

Modeling of Bleach Plant Washer Mineral Scale

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Abstract: One of the more common areas of mineral scale formation in bleach plants is on washer face wires and the extraction rings of diffusion washers. Whereas most scale problems can be understood as a mixing of two streams that increase the concentrations of anions and cations and exceed a solubility product, washer problems are often more difficult to understand. The behavior of the pulp mat as a cation exchange resin makes these devices operate as an ion exchange column. This feature has the effect of delaying the release of cations into the filtrate and can cause a high concentration of a scaling cation to be released into a filtrate stream containing a higher concentration of the scaling anion. This ion exchange column process is proposed as a critical element in understanding scaling problems on washers. To test the hypothesis, a finite element model of a bleach plant washer has been prepared. This model divided the mat into thickness increments and modeled the ion exchange and precipitation equilibrium for each increment. The soluble fraction was passed on to the next increment using a washing efficiency factor to apportion the displacement and mixing of the input and output streams for each increment. The model has been tested against laboratory washing data and has been validated against two extraction stage washers in the MeadWestvaco Covington, VA mill.

Introduction: To comply with the U.S. Cluster Rules, bleach plants had to reduce or eliminate the use of chlorine as a bleaching chemical. In most cases this was accomplished by substituting chlorine dioxide for the chlorine used in the first stage of the bleach plant. In many cases, mills also improved spill collection and increased filtrate recycle in the bleach plant to further reduce effluent volume. The combination of the reduced formation of hydrochloric acid as a reaction by-product, the need for sulfuric acid for pH management in the first stage, the higher target pH in the first stage, and the tighter filtrate recycle, increased the incidence of mineral scale problems in bleach plants significantly. A number of research groups responded by trying to improve the understanding of barium sulfate, calcium oxalate and calcium carbonate precipitation,^{1,2,3} ion exchange processes of trace metals with wood pulp,^{4,5,6,7} equilibrium modeling of bleach plant conditions, and mass balance equilibrium modeling of bleach plants.^{8,9,10} These efforts have gone a long way to assisting scientists and engineers in understanding and correcting process conditions that favor mineral scale formation. However, bleach plant washers remain as an area where there remains insufficient understanding of the chemical processes that promote scale formation. This is unfortunate because washers are one of the most prevalent locations for mineral deposits in bleach plants. Having recently succeeded in modeling and predicting changes in trace metal accumulation and scale potential for an overall-bleach plant,¹⁰ it was decided to apply similar methods in an effort to understand scale formation on bleach plant washers.

One of the features of wood pulp that fosters mineral scale problems is the ion exchange behavior of the acid functional groups.^{4,5} Electroneutrality requires pulp to collect enough cations to balance or neutralize the charged groups. 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.¹¹ 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 byproduct of the chlorine reactions. At a pH below 2, 90-99% of the trace metals are freed from the fibers and available to be washed from the pulp.^{12,13} For a chlorine dioxide initiated bleach sequence, there is not sufficient acid formed in bleaching to maintain the target pH and sulfuric acid is needed. This raises the sulfate ion concentration in the bleach plant considerably and is probably the biggest single contributor to the increase in Barium/Radium Sulfate scales. The optimal pH for a chlorine dioxide initiated bleach sequence adds a second problem. Whereas the ideal pH for chlorine was 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^{12,13} and will be carried further into the bleach plant. Typical limits on washing efficiency increase this value significantly. The nature of the ion exchange process is such that it favors ions of high charge, preferring divalent cations like Ca^{2+} and Ba^{2+} by about a factor of four over Na^{2+} .⁴ This results in a significant carryover of scale forming trace metals. Many of these will be released from the pulp and washed out in later chlorine dioxide stages, only to be returned to the first stage in wash filtrate. This filtrate recycle further contributes to the accumulation of trace metals in the first stage and in the bleach plant as a whole. The final chemical contributions to the scale forming process are the anions - oxalate and carbonate are formed as by-products of the bleaching reactions. Any sulfur/sulfide carried over from the kraft process will be oxidized to sulfate in the bleach plant, adding to the sulfate load of the process.

