

Modeling and Minimization of Barium Sulfate Scale

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Abstract

The majority of the barium present in the pulping process exits the digester as barium carbonate. Barium carbonate dissolves in the bleach plant when the pH drops below 7 and, if barium and sulfate concentrations are too high, begins to precipitate as barium sulfate. Barium is difficult to control because a mill cannot avoid this carbonate-to-sulfate transition using common bleaching technology. An advantage in controlling barium scales is that the sulfate, once formed, will not redissolve to any appreciable extent, and this reduces the rate at which barite scale can form in other locations in the bleach plant. A mill has relatively few options for controlling barium sulfate scale. The first is to ensure very good debarking to minimize barium entering the mill with the wood. The second option is to minimize sulfate content of the first chlorine dioxide stage in the bleach plant. Sulfate is minimized through good brown stock washing and by using sulfuric acid for pH control instead of chlorine dioxide generator spent acid. Sulfate can also be reduced by operating the initial chlorine dioxide stage at higher pH, but this will work only in mills where calcium scales are not a concern. A third option is to use crystal modifiers (scale inhibitors). Scale inhibitors can be an expensive solution but are effective at delaying precipitation, and if the location can be moved from pumps and process piping into a tower, the impact of the scale is reduced. Because barium sulfate will not redissolve in the bleach plant, a barite deposit is less likely to reoccur somewhere else in the bleach plant.

Introduction

Pulp mill bleach plants have experienced problems with barium sulfate mineral scale since the advent of continuous bleaching. However, the change to chlorine dioxide initiated bleaching sequences in the 1990s resulted in an unanticipated increase in mineral scale problems, including several mills with significant barium sulfate scale. Of the three common mineral scales encountered in bleach plants (barium sulfate, calcium oxalate, and calcium carbonate), barium sulfate is the most difficult to remove and the most difficult to prevent. It also tends to co-precipitate radium sulfate, which results in a radioactive deposit that requires special handling when removed.

Preventing barium sulfate scales is difficult because the sulfate ion is ubiquitous in a pulp mill and bleach plant. The sulfate dianion is the net product of bound sulfur on brown stock pulp, sulfur carryover from brown stock washing, and acid used for pH adjustment in the bleach plant. Barium sulfate scale is difficult to remove because sulfate is a strong acid and the dianion persists to a pH below 2. Barite scale requires strong acids to dissolve, and the acid used cannot be sulfuric acid. The usual treatment is more mechanical—fracturing and removing deposits with intense water washing, usually referred to as hydroblasting. This is akin to trying to demolish a concrete driveway with a pressure washer.

A mill can take a few somewhat simple steps to try to eliminate barium sulfate scale. The first is to minimize the bark content of the wood. Trace metals are at significantly higher concentrations in the bark than they are in clean wood.^{1,2} Good debarking is the only effective way to reduce barium in the mill. For mills that are experiencing barium sulfate scale, a reduction of barium taken into the mill directly decreases the amount of scale.

Having ensured effective bark removal, the next most effective means of reducing or eliminating barium sulfate scale is to eliminate the use of spent acid from the chlorine dioxide generator for pH adjustment in the bleach plant. Spent acid is a mixture of sodium sulfate (Na_2SO_4) and sodium bisulfate (NaHSO_4) and adds four times as much sulfate to a bleach plant as does commercial sulfuric acid (detailed later in this paper). Sulfate concentration in the first chlorine dioxide stage can also be reduced by optimizing brown stock washing. Sulfide used in kraft pulping is S(-II) (sulfur in the -2 oxidation state), the most reduced state sulfur is commonly found in. Sulfate from sulfuric acid, S(VI), is the most oxidized state that sulfur is typically found in. Because chlorine dioxide is a strong oxidizing chemical, it oxidizes all forms of sulfur that enter the bleach plant to sulfate. Other than installing an oxygen stage, the mill cannot do anything about the sulfur that is physically bound to pulp as thiols, but it can wash out the sulfide, sulfate, and intermediate oxidation state sulfur-containing anions. A mill can realize at least three benefits by improving brown stock washing:

1. Less chlorine dioxide is wasted oxidizing reduced sulfur compounds.
2. Less base (NaOH , Na_2CO_3 , and NaHCO_3) will carryover into the bleach plant. This reduces the amount of sulfuric acid needed to attain the D_0 stage target pH.
3. Risk of barium sulfate scale is reduced and, if not eliminated, deposition is slowed.

