Bleach Plant Scale Control Best Practices to Minimize Barium Sulfate and Calcium Oxalate Scale, Down Time and Cost

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ABSTRACT

Chlorine dioxide used as a delignification agent in the first stage (D0) of a bleach plant is a common practice in North America. Compared to a conventional chlorination stage, using chlorine dioxide at the D0 stage requires a relatively high pH (2.5 – 4.5) to achieve maximum delignification and bleaching efficiency. These operating conditions often result in an increased risk of developing either barium sulphate and/or calcium oxalate scale, depending on the operating pH range. This can lead to significant production losses, extra maintenance costs, high bleaching chemical costs and quality issues. Through process modification, many mills are able to reduce or eliminate calcium oxalate scale formation by running the D0 stage at a relatively low pH. These same mills incur higher costs though as a result of higher acid and caustic costs. For mills with higher barium levels, lowering the pH in the first chlorine dioxide (D0) stage will also increase the risk of barium sulphate scale, particularly if the mill uses spent acid from chlorine dioxide generation. For mills having limited water supply or using water with high hardness, calcium oxalate issues can be even more problematic when those mills operate at the higher end of the pH range (3.5 – 4.5). This paper will discuss how several mills have improved their bleach operation efficiency, reduced down time and decreased maintenance costs with a scale control program that manages both barium sulphate and calcium oxalate scale. The program provides additional benefit by allowing the D0 stage to operate at a slightly higher pH, in resulting in incremental of caustic and acid savings.

Keywords: D0 Stage, Scale Control, Bleaching, Cost Reduction, Best Practice, Calcium Oxalate, Barium Sulfate

INTRODUCTION

The operating conditions of a chlorination stage in a conventional bleach sequence are very acidic with the pH typically below 2 [1]. The low pH enables chlorine substitution and oxidation reactions to complete in a very short time. Chlorinated lignin is hydrolyzed and dissolved in an alkaline medium through the subsequent extraction stage. At the very low chlorination stage pH, more metal ions become soluble and are removed during washing. The low pH also minimizes the concentration of oxalate anion such that calcium oxalate scale rarely becomes an issue. On the other hand, barium sulfate scale at this low pH

can be problematic for some bleach plants, especially mills that use spent acid from the chlorine dioxide plant to control D0 pH.

When the industry eliminated elemental chlorine to minimize AOX formation from bleach plants, chlorine dioxide was introduced to replace chlorine at the first stage (D0) of the bleach plant. Industry researchers [2] examined the effect of pH, kappa factor, and temperature on chlorine dioxide decomposition and DED bleach sequence performance. They concluded that at a given charge of ClO2, maximum final pulp brightness was achieved when the D0 stage was operated at pH 4.5 within the range of 2.5 – 7.5. When the D0 stage is operated in an acidic media, the reactive species ClO_2, $HClO_2$, HClO, and Cl_2 are all present in the system no matter whether ClO_2 or ClO_2^- are used initially. At the pH below 2.5, chlorine will be the major reactive species, which will lead to a decrease in the delignification and an increase in formation of AOX [3]. To make chlorine dioxide (as the major reactive species) react with free phenolic and etherified units of lignin [4], the D0 stage pH needs to be higher than 2.5. As the pH rises to above 4.5, chlorine dioxide will convert to chlorite, which reacts only with free phenolic hydroxyl groups and this reaction stops when pH is above 7. Therefore, chlorine dioxide delignification should be operated below pH 4.5 to minimize chlorine dioxide decomposition [1, 4]. However, by increasing D0 pH to around 4, the solubility of the metal ions (calcium and barium) are decreased. This pH is not low enough to protonate the oxalate anion, resulting in the formation of calcium oxalate [5, 6]. Consequently, some mills face serious calcium oxalate scale problems in the D0 stage. Furthermore, precipitated calcium oxalate trapped in the fibers at the D0 stage becomes a major calcium source contributing to the formation of carbonate scale in the following extraction stages [5].

To reduce the formation of calcium oxalate and barium sulfate scales, industry researchers initially focused on metal ion and anion sources and their distributions in the system [7,8]; the impact of ion-exchange on metal ions release [9, 10] and oxalic acid formation during the bleaching process [11], as well as the scaling component balance in the bleaching process [12,13]. Based on calcium and oxalate concentrations from mill surveys and pH impact, the mill conditions are simulated to predict where the supersaturation point is reached [14]. Researchers concluded that most of the calcium oxalate scale at the mill can be eliminated by operating the D0 stage pH around 2.5 - 2.8, which still puts the D0 stage pH within the target optimal pH for chlorine dioxide [15, 16]. Within this pH range, calcium remains soluble and can be removed at the D0 washer. It also keeps the oxalate anion concentration at an acceptable level. If a bleach plant suffers from both calcium oxalate and barium sulfate scales, lowering the D0 pH cannot prevent barium sulfate scale from formation. A process-based control strategy to eliminate sulfate [17, 18] is required at very low pH.

Besides process optimization to control bleach plant scale, industry researchers also developed numerous antiscale additives to reduce or eliminate mineral deposit problems based on effect of inhibitors functional group, molecular weight, and concentration on scale crystal structure modification [16, 19-20]. The scale inhibitors offer an alternative approach to barium sulfate scale control if the mill is unable to invest the capital to improve brownstock washing or to install an oxygen delignification.

Sources of metal ions (Ca and Ba) and anions (Oxalate and Sulfate)

The majority of calcium brought into the bleach plant is from the wood. Calcium concentration ranges from 1,000 ppm to 30,000 ppm depending on wood species. Hardwoods typically have a higher level of calcium concentration with an average ranging from 2000 ppm to 6000 ppm, and softwoods about 1000 ppm to 4000 ppm. Usually calcium ions are associated with anionic groups within the fibers such as carboxylic, phenolic, hexenuronic, carbonyl etc. [9-10, 12]. The calcium ions begin to dissociate when the process pH drops below 7. At a low pH, calcium ions can be replaced with protons and be released. Through washing, they can be removed via the filtrate. When the bleach plant reuses this filtrate, the calcium ion concentration within the loop can build up to a very high level. Because bark typically contains more than 10 times the calcium and oxalate anions than the wood chips, reducing bark content is an effective way to control calcium scale. Table 1 shows metal ions concentration in various wood species [20]. In an average mill it can reach as much as 3000 mg/kg in hardwood brownstock pulp [14]. Even if it diluted to 3%, the calcium concentration still reaches 100 mg/l. Once calcium is released and meets the oxalate anion, they will couple to form calcium oxalate. High levels of calcium in the system are a major contributor to calcium oxalate formation.