The above list of issues may seem imposing, but paints an overly dire picture of metals control in the process. The first and foremost element of control is pH. Carbonate is unlikely to form lime scale at a pH below 7, and oxalate scale is unlikely to form below a pH around 4.¹⁴ Furthermore, low pH in the initial chlorine dioxide stage helps to remove metals, so the first line of control is the initial chlorine dioxide stage. Although the optimum bleaching pH may be higher, for purposes of trace metal control it is beneficial to operate this stage at a pH between 2 and 3. That is of course unless the mill is a victim of high barium content wood in which case the extra sulfuric acid needed to obtain this pH will aggravate barite formation in the stage. The best way to reduce barium scale problems are to insure good brown stock washing to minimize the sulfur/sulfate carryover into the bleach plant, and maximize acid filtrate reuse from later stages to minimize the need for sulfuric acid for pH control. It is also important to control sodium hydroxide use since this invariably needs to be neutralized somewhere else with sulfuric acid. Even with this issue - barium concentrations are typically 1/100 of the calcium concentration^{15,16} and it may benefit the mill to tolerate a barium scale problem to avoid oxalate scale which can build up at a significantly faster rate. But for mills without significant barium sulfate scale concerns, typically lowering the first stage pH will reduce or eliminate oxalate scale formation in this stage and will help to reduce the trace metal concentrations in the finishing stages of the bleach plant. This is also the first line of defense to reduce or eliminate calcium carbonate scale problems in the extraction stages. It is unrealistic to lower the pH at the mixers or discharge of an extraction stage to below 7. Therefore, the best solution is to remove as much calcium in the preceding stages with a low pH and improved washing to prevent it carrying into the extraction stage in the first place. Other changes that will help to eliminate scale in extraction stages are to avoid using chlorine dioxide stage or other low pH stage filtrates on the showers of the washers or otherwise as water makeup to the stage. Low pH stage filtrates invariably have a higher dissolved Ca^{2+} concentration than filtrates from neutral or alkaline stages and will aggravate calcium accumulation in the extraction stage.

Consideration of these issues, the pH response of the anions, the ion exchange process, filtrate recycle, and use and distribution of sulfuric acid can help reduce mineral deposits in most locations. But the source of mineral deposits on bleach plant washers often escapes such a simple analysis. The premise of this study is that the chemical process that promotes scale formation in bleach plant washers is an ion exchange chromatography effect that increases cation concentrations and delays their release into filtrates that often contain higher concentrations of the scale forming anions.

The project established to test this hypothesis consisted of four tasks:

1. Evaluate the rate for the ion exchange reaction of wood pulp
2. Conduct laboratory washing experiments using a mat consisting of layers that can be readily separated to determine the penetration of wash water into the mat and displacement of filtrate for the modeling effort.
3. Prepare and test a finite element model of the washing process that is capable of mimicking the ion exchange chromatography effect.
4. Use the model to evaluate conditions on known washers and test the models ability to identify conditions that will reduce scale buildup.

Experimental: The collaboration for the project is between the USDA Forest Service, Forest Products Laboratory and the MeadWestvaco mill in Covington, Virginia. Two E (extraction) stage washers were selected for study. Both washers experience periodic scale problems and the mill has collected both calcium carbonate and calcium oxalate scale from the vats, wires, repulpers and filtrate chests. Six total samples sets were collected from the A line (softwood) extraction stage washer and B line (hardwood) E(OP) washer over two distinct sample periods. Each sample collection consisted of a vat, mat, shower and filtrate sample and all were analyzed for trace metals (Na^+ , Mg^{2+} , K^+ , Ca^{2+} , Mn^{2+} , and Ba^{2+}). The shower, washer filtrate and pulp filtrates (squeezed from the pulp samples) were also analyzed for anions: CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, and SO_4^{2-} . Large samples of both hardwood and softwood were collected from the washer mats during the first run and sent to the Forest Products Laboratory for use in the laboratory experiments. The softwood sample was selected for the lab experiments. All analysis of the mill samples were carried out by the MeadWestvaco Corporate Research Center in Chillicothe, OH. Samples were prepared for cation analysis by weighing the sample into a platinum crucible for drying and combustion in a muffle furnace. The ash was dissolved in acid and the resulting solutions analyzed by ICP. Anions were determined directly from the process and pulp filtrates by HPIC. Laboratory samples were analyzed at the Forest Products Laboratory on air dried samples using acid digestion and an ICP.