As part of a barium sulfate scale reduction process, the mill should evaluate acid use and, importantly, caustic use in the bleach plant. The caustic must be neutralized somewhere, and one method of reducing the demand for sulfuric acid is to reduce the use of sodium hydroxide. Good washing is important, particularly after the D_0 stage because this is the best place to remove barium from the bleach plant. The countercurrent use of wash water can also contribute to problems. Direct countercurrent washing, where E_1 stage filtrate is used to wash D_0 pulp and D_1 filtrate is used to wash E_0 pulp, helps to trap alkali-insoluble trace metals in the extraction stage. The alkaline extraction stage filtrate promotes oxalate and sulfate precipitation on the D_0 stage mat, increasing the amount of barium and calcium entrained in the pulp and carried into the extraction stage. It also raises the pH of the D_0 filtrate, which increases the need for sulfuric acid in this stage. The acidic D_1 filtrate used on the extraction stage washer causes calcium and barium carbonate to dissolve. Some is washed through into the extraction stage washer seal tank, and the rest ends up in the D_1 stage filtrate, where it returns to the extraction stage in the shower water. Jump stage and split stage filtrate recycle methods have fewer problems with trace metals.

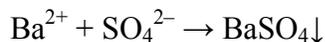
The remainder of this paper will present the supporting science for these recommendations, starting with a brief review of the chemical theory of precipitation and then discussing various aspects of barium in the pulp mill and bleach plant:

- Barium sulfate solubility (solubility product)
- The state of barium in the digester (part of the problem)

- □ Acid base chemistry for sulfate and why spent acid contributes to barium scale
- □ Barium sulfate scale on washers

Chemistry Review

Chemical solubility is defined by an equilibrium expression known as the solubility product. The chemical equation for precipitation of barium sulfate is



The equation specifies the divalent cation, barium, and the divalent anion, sulfate. Bisulfate (HSO_4^-) does not participate directly in the precipitation process. The down arrow following BaSO_4 indicates that it is a precipitate.

Monovalent cations such as sodium and potassium rarely form complexes, and the total solution concentration is very close to the concentration of monovalent cation. With divalent cations such as Ca^{2+} and Ba^{2+} , this is not quite the case. Divalent cations form weak complexes with the base form of organic acids and with the hydroxide anion. The formation constant of barium with acetate is 2.6, with oxalate is 204, and with catechols, around 10,000. They also form strong complexes with chelating chemicals such as ethylenediaminetetraacetic acid (EDTA, 6×10^7) and diethylenetriaminepenta-acetic acid (DTPA, 6×10^8). In a painfully rigorous analysis, all these potential complexes must be evaluated as interdependent equilibria to arrive at the true free divalent cation concentration. For the D_0 stage, it is appropriate to ignore these equilibria. Persson and Ulmgren have shown an effect of bleach plant chemical oxygen demand (COD) increasing the apparent solubility of barium sulfate. This is probably due to the relatively weak complexes formed between barium and the organic acids common in bleach plant filtrates.³ The organic acids are largely protonated at a pH of 3 and below. Even if DTPA or EDTA is present, they are not very effective as chelating agents at low pH.³ The resulting analysis provides a worst case for scale problems. Trivalent cations such as Fe^{3+} and Al^{3+} rarely exist in the trivalent state, and the solution chemistry of these metals is quite complex. Fortunately, these rarely occur in bleach plant scales.

With the anion, the competing equilibria are a concern. The most significant competing equilibrium is the acid–base equilibrium (discussed in detail in a previous paper and not reiterated here⁴). But sulfate is in equilibrium with bisulfate (HSO_4^-) at pH around 2. This equilibrium is the source of the buffering effect of spent acid and has been accounted for in determining the divalent sulfate anion concentrations used in this paper. At a pH of 2.5, about 80% of the total sulfate ($\text{H}_2\text{SO}_4 + \text{HSO}_4^- + \text{SO}_4^{2-}$) is in the divalent state.