Table 1. Trace Metal Ions Concentration in various Wood Species

Species	Ca mg/kg	K mg/kg	Mg mg/kg	Na mg/kg	Mn mg/kg	Fe mg/kg	Al mg/kg
Green ash	1992	1560	467	238	23	70	25
Red maple	1937	974	290	198	82	75	22
Red oak	908	998	139	149	183	77	34
White birch	740	270	180	—	34	—	23
Aspen	1130	1230	270	—	29	—	—
Loblolly pine	1155-889	125-104	311-250	256-197	112-95	68-56	—
Red spruce	820	200	70	—	144	—	—
Balsam fir	830	770	270	—	127	—	—
Eastern hemlock	750	400	110	—	145	—	—

Compared to calcium concentration, barium content in wood is at a much lower level. The typical hardwood pulp contains 20-60 ppm of barium and only about 10 ppm of barium for softwood [14]. Therefore, the influence of barium concentration on scale formation is much smaller than that of the sulfate anion. Because barium content in the bark is significantly higher than in the wood [22], to minimize barium content in the pulp, the first step is to minimize bark content in the wood chips. Debarking is the only effective way to reduce the barium concentration in the mill. The major form of the barium present in the pulping process is barium carbonate. It was reported [14] that the bulk of the barium carbonate is inside the fibers and cannot be washed out without lowering the system pH to dissolve the barium carbonate. When the system pH drops below 7, barium carbonate starts to dissolve and barium is released. If sulfate ion is high enough, they will couple and form barium sulfate that will not be dissolved again.

The majority of the oxalic acid is coming from wood bark, pulping and the bleaching reactions. It is reported [23] that maple bark contains approximately 100 times more oxalic acid than that from the wood stem. Keeping a low bark content is therefore also important to reduce oxalate content. Besides wood bark carrying oxalic acid into the process, the majority of the oxalic acid is generated from oxidizing reactions. All oxidizing stages generate oxalic acid typically about 250 to 500 g/metric ton of brown stock pulp [11, 23]. In the first stage of bleaching, the concentration of oxalate in the filtrates ranges from 35 to 90 mg/l. Elsander, et al. [11] have studied a number of bleaching agents and determined that the amount of oxalic acid generated directly correlates with the kappa number reduction, with the exception of peracetic acid, which further oxidizes oxalate to carboxylic acid. It accounts for about 80 g/kg oxalic acid per kappa number reduction. To reduce oxalic acid concentration, oxygen delignification is a good option to reduce kappa number of the pulps entering the bleach plant.

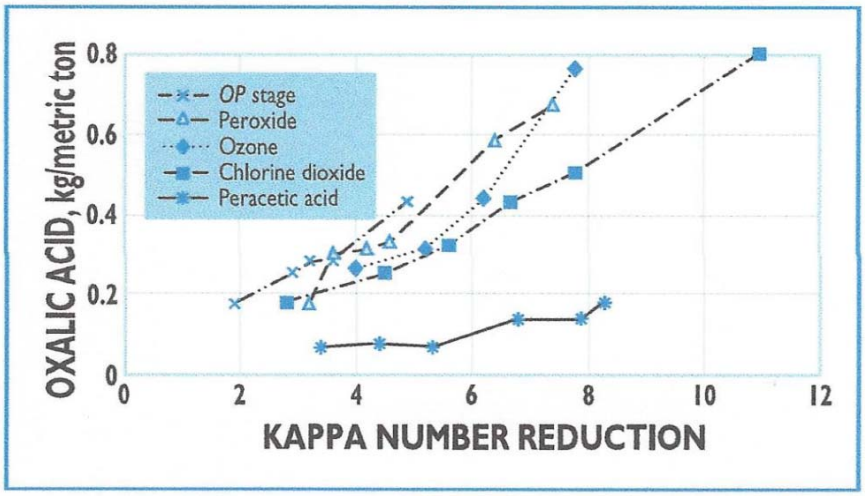

Figure 1. Relationship of oxalic acid generation and kappa number reduction [11]

Because low concentration of barium ion contributes less to scale formation, controlling the sulfate anion concentration is an essential step to control barium sulfate scale. The majority of the sulfate anion is coming from the acid used for D0 pH control. Operating the D0 stage at a higher pH can reduce sulfuric acid charge. Improvements in brown stock washing can remove more caustic, which need less sulfuric acid to neutralize. In addition, improved brown stock washing can reduce carryover of sulfur containing compounds to the D0 stage which can be converted to sulfate after chlorine dioxide oxidation. For the same reason, the addition of oxygen delignification will reduce sulfate anion concentration because additional washing capacity will be added through O2 delignification. Making use of spent acid to control D0 pH contributes an excess of sulfate anions. Depending on the D0 pH, spent acid brings 4-8 times the sulfate anions into the bleach plant as sulfuric acid. For mill lacking water resources, the practices of conducting countercurrent bleach plant washing or using paper machine white water, will build up either barium ion or/and sulfate anion concentration if the paper machine uses alum.