Laboratory Experiments: A pulp with a known metal content and free from barium and calcium precipitates was needed for the laboratory work. The softwood sample from the Covington mill was soaked in dilute hydrochloric acid at pH 1.5 and 6% consistency for six hours at room temperature. The acid treated sample was washed twice with deionized water (Millipore). The second wash filtrate gave a final pH of 2.5. The pulp was then treated at 10% consistency with a metal solution to give a total concentration of approximately 20 mM in Ca^{2+} , and Na^+ , 10 mM in Mg^{2+} and 0.2 mM in Ba^{2+} and Mn^{2+} . This suspension was then adjusted with sodium hydroxide to a neutral pH and allowed to soak with periodic agitation for 1 hour. Again, the pulp was filtered and washed twice with deionized water giving a final filtrate pH of 6.5. This pulp analyzed for 804 ppm Ca^{2+} , 225 ppm Mg^{2+} , 38 ppm Na^+ , 39 ppm Mn^{2+} and 68 ppm Ba^{2+} . Prepared in this manner, the pulp metal analysis is suitable for determining the acid group content¹⁷ which calculates to 62.1 meq/kg.

Kinetic Experiments were carried out by mixing 0.75 OD g of treated pulp in 400 ml of deionized water and filtering onto a 12.5 cm Büchner funnel with a glass fiber filter. A second glass filter was placed on top and the mat washed with 250 ml of deionized water. The filtration rate was measured to provide an estimate of the flow rate and as a cross check for good formation of the sheet. Washing was carried out using 25 and 250 ml of deionized water adjusted to pH 2.0 with sulfuric acid. This pH is sufficiently low to insure near total removal of trace metals. The 25 ml wash required 2.3 seconds and the 250 ml wash 21 seconds to complete. The experiments were carried out both at room temperature and using chilled water to make up the samples and for the wash, 10° to 14° C. Pulp samples were collected, dried and analyzed at FPL for the trace metals remaining in the pulp.

Washing experiments were conducted by preparing five 2.5 OD gram pulp pads on the 12.5 cm Büchner funnel with glass fiber filters. Each layer was formed by pouring it into the filter and letting it gravity drain until filtrate stopped dripping from the funnel. After forming the first layer, a glass filter was placed over the pulp and a second layer added. This process was continued until five layers were built up providing a pulp mat about 16 mm (5/8") thick. The mat was covered with a final glass filter sheet to avoid disrupting the top layer when the wash water was added. The mat was washed with 110 ml of pH 3 deionized water requiring 15.7 seconds to complete. The end point was taken when air penetrated the washer mat. The funnel was then inverted in a glass crystallizing dish, the pulp pad blown out and the layers separated. Each layer was checked for wet weight, dry weight, filtrate pH and metals analysis. The make-up filtrates were checked to make sure the metals loss from the starting condition was minimal, and the final filtrate was analyzed for removed metals. The consistency and pH for each layer in the pH 3 experiment were (top to bottom): 12.3%, 3.35; 14.6%, 3.97; 16.7%, 5.09; 17.4%, 5.10; 19.4%, 5.74.