The equilibrium expression for barium sulfate precipitation is

$$[\text{Ba}^{2+}]f_{\text{Ba}}[\text{SO}_4^{2-}]f_{\text{SO}_4} = K_{\text{sp}}$$

The precipitate is not shown in the equilibrium expression because it is not present in solution and is assigned an activity of 1. Following standard chemical usage, the square brackets are used

to indicate molar or molal concentration. The terms f_{Ba} and f_{SO_4} are activity coefficients and convert the ions to their respective molar activities. Activity has also been discussed in the previous paper.⁴ At bleach plant ion concentrations, the activity of a divalent ion is approximately half of the molar concentration. In this paper, f_{Ba} and f_{SO_4} are assumed to be ~ 0.5 .^{5,6}

Brown Stock Barium

Of the trace metals common in wood, barium is typically present at the lowest concentration and is usually of concern only in hardwoods. Analysis of brown stock from four hardwood mills gave an average barium concentration of 42 mg/kg on an oven-dry basis, with a high concentration of 61 mg/kg and a low concentration of 21 mg/kg. Analysis of five softwood lines gave an average of 9.2 mg/kg in the brown stock pulp. The vast majority of this barium entered the mill with the chips and—like calcium—precipitated in the digester. Because of the very low concentration, the state of barium in the wood is not known, but in the hardwood lines it is present at about 4×10^{-5} molar total concentration in the digester. Two likely alternatives for the state of barium in the digester are barium sulfate and barium carbonate. At room temperature, barium sulfate has a solubility product of 1.1×10^{-10} , and the solubility product for barium carbonate is 2.6×10^{-9} .⁷ At the cooking temperature, the solubility products for barium carbonate and barium sulfate are nearly equal, $\sim 3 \times 10^{-9}$ (Figure 1). At the end of a typical conventional kraft cook, carbonate concentration is around 33 gpl (0.31 M) and sulfate around 0.88 gpl (0.0062 M). Ignoring ion activities and competing equilibria, these anion concentrations limit the soluble barium to about 9.7×10^{-9} molar barium as carbonate and 4.8×10^{-7} molar as sulfate. Under these conditions, the bulk of the barium is

expected to be as insoluble barium carbonate. This is critical to understanding the barium scale problem. If barium precipitated in the digester as the sulfate, it would not dissolve to any appreciable extent in the D_0 stage and mills would not suffer from significant barium sulfate scale problems. The location where the barium carbonate should precipitate is

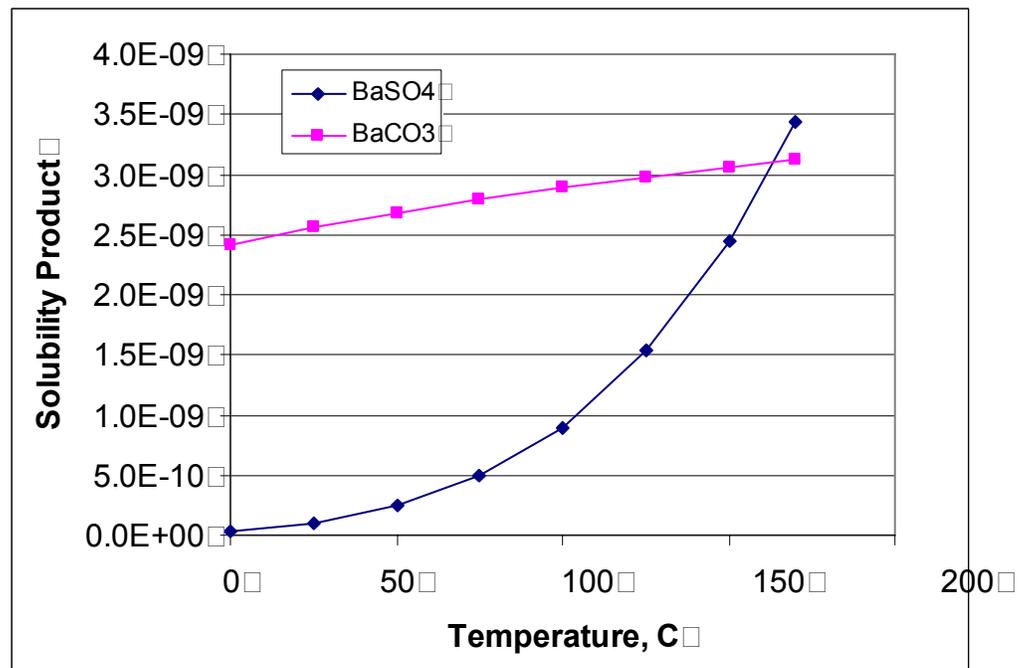


Figure 1. Influence of temperature on the solubility product of barium sulfate and barium carbonate. K_{sp} calculated from the free energy.

also critical to understanding the barium scale problem. With the exception of the outer cell wall of the perimeter fibers on a chip, barium in the fibers is closer to a cell lumen than the exterior of the chip. There is no exterior fiber surface inside the chip, just the lumens. By default, the bulk of the barium carbonate has to be inside the fibers and cannot be washed out without lowering the pH to dissolve the carbonate. These two critical factors cannot be changed and force mills to deal with barium in the bleach plant.

