Inorganic scale buildup in a bleach plant—a mill case study

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ABSTRACT: When a particular mill modified its bleaching process, the changes led to the buildup of calcium carbonate scale. Scale built up in the chute and in the thick stock pump leading from the discharge of the washer for the alkaline extraction stage to the inlet of the up-flow tube of the D_1 chlorine dioxide stage. The buildup of scale restricts the stock flow and ultimately the production. The mill was shutting down to clean the bleach plant every seven weeks, but there were some times when the mill had to shut down prematurely because of excessive scaling. The last occurrence of unscheduled downtime prompted the mill personnel to try an antiscalant in the bleaching process. The rate of antiscalant addition was varied to optimize it, and the discharge pressure of the thick stock pump was monitored along with the daily production rate. Adding the antiscalant at the upper pond flow on the alkaline extraction washer controlled the excessive buildup of scale and resulted in a daily production increase of 10–50 tons/day.

Application: Antiscalant can inhibit scale formation in the bleach plant to improve washing, reduce chemical consumption, and increase production.

To meet the requirements of the EPA cluster rules, mills have modified their bleaching sequences and have recycled more machine white water back to the bleach plant. Integrated mills have recycled their white water laden with clay or precipitated calcium carbonate (PCC) and other organic and inorganic material back to the last washer of the bleaching process to reduce the amount of water being discharged as effluent.

Mills that used considerable amounts of chlorine have replaced part or all of it with chlorine dioxide. Mills have upgraded existing facilities or installed new facilities for generating chlorine dioxide. However, mills that were capital limited sought other means, such as using oxidizing agents like hydrogen peroxide, ozone, and oxygen to replace part of the chlorine dioxide and all or part of the chlorine. Of the three candidates, hydrogen peroxide and oxygen were successful at replacing both the chlorine and the chlorine dioxide.

Modifying the bleaching sequence and recycling the white water satisfied the regulations but created another operating snag. The oxidative bleaching chemicals reacted with the lignin molecules and generated substances such as oxalic acid [1], which adds to the oxalic acid coming through with the brownstock from the cooking process. It also instigates the formation of calcium oxalate deposits in acidic stages where the pH varies between 3 and 6 [2]. The recycled white water is high in Ca^{2+} and CO_3^{2-} ions, which precipitate at a pH greater than 8 in the first extraction stage [2].

Various problematic scales such as barium sulfate, calcium carbonate, and calcium oxalate have been observed in the bleaching process in some mills that have made the conversion [3]. Some mills have found that the generation of scales has been such a hindrance that it affects the operation and results in production loss and high production cost. Some mills have assuaged the problem by altering the filtrate circuit in the bleach plant [4–6].

To achieve elemental chlorine-free bleaching (ECF), the mill of this study modified its bleaching sequence from (CD)ED to D(EOP)D and increased the closure of its white water loop. This modification meant recycling from the paper machines part of the white water laden with PCC and other trash (anywhere from 0.05% to 0.15% solids). This white water was sent back to the bleach plant as wash water on the last bleaching stage and as broke dilution. The broke, depending on the tank levels, is also recycled back to the front of the bleach plant at the discharge of the pre-washer repulper.

Converting the bleach plant to ECF bleaching and closing the white water loop has led to a serious inorganic deposit problem between the discharge of the washer of the alkaline extraction stage and the D_1 chlorine dioxide mixer. The scale builds up on the inside of the chute leading from the E-stage repulper to the mixer and causes the pressure drop in the piping to increase. The scale also deposits inside the thick stock pump on the screw and wears the screw down.

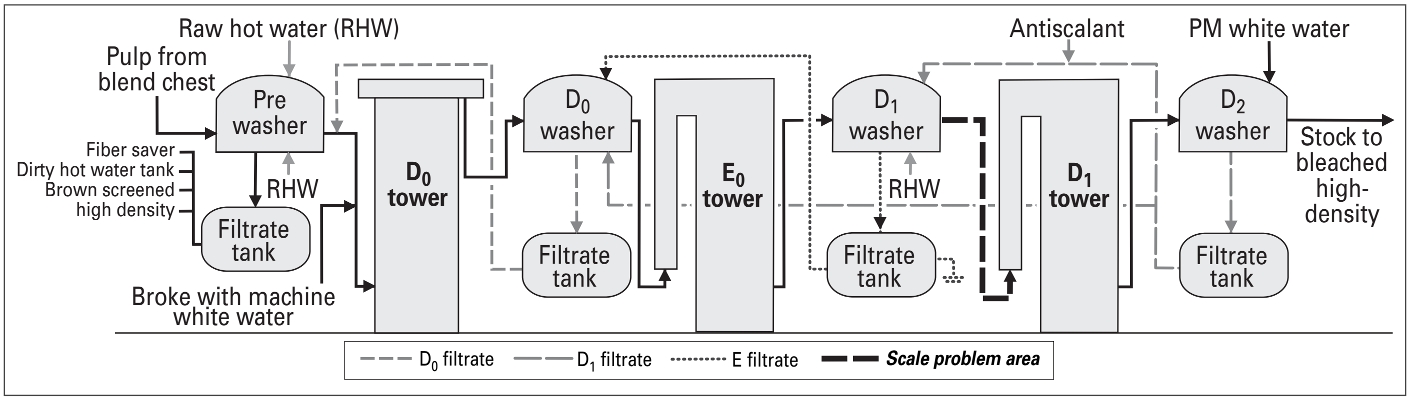
There are several factors that contribute to the formation of scale in the bleaching process. These include the pH, the temperature, and the concentration of cations and anions. Since the mill switched to ECF bleaching from conventional bleaching, the pH in the first stage changed. With conventional bleaching, chlorine hydrolyzes and lowers the pH of the process below 1.8 by Reaction 1:

$$Cl_2 + H_2O \rightarrow HCl + HOCl \quad (1)$$

However, switching to chlorine dioxide bleaching raises the pH higher than 3. To compensate for the higher pH, the mill adds sulfuric acid and sodium sesquisalt from the ClO_2 generator to lower and control the pH at 2. The sulfuric acid is combined with the sesquisalt, and this combined solution is added to the chute of the pre-washer repulper. With the addition of the acid and the sesquisalt, which is 18.7% sulfuric acid by weight (Reaction 2), the pH at the bottom of the chlorine dioxide tower decreases and varies between 2.0 and 2.2.

$$2Na_3H(SO_4)_2 \rightarrow H_2SO_4 + 3\ Na_2SO_4 \quad (2)$$

The recycling of PCC-laden white water causes large deposits of calcium carbonate in the piping between the E-stage washer discharge and the up-flow tube of the D_1 chlorine dioxide stage. (The PCC-laden white water comes into



1. Bleach plant layout.

the bleach plant via the broke and the wash water on the upper pond flow of the D_1 washer). The scale that forms can be as thick as 15 cm in some places. The thick scale causes many problems that limit the production rate, such as restricting the stock flow from the washer to the D_1 tower. This problem with the stock flow was discerned from the pressure gauge at the discharge of the thick stock pump.

When the scale buildup causes problems, the mill shuts down to clean the deposits in the chute and the thick stock pump. Because of this predicament, the mill shuts down the bleach plant every seven weeks for maintenance. However, the mill has had one occurrence of having to deal with a very thick deposit prior to the scheduled down day. The mill had to take an unscheduled shutdown to clean the chute and the piping between the E-stage washer and the D_1 mixer. Each time the mill goes down, it costs 6–8 h of lost production and several person-hours of labor. The lost production and labor costs the mill approximately US$ 62,000 each time, and the seven schedule shutdowns cost the mill approximately US$ 434,000 annually.

As a result of the unscheduled shutdown in April 2004, the mill personnel decided to try using an antiscalant. The objective was to prevent excessive buildup of calcium carbonate scale between the E-stage washer and the D_1 up-flow tube and to evaluate the effectiveness of the antiscalant program. To determine the effectiveness of the antiscalant program, the discharge pressure of the thick stock pump was monitored together with the daily production rate.

SCALING PARAMETERS

Several changes to the bleaching process over the last few years have caused severe operational problems for the mill staff. These changes are:

- Conversion from conventional bleaching to ECF/TCF bleaching.
- Closure of the white water system and screen room system.
- More emphasis on oxidative bleaching to meet the environmental discharge regulations and to reduce the bleaching cost.

All of these changes have resulted in more metal earth cations such as Ca^{2+}, Ba^{2+}, and Mg^{2+} coming into the bleach plant and circulating around in the filtrates. With increased emphasis on oxidative bleaching, more oxalic acid is generated by the hydrogen peroxide reacting with lignin. The closure of the machine room has led mills to recycle their white water, which tends to be dirty and which contains chemicals that promote scaling under the ECF bleaching environment. Some conditions promote calcium carbonate scale, and others promote calcium oxalate scale.

Calcium carbonate scale

Temperature, pH, and the chemical composition of the solution play a predominant role in the formation of calcium carbonate scale. Since calcium carbonate has a negative solubility, it tends to precipitate under a high temperature.

As the pH of a solution containing carbonate anion increases above 8, the predominant species in the solution is the carbonate ion [7]. Carbonate ion precipitates as calcium carbonate if calcium cations are present and if the concentrations of both the calcium and the carbonate ions exceed certain critical values.

Based on the parameters, calcium carbonate scale will appear in the alkaline stage of bleaching.

