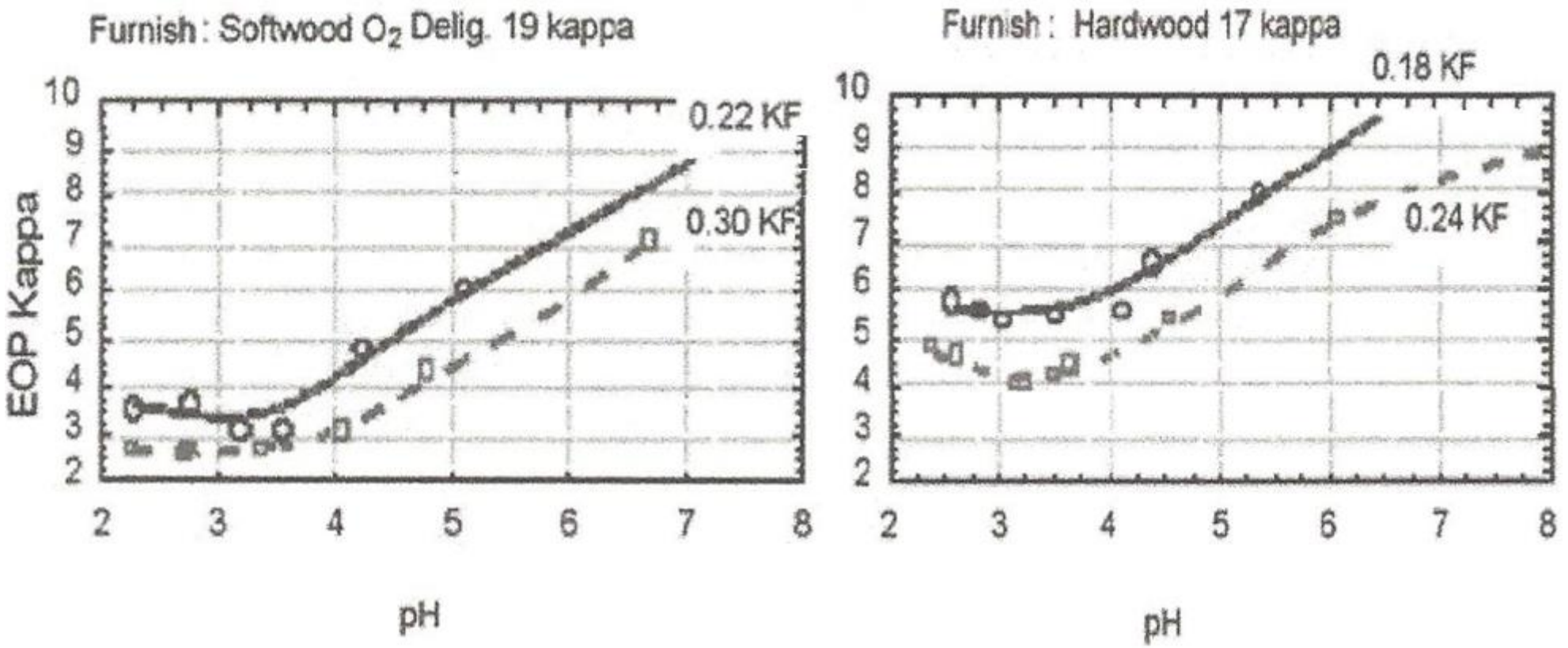
$2\ HClO_2 \rightarrow H^+ + HClO + ClO_3^-$ pKa = 1.96