Bleaching and Barium

The first chlorine dioxide stage operates with a typical target end pH of 2.5 to 4.0. For mills with calcium oxalate scale problems, the recommendation is generally to lower the pH to 2.5.^{8,9} Carbonates are not stable at pH below neutral. At this pH, much of the carbonate is in the form of carbonic acid, which disproportionates into CO₂ and water. CO₂ has low solubility in water, particularly at higher temperatures, and ends up released to the atmosphere. This reaction forces barium into solution, where it is free to be washed out at the end of the D₀ stage or to react with other molecules—such as the sulfate anion. Using the nominal 4×10^{-5} M barium concentration in the digester and adjusting for the difference in consistency, the average mill will have a barium concentration around 2×10^{-5} M. Actual values in the acid sewer from the four hardwood mills ranged from 1 to 2 mg/kg or about 1×10^{-5} M. Up to this point in the process, the mill has not had much real ability to control or minimize barium scale. The D₀ stage is the first and best opportunity to control barium. If barium sulfate precipitates in the D₀ stage, it ensures that the rest of the process will operate saturated in barium and sulfate and any process changes that reduce solubility will likely encounter some scaling. An acid sized papermachine using alum is a common place to observe this sad fact.

In-process management of barium in the D₀ stage is limited to controlling the sulfate anion. Secondary control possibilities include reducing the soluble barium using chelants or controlling precipitation using chemical inhibitors.

Sulfate Control

Eliminating barium sulfate scale in the D₀ stage means minimizing sulfate. For mills that do not also suffer from calcium oxalate precipitation, this can be accomplished by operating the D₀ stage at the high pH side of the optimization window—near pH 4.0. The second critical change (stated in the introduction) is to eliminate the use of spent acid from the chlorine dioxide generator for pH control in the bleach plant.¹⁰ Spent acid, also referred to as sodium sesquisulfate, is a mixture of sodium sulfate and sodium bisulfate. The composition is variable but is often listed as Na₃HS₂O₈. More accurately, it is (Na₂SO₄)_n(NaHSO₄)_m. The first half of the chemical formula is just sodium sulfate. It contributes nothing to adjusting the pH and serves only to increase sulfate concentration and the potential for barium to precipitate and form scale. The second part is sodium bisulfate—it contributes one mole of acid for each mole of sulfate. Compare this to sulfuric acid, which contributes just ½ mole of sulfate for each mole of acid and it is easy to see why spent acid is a barium scale problem waiting to happen. At higher pH targets—around pH 4—spent acid adds four times as much sulfate to the D₀ stage as does pH control with sulfuric acid. At the low target range—pH 2.5—the situation is even worse. Spent acid is a

buffer that cannot produce a pH below about 2.0. At pH 2.5, the amount of sulfate added is six times the amount needed to reach this pH with sulfuric acid (Figure 2).

The sulfate concentration at pH 2.5 from Figure 2 is 1.4 mM when using sulfuric acid and 9 mM when using spent acid.¹¹ Using the average barium concentration of 1×10^{-5} and activity coefficients of 0.5, the ion

product using sulfuric acid is $(1 \times 10^{-5})(0.5)(1.4 \times 10^{-3})(0.5) = 3.5 \times 10^{-9}$. With spent acid, the ion product is 2.2×10^{-8} . At 75°C, the solubility product for barium sulfate is 5×10^{-10} . Using sulfuric acid, the ion product for barium sulfate exceeds the solubility product by a factor of 7. Due to a number of factors, including supersaturation and complex formation, scale problems are often not encountered until the ion product exceeds the solubility product by an order of magnitude or more (a factor of 10). With spent acid, the ion product exceeds the solubility product by a factor of 40. This condition is much more likely to result in precipitation and often scale.