Washer modeling was carried out in Excel as a single dimension, 10 layer (increment) finite element approach. Each wash/time increment was calculated as addition of enough filtrate to exactly match the filtrate in the first layer/increment of the model. Thus, each iteration of the model produced a washing effect of 0.1 wash liquor ratio and 10 to 12 iterations were required to model the typical washer. The model consisted of two linked spreadsheets, the iteration control which handled the iterations, and wash increment mass balances, and the equilibrium calculator which handled the ion exchange and precipitation equilibria. The finite element wash model was set up to calculate a washing effect that combined mixing, displacement and layer channeling or by-pass. The best fit was with each layer operating as a mixed increment without displacement or by-pass. The wash process is only applied to the cations in the soluble or free state. The equilibrium calculator was based off the Excel spreadsheet developed for the WinGEMS dynamic data link model reported last year,¹⁰ but has been upgraded to include calcium carbonate precipitation. The solubility product for calcium oxalate precipitation was also changed to the dihydrate polymorph which is the common crystalline form found in the bleach plant.¹ For routine mass balance modeling, the equilibrium spreadsheet used the processes pH and did not attempt to calculate the proton mass balance. Since this is changing in the washer mat and is a key part of the ion exchange process, this macro was changed to one that calculated the proton mass balance as well as the ion exchange equilibrium. Several approaches were tried for controlling the iteration of the model. The washer model requires single step iterations, each equivalent to 0.1 in wash liquor ratio. The equilibrium model requires typically 60 to 100 iterations to converge. The most successful strategy was to open both files in one Excel window. setting the increment to 1 (on manual). The wash model was updated by one increment and closed. The iteration count was increased to 100 and the equilibrium model run until converged. Then the increment was set back to one, the wash model reopened and advanced again by one increment. Repeating this process 12 to 13 times completed the analysis.

Results and Discussion:

The residence time in the shower zone of a typical drum washer is on the order of 4-6 seconds.¹⁸ Since ion exchange is a chemical process subject to diffusion and kinetics, 4-6 seconds is likely to be insufficient for the pulp and filtrate to maintain equilibrium during the washing process. Viewed as a dynamic process with wash water and filtrate flowing continuously through a fiber network, the fibers and surrounding solution are certainly not at equilibrium. Yantasee and Rorrer show that the ion exchange process reaches equilibrium very quickly and is essentially complete within the 1 minute minimum time frame of their experiments.¹ This data is clearly not applicable to the very short time frames encountered in vacuum drum in washing. The kinetic experiments were performed to determine the reaction rate at shorter time intervals. For this experiment, it was important to be able to prepare a pulp sheet with a known starting cation concentration. Since the kinetics for dissolving calcium carbonate or calcium oxalate precipitates is different from the ion exchange kinetics, it was also important to pretreat the pulp to remove any acid soluble precipitates.

Using the pretreated pulp, a 0.75 g (OD) weight pad was formed on a glass fiber filter and pH 2.0 wash water filtered through the pulp. Retention time was controlled by the amount of wash water used in the experiment with the apparatus typically using about 10 ml of wash water per second. Experiments with 10 ml aliquots of wash water were not successful since the volume was not sufficient to flood the pulp pad. Experiments with 25 ml of wash water were found to be the minimum practical volume, giving about 2.5 seconds retention time. Results are shown in Figure 1 for both room temperature and chilled (10-14° C) experiments. The equilibrium reaction is nearly complete in the 2.5 second minimum time frame and since the low temperature experiments have given lower trace calcium concentrations than the room temperature experiments, it can be concluded that much of the differences between data point is experimental variation. For the room temperature experiment, 86% of the change observed at 20 seconds is obtained in 2.5 seconds. For the chilled experiments, 94% of the change is obtained in 2.5 seconds. The data – although limited – does not follow first order kinetics.

The data in Figure 1 clearly shows that equilibrium in the ion exchange is obtained very quickly, on the order of several seconds. A kinetic factor was subsequently built into the washer model but was set at 90% of equilibrium and not used as a tuning factor in modeling. To calculate the bound and free cation concentration in each increment of the model, the ion exchange equilibrium condition was determined and the bound cation concentrations were calculated as 90% of the difference between the status at t_{i+1} and t_i (where t represents the time and the subscript indicates the time (increment) which is actually spreadsheet iteration). The free cation concentration was then determined from the total cation concentration entering the increment and the estimated bound cation concentration exiting. The laboratory washing experiments were carried out to determine the change in metal profile through the pulp mat. In particular, there was a concern about how much each element of the model should be regarded as a stirred tank, how much displacement and how much filtrate bypass (channeling) occur in washing. Two nearly identical experiments were carried out with the only significant change being that the wash water in one was adjusted to pH 2, and to a pH of 3 in the other. Results for Calcium and