Calcium oxalate scale

The calcium oxalate scale is affected by the temperature, the pH, and the presence of calcium cations and oxalate anions. The main parameter controlling the oxalate scale is the solution pH. In a highly acidic solution, calcium oxalate scale is absent. As the pH increases, the dihydrate form precipitates between pH 2.5 and pH 4. Above pH 4 ,the monohydrate form of calcium oxalate predominates and will appear in the acidic stages where the pH varies from 4 to 6.

THE MILL PROCESS

Figure 1 illustrates the bleaching process. The pulp comes from the unbleached decker and is stored in the unbleached high-density storage tank. From the unbleached high-density storage tank, the pulp is conveyed to a blend chest and then to the pre-washer. From the pre-washer, a thick stock pump conveys the stock to the D_0 chlorine dioxide tower. The retention time in the tower is about 30 min, the pH at the bottom of the tower is 2.0, and the temperature is 60°C. The tower is an up-flow tower, which discharges to the D_0 washer.

From the washer the stock is sent to the up-flow tube of the alkaline extraction tower. The pH at the bottom of the tower is controlled at 11.0, the temperature is 68°C, and the tower retention time is 60 min. Stock from the bottom of the tower is sent to the E-stage washer. The washer has two sources of washing medium. The lower pond source is the raw hot water running at 2950 L/min, and the upper pond source is the D_1 filtrate running at 1590 L/min. To control the buildup of scale between the E-stage washer and the D_1 up-flow tube, the mill applied antiscalant to the upper pond flow stream.

A thick stock pump transfers the stock from the E-stage washer outlet to the inlet of the D_1 tube. The pressure at the discharge of the thick stock pump is monitored to indicate the degree of scaling that has occurred in the piping.

The pH at the bottom of the D_1 tube is controlled at 4.5, and the outlet is at pH 6.5. The tower is maintained at a temperature of 68°C. The retention time of the stock in D_1 is 270 min. The stock from the tower is discharged into the D_1 washer and from there is transferred to the bleached high-density storage tank. The filtrate flow is countercurrent with the E-stage filtrate tank overflowing to sewer and the pre-washer filtrate tank transferring the filtrate to a fiber-saving unit. The screened filtrate is discharged to sewer.

Calcium carbonate comes into the bleach plant in the broke diluted with paper machine white water. The white water is used as a washing source for the pulp on the upper pond flow of the D_1 washer. The white water contains residual PCC and fiber, which can vary from 0.05% to 0.15%.

LABORATORY ANALYSIS

A sample of the deposit from the E-stage discharge chute was collected and sent to a laboratory for analysis. A simple test of adding concentrated hydrochloric acid on the scale revealed the deposit to be predominantly calcium carbonate.

MILL TRIAL PROCEDURE

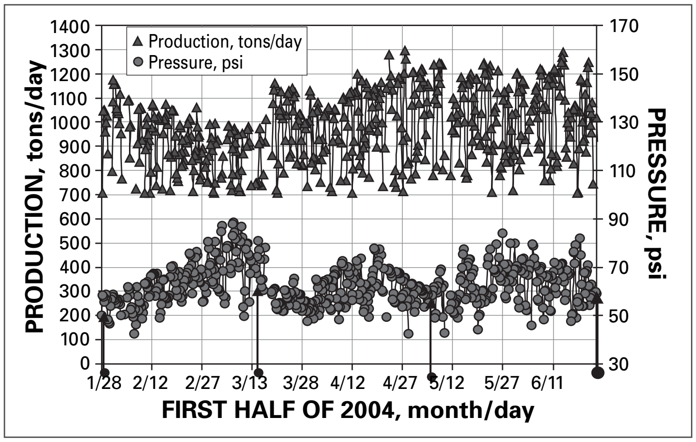
The feed point for antiscalant is shown in Fig. 1. The addition rate was initiated at 220 mL/min (142 ppm) on May 5 in the upper pond flow of the E-stage washer. This addition rate was maintained constant even if the production varied as a result of the pump being operated on manual control. This rate amounted to an addition rate of 0.295 kg/ton of pulp (where the ton is a short ton).

On May 9, the bleach plant was down because of some problem with the evaporators. At this time the antiscalant was shut off. When the mill started up again, the antiscalant was not turned on until May 14, and then it was turned on at a lower dosage rate. The application rate of antiscalant at this time was 180 mL/min (117 ppm, 0.240 kg/ton). This rate was maintained until June 11, at which time the application rate was further reduced to 120 mL/min (78 ppm, 0.161 kg/ton). This rate was maintained until June 23.

The dosage rates are summarized in **Table I**. The dosage rate appears to be high in the upper pond flow. However, the actual concentration in the washer and with the stock in the piping leading to the D_1 up-flow tube is much lower because of the mixing of several flows in the E-stage washer.

