

## **Application of Fundamental Principles to Mineral Scale Reduction – Case Studies**

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### **Abstract**

This paper will present several successful case studies where scale has been eliminated in mills including calcium carbonate scale in a white liquor strainer, calcium oxalate scale in the D<sub>0</sub> stage, enzymatic treatment of brown stock to eliminate oxalate scale, and control of barium sulfate scale.

### **Introduction**

Over the course of a single day of operation, thousands of pounds of calcium pass through a pulp mill and bleach plant. If process conditions are not properly maintained throughout the entire pulping and bleaching process, relatively small amounts of these materials may precipitate onto various process surfaces. Even though only small percentages of these minerals precipitate in troublesome areas to form process scale, extensive upsets in process operation and increases in operating costs result. Ironically, typical minor adjustments in operational conditions may be required to substantially reduce or eliminate scale formation. It is possible to predict what these process changes should be if one has a good understanding of the fundamental chemistry behind mineral-scale formation. In at least one reported study, the ability to *a priori* predict the onset of scale formation and changes in operating conditions needed to eliminate this scale formation has been documented.

In addition to understanding the fundamentals of mineral scale formation, it is important to know the type of scale that is forming in various places. Typically, scale formation in the pulp mill area is calcium carbonate or lime scale. Scale formation on the acid stages of the bleach plant can be either calcium oxalate or barium sulfate. Under specific circumstances, lime scale can form on parts of acid stage equipment. Scale formation on the caustic extraction stages is typically lime scale. The current work examines various case studies of scale formation and elimination from the digester through the bleach plant. In all of these case studies, process changes and the fundamental understanding of why these process changes were successful are examined.

The majority of non-process elements enter the pulp mill with the wood.<sup>1</sup> Vast amounts of calcium enter the digester with the wood chips. This calcium reacts with the white liquor to form calcium carbonate or lime scale.<sup>2</sup> The calcium precipitates on any readily available surface. By far the highest surface area present in the digester is the fiber. Thus, the majority of the lime-scale forms on the fibers. Some specificity for heating surfaces exists because calcium carbonate exhibits an inverse solubility. For instance, as a calcium carbonate solution gets hotter, the solubility of calcium carbonate decreases.<sup>3</sup> Because the solubility decreases with temperature, lime scale tends to form on liquor heaters.

### **Calcium Carbonate Scale Formation in a Kamyr Digester White Liquor Strainer**

Mill A was operating a continuous digester with a frequent, reoccurring problem with lime scale forming in the white liquor strainer associated with the white liquor level tank. One of the strainers built up sufficient lime scale to require hydroblasting every 5 days. The digester had two liquor strainers operating in parallel. As a result, no lost production time has been associated with the need to isolate and clean the strainer. Extensive long-term maintenance costs resulted from the need to routinely isolate the scaled strainer, extract the internals of the strainer, hydroblast the strainer to remove the scale, and finally to put the system back together. Initially, the mill attempted to control the scale formation with commercially available crystal modifiers. The use of an anti-scalant further increased the cost associated with scale formation. Even with the anti-scale chemical, the white liquor strainer still required hydroblasting every 5 to 7 days.

Normally, no chemicals are added or mixed in the white liquor strainer. This ruled out typical chemical concentration changes as the source or initiator of the scale. The understanding of the inverse temperature solubility of calcium carbonate suggested that some form of heat intrusion might be occurring in the white liquor strainer. Careful observation of the strainer over several weeks showed that one side of the strainer

was always scaling far more than the other side. The side of the strainer housing with the thickest scale was carefully examined. Finally, a steam leak was found in the strainer housing. Once the steam injection into the strainer was eliminated, the strainer stopped scaling. The additional anti-scale chemical was eliminated with no detrimental effect on scale formation. The fundamental understanding of the inverse solubility of calcium carbonate was used to understand how the scale was forming and suggest steps to eliminate the problem.

### **Lime Scale on a Caustic Extraction Stage Washer**

Mill B routinely experienced lime scale formation on the face wire of the first caustic extraction stage. The scale started forming shortly after the mill migrated from a chlorine-based bleaching sequence to an ECF bleaching sequence using chlorine dioxide. When Mill B converted to chlorine dioxide bleaching they also introduced, D<sub>0</sub> stage filtrate recycle. The mill had used strict pH control in the chlorine stage as part of its dioxin-control program. In general, the terminal pH of the chlorine bleaching stage was maintained in the 2.1–2.3 range. But when the mill converted to chlorine dioxide bleaching, no pH control was used. The natural terminal pH of the first bleaching stage increased to a range of about 3.1–3.3. Fresh caustic for the first caustic extraction stage was applied to the pulp by a spray bar directed into the repulper of the D<sub>0</sub> stage. In addition to fresh caustic, blow-down from the bleach plant scrubber was added to the D<sub>0</sub> repulper. The caustic source for the bleach plant scrubber was white liquor.