Effect of D0 pH on Calcium Oxalate and Barium Sulfate Scale Formation

Metal ions are present in fibers either in free form or bonded to anionic groups. If they are in free form, they can be removed through washing. The form the metal ions exist in the fibers is governed by the system pH. Altering of the system pH changes the metal ion status in the fiber. Based on *Donnan Approximation and Selectivity Coefficient Method* theory, affinity of metal ions to the fiber follows the following order [6]: $H^+ > Ca^{2+} > Na^+ > Mg^{2+} > Ba^{2+}$. At the low D0 pH, metal ions can be easily released from the anionic groups and then removed in the following washing operation. When the D0 pH is increased to above 3.5, the solubility of calcium and barium are dramatically reduced and both metal ions are unlikely to be removed in the following washing. On the other hand, the D0 pH has an even greater impact on the anion concentration through equilibrium. Altering the system pH can increase or decrease the anions concentration dramatically. This is a critical step to create or eliminate the scale in the system. Figures 2 showed that the majority of the oxalic acid are in the form of bioxalate when the system pH is around 3. When the system pH increases to 4.5 the oxalate anion becomes the major form that leads to more scale. Figure 3 shows various forms of dissociated sulfuric acid. When the system pH reaches 2, the sulfate anion becomes the major form that leads to potential scale formation. Table 2 shows dissociation constants of oxalic acid and sulfuric acid at room temperature. When the system pH equals to pKa_2, about 50% of the anions exist in the system.

Table 2. Acid dissociation constants for anions in common bleach plant scales [24].

	pK_{a1}	pK_{a2}
H_2CO_3	6.352	10.329
$H_2C_2O_4$	1.271	4.272
H_2SO_4	—	1.99

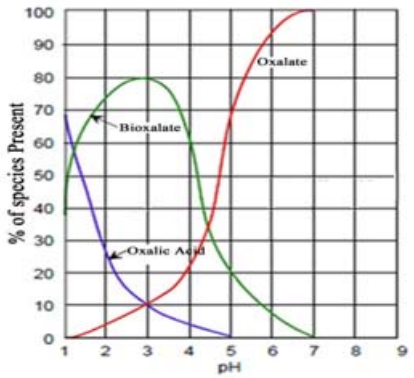

Figure 2. Effect of solution pH on concentrations of oxalic acid and its anions

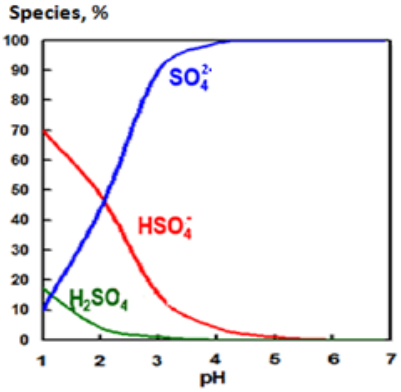

Figure 3. Effect of solution pH on concentrations of sulfuric acid and its anions

If solubility products are reached and enough contact time is given, scales are more likely to form. To eliminate scale, controlling two pH units away from this critical pH is a good rule of thumb. There are two critical pHs that need to remember: 4.5 for calcium oxalate and 2.0 for barium sulfate. If the system only has calcium oxalate scale, the system is decreased to pH 2.5 and most of the calcium can be dissolved. If the system only experiences barium sulfate scale, increase in the D0 pH to 4.0 would reduce sulfuric acid usage and sulfate anion concentration. Barium sulfate scale should be reduced or eliminated. The system pH also influences scale deposition form. In the cooking and washing processes, majority of barium deposits are in the form of barium carbonate. In a bleach plant when the system pH is below 7, barium carbonate starts to dissolve and converts to barium sulfate. After they become barium sulfate, they will not dissolve again. Increase in the D0 pH may start to form calcium oxalate scale, but they may not grow big enough to precipitate from the system. The small microcrystal calcium oxalate may carry over to the Eop stage to facilitate calcium carbonate formation.

Comparison between Calcium Oxalate and Barium Sulfate

We can control a single scale in a bleach plant through modifying the D0 pH within a reasonable range to reduce anion concentration and its solubility product. If the system has both calcium oxalate and barium sulfate scales, changes in the system pH may not able to solve the problem. So, we need to understand the difference between calcium oxalate and barium sulfate because they have different chemical properties in the process of scale formation. Table 3 shows solubility products for common bleach plant scales. Calcium oxalate has a *Ksp* product of 1.7×10^{-9} and the scale has inverse solubility. It forms wherever the system temperature is high. Calcium oxalate can be dissolved by lowering the system pH. By contrast, the solubility product for barium sulfate is only one sixth of calcium oxalate. Its solubility increases as the system temperature increases. But barium sulfate cannot dissolve again when it is formed.

Table 3. Solubility products for common bleach plant scale

	K_{sp}	pK_{sp}
$CaCO_3$	4.5×10^{-9}	8.35
$CaC_2O_4 \cdot H_2O$	1.7×10^{-9}	8.77
$CaC_2O_4 \cdot 2H_2O$	4.6×10^{-9}	8.34
$BaSO_4$	1.1×10^{-10}	9.96

Calcium ions have a high affinity to fibers compared to barium. This implies that calcium ions form is more sensitive to the system pH. Therefore, calcium ions can be removed easily through altering the system pH. On the other hand, barium ion has lower affinity to fibers and its solubility increases as the system temperature increase. It is relatively easy to be removed in the brown stock washing process. The majority of barium present in the brown stock washing process are as barium carbonate. When they enter bleach plant with a low pH, it converts to barium sulfate that cannot be dissolved again. Due to this property, we can manipulate the scale precipitation location by applying a crystal modifier.

Comparing the level of metal ion concentrations in the system, the calcium concentration is hundreds of times higher than barium. Therefore, removal of calcium is an effective way to control oxalate scale. The system pH can change the calcium forms that are free or bonded to the fibers. Therefore, calcium concentration can build up when filtrate is reused or re-circulated. On the other hand, oxalate concentration is dependent on bark content, bleaching chemical applied and magnitude of kappa reduction during the bleaching process. Both calcium and oxalate concentrations are large contributor to the scale formation. Compared to calcium, barium concentration in the pulp is very low - ranging from 20 ppm to 60 ppm in the hardwood and even less in the softwood. The only way to limit barium entering the bleach plant is through a good debarking.

The major contributor to the barium sulfate scale is the sulfate anion concentration. Several process steps may reduce sulfate anion concentrations. The first process affecting sulfate concentration is brown stock washing. Sulfur compounds carried with the stock will convert to sulfate anions in the D0 stage. Higher alkalinity of the stock entering the bleach plant requires more sulfuric acid to neutralize in the D0 stage. Conversely, good brown stock washing can remove more barium from the pulp. The second step impacting sulfate concentration is the D0 stage pH. A lower pH target in the D0 stage requires more sulfuric acid which increases the concentration of sulfate ions. When spent acid from chlorine dioxide generator is use to control D0 stage pH, it brings 4 – 8 times of sulfate anions. The third step is to eliminate sulfate anion is avoidance of using paper machine white water as bleach plant washer shower when the paper mill uses alum.