$HClO \rightleftharpoons H^+ + ClO^-$ pKa = 7.54

Chlorine Dioxide Delignification Reactions at D0

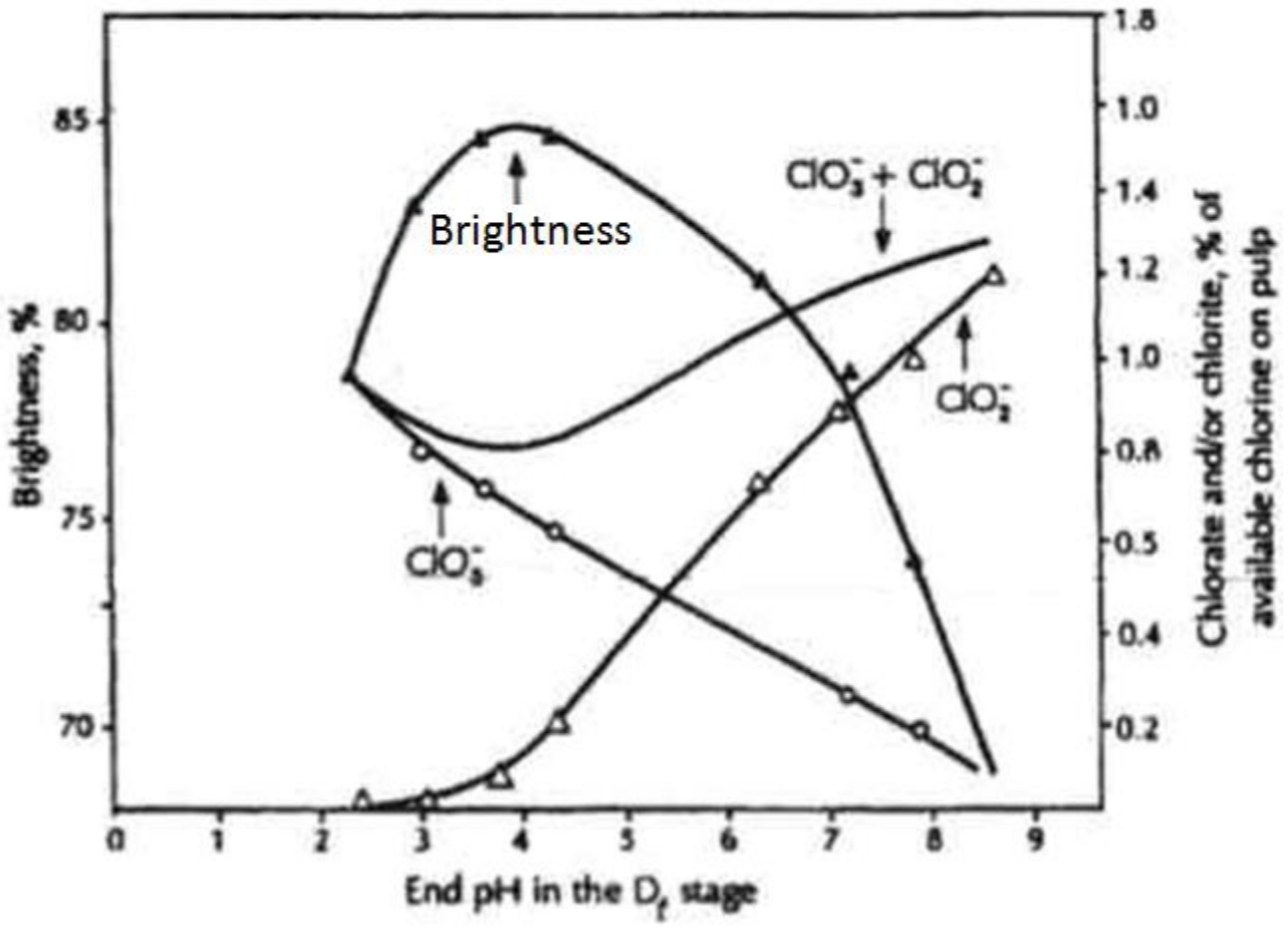
- ClO_2, $HClO_2$, HClO, and Cl_2 are all present no matter whether ClO_2 or ClO_2^- are used initially (acidic medium)
- ClO_2 reacts with both free phenolic and etherified units.
- Cl_2 (low pH) delignification is through substitution and oxidation
- High pH (>4.5) favors to generate ClO_2^-. Chlorite reacts only with free phenolic hydroxyl group and very slow (stop when pH>7)
- Oxidations contributes little to delignification in the subsequent extraction stage

Impact of D0 pH on Eop Kappa Reduction



Hart, P. & Connell, D. July 2008 Tappi Journal

Effect of End pH on Pulp Brightness and Chlorite & Chlorate Formation



Rapson at. el.

What happen when ClO_2 is operated under elevated pH?