After the ECF conversion, lime scale slowly formed on the face wire of the caustic extraction stage washer. One unintended result of the ECF conversion was that the calcium concentration in the caustic extraction stage increased substantially. The higher terminal pH of the first stage decreased the amount of calcium removed in the first bleaching stage effluent. D<sub>0</sub> filtrate recycle also increased the non-process elements (NPE) content of the stock. One of the features of wood pulp that fosters mineral scale problems is the ion exchange behavior of the acid-functional groups.<sup>4,5</sup> Electroneutrality requires pulp to collect enough cations to balance or neutralize the charged groups.<sup>6</sup> At pH below about 4, protons provide the majority of this charge balance, but at pH above 4, cations in solution must be absorbed by the pulp to maintain the charge neutrality of the fiber. In the traditional chlorine-initiated bleach plant, the first stage operated at a pH between 1.5 and 2.0, and the acid required to maintain the low pH was a by-product of the chlorine reactions. At a pH below 2, 90% to 99% of the trace metals are freed from the fibers and available to be washed from the pulp.<sup>5,7,8</sup>

When the mill changed to ECF bleaching, the cation concentration on the fiber increased substantially. The optimal pH for a chlorine-dioxide-initiated bleach sequence was one problem. Whereas the ideal pH for chlorine is about 1.5, the ideal pH for chlorine dioxide is typically closer to 4. At this pH, 50% of the trace metals are still “bound” to pulp<sup>5,7,8</sup> and will be carried further into the bleach plant. Typical limits on washing efficiency increase this value significantly.

Recycle of the first stage effluent to help dilute the incoming brownstock pulp was another contributor to the problem. The decreased volume of first stage effluent being seweraged increased the concentration of calcium in the D<sub>0</sub> stage. The results of these changes were a substantial increase in the calcium content of the pulp passing through the bleach plant. The increased calcium content in conjunction with substantial carbonate levels in the caustic and scrubber blow-down resulted in a saturated system prone to scale formation with scale forming on the extraction stage washer wire. This washer operates with mill water on the first three shower bars, and D<sub>1</sub> filtrate on the final two bars. The mill water is pH controlled to near neutral and the D<sub>1</sub> filtrate runs around pH 3.8.

This bleach stage was not modeled, and the chemistry explanation that follows is somewhat speculative, but consistent with a case that has been modeled.<sup>9</sup> The extraction stage seems to be well set up to precipitate calcium carbonate early in the stage, probably at the D<sub>0</sub> repulper where the scrubber blowdown was added to the pulp. CO<sub>2</sub> forms in extraction stages, so continued formation of carbonate in the tower would continue to reduce calcium solubility and add more lime to the pulp suspension. At the extraction stage pH, along with carboxylic acid groups are the deprotonated phenolic groups that have a pK<sub>a</sub> near 10. These charges also need to be neutralized, which typically means more calcium ions are bound to the fiber entering the washer. The initial wash water is at about pH 7, low enough to exchange protons on the

phenolic groups, adding calcium to solution. This calcium is subject to an ion exchange chromatography effect that slows movement through the pulp mat. The D<sub>1</sub> filtrate is low enough pH to dissolve some of the precipitated calcium carbonate, pumping even more free calcium into solution. The resulting bicarbonate anions are not subject to ion exchange and wash freely through the pulp. As they penetrate the mat, the anions encounter a filtrate at higher pH (because of the proton ion exchange effect, the pulp provides a fairly good pH buffer at both the phenolic pK<sub>a</sub> around pH 10, and carboxylate pK<sub>a</sub> at pH around 4). The anions convert back to carbonate as they catch up to the calcium delayed by the ion exchange chromatography effect. The net result is a higher concentration of calcium mixing with a higher concentration of carbonate in the bottom of the pulp mat, near the washer wire. As the filtrate passes through the face wire of the washer drum, it flashes into a partial vacuum zone. The partial vacuum evaporates some of the water, causing the concentrations to increase and helping scale to form on the wire.

The routine formation of lime scale on the caustic extraction stage washer resulted in substantial increases in operating cost for the bleach plant. As the washer became more and more scaled, the washing efficiency of the extraction stage decreased, resulting in increased carryover into the D<sub>1</sub> stage. Mill B was required to schedule maintenance outages every 6 weeks to remove the scale with an acid wash.