Minimize D0 Stage Scale Formation through Process Optimization

The best way to control bleach scale is through process optimization. Based on scale formation mechanisms, the first step is to control concentration of scale components. This step includes controlling bark content to reduce calcium, barium and oxalate content. Installation of oxygen delignification to reduce pulp kappa number entering the bleach plant leads to less oxalate generation during the bleaching process. Optimization of brown stock washing to remove as much alkalinity and sulfur containing compounds results in less acid being used in the D0 stage, and less sulfate anion conversion during the D0 chlorine dioxide oxidation. Better washing also provides a good opportunity to remove additional barium carbonate. Elimination of the use of spent acid from chlorine dioxide generator to control D0 stage pH reduces the sulfate concentration in D0 stage.

Modifying the system pH can be leveraged to convert oxalate and sulfate to other forms to reduce solubility products. For most bleach plants, decreasing the D0 stage pH to 2.5 to 2.8 is low enough to dissolve calcium oxalate. For the mills having barium sulfate scale issues, increasing D0 pH to 3.5 to 4 will reduce or eliminate the scale.

To avoid calcium build up, the reuse of filtrates should be minimized and fully countercurrent washing should be avoided. Mills that have calcium oxalate scale should establish a scale formation chart [25] (Figure 4) and routinely check calcium and oxalate concentrations. Comparing the process solubility product to supersaturation point, the mill can periodically purge the D0 filtrate and minimize calcium/barium built up.

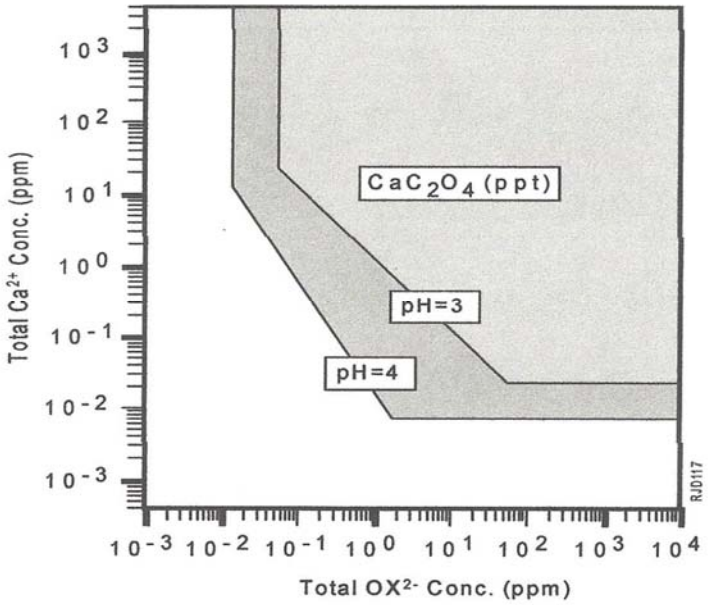

Figure 4. Predict calcium oxalate scale in the mill conditions

Situations that the Mills Need a Scale Inhibitor and Case Histories

Process modification can prevent some bleach plant scale formation, but there are many situations that bleach plant scale issue cannot be resolved. Therefore, a chemical scale control program is the best solution to provide exceptional investment returns. When the following conditions exist, a mill will benefit from a scale control program:

- Multiple scales occurring in the process - calcium carbonate and/or barium sulfate and/or calcium oxalate.
- High operational cost of caustic and acid that challenges maintaining optimal pH targets.
- When chlorine dioxide generator has limited capacity, reduction of chlorine dioxide consumption (by raising D0 pH) becomes essential.
- Rapid scale formation causes quality issues and requires very frequent cleaning.
- Limited water resources or effluent discharge allowance forces the mill to reuse filtrates with high calcium or barium concentration.
- Desire to move scale location away from where is difficult or impossible to clean.

A number of scale inhibitors are available in the present market with a wide range of chemistries. Table 4 shows various industry antiscale chemistries used on calcium oxalate and the impact of pH on their efficiency [26]. All of the scale inhibitors work adequately at a very low pH where calcium oxalate scaling is minimal. General speaking, polyacrylate (PAA) is a common calcium oxalate treatment used by many chemical suppliers though the molecular weight of competitive products may vary. As the pH increases above 3 the dosing requirements of the PAA increase by more than 10 fold to control the calcium oxalate scale before dropping again as the pH nears neutral.

Table 3 Inhibitor required (mg/L) for 100% CaC_2O_4 inhibition at varying pH

	Inhibitor (mg/L)						
				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 Ca 16mg/L, Total Oxalate - 35.2 mg/L Temperature – 60 °C

While still effective, the dosing requirements at the pH range of concern in a bleach plant can be cost prohibitive. SHMP, sodium hexametaphosphate, is very effective in the desired pH range but is not considered environmentally acceptable in many applications due to concerns of eutrophication from phosphates.

Alternative chemistries have been developed which address cost effectiveness, effective in control both calcium carbonate and barium sulfate and avoidance of phosphates. Utilizing the appropriate chemistry can provide the desired performance and exceptional return of investment for many mills. Tables 4 and 5 show results of mill programs utilizing the appropriate chemistry for their scale issues. In both cases, the mills had both calcium oxalate and barium sulfate scale. The chemistry of these scale inhibitors control scale efficiently at low chemical dosing rate and cost. The programs were able to reduce chlorine dioxide demand, sulfuric acid or caustic usage; and boilout chemicals. Less down time and higher operating efficiency enabled the mills to increase pulp production.