The above analysis is for pH adjustment of water and contains a number of simplifications that need to be discussed:

- Much of the acid in a D₀ stage is by-product hydrochloric acid. For a hardwood line with a 16 incoming kappa and a kappa factor of 0.2, this contributes 0.018 mol/L of acid. If not for other issues (discussed below), this is enough acid to provide a pH below 2 and eliminate the need for sulfuric acid in the D₀ stage.
- Wood pulp contains phenolic and carboxylic acid groups that make it behave as an ion exchange resin. The phenolic acids go from the base state to the acid state as the pH falls below 10. The majority of the carboxylate anions are protonated at a pH below 4. At pH 3, 100% of the phenols and 90% of the carboxylic acids are in the acid form, and we can pretty much ignore the ion exchange effect on barium. But we cannot ignore the acid–base chemistry. A typical brown stock has about 100 meq of carboxylic acid groups for every kilogram of pulp and nominally an equal number of phenols. At 10% consistency, this

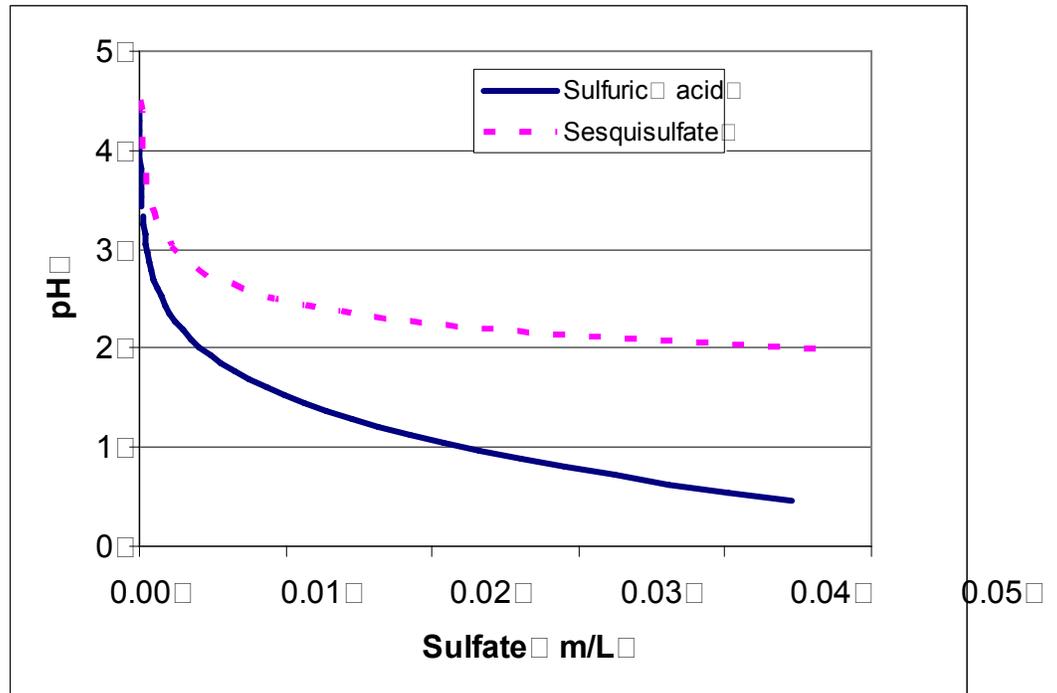


Figure 2. Concentration of sulfate anion when using sulfuric acid and sodium sesquisulfate for pH control.

amounts to about 0.01 to 0.02 moles of base per liter of pulp. The vast majority of these carboxylate groups need to be neutralized to reach a solution pH of 2.5. This adds 5 to 10 mM sulfate to the solution.

- Brown stock does not enter the bleach plant free of sulfur, and as pointed out in the introduction, all the sulfur compounds are oxidized to sulfate by chlorine dioxide. For the hardwood mills in the analysis pool, the brown stock pulp averages 300 mg/kg total sulfur. At 10% consistency, this adds another 1 mM of sulfate to the D₀ stage.
- Few mills operate with mill water as the only water added to the D₀ stage. Most use D₁ filtrate on the washer showers and some cascade extra D₁ filtrate from the washer seal tank into the D₀ stage. Ideally, the only sulfate in the D₁ stage is what carries through the bleach plant from D₀, but mills using papermachine whitewater on bleach plant washers can be adding considerable sulfate to the D₁ or D₂ stages. This sulfate will work back to the D₀ in the countercurrent wash process.

