

MANAGING CALCIUM OXALATE SCALE IN THE BLEACH PLANT

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To comply with the U.S. Environmental Protection Agency's "Cluster Rule," most U.S. mills have switched from the use of chlorine to chlorine dioxide as the oxidant in the first stage of bleaching. This process change has a downside. It increases the formation of mineral scale in bleach plants. Typically, calcium oxalate forms in the chlorine dioxide stages and calcium carbonate in the extraction stages.

Many mills have directly linked significant production losses, increased maintenance costs, and increased bleach chemical costs to calcium-based scale formation.

CONDITIONS THAT LEAD TO SCALE

Most of the calcium entering the bleach plant comes into the mill with the wood (1). Calcium precipitates as calcium carbonate in the digester and is carried into the bleach plant. The calcium then dissolves once the pH drops below 7. Once calcium is dissolved, it is capable of reacting with oxalic acid to form calcium oxalate. Oxalic acid is found in wood and also forms in the pulping process, but conditions in the digester strongly favor calcium carbonate and the oxalate is left in solution (2) and is removed by brown stock washing. The majority of the oxalate in a bleach plant is formed during bleaching. All oxidizing stages generate oxalic

acid typically about 250 to 500 g/metric ton of brown stock pulp (2,3). In the first stage of bleaching, the concentration of oxalate in the filtrates ranges from 35 to 90 mg per liter of filtrate.

Due to recycle concentration, an average mill can have as much as 3000 mg/kg of calcium in hardwood brownstock pulp. This is diluted to a concentration of about 300 mg/L at 10% consistency or about 100 mg/L at 3% consistency. A softwood line will usually have about half this amount.

PROCESS INFLUENCE ON CALCIUM OXALATE PRECIPITATION

The data for this paper was obtained with an Excel-based equilibrium model that accounts for ion exchange, ion activities, oxalic acid speciation and precipitation (4). Figure 1 shows the effect of pH and total oxalate ion concentration on calcium oxalate precipitation. These results are for a calcium concentration of 100 mg/L. A mill with a low oxalate concentration of 10 to 20 mg/L has the potential to encounter scale problems when the pH in the first chlorine dioxide stage is above about 3.5. Mills with more typical oxalate concentrations of 50 mg/L or 100 mg/L (5) can reduce scale by lowering the pH to about 2.5. What these data mean to a mill that is experiencing calcium oxalate scale formation is that simply by lowering the pH of the bleaching stage, mills may be able to either eliminate or substantially reduce scale formation.

However, another phenomenon makes it more difficult to eliminate calcium oxalate scale by simply lowering the target pH in the bleach stage. Calcium precipitates with oxalate in three crystal morphologies that differ in the number of water molecules included in the crystal. Two of these morphologies are found in bleach plants. Under most bleaching conditions, the preferred morphology is the monohydrate, but at pH below 4, the less soluble dihydrate also begins to form (6). This increases the amount of calcium oxalate that precipitates between the pH of 2.5 and 4, but has little impact on the pH at which scale problems should cease. This effect is shown in Figure 1 as the dihydrate case and was modeled assuming 50 mg/kg of total oxalate in solution. Even with the dihydrate, it should be possible to eliminate the formation of calcium oxalate scale by lowering the pH to 2.5.

EFFECT OF CALCIUM CONCENTRATION

The amount of calcium in the bleaching system also has an effect on the formation of scale. In unbleached softwoods, calcium content varies from 1000 to about 4000

WHAT YOU WILL LEARN

- How the switch to chlorine dioxide from chlorine can increase the formation of mineral scale in bleach plant.
- Why by lowering the pH of the bleaching stage, mills may be able to either eliminate or substantially reduce this scale formation.
- Why another phenomenon can make it more difficult to eliminate calcium oxalate scale by simply lowering the target pH.