Understanding how the changes in the bleach plant contributed to the lime scale formation allowed the mill to consider various options to eliminate the scale. One potential solution was to eliminate the filtrate recycle associated with the D<sub>0</sub> bleaching stage. Another solution was to lower the terminal pH of the D<sub>0</sub> stage through the addition of sulfuric acid to remove more calcium from the system prior to the caustic extraction stage.

A third potential solution was investigated. Mill B was in the process of installing an enzyme-bleaching stage into the third of its four-stage brownstock washing line. The enzyme-bleaching stage required the brownstock pulp to be treated with sulfuric acid to lower the pH of the brownstock to about 6.5. The pH was adjusted by mixing sulfuric acid into the repulper water being applied to the third-stage brownstock washer. Enzymes were also added into the repulper water. The resulting reduced pH stock was held in a tower for at least 15 minutes, then subjected to a fourth stage of brownstock washing. Lowering the pH of the brownstock in the middle of the washer line desorbed a substantial amount of sodium from the fiber and retained the sodium in the black liquor cycle.

Lowering the pH of the brownstock washing line to 6.5 is not sufficient to remove a substantial amount of bound calcium from the pulp going to the bleach plant. Most of the ion exchange sites are carboxylic acids that remain in the base (anion) form until the pH gets closer to pH 4. But the lignin phenolics are also deprotonated, existing as anions at pH levels around 10 and above. Lowering the brownstock pH to 6.5 frees all cations balancing the charge of the phenolic sites on the pulp. This can be about a 50% reduction in bound metals. Also, as stated in the introduction, much of the calcium in brownstock pulp appears to exist as precipitated calcium carbonate (PCC). Just like on a paper machine, PCC becomes unstable when the pH drops below 7, and with 15 minutes retention time, some of the PCC will dissolve and become free to be washed from the pulp in the final washer. Although much of this calcium will precipitate again in the first or second stage of brownstock washers, the reprecipitated calcium carbonate often remains suspended in solution and is more effectively washed from the pulp than the lime that forms in the digester where it is often inside the fibers.

When the enzyme-bleaching stage with brownstock pH control was initiated, the sodium content of the bleach plant acid sewer decreased considerably. This is consistent with the proposed scenario. The acid treatment was removing a considerable portion of the sodium from the fiber surface. Some calcium also became soluble and was washed from the pulp, lowering the calcium input to the bleach plant. The sodium content of the bleach plant acid sewer dropped from about 16,000 mg/L of sodium to averaging about 2,500 mg/L of sodium with no significant change in effluent volume. Lime scale no longer precipitated on the extraction stage washer. In fact, a small amount of lime scale that was present on the extraction stage-face wire actually dissolved and disappeared. The positive aspect of this solution is that some calcium is removed in brownstock washing. This reduces the risk of calcium scale throughout the bleach plant, not just the lime scale problem on the extraction stage washer.

## Calcium Oxalate Scale Formation in the D<sub>0</sub> Bleach Stage

Lime scale is not the only non-process element mineral scale that causes problems in an ECF bleach plant. Calcium oxalate formation has also been documented to cause extensive lost time and increased operating costs. For most mills, the majority of the calcium entering the bleach plant comes with the wood.<sup>1</sup> It precipitates as calcium carbonate in the digester and is carried into the bleach plant to dissolve once the pH drops below 7. Once the calcium is dissolved, it is capable of reacting with oxalic acid to form calcium oxalate and precipitate onto process equipment. Oxalic acid is found in wood and also forms in the pulping process. But the conditions in the digester strongly favor calcium carbonate formation<sup>2</sup>, and the oxalate is left in solution where it can be removed by good brownstock washing. The majority of the oxalate in the bleach plant is a by-product of the bleaching chemistry. All oxidizing stages generate oxalic acid, typically about 250 to 500 g per metric ton of brownstock pulp.<sup>10,11</sup> With filtrate recycle and technical washing conditions, this provides for an oxalate concentration in bleach plant filtrate in the range of 35–90 mg of oxalate/kg of material (filtrate and pulp) in the first stage of bleaching. Filtrate recycle can increase the concentration of calcium to as much as 3000 mg/kg in hardwood pulp.

A mill with a low oxalate concentration, 10–20 mg/L has the potential to encounter scale problems when the pH in the first chlorine dioxide stage is above about 3.5. With a more typical mill concentration around 50 mg/L to 100 mg/L,<sup>12</sup> the mill can still reduce the oxalate scale by lowering the pH to about 2.5. Applying these data to a mill experiencing calcium oxalate scale formation indicates that simply by lowering the pH of the bleaching stage, the mill may be able to either eliminate or substantially reduce scale formation.

Another effect 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. Under most bleaching conditions, the preferred form is the monohydrate, but at pH below 4, the less soluble dihydrate also begins to form.<sup>13</sup> This effect increases the amount of calcium oxalate that precipitates between the pH of 2.5 and 4, but has little effect on the pH at which scale problems should cease.