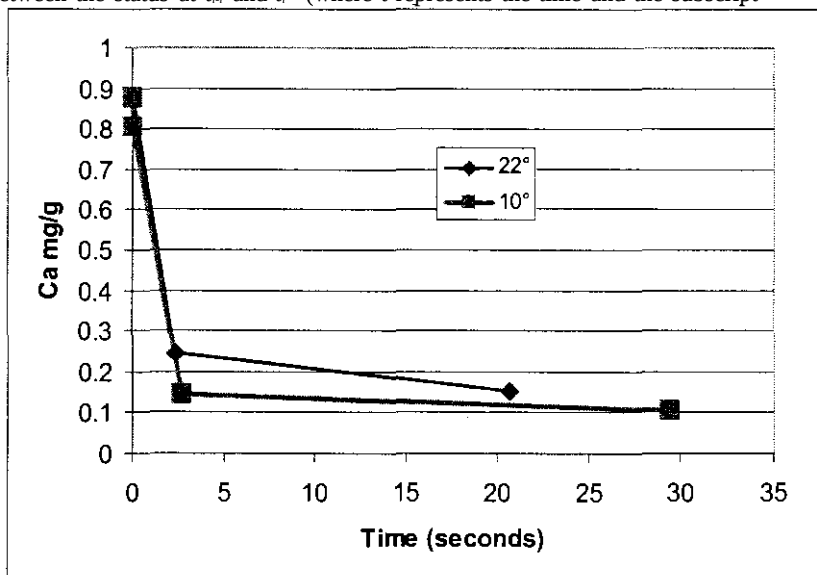


Figure 1. Residual Calcium after washing with pH 2.0 water

Magnesium are shown in Figure 2 for the pH 3 experiment. Calcium, magnesium and pH (not shown) all show a regular progression from the top of the mat to the bottom. The lines in Figure 2 are from the model (*vide infra*).

The most interesting feature of the washing experiment is that the calcium content of layers 3, 4 and 5 is higher than the starting pulp: 0.0923 % on OD pulp for layers 3, 4 and 5 (0.0012 standard deviations) vs. 0.0828% on OD pulp ($s = 0.00415$ for three analysis) for the starting pulp. As a one-tailed test, the bottom of the washed pulp mat has a higher calcium concentration than the starting pulp at a 95% confidence level. This is direct evidence that the pulp mat is behaving as an ion exchange “chromatography” column in the washing environment and that trace metals are concentrated by the process. There is some evidence that magnesium and manganese have also been concentrated in the bottom three layers of the

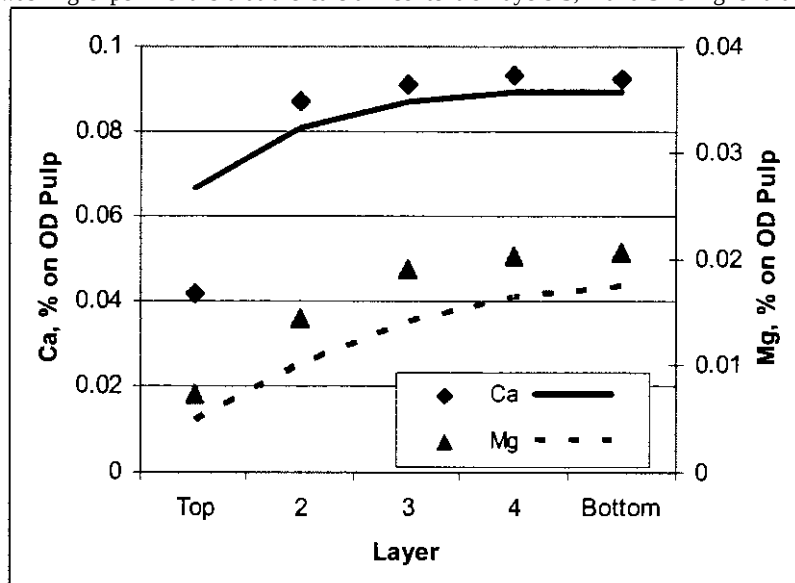


Figure 2. Ca and Mg content of washed pulps by layer.

pulp mat in this experiment, but the increases are not statistically significant.