- Calcium oxalate is formed when the pH is above 3.5
- Barium sulphate scale may appear below pH 3.5
- Calcium carbonate scale in Eop may increase due to CaC_2O_4 carryover

Comparison of Calcium Oxalate and Barium Sulfate

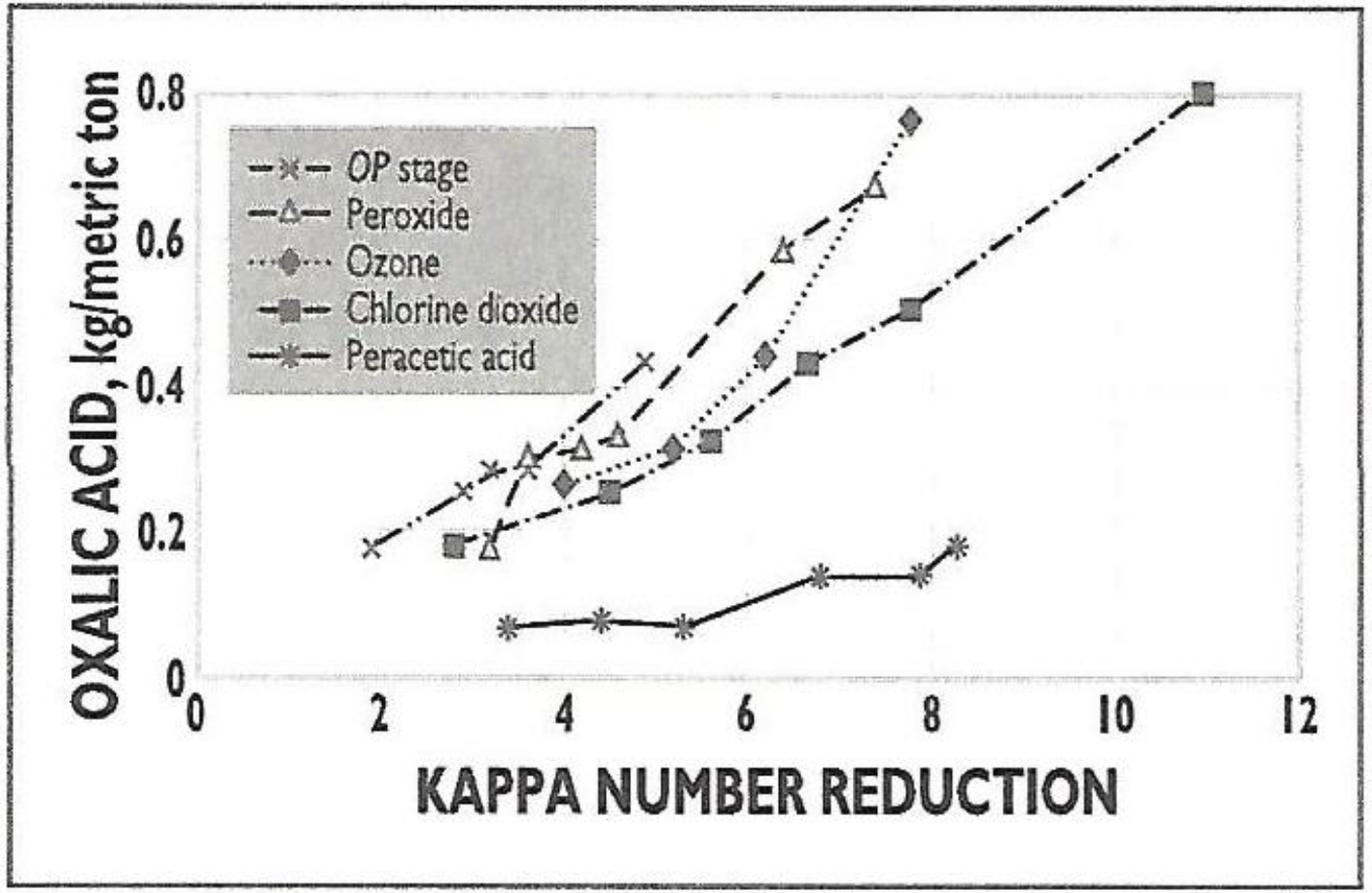
- Major source of Ca ions are from wood chips, especially bark. Typical HW pulp contains 2000 – 6000 ppm, 1000 – 4000 ppm for SW. Ca is associated with anionic groups in the pulp
- Calcium scale has inverse solubility (higher temperature = lower solubility).
- Majority of $C_2O_4^{2-}$ are coming from wood bark, cooking and oxygen delignification.
- K_{sp} for Ca C_2O_4 is $1.7x\ 10^{-9}$.
- Infinity of ions to fiber follows the following order:

  $H^+ > Ca^{2+} > Na^+ > Mg^{2+} > Ba^{2+}$

- CaC_2O_4 will be dissolved when the system pH drops to 2.8

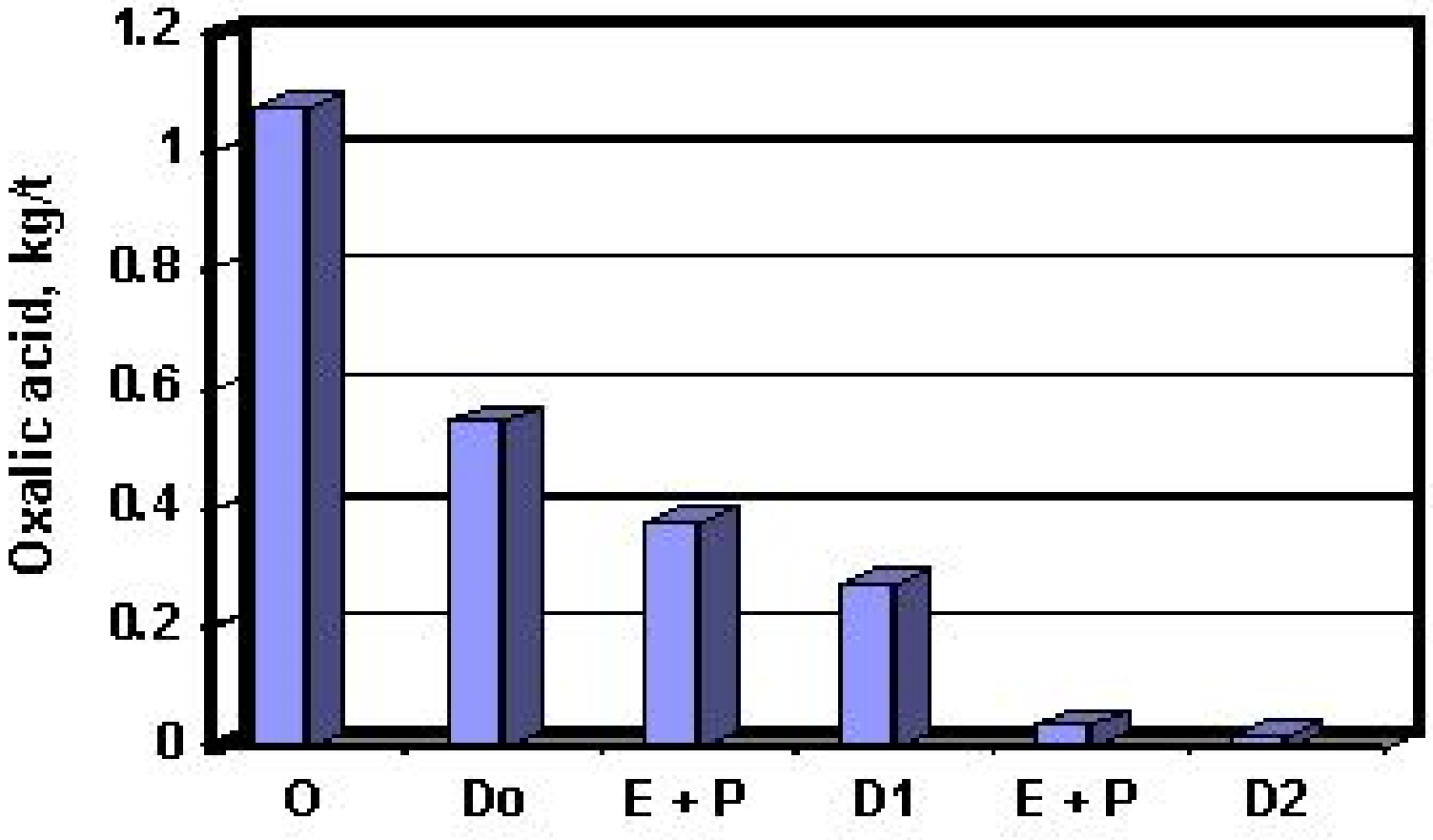
- Major sources of barium are from wood and bark. Typical HW pulp contains 20-60 ppm and 10 ppm for SW pulp.
- Majority of barium present in pulping process in $BaCO_3$ form. It will be dissolved when the system pH is below 7 and converted to BaSO4 that will not be dissolved again.
- Majority of SO_4 comes from acid used to control D0 pH. Additional sulphate may come from carryover from brown stock, paper machine white water. $BaCO_3$ scale carried
- $BaSO_4$ solubility increases with increasing temperature, ionic strength and organic substances.
- K_{sp} for $BaSO_4$ is $1.1x\ 10^{-10}$, lower than CaC_2O_4