Table 4 Case 1. Effective D0 Scale Control Program Creates Huge ROIs

Items	Pre-treated	Present	ROIs
D0 pH	2.5	3.5	
H_2SO_4, lb/t	16.4	5.4	$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

* Provided additional non-monetized benefits to the mill

Table 5 Case 2: Reduce ClO_2 Usage, Maintenance and Down Time

Chemical	Pre- treated	Present	Value
Boilout	once 8 weeks	once 26 weeks	$150k/y
ClO_2	baseline	-1.5 lb/t	$350k/y
Caustic	baseline	-3.0 lb/t	$650 k/y
Scale	$BaSO_4$, CaC_2O_4	Significantly reduced	
Total saving			$1,150 k/y

Note: This is a 1600 tpd HW/SW mill

INDUSTRY BEST PRACTICE ON SCALE CONTROL

The start to any scale control program is optimization of the system parameters to reduce scale components entering the process and minimize scale formation. Since barks contain 10 times more metal ions than wood chips and controlling bark content is only way to prevent barium entering bleach plant, controlling bark contamination to less than 0.5% is ideal. Bark also contains more oxalate than wood chips; therefore, less bark content in the wood chips helps to reduce oxalate concentration in the system. The majority of metal ions, especially calcium ions, are carried by wood materials and most of them are bonded with anionic groups within pulps. Effective washing can dramatically reduce calcium concentration. Optimization of the washing process will maximize removal of sulfur containing compounds, caustic, metal ions and anions which have an impact on barium sulfate scale formation.

The system pH has tremendous impact on metal ions form (free or bonded). Running a lower D0 pH increases metal ions solubility and allows them to be removed in the subsequent washing operations. Therefore, recycled or reused filtrates can increase the metal ion concentrations in a given loop. Following the same logic, fully countercurrent washing should be avoided in the bleach plant. If a mill experiences only calcium oxalate scale, lowering the system pH below 2.5 to 2.8 can protonate the oxalate anion and reduce calcium oxalate scale formation. If a mill experiences only barium sulfate, raising the system pH to approximately 3.5 to 4 will reduce barium sulfate scale formation.

Limited water resources and reuse of filtrate or white water to wash pulp, promotes buildup of ion concentrations in the bleach plant and can initiate scale formation. A profile of metal ions and anions can be checked periodically to identify supersaturation point locations. These data points can be utilized to trigger periodic purging of filtrate to reduce the potential of scale formation.

Chemical scale control programs can allow a mill to operate the D0 stage at any pH range without having scale issue. Scale inhibition programs should be implemented in the following situations: both calcium oxalate and barium sulfate scales present; a mill has limited chlorine dioxide production capacity and wants to save chlorine dioxide; a mill wants to reduce high cost of caustic and acid in the Eop stage by raising D0 pH scale accumulation is faster than can be managed and causing pulp quality issues; or the scaling location does not allow for effective cleaning. It also provides additional benefit in instances where system controls are inadequate or unavailable to prevent scale formation.

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

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Agenda

- Ideal condition of the first stage in multiply bleaching sequence
- Effect of pH on chlorine dioxide delignification reaction
  - ✓ *Effect of pH on chlorite and chlorate formation*
  - ✓ *Best pH in terms of best efficiency on delignification and brightness*
- Impact of raising D0 stage pH on scale formation
- Comparison between calcium oxalate and barium sulfate
  - ✓ *Properties difference between calcium oxalate and barium sulfate*
  - ✓ *Major sources of Calcium and Barium ions*
  - ✓ *Major sources of Oxalate and Sulfate anions*
- Minimize scale through modifying bleaching conditions
- Situations you may need a scale control program
- Present scale inhibitors used in the industry and case histories
  - ✓ *Comparison of various scale inhibitors at various pH*
  - ✓ *Case studies with advanced scale control technology*
- Industry best practice

Ideal conditions of the first bleaching stage

- In conventional bleaching sequence, chlorine water is used as a delignification agent. Ideal conditions are as follow
  - ✓The pH of chlorination: <2
  - ✓Pulp consistency: 3%
  - ✓Retention time: ~ 30 min.
  - ✓Temperature: <50° C
  - ✓Impact on calcium solubility

Ideal conditions of the first bleaching stage

- In ECF bleaching sequence, chlorine dioxide replaced chlorine. Ideal conditions are as follow
  - ✓The pH of D0 stage: 2.5 ~ 4.5
  - ✓Pulp consistency: 10%
  - ✓Retention time: 30 ~ 80 min.
  - ✓Temperature: ~70° 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

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

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

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

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

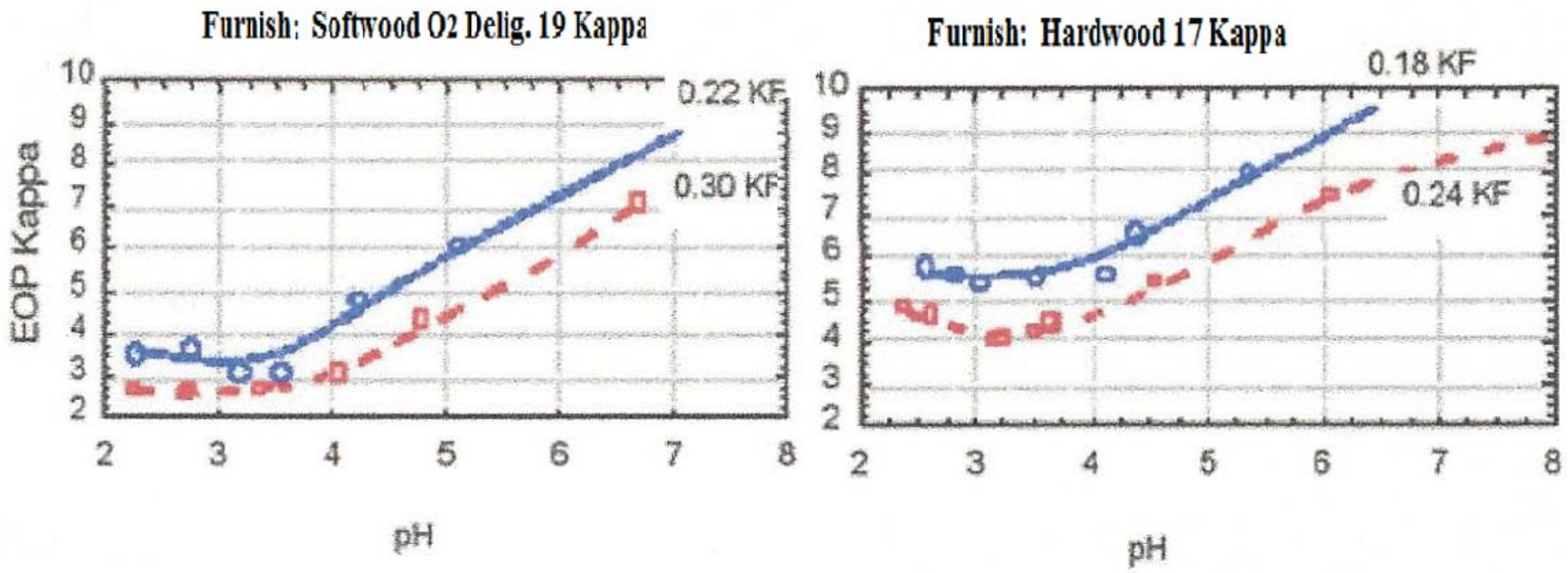
$2\,HClO_2 \rightarrow H^+ + HClO + ClO_3^-$ pKa = 1.96