Mill C started experiencing calcium oxalate scale formation about the time it converted to ECF bleaching. The scale was prevalent enough to extend the length of scheduled bleach plant outages by a couple of hours every 8 weeks. As oxalate scale formed on the washers during the 8 weeks between acid washes, the washing performance deteriorated and bleaching costs increased. After removing the scale from the washer, bleaching costs would drop then slowly climb again. Thus, calcium oxalate scale formation was responsible for increased operating costs and increased downtime.

When the mill originally converted from chlorine-based bleaching to ECF bleaching, no pH adjustment was employed. The natural terminal pH of the D<sub>0</sub> stage was about 3.0–3.4. In this pH range, about 10% of the oxalate is still in the divalent anion form. By reducing the pH to 2.5, this can be reduced to 2% or less. The mill piped a sulfuric acid line to the blend chest where brownstock pulp was diluted and fed to a chlorine dioxide mixer. A simple feedback control system and pH probe was installed approximately 30 seconds downstream of the chemical mixer. Manual tests were conducted to correlate the pH of the stock 30 seconds after chlorine dioxide addition to the terminal pH of the D<sub>0</sub> stage. Simple proportional feedback control was used, maintaining the sulfuric acid flow to keep the terminal pH of the D<sub>0</sub> stage in the 2.5–2.8 range. Good control of the terminal pH from about 2.4–2.9 resulted from the use of this sulfuric acid control system. Calcium oxalate scale formation on the D<sub>0</sub> washer was eliminated.

After about 11 months of operation, the D<sub>0</sub> stage started to scale again. Laboratory analysis of the scale indicated that calcium oxalate was again precipitating onto the D<sub>0</sub> washer. The pH measurements of the washer vat indicated that the terminal pH had increased to about 3.1–3.2. Troubleshooting of the pH control system found that the calibration of the pH probe had drifted. Thus, the probe was recording lower pH values than really existed. Several preventive maintenance procedures were implemented: the pH probe was correctly calibrated and a routine probe calibration protocol was established. Calcium oxalate scale formation stopped once again.

## **Prediction of Oxalate Scale Formation Conditions as Part of a Construction Job**

Mill D had been experiencing exceptional levels of calcium oxalate scaling over the course of 2 years. Scale formation started about the time the mill converted to ECF bleaching. Stock lines were depositing scale several inches thick, and the D<sub>0</sub> washer was routinely being taken out of service to be cleaned. Long segments of the D<sub>0</sub> stage stock lines were routinely replaced because they were too thickly scaled to be successfully hydroblasted or acid cleaned. Bleach plant operating costs were exceptionally high because of excessive carryover between washing stages. Every time the mill shut down or experienced large production swings in the bleach plant, some amount of scale would mechanically crack off the internal piping and send small particles of scale to the paper machine for several hours after the event.

The mill attempted to implement a pH control scheme similar to the one described above, resulting in a significant decrease in the amount of scale forming in the piping system. The oxalate scale associated with the washer did not decrease, and the amount of lime scale in the extraction stage increased. Except for the reduction in calcium oxalate scale formation in the D<sub>0</sub> piping system, the attempt to control scale formation by pH control was not successful.

The mill used atmospheric diffusion washers in the bleach plant. Filtrate obtained from a washing stage following the caustic extraction stage was used as wash water in the D<sub>0</sub> stage. The pH of this wash water was slightly alkaline. Poor pulp-washing efficiency was exhibited in this bleach plant. To simulate mill bleaching conditions in the laboratory, the D<sub>0</sub>, EOP bleach sequence required at least 45%–55% filtrate carryover from the D<sub>0</sub> stage to the EOP stage. The poor washing conditions in this bleach plant and high wash water pH were responsible for the failure of pH control to substantially reduce or eliminate calcium oxalate scale formation. Even though oxalate scale formation was eliminated in the D<sub>0</sub> stage piping and tower, the alkaline wash water, in conjunction with the inability to remove the dissolved calcium in the washer, resulted in extensive oxalate scale formation. The calcium that had been scaling onto the D<sub>0</sub> piping system was simply carried through the D<sub>0</sub> stage and formed calcium carbonate in the extraction stage. In order to eliminate the excessive down time associated with hydroblasting scale off of the atmospheric diffusion washers, and to substantially reduce the operating cost of the bleach plant, the mill decided to replace the D<sub>0</sub> and EOP stage washers with twin-roll presses.