Oxalic Acid Formed kg/t vs Kappa Reduction with Different Bleaching Agents



A.Elsander, M. Ek, G. Gellerstedt
TAPPI J., Vol. 83, (2) 73-77

Oxalic Acid Concentration in Each Bleaching Stage



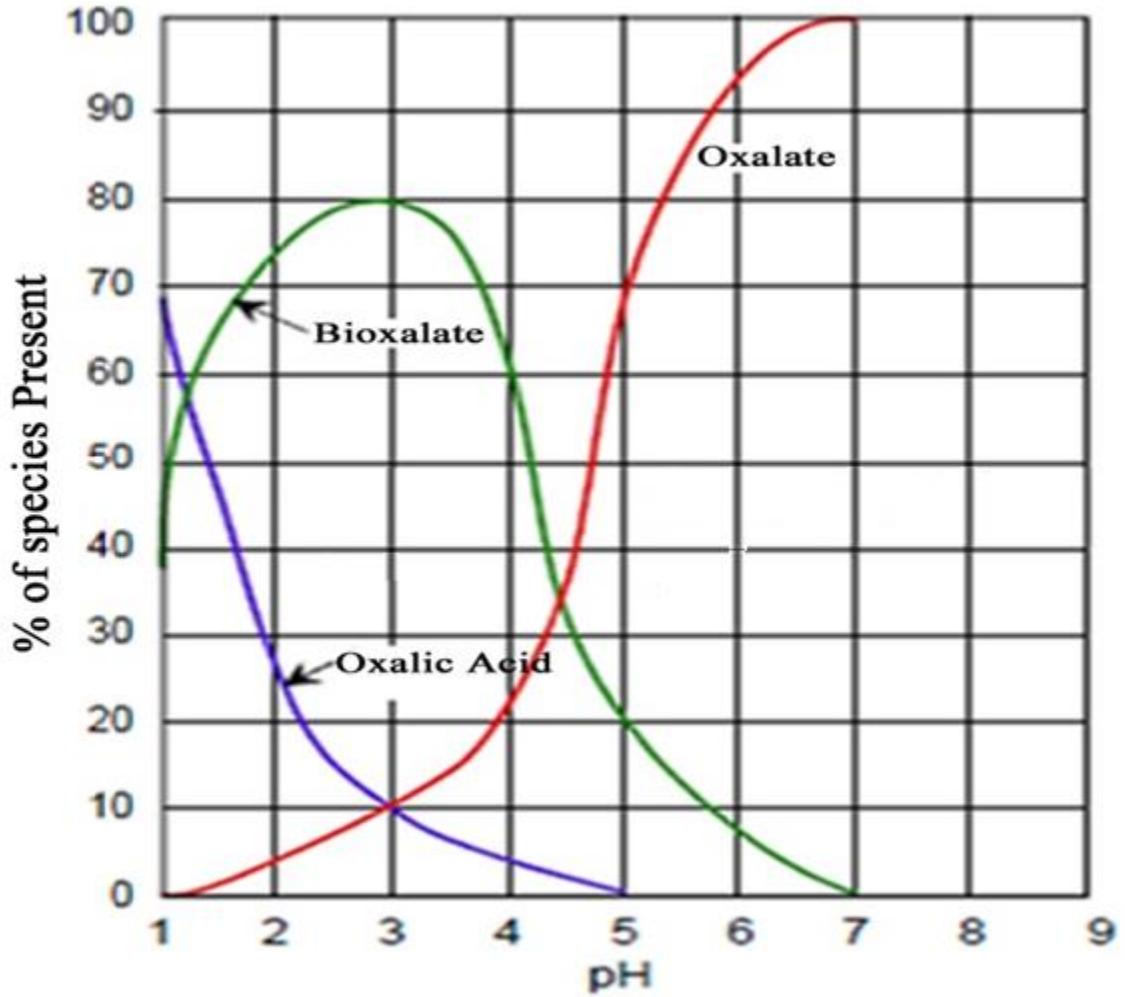
A.Elsander, M. Ek, G. Gellerstedt
TAPPI J., Vol. 83, (2) 73-77