Period	Dosage, mL/min	Dosage, ppm	Dosage, kg/ton
May 5 – May 9	220	142	0.295
May 14 – June 11	180	117	0.240
June 12 – June 22	120	78	0.161

I. Antiscalant dosage rate.



2. Production rate vs. discharge pressure for the thick stock pump.

Period	Pressure, psi	Production, tons/day
Jan. 28 – Mar. 16[a]	64±10	910±117
Mar. 17 – May 5[a]	60±7	995±145
May 5 – June 23[a]	63±8	1027±149
Mar. 17– Apr. 22[b]	61±7	979±130
Apr. 23 – May 4[c]	60±6	1034±173
Jan. 28 – May 4[d]	62±8	955±139

[a]Scheduled operating periods, with down days slated for Mar. 16 and May 5. [b]Period of high deposits of scale leading to an unscheduled down on April 22. [c]Period after unscheduled down day on April 22. [d]Period with two down days, one on Mar. 16 and one on Apr. 22.

II. Mill operating data over different intervals.

MILL TRIAL RESULTS

Data presented in **Fig. 2** are summarized in **Table II**. The graph in Fig. 2 shows how the pressure in the thick stock pump varied prior to and after antiscalant was applied. The discharge pressure is initially low after the shutdown, and it builds up until the next scheduled down day. As the graph also shows, the production rate decreases as the pressure increases.

After the scheduled down day, the pressure increased with the growth of calcium carbonate scale. The scale plates on the inside of the piping and the thick stock pump between the E-stage washer discharge and the up-flow tube of the D_1 stage.

Between March 17 and May 5, the mill had to take an unscheduled down day because of excessive scale buildup restricting the production rate. On April 22, the bleach plant was taken down and cleaned. After the cleanup, the pressure at the discharge of the thick stock pump decreased as expected. After this incident, the mill personnel decided to administer an antiscalant program to see if it would be effective in enhancing production and preventing excessive calcium carbonate deposits in the piping and the thick stock pump.

On May 5, the mill went down again as a schedule downtime. During the startup, antiscalant was applied at a rate of 220 mL/min into the upper pond flow of the E-stage washer. It ran at this rate for four days, but on the fourth day the mill had some troubles with the evaporators and had to shut down. Antiscalant addition was also stopped.

When the mill started up again, it did not start applying antiscalant immediately. Four days later the antiscalant addition was initiated again, when the mill personnel realized that the pressure at the discharge of the thick stock pump was increasing. The first thing they checked was to see if the antiscalant application was on. To optimize the application rate, they set the flow at 180 mL/min. At this addition rate, the pressure from the discharge of the thick stock pump started to decrease.

Because the scale was reduced in the piping and the thick stock pump screw, the clearance increased between the screw and the wall of the thick stock pump. Subsequently the production could not be raised because the screw had worn out over years of operation. With increasing clearance, the efficiency of the thick stock pump decreased, and production started to suffer. The mill personnel decided to reduce the antiscalant flow to build up some scale on the screw to improve tolerances so that the thick stock pump would work efficiently. The flow of antiscalant was reduced to 120 mL/min. A day later the production improved. The discharge pressure of the thick stock pump fluctuated after this day but never again got as high as it had been.

To summarize, the mill produced 10–50 more tons of pulp per day when antiscalant was applied, and the discharge pressure from the thick stock pump did not increase to the point at which the mill had to be taken down. This increase meant that the mill could run longer before a scheduled downtime or run at the same schedule and make more product during the operating period. **TJ**

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INSIGHTS FROM THE AUTHORS

Many mills have encountered scale problems after switching from a conventional bleaching sequence to either ECF or TCF bleaching. Since little information has been published on this topic, we decided to study the cause of scaling during oxidative bleaching. A lot of work has been done on scale formation and its prevention, but little work has been carried out on preventing scales in the bleaching process after a mill converts to ECF or TCF bleaching.

The mill in this particular study had only a single problem site with only one kind of scale formation (calcium carbonate). However, we are now addressing problems in mills with multiple sites of scale buildup. Mills being evaluated have scale problems in the front end of the bleach plant (barium sulfate scale), after the EOP stage (calcium carbonate and pitch), and in the D stages (calcium oxalate). We have found that most of these scales can be controlled with the right kind of antiscalant.

For mills, this information offers a way to control scale. In most mills where there is scale in the bleach plant, there are also other problems associated with it, such as production loss, poor washing, and high chemical consumption. The proper antiscalant can prevent or inhibit scale formation in the bleach plant and improve washing, reduce chemical consumption, stabilize variation in final brightness, reduce dirt, and increase production.

The next step for us is to formulate a product that is applicable not only in the bleaching process but also throughout the entire pulping and papermaking processes. This product should prevent or inhibit the formation of various kinds of scales.

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