Taking these values as a good estimate, the brown stock requires ~0.015 moles of acid to neutralize the ion exchange sites. The chlorine dioxide provides 0.018 moles, leaving 0.003 moles excess acid. With water, sulfuric acid needed 0.0018 moles of H₂SO₄ or 0.0035 moles of acid to achieve a pH of 2.5.¹¹ Subtracting the excess HCl leaves 0.0005 moles of additional acid needed in the stage, which is 0.25 mM of sulfuric acid or sulfate added. This is about 0.25% sulfuric acid on pulp and is in the normal range for acid requirements in a hardwood D₀ stage. Total sulfate is now 0.25 mM, plus 1 mM from the sulfur in brown stock, for a total of 1.25 mM. This case would provide a filtrate sulfur analysis of 40 mg/kg. Four of the six bleach lines that have been analyzed have concentration of 30–50 mg/kg of sulfur in the acid sewers. The net effect of the factors listed is to reduce sulfate concentration from 1.4 mM for the pure water case to 1.25 mM, and 80% of the sulfate is from brown stock carryover.

The case using spent acid for pH adjustment is similar. Water required 0.0055 moles of spent acid to reach a pH of 2.5. There is 0.003 moles of HCl generated by the ClO₂, leaving 0.0025 moles of spent acid needed for pH adjustment. That produces between 4 and 5 mM of sulfate. In this case, 75% of the sulfate is from the spent acid. The ion product is around 1×10^{-8} for the spent acid case. ($0.004 \times 0.5 \times 0.00001 \times 0.5 = 1 \times 10^{-8}$). With the solubility product for barium sulfate at 75°C as 5×10^{-10} , with spent acid for pH control, the hypothetical mill exceeds the stable barium and sulfate concentration by a factor of about 20.

Barium on Washers

The cases of barium scale reported in the case studies⁸ all occurred on the first chlorine dioxide stage washer. A number of chemical changes occur in the D₀ stage that can contribute to this problem. But note that all three mills were able to eliminate their barium sulfate scale by operating at an appropriate pH and not using spent acid for pH control.

The barium enters the bleach plant as barium carbonate in unbleached pulp that is usually at a pH above 9. The sulfuric acid charged to the chlorine dioxide stage may be sufficient to lower the pH below 7, but the stage is ultimately dependant on by-product HCl to achieve a final pH between about 2.5 and 4. This means that the pH change from above 9 to below 4 occurs over a

period of time and with it the acid–base reaction of carbonate that causes the calcium and barium carbonates to dissolve. Chlorine dioxide reacts with carryover sulfur, oxidizing it to the sulfate anion. The result is that the concentration of both barium and sulfate can increase during the D₀ stage and the barium sulfate can precipitate when inside the D₀ tower where pulp surface area is large and the process surface area is very minimal. Among possible outcomes, this is not bad, but it almost ensures that the rest of the process, bleach plant and paper mill, are operating saturated in barium and sulfate.

At the discharge of the tower, D₀ filtrate is used to dilute pulp in the tower and this is also saturated in barium sulfate. It is likely a little cooler than the tower and will lower the solubility product, which might cause some precipitation or a little scale around the discharge device. At the washer, the fiber mat thickens to 10% to 15% consistency. Filtrate sucked through the mat cools as it reaches the low pressure side of the drum. This is most pronounced in vacuum washers, where the drop leg can flash some steam to increase cooling. In a laboratory attempt to mimic a vacuum washer, 55°C water dropped 4°C to 5°C degrees when filtered through a standard glass fritted disk filter using a laboratory aspirator. The 5°C temperature change reduces the solubility product from 2.9×10^{-10} to 2.6×10^{-10} . The lower temperature causes additional precipitation which would occur at the washer wire and in the drop leg. This is the most likely reason for scale forming on the wire.