ADDITIONAL RESOURCES

- "Bleaching 101: The basic of bleaching," by Wayne Bucher. Solutions!, February 2004. To access this article, enter the following Product Code in the search field on www.tappi.org : 04FEB036
- "Beyond the Cluster Rule: New bleaching challenges," by Alan Rooks, Solutions!, November 2003. Product Code: 03NOVS033
- "Bleaching and environment in the 21st Century," by Donald G. Meadows, Solutions!, June 2003. Product Code: 02JUNS064.

mg/kg of oven dried pulp. Calcium is typically much higher in hardwoods, varying from about 2000 to about 6000 mg/kg oven-dry pulp. These ranges were obtained from analyses of 5 softwood lines and 4 hardwood lines around the United States. The first chlorine dioxide stage filtrate concentrations in these mills ranged from about 30 to 600 mg of calcium/L of filtrate. Most of the samples we have analyzed are on the low end of this range, between 100 to 250 mg/L of filtrate.

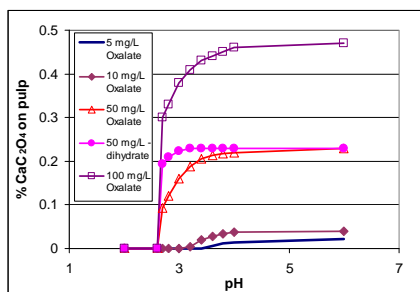


Figure 1. Concentration of calcium oxalate (% on pulp) with 100 mg/L total calcium concentration as a function of pH for various total oxalate ion concentrations. In the 50 mg/L dihydrate case, the solubility product used is for the dihydrate crystal morphology.

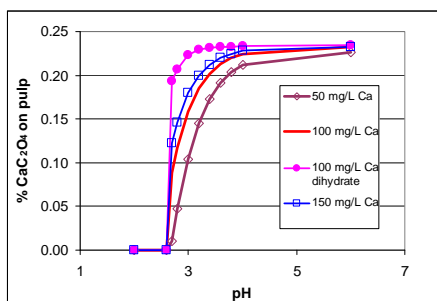


Figure 2. Calcium oxalate precipitation with a total oxalate concentration of 50 mg/L as a function of pH for various total calcium concentrations. The 100 mg/L Ca dihydrate case uses the solubility product of the dihydrate crystal morphology.

The influence of calcium concentration is shown in **Figure 2**. We have graphed model results for a case with 50 mg/L oxalate concentration and calcium concentrations varying from 50 to 150 mg/L. Again, pH is the control parameter. In the examples shown in Figure 2, the oxalate anion is the limiting ingredient, even low levels of calcium produce high levels of calcium oxalate precipitation at high pH. All three scenarios would likely produce scale at any pH above 4. To significantly reduce the potential for scale formation, the pH needs to be below 3. The case assuming dihydrate formation shows no reduction in the amount of precipitation until a pH of 2.8. All cases indicate no precipitation at pH of 2.6 or below.

CONCLUSION

As presented in the 2003 TAPPI Fall Technical Conference, the model used in this analysis has been successfully used to evaluate scale problems at various mills around the United States (4). Since implementing the suggested solution and lowering the initial chlorine dioxide stage pH target to 2.5-2.8, many bleach plants have either substantially reduced or eliminated the formation of cal-

cium oxalate scale. However, for mills with high barium levels, lowering the pH in the first chlorine dioxide stage will increase the risk of barium sulfate scale, particularly if the mill uses spent acid for pH control in the bleach plant. **SI**

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Dr. Hart and Dr. Rudie have been collaborating on the management of trace metals and control of mineral scale control since 2000 and presented papers at the TAPPI Fall Technical Conference in 2003 and 2004. With coauthor Chris Livay, Drs. Hart and Rudie received the Alkaline Pulping Committee David Weatherhorn Award and the Pulp Manufacturing Division High Impact Paper Award for the paper presented at the 2003 Fall Technical Conference. Contact Dr. Rudie at USDA Forest Service Forest Products Laboratory, One Gifford Pinchot Drive, Madison, WI 53726-2398, +1 608 231-9496, Email: arudie@fs.fed.us.