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

Chlorine Dioxide Delignification Reactions at D_0 Stage

- 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
- 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

Impact of raising D0 stage pH on scale formation

•Calcium solubility was greatly reduced When pH is above 3.5. Calcium and barium are difficult to remove in the D0 stage washing

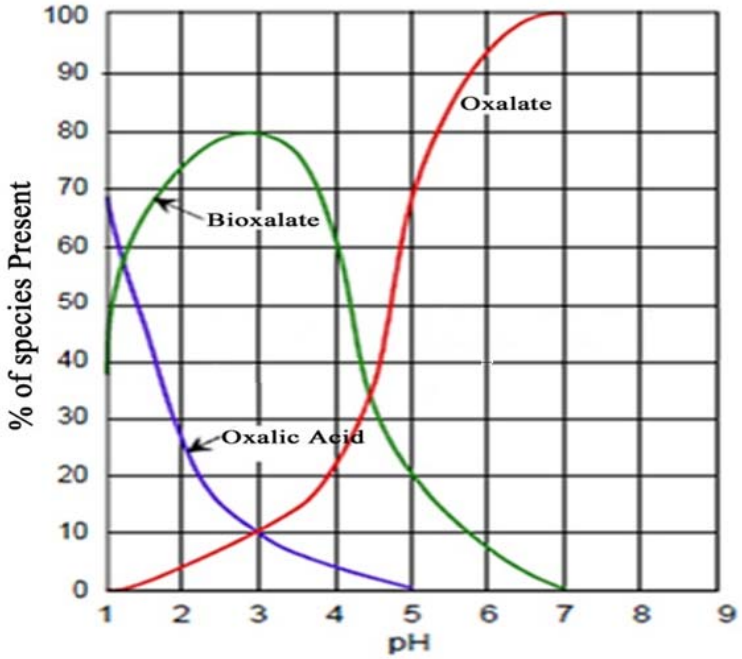
•Oxalate anion concentrations increased at this pH

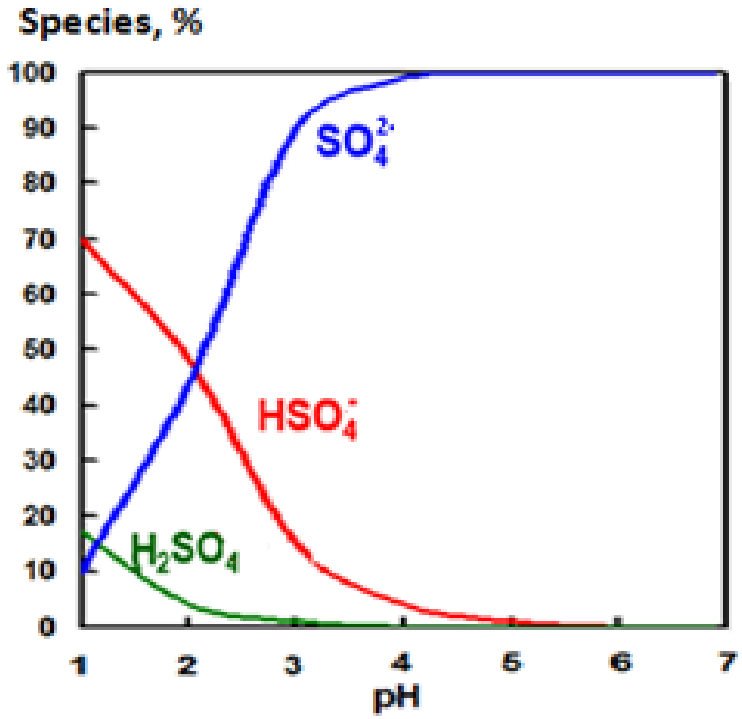
• Less sulfuric acid is needed at a high D0 pH

• Temperature was also increased after switching to chlorine dioxide

•Microcrystal calcium oxalate formed in D0 may carry over to extraction stage to form calcium carbonate

Effect of pH on Concentrations of oxalic acid and sulfuric acid





Comparison between calcium oxalate and barium sulfate

•Major calcium source is wood, especially bark. HW: 2000–6000 ppm, SW:1000–4000 ppm.

•Major source of oxalic acid is from bark and oxidation reactions: 80 g/kg oxalic acid for one kappa reduction.

• Both calcium and oxalate, having a high concentration in the system, are contributing to the scale formation.

•Calcium scale has inverse solubility (higher temperature = lower solubility). Scale formed when temperature is high.

•Major barium source is wood, especially barks. HW: 20-60 ppm, SW: ~10 ppm.

•Major source of sulfate is from acid used to control D0 pH, oxidized sulfur compounds carried from brown stock, white water containing alum.

•Sulfate is the major contributor to the scale formation. Control sulfate is the key to control barium sulfate.

•Barium sulfate solubility increases as increasing of temperature, ionic strength and or organic substance.

Comparison between calcium oxalate and barium sulfate (cont.)

- K_{sp} for Ca C_2O_4 is 1.7x 10^{-9}. Dissolved calcium presents in the system that can build up to a very high level.