Oxalic acid is formed in the O2 stage(s) due to oxidation of lignin - 250 – 500 g/ton of pulp.

Impact of Raising D0 pH on Scale Formation

- Bleach stage pH changes the cat ions solubility and cannot be removed during washing
- The process pH alters anions concentration through equilibrium
- Low D0 pH needs more acid – increase sulphate anions concentration
- The process pH also changes the deposit form
  - pH >7 $BaCO_3$, pH <3.5 $BaSO_4$
  - Microcrystal calcium oxalate formed in D0 may carry over to extraction stage to form calcium carbonate in Eop stage

Effect of pH on Concentrations of Oxalic Acid, the Bioxalate, and Oxalate



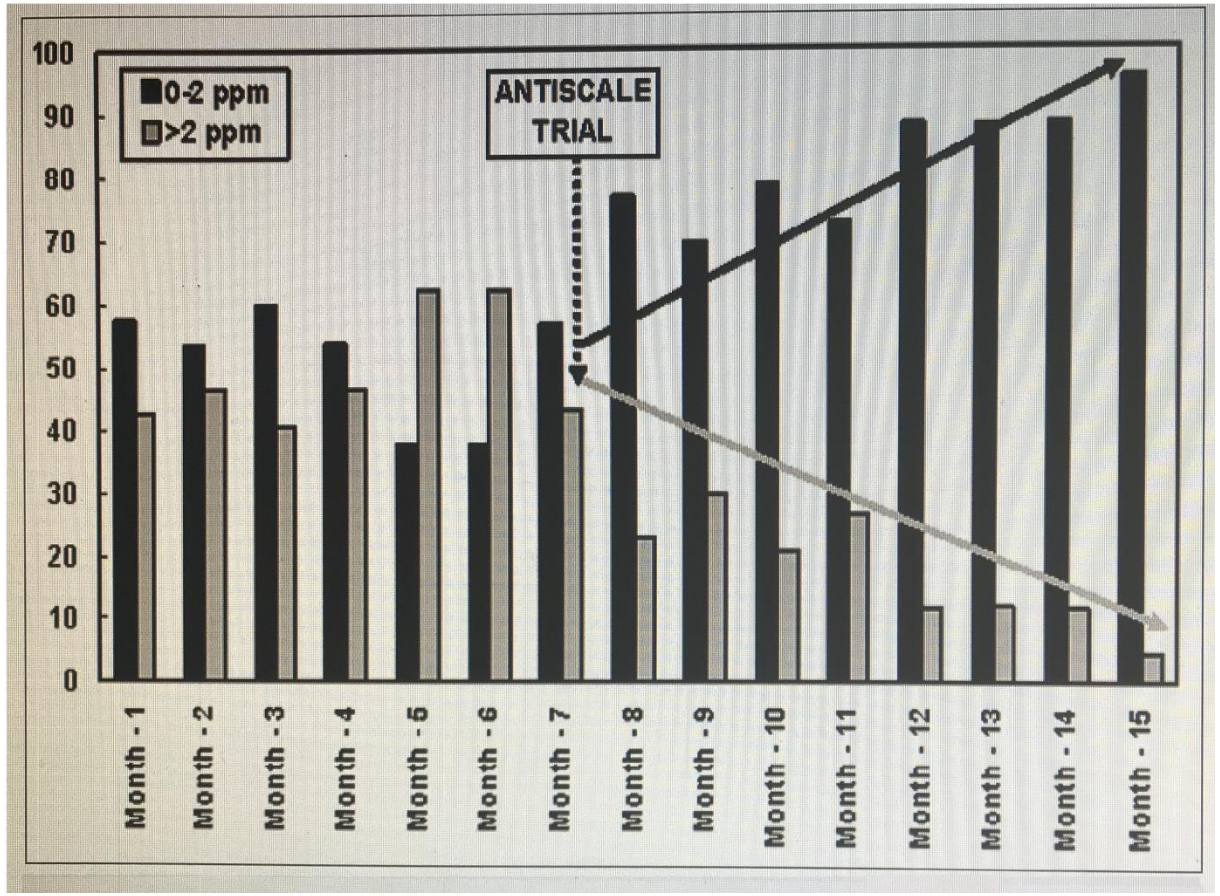
Minimize Deposit Formation via Process Optimization