In some cases, the mat can behave as an ion exchange resin, and this provides another mechanism for scale forming on washers.¹² This was observed on an extraction stage washer where calcium carbonate scale was found in the vat and calcium oxalate scale formed in the filtrate tank. The ion exchange mechanism is not expected to contribute to barium sulfate scale forming in a D₀ stage. The shower water is usually at a higher pH than the pulp on the mat. The increase in pH increases the ion exchange capacity available to adsorb barium and will reduce the concentration penetrating the mat in the wash zone. There is also no reason for the D₁ filtrate typically used as shower water on D₀ to be high in sulfate because acid is usually not needed in the later stages of the bleach plant. An obvious exception is a mill receiving papermachine whitewater on late stage bleach washers but only if the mill is still running an acid headbox. Both of these conditions were reversed when ion exchange appeared to be contributing to the scale.

Scale Suppressants and Crystallization Inhibitors

The authors have no direct experience controlling barium sulfate scale with crystallization inhibitors or scale suppressants. Scale suppressants used on calcium carbonate scale in digesters have reduced scale-related digester outages, but experience with scale suppressants to control calcium oxalate scale in various locations in the bleach plant has generally not been positive, suppressing scale formation in one location only to have it show up later in the bleach plant. Reports from mills using scale suppressants on barium sulfate have been favorable.

Scale suppressants or more accurately, crystallization inhibitors, appear to work by several different mechanisms.¹³ They usually do not prevent crystals from forming but rather prevent them from growing and can prevent them from attaching to surfaces. Effectively, the active chemical attaches or coordinates to the surface of a crystal and blocks either the cations or anions

from attaching and preventing further growth. Because crystals do not grow, many more need to form to reach equilibrium, but they remain very small and easily suspended. If a scale begins to form, the inhibitor attaches to the surface of the scale and it remains as a film or grows very slowly and can be handled within a normal maintenance schedule.

There are several reasons why scale suppressants should be more effective with barium sulfate than calcium scales:

1. The amount of barium sulfate that can form is small relative to the potential amount of calcium oxalate or calcium carbonate scale. This means that the ratio of suppressant to crystal surface area is usually more favorable.
2. Once formed, barium sulfate is nearly inert at pH above 3. Since the later stages of the bleach plant never go below this pH, the soluble barium concentration remains too low to form an appreciable amount of scale.
3. The higher temperature and lower sulfate concentration of the later stages favor dissolving some of the entrained barium sulfate. There are no places in the late stages where the trend reverses and precipitation would occur (other than the thermal mechanism on vacuum washers). This is definitely not the case with calcium, where additional oxalate (and carbonate) form in later stages.

For mills with high barium concentrations in the wood and where other control methods have failed, the use of scale suppressants can provide considerable relief from scale problems. Process changes are usually the more cost-effective approach to solving scale problems, but when these fail, polymer suppressants have succeeded in controlling barium sulfate scale.

Summary

Most of the barium encountered in a mill bleach plant enters with the wood. It is expected to precipitate in the digester as barium carbonate, and much of this precipitate should be trapped in the fibers. The barium carbonate dissolves when the pH drops below 7 in the first chlorine dioxide stage. This stage is well designed to experience barium sulfate precipitation. The soluble barium concentration is at the highest point in the mill because adsorption on pulp ion exchange sites is suppressed by the low pH and there has not been much opportunity to wash the barium from the pulp. In addition, the first chlorine dioxide stage typically requires addition of sulfuric acid to reach the target end stage pH needed to control calcium oxalate scale. Finally, all the sulfur compounds that carry into the D₀ stage with the brown stock are oxidized to sulfate in this stage, further adding to the sulfate concentration.

A mill has a number of opportunities to reduce or eliminate barium sulfate scale. Trace metals in bark are at higher concentration than in the wood, and the mill may achieve some reduction by improving the debarking. Improved brown stock washing helps by removing sulfur compounds that will otherwise oxidize to sulfate in the D₀ stage. The mill can also reduce sulfate by controlling the use of sulfuric acid in the bleach plant. The D₀ pH can be increased if the mill does not have problems with calcium oxalate. If the mill uses chlorine dioxide generator spent acid for pH control, this adds four times more sulfate to the bleach plant than sulfuric acid. Switching to sulfuric acid has eliminated barium sulfate scale in several mills. Polymer scale

inhibitors can be effective, but this route is usually more costly and mills should attempt to resolve the problem with process changes before resorting to this alternative.

Note: The Forest Products Laboratory is maintained in cooperation with the University of Wisconsin. This article was written and prepared by U.S. Government employees on official time, and it is therefore in the public domain and not subject to copyright.

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