- Calcium oxalate scale can be eliminated when the D0 pH drops to 2.5 - 2.8.

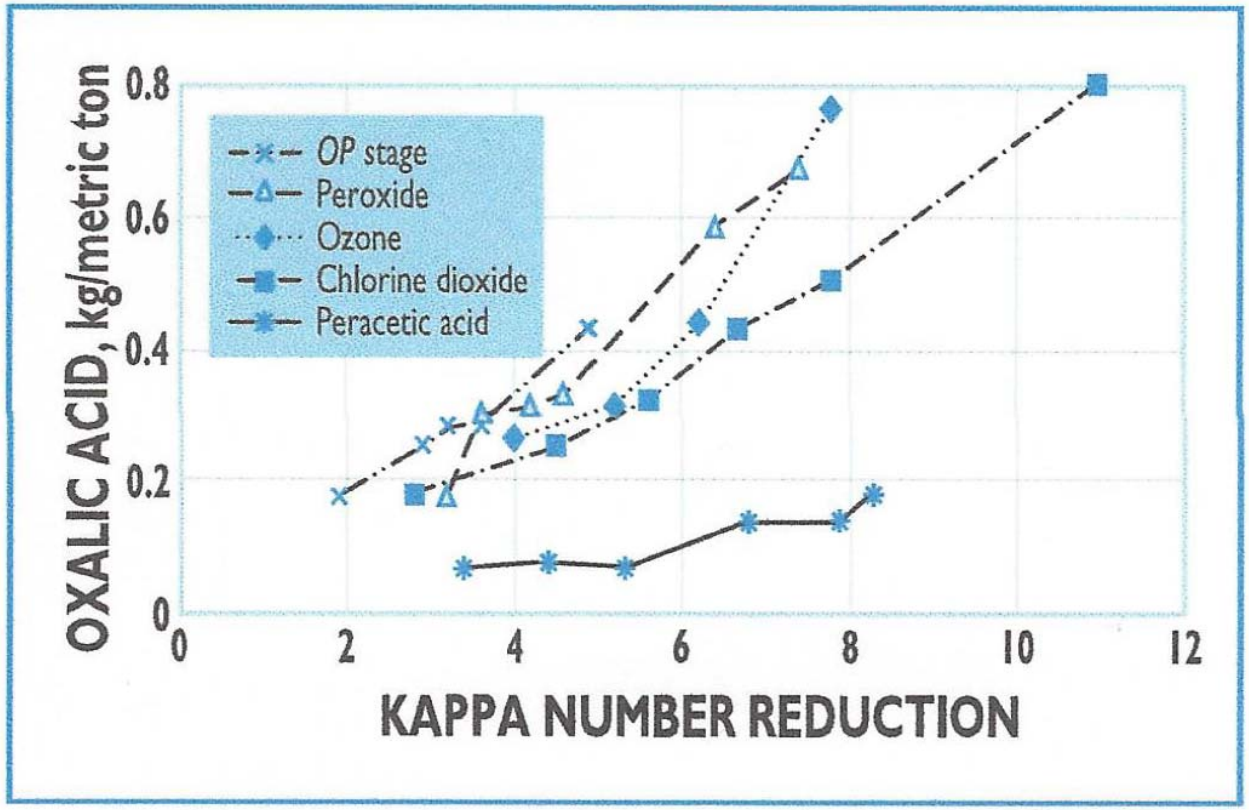
- Affinity of ions to fiber follows the following order: $H^+ > Ca^{2+} > Na^+ > Mg^{2+} > Ba^{2+}$. Calcium is more sensitive to the process pH.

- K_{sp} for $BaSO_4$ is 1.1x 10^{-10} . One sixth of calcium oxalate. When barium sulfate formed, it cannot be dissolved again.

- Barium sulfate scale can be reduced or eliminated when the system pH increases to 3.5 -4.0.

- Affinity of ions to fiber follows the following order: $H^+ > Ca^{2+} > Na^+ > Mg^{2+} > Ba^{2+}$.

Oxalic acid formed kg/t v.s. kappa reduction with different bleaching agents



Elsander, A. Ek, M. Gellerstedt,G.
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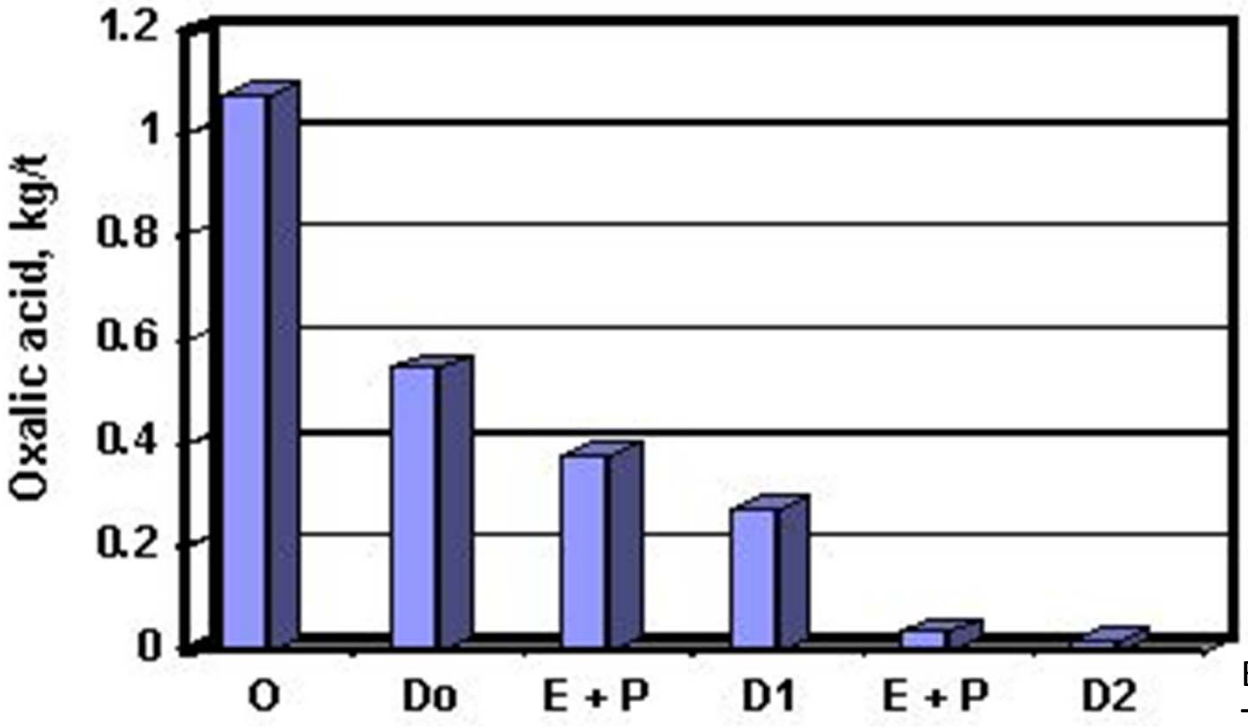
Oxalic acid concentration in each bleaching stage