Shortly before the mill started engineering the press retrofit project for the hardwood bleach plant, the mill had been engaged in a project to model the non-process element behavior of the hardwood bleach plant. A WinGEMS model of the mill was connected through dynamic data exchange to an Excel equilibrium calculation developed at the Institute of Paper Science and Technology. The operating bleach plant and the model were in agreement. Details of the model development, calibration, and performance are documented in the literature.<sup>14</sup> The mill was interested in predicting what effect the replacement of the D<sub>0</sub> and EOP stage washers with presses would have on non-process elements and NPE scale formation. The existing washer blocks were replaced in the model with split-blocks that split off filtrate to model the press discharge consistency of 30%. Two models were run: the ion exchange model with calcium oxalate precipitation and an exchange with the lime precipitation model in EOP. Laboratory work, in conjunction with vendor recommendations, was used to determine the initial operating conditions of the new bleach plant. These were used in the NPE model for the mill. The model results suggested the mill would be operating at a risk for calcium oxalate scale formation under their planned start-up conditions. Alternate operating scenarios were modeled in an attempt to develop non-scaling operating conditions that would be acceptable to the mill. These conditions suggested that pH control of the D<sub>0</sub> stage would be sufficient to eliminate the potential for calcium oxalate scale formation in the new bleach plant.

As the mill had previously been unsuccessful with pH control as a method of controlling scale formation, the initial suggestion was discarded, and the mill used the initial start-up conditions suggested by the project vendor. Excellent chemical reduction and good washing were obtained immediately upon start-up. The mill also started to form calcium oxalate scale on the D<sub>0</sub> press rolls. The mill data collected during this period were used in the equilibrium calculation presented in the second paper of this series.<sup>15</sup> After a couple of months of operation, the mill had to hydroblast the press rolls to remove the oxalate scale. The mill then initiated pH control and scheduled a maintenance outage to perform needed repairs and to hydroblast the press rolls for the next 8-week operating period. When the press was opened up for hydroblasting, no scale

was found. Good washing in conjunction with pH control was sufficient to eliminate calcium oxalate scale formation in this bleach plant.

WinGEMS modeling enhanced with the equilibrium calculation was able to successfully predict the behavior of the non-process elements and the potential for scale formation in the bleach plant.<sup>14</sup> Manipulation of the model parameters allowed mill personnel to *a priori* develop operating conditions that would alleviate the potential to form scale. The model predicted that the start-up conditions used by the mill would form calcium oxalate scale. This prediction was proven to be accurate. The modified conditions using pH control predicted that calcium oxalate scaling could be eliminated through the implementation of pH control. Mill operating conditions verified this finding also.

### **Calcium Oxalate Scale Formation in Piping Leading to the Caustic Extraction Stage Tower**

Mill E was experiencing extensive calcium oxalate scaling in the piping and MC pump going to the first caustic extraction stage bleaching tower. Extensive scale was forming at the inlet of the bowl of the pump. Caustic was being added at about the same location for the extraction stage. The scale was reoccurring to the point where the pump had to be opened up and hydroblasted every few weeks. The need to descale this pump was resulting in extensive downtime and maintenance. The mill was operating the D<sub>0</sub> stage well within the desired terminal pH range of 2.5–2.8, and no oxalate scale was forming on the washer drum. The wash water being applied to the D<sub>0</sub> stage was a combination of D<sub>1</sub> filtrate and paper machine whitewater. The paper machine operated at acid pH, around 5, and the whitewater contained a fairly high calcium concentration. Samples of the pulp leaving the repulper of the D<sub>0</sub> stage were collected. The pH of this pulp was about 3.5–4.0. Oxalic acid that was not washed out in the first chlorine dioxide stage was reacting with dissolved calcium in the paper machine whitewater and in the D<sub>1</sub> filtrate to form calcium oxalate scale. The leading edge of the pump had some amount of caustic dispersion and was operating at a pH closer to 4.0–4.5. Oxalate scale growth was prevalent under these conditions. The majority of the scale was forming in the bowl of the pump in the pH 4.0–4.5 location. The mill was not able to alter their wash water sources or improve their existing washing capabilities. Thus, the only option left to them was to relocate the caustic addition source. The mill decided to relocate the caustic addition point from the impeller of the MC pump to the repulper of the D<sub>0</sub> stage. It was well understood that this change might just move the scale formation to the D<sub>0</sub> repulper, but this area was at least easier to maintain. The hope was that by adding the caustic through a shower bar across the entire length of the washer repulper, the majority of any precipitate would collect on the material with the highest amount of surface area, the pulp fibers themselves. To date, the mill has not experienced any significant scaling problems in the D<sub>0</sub> repulper, and the oxalate scale formation in the piping and in the bowl of the MC pump have not reappeared.