- Control bark content –less calcium, barium and carbonate
- Improve brown stock washing to reduce any form of caustic and sulphur containing compound, and barium
- The pH of the bleaching is a very important factor. Lowering D0 pH to 2.5 – 2.8 can minimize calcium oxalate
- Predict where scale reaches the supersaturation point. Purge D0 filtrate partially to avoid calcium/barium build up
- Avoid running countercurrent washing in the bleaching plant
- Avoid controlling D0 pH with spent acid from ClO2 plant

Benefit of Adopting a Scale Control Program

- Improve ClO_2 bleaching efficiency and reduce ClO_2 consumption
- Reduce operating costs by lowering acid and caustic usage
- Minimize down time and save water - reused water calcium concentration reaches a very high level
- Lower maintenance cost due to high metal ion levels (resulting from a higher D0 pH, high bark content and water shortage)
- Use crystal modifier to push scale location from a pump to storage tank or pipeline etc.
- When a bleach plant faces both calcium oxalate and barium sulphate scales

Benefit of Lower Dirt Levels in the Final Pulp, Less Deposits in Pump



No Scale Control

With Scale Control

M.H. OLIVEIRA, J-FOR, VOL.2, NO.1, 2012

Effect of pH on Various Calcium Oxalate Inhibitors Performance

Inhibitor required (mg/L) for 100% Calcium Oxalate inhibition at varying pH.

	Inhibitor (mgL)						
	pH						
Inhibitor	3	4	5	6	7	9	9.5
SHMP	0.1	0.5	8.0	10.0	>10	>10	
STP	0.1	>5	>10	>10	>10		
PAA*	0.5	>5	>5	3.5	1.5	1.2	2.5
SHMP/PAA	0.2	1.0	10.0	6.0	3.0		
SHMP/CP**	0.2	1.0	10.0	7.5	4.0		

*PAA = Polyacrylic acid (8-12K Mol. Wt.) **CP = Copolymer of AA and AMPS

Experimental Conditions: Total Calcium - 16mg/L, Total Oxalate - 35.2 mg/L Temperature - 60 oC

Advances in Crystal Growth Inhibition Technologies edited by Zahid Amjad

Case 1. Effective Program Creates Huge ROIs

Items	Pre-treated	Present	ROIs
D0 pH	*2.5*	*3.5*	
H_2SO_4, lb/t	*16.42*	*5.42*	*$165 k/y*
ClO_2, lb/t	*38*	*33.2*	*$700 k/y*
Cleaning Schedule	*2 weeks*	*7-8 weeks*	*
Boilout	*Each shut down*	*Every other shutdown*	*$54k/y*
Scale	*$BaSO_4$, CaC_2O_4*	*Significantly reduced*	*
Production, t/d	*980*	*1020*	*$423k/y*