Modeling of the Laboratory Experiments

Equilibrium modeling results for calcium in the pH 3 experiment are provided in Figures 2 and 3. In Figure 2, the results of the model are displayed as lines, and the data from the experiment as points. Several features merit discussion. The first feature is that the model predicts low calcium and magnesium contents for all but one layer of the experiment. This is an artifact of the ion exchange process. For an ion exchange resin, all of the fixed anionic sites have to be neutralized by a cation.¹¹ In the laboratory washing experiment, the pulp had been washed several times with deionized water, and the only cation present in the wash water (to any appreciable extent) was the acid. Following these parameters as inputs to the equilibrium model produces a situation where the cation concentrations are very low, just barely enough to neutralize the acid sites on the pulp. This makes the equilibrium model unstable since as it progresses through an iteration, it can end up with negative concentrations. To improve the stability of the equilibrium calculation, it was necessary to reduce the acid content of the pulp slightly from the actual experiment (60 meq/kg whereas the experimental results dictate 62 meq/kg) and increase the sodium concentration of the wash water above the actual analyzed concentration of the deionized water used in the experiment. Although the net effect of these changes is small, they both reduce the ion exchange sites available to sequester calcium and magnesium and result in slightly low estimates for bound cation concentrations. For calcium, with the exception of layer 1, the model underestimates the Concentration by about 5%, and for magnesium the estimate is low by about 10%.

The second issue is that errors are considerably higher in the first layers of the model. For magnesium, the first layer has a very low concentration, but the model underestimates it by almost 50%. For mill modeling, this error is not an issue because the absolute error is very small and will not have a measurable impact on the overall mass balance. Furthermore, the difference between a low concentration and a very low concentration for any of the trace metals is the difference between two highly desirable outcomes. For calcium, the error is opposite, over estimating the layer concentration by about 50%. In this case, the error is more significant and may indicate that the selectivity coefficient for magnesium and calcium or magnesium and protons is not accurate for the conditions of the experiment. Overall however, the model has done a credible job of fitting the outcome of the layer experiment. Among other features, it does show the selective removal of bound cations from the top layer(s) and an increase in concentration of cations in the middle and bottom layers. As is true of the experimental data, the calcium concentration of the lower layers of the pulp mat are estimated to be higher than the calcium concentration in the starting pulp. The model

therefore represents a conservative estimate of the cation concentrating effect observed in washing.

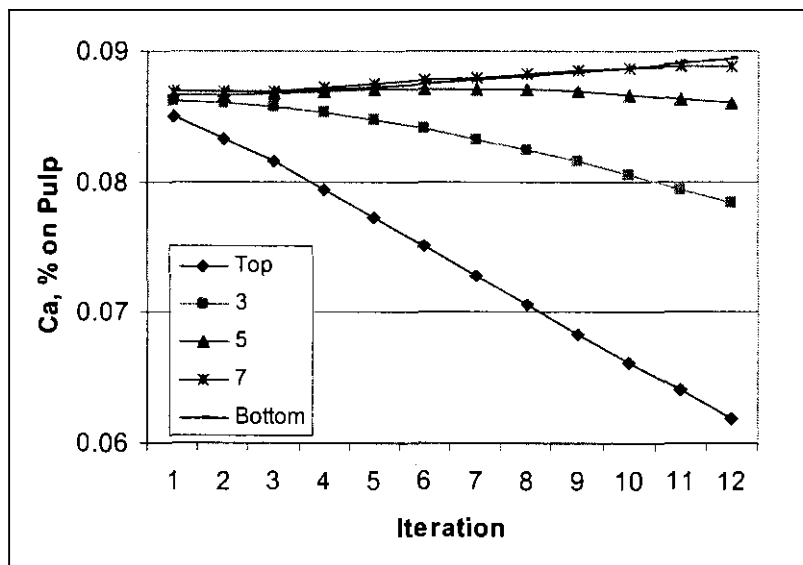


Figure 3. Calcium content by layer as the wash liquor ratio increases. Wash liquor ratio is 0.1 times the iteration number.