### **Barium Sulfate Scale Formation in the D<sub>0</sub> Washer Face Wire**

Mill F was having difficulties with calcium oxalate scale formation on the face wire of the D<sub>0</sub> washer. Shortly after another mill explained their success in scale control by regulating the terminal pH of the D<sub>0</sub> stage, Mill F decided to try the same thing. After several months of operation, Mill F decided to stop using pH control because they had simply traded one scale problem, calcium oxalate, for a worse scale problem, barium sulfate. This literally put the bleach plant operators between a rock and a hard place. The barium sulfate was forming in the weave of the D<sub>0</sub> washer face wire. The scale was so tightly packed into the face wire that the mill was not able to scrape a sample of the scaling material off the drum for analysis. The face wire developed a shiny finish to it, and the small amounts of scale were sealing the washer drum and drastically impeding production as well as increasing bleach plant operating costs.

The barium sulfate would not come out with a simple acid wash either. The mill had to apply a hydroblasting technique using a caustic detergent wash aid with chelant. The hydroblasting solution also added substantial cost to the operation. Faced with the prospect of dealing with barium sulfate with their pH control system or working with the more manageable calcium oxalate scale, the mill abandoned pH control of the D<sub>0</sub> stage.

The mill had been controlling the terminal pH of the D<sub>0</sub> stage to 2.0–2.5. The mill was attempting to operate at the lower end of the pH range to ensure they would not get into a pH range friendly to calcium

oxalate scale formation. Frequently, the terminal pH of the D<sub>0</sub> stage would swing as low as 1.9. By adding enough sulfuric acid to drive the pH into this lower range, the mill was establishing excellent conditions for barium sulfate scale to form. The addition of excessive amounts of sulfuric acid substantially increased the sulfate ion concentration in the D<sub>0</sub> bleaching stage. Several fairly subtle effects also occur on washers to increase the probability of scale formation. The second pK<sub>a</sub> for sulfuric acid is about 1.9, so at this pH, half the acid is dissociated to the sulfate dianion and half is still associated as the bisulfate monoanion. The D<sub>1</sub> wash water at higher pH of 3.9 shifts this equilibrium to produce more sulfate. Secondly, both the pK<sub>a</sub> and the solubility product are temperature sensitive. Lowering the temperature decreases the solubility and increases the acidity, moving the acid–base equilibrium to produce more sulfate, and the precipitation equilibrium to favor precipitation. The high sulfate concentration and shift in equilibria associated with a cooler and higher pH wash water was enough to initiate precipitation of barium sulfate on the washer.

Eventually, this mill re-implemented pH control for the D<sub>0</sub> stage with a significantly higher target and tighter range. The mill now operates their pH control in the range of 2.4–2.8 with a target of 2.6. To date, the mill does not experience scaling problems on the D<sub>0</sub> washer.

### **Use of Sodium Sesquisulfate for pH Control in the D<sub>0</sub> Stage**

Mills G and H decided to reduce bleaching costs by substituting chlorine dioxide generator-spent acid for the sulfuric acid normally used in pH control of the D<sub>0</sub> stage. These mills operate an Erco R8 process. Another mill, operating an EKA SVP process also had similar cost-reduction thoughts. Both of these types of generators produce an acid salt by-product, a bi-salt of sodium sulfate and sodium bisulfate known as sodium sesquisulfate. The chemical structure of this generator by-product is Na<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub>. Some mills use a portion of the spent generator acid as a source of sodium make-up in the liquor cycle. Other mills sewer some or all of the spent acid, but some use the spent acid in the bleach plant for pH control. The mills that used spent acid for pH control developed recurring problems with D<sub>0</sub> stage face-wire plugging. The face wire of the D<sub>0</sub> bleaching stage developed a shiny appearance and stop draining, similar to the deposits described for Mill F. The drainage could be re-established by hydroblasting the face wire with a detergent/chealant material.

Based upon experiences at other mills that had run into similar difficulties, the pH control system used for the D<sub>0</sub> stage was evaluated. The mill was found to have been operating in a pH range that was considered “safe” for barium sulfate scale. After several months of difficulties, the mill finally got a sample of the scale material large enough for analysis. The majority of the material present was found to be barium sulfate. The mill tried to raise the pH of the D<sub>0</sub> stage slightly to no effect. Finally, they replace the spent generator acid with sulfuric acid and the barium sulfate scaling problem went away.