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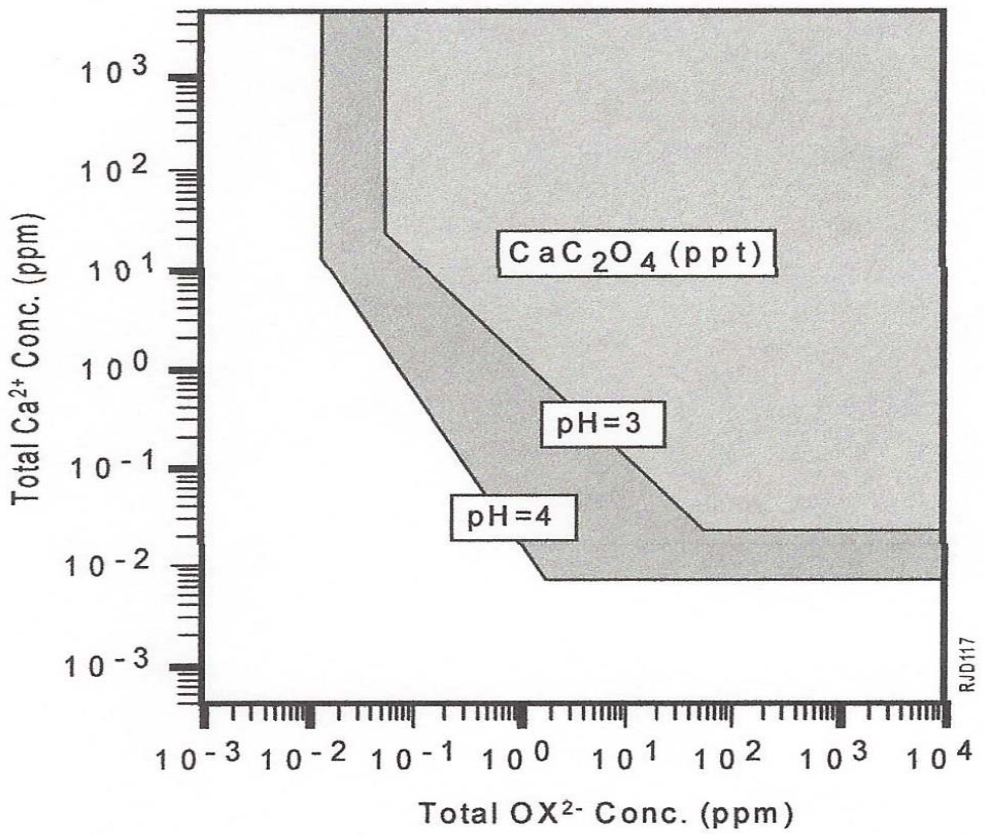
Oxalic acid is formed in the O_2 stage(s) due to oxidation of lignin - 250 – 500 g/ton of pulp.

Minimize scale formation via process optimization

- Control bark content – less calcium, barium and carbonate
- Improve brown stock washing to reduce barium, caustic and sulfur containing compounds
- Lower D0 pH to 2.5 – 2.8 to minimize or eliminate calcium oxalate scale.
- If barium sulphate is the only scale, increase D0 pH to 3.5–4.0 to minimize or eliminate scale.
- Monitor scale supersaturation point by purging D0 filtrate partially to avoid cation build up
- Avoid controlling D0 pH with spent acid from ClO_2 plant
- Avoid running countercurrent washing in bleach plant; Avoid using white water that contains alum

Calcium oxalic formation at different pH and concentration



R. Dexter, X.H. Wang

Situations you may need a scale control program

• When bleach plant has both calcium oxalate and barium sulfate scales, altering the system pH cannot eliminate scale

• High operational cost of caustic and acid that challenges maintaining optimal pH targets

• Chlorine dioxide plant capacity cannot supply enough chlorine dioxide

• Limited water resources or effluent discharge allowance forced the mill to reuse filtrates with high calcium or barium concentration

• Rapid scale formation caused quality issue and required frequent cleaning

• Present scale location is hard to clean and need to move scale location

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 Create Huge ROIs

Items	Pre-treated	Present	ROIs
D0 pH	2.5	3.5	
H_2SO_4, lb/t	16.4	5.4	$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

* Provided additional ROIs to the mill

Case 2. Reduce ClO2 usage, maintenance cost and down time

- Production: 1600 t/d Kraft SW/HW pulp with D0EopDED bleaching
- Chelant boilout 5-6 times a year at D0 stage limited pulp production. Scale problem needs more down time, and has safety risk in acid handling
- Benefits delivered after applied scale control program
  - Chelant boilout reduced from 5-6 times to 1-2 times.
  - Reduced ClO_2 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 $BaSO_4$ in bleach plant

- Control bark contamination at less than 0.5%
- Improve washing to remove sulfur containing compounds, caustic, calcium and barium
- Lower D0 pH around 2.5 - 2.8 when calcium oxalate is the only scale in the system
- Monitor scale supersaturation point by purging filtrate partially to remove calcium and barium
- Avoid to run countercurrent washing in the bleach plant, avoid using white water that contains alum
- Control D0 pH around 3.5 – 4.0 when $BaSO_4$ is the only scale in the system
- Avoid to control 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

- Thank You!

- Any Questions?