Figure 3 shows the model calcium results for the top layer, 3rd, 5th, 7th and bottom layers of the washer model. The top layer shows a smooth, almost linear progression with a decrease in calcium content from 0.087% to about 0.06% on OD pulp. Layer 5 shows a very slight increase in iteration 6 and 7 corresponding to a wash liquor ratio of about 0.6, but declines to about the starting concentration by iteration 12. Layers 7, 8, 9 and 10 (bottom) all show increases in calcium concentration as the wash liquor ratio increases

The predicted increases in soluble calcium concentration are more dramatic. These are shown in Figure 4, again for the

pH 3 experiment. All layers show increases in the soluble calcium concentrations with the highest concentrations in layers 3 through 5. Since the soluble calcium concentration in the wash water was just 0.15 mg/kg, nearly all the increase in soluble calcium observed in this experiment is from acid displacement of adsorbed calcium in the ion exchange process. Although the 4-6 mg/kg increase in soluble calcium looks dramatic, this represents less than 10% of the calcium in the pulp. In terms of the potential for mineral scale formation this increase does have a dramatic effect. A pulp suspension that was in equilibrium at the solubility limit in the washer vat, would become supersaturated by a factor of 2-3 at the washer wire.

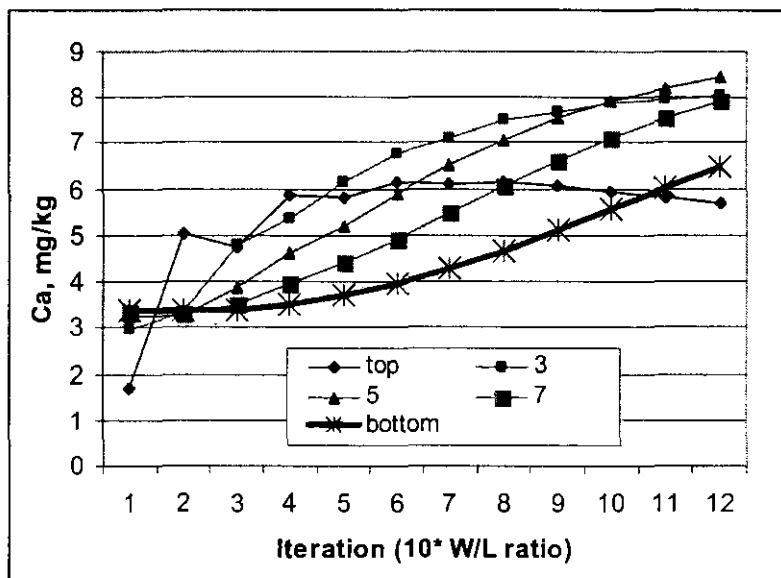


Figure 4. Calculated soluble calcium in the pulp layers of the washing experiment.

Modeling of Mill Data

The MeadWestvaco samples from Covington were evaluated using the finite element model. The pine line is an OD(EO+P)D bleach line using conventional vacuum drum washers. The extraction stage washer has periodic calcium oxalate scale buildup on the wire, the repulper and the filtrate tank. It had also been shut down the week before the initial sample collection to remove calcium carbonate scale from the vat. This washer is overloaded and operates with an average wash liquor ratio around 0.8. The

hardwood line is also OD(EO+P)D with vacuum washers on all states. It also has experienced calcium oxalate scale problems, primarily in the repulper. This washer is also overloaded and operates with an estimated wash liquor ratio of about 0.4. In both cases, the trace metals analysis for the washer vat and shower water were entered into the model. The model calculated the trace metal concentrations of the mat and filtrate. No effort was made to tune up the results other than to test the model with and without CaCO_3 precipitation included in the equilibrium calculation for the vat. The models were run to the mill estimated wash liquor ratio in each case.

The modeling effort required an evaluation of how precipitates partition in the washer. The model was assembled with three alternatives for dealing with precipitates: (1) include precipitates as a solid attached to fiber and subject