* Provide additional ROIs to the mill

Case 2. Reduce ClO2 Usage, Maintenance and Down Time

- Production: 1600 t/d Kraft SW/HW pulp with D0EopDED bleaching

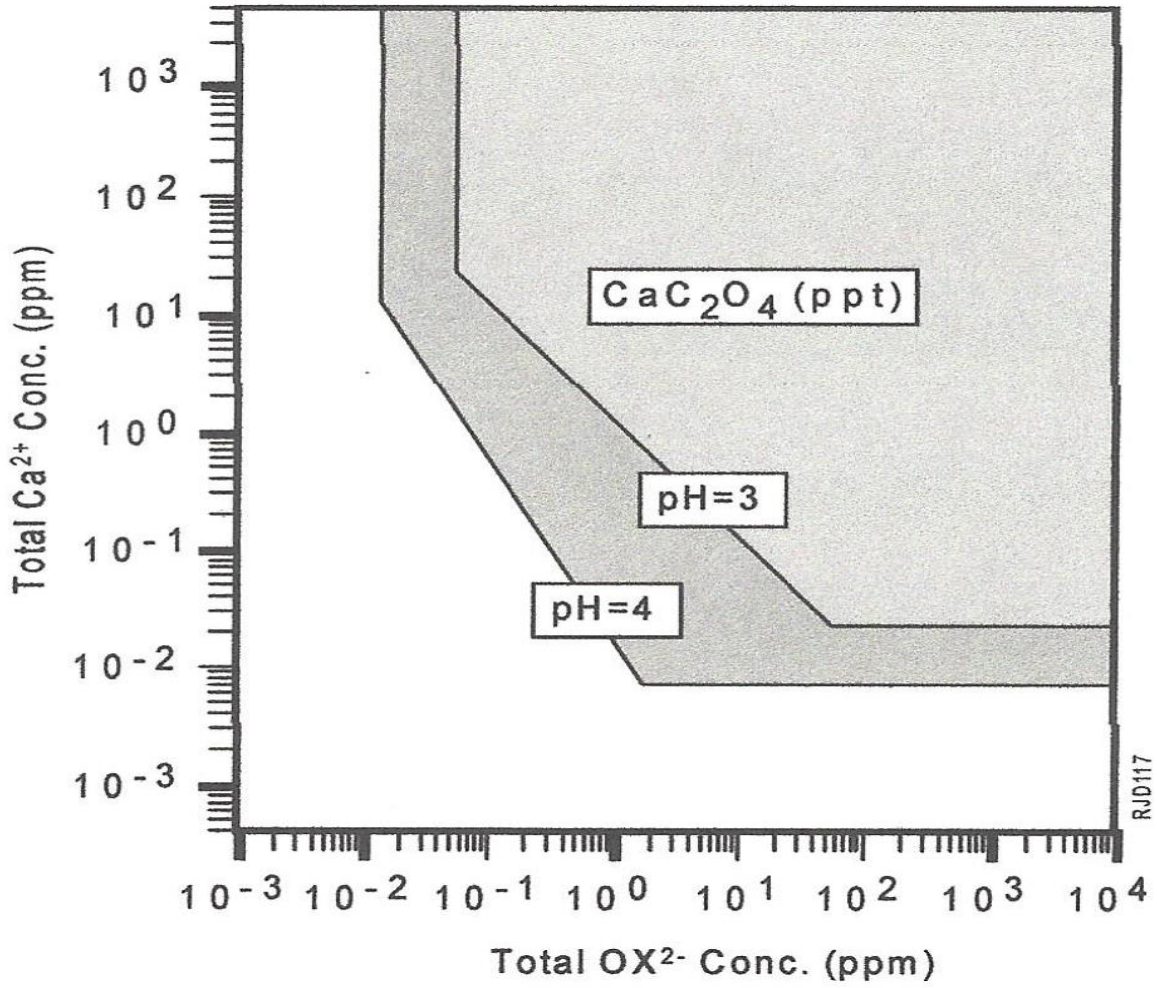
- Chelant boilout 5-6 times a year at D0 scale, Eop scale limited pulp production. Scale problem needs more down time, acid and safety risk

- Benefits delivered after applied 0.1-0.4 kg/t of scale control product
  - Chelant boilout reduced from 5-6 times to 1-2 times.
  - Reduced ClO2 1.5 kg/t and 3 kg/t NaOH at Eop stage
  - Purge partial filtrate from D0 to remove Ca
  - ROIs for the program are over $1,000,000 a year

Best Practice to Control CaC_2O_4 and $BaSO_4$

- Control bark contamination to less than 0.5%
- Improve brown stock washing to remove as much sulphur containing compounds, caustic and barium, calcium as possible
- Control the first bleaching stage end pH to 2.5 - 2.8
- Predict where metal ions reached supersaturation and purge filtrate from process partially to remove calcium and barium
- Avoid running countercurrent washing in the bleach plant
- Avoid controlling D0 pH with spend acid from ClO_2 plant
- Raise D0 pH to around 3 – 4 to save ClO_2, caustic and acid and improve D0 efficiency while using crystal modifier antiscalant

Predict calcium oxalate scale in the mill conditions



R. Dexter, X.H. Wang

- Thank You!

- Any Questions?