By using spent generator acid in place of concentrated sulfuric acid for pH control, the mill was effectively increasing the sulfate ion concentration in the bleaching stage at a dramatic rate. When using sulfuric acid, the mill adds a half of a sulfate ion for each proton added. When spent generator acid is used, two sulfate ions are added for each proton. Hence, by using spent acid, the mill was adding four times as much sulfate ion as it would have with sulfuric acid. This drastic increase in sulfate ion often results in barium sulfate scale even at higher pH values. For mills with barium sulfate scale, the best solution for controlling bleach plant pH would be to use hydrochloric acid (HCl), but as this tends to be cost prohibitive, concentrated sulfuric acid is used. In general, if a mill has any amount of barium entering with their wood basket, they should avoid using spent generator acid for pH content.

### **Conclusions**

Several mill case studies have been examined where some form of non-process element mineral scale has resulted in increased operating costs, extended downtime (both planned and unplanned), and substantially increased maintenance requirements. Mineral scale can form in the digesters, chlorine dioxide stages, and caustic extraction stages. Typical forms of scale include calcium carbonate or lime scale, calcium oxalate, or barium sulfate. In all cases, an understanding of the fundamental principles of scale formation has minimized or eliminated scale formation. In one reported case study, it was possible to apply first principle

understanding to a material and energy balance model. The mill could then predict *a priori* that proposed operating conditions would cause scale and develop alternate conditions that would be relatively scale free.

The fundamental aspects associated with scale formation and what works as a solution at one mill may not work at another because of variations in process conditions and equipment layout. It is also important to understand exactly what type of scale is in question. Just because a scale is forming in equipment associated with an extraction stage does not mean the scale that is forming is lime scale. As one case study above demonstrated, it is possible for calcium oxalate to form in portions of the extraction stage.

In short, by studying and understanding the fundamental aspects of mineral-scale formation, it is possible to minimize the cost of NPE's associated with bleaching. In some cases, it may not be possible to eliminate scale formation without radically altering the bleach plant water sources or operating conditions, but modeling and first principle predictions may be used to minimize the number of changes required to obtain minimal scale operation.

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## Fundamental Chemistry of Precipitation and Mineral Scale Formation

Session 3 of a tutorial on mineral scale

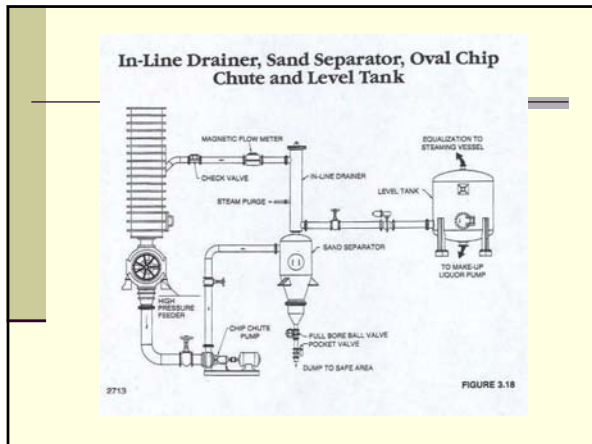
Alan W. Rudie  
USDA, Forest Service, Forest Products Laboratory  
Peter W. Hart  
Meadwestvaco Corp., Corporate Research Center, Chillicothe, OH

### What will we learn

- Understanding the Fundamentals will allow you to fix process related scale problems
- 3 mill case studies will be examined.
  - Note 7 examples in manuscript
  - Calcium Carbonate
  - Calcium Oxalate
  - Barium Sulfate

## Calcium Carbonate

Typical Locations -  
Digester  
Caustic Extraction Stages

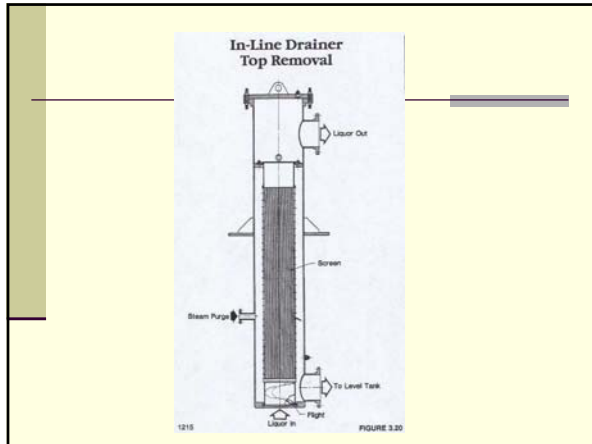


## Calcium Carbonate in White Liquor Strainer

- Liquor Strainer Used to Prevent Pins and Fines from Entering the Mixed Liquor Pump
- Routinely Plugging - Had to be Removed and Hydroblasted every 5 Days
- Antiscale Addition did not alleviate problem
  - Did Increase Operating Costs

## Calcium Carbonate

- No Chemical Addition or Mixing
  - Not chemical concentration change driven
  - May be a temperature change
  - May be a slow reaction like absorption of CO<sub>2</sub> from the atmosphere
  - Could be precipitation from a supersaturated condition
- After Several Weeks of Observation
  - Scale typically more prevalent in one location



## Calcium Carbonate

- Careful Observation Revealed Steam Leak
- Understanding of Inverse Solubility of Carbonate
- Fixed Steam Leak - problem went away
  - even when antiscaling was discontinued

## Calcium Oxalate

Typical Locations -  
Acid Stage Washers & Filtrate Tanks  
Caustic Stage Piping prior to NaOH

## Calcium Oxalate - Do Stage Washer

- Causes Excessive Downtime - every 8 weeks
  - hydroblasting - extended outages
  - removal from filtrate tanks
- Causes Excessive Chemical Consumption
  - poor washing through plugged wires

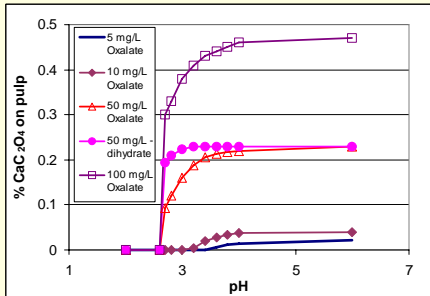
## Calcium Oxalate

- Generated as by-product of bleaching
  - 250 - 500 g/metric ton
    - 30 - 90 mg/Kg
- Recycle Concentration
  - can increase concentration to 3000 mg/Kg
    - typical concentrations in the 50 - 100 mg/L
- Crystal Structure and solubility product are very pH dependent
  - pH < 4 starts to form dihydrate

## Calcium Oxalate

- Scale Started after ECF conversion
  - Do Stage Terminal pH  $\approx$  3.0 - 3.4
    - about 10% of oxalate in divalent form
- Theory Suggests that reducing the Terminal pH to 2.5 will reduce this to 2% or less

## Calcium Oxalate - pH Dependence



## Calcium Oxalate

- Mill Solution
  - Feedback Control Sulfuric Acid Addition System
- Results - pH Controlled to 2.4 - 2.9
- Calcium Oxalate Scale Eliminated!

## Calcium Oxalate

- Scale Started to Appear again after 11 months of operation
  - Data Historian still showing good pH control
  - Lab Tests showed vat pH 3.1 - 3.2
  - pH probe calibration had drifted.
- Scale Eliminated after Recalibration of Probe

## Calcium Oxalate - Predicted

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- Understood Well Enough to be Modeled
  - C. Litvay, A. Rudie, P. Hart, "Use of Excel Ion Exchange Equilibrium Solver with WinGEMS to Model and Predict NPE Distribution in the MeadWestvaco Evadale, TX Hardwood Bleach Plant," TAPPI 2003 Fall Conference, Chicago, IL, October 2003.
- Used to Model Bleach Plant Washer Changes
  - Predicted Boarder line Scaling Conditions
  - Predicted pH control would eliminate problem
  - The solubility for this case is analyzed in the second paper

## Barium Sulfate

Typical Location -  
Do Washers

## Barium Sulfate

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- Mill experiencing excessive oxalate scale
  - Implemented pH control
  - Target pH of 2.0 - 2.5
- Started forming a hard to remove scale in the weave of the face wire of the Do washer
  - Completely sealed face wire
  - had to hydroblast with chelant and caustic detergent to remove

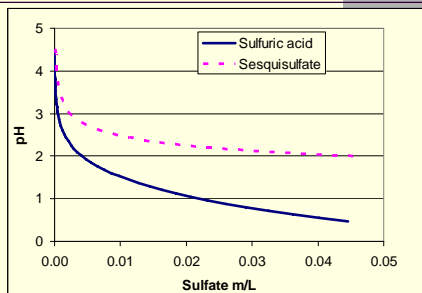
## Barium Sulfate

- Low pH target required large amounts of Sulfuric Acid Addition - Increased Sulfate Ion
- Re-implemented pH control with 2.6 target
- All Scale Eliminated

## Barium Sulfate - Sesquisulfate for pH Control

- Mill experiencing oxalate scale
  - Implemented pH control with a 2.6 target
  - Employed Spent Generator Acid as Acidification Method to reduce chemical costs
- Formed Barium Sulfate Scale
- Replaced with Sulfuric Acid at same pH target
- Eliminated Scale Problems

## Entire pH range



## Conclusions

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- Several Mills have experienced Scale Formation from NPE's
  - Calcium Carbonate
  - Calcium Oxalate
  - Barium Sulfate
- It is possible through application of fundamental understanding to predict scale formation and determine methods to eliminate scale formation

## Conclusions

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- NPE Scale Formation is non-trivial
- Subtle Interactions complicate predictions and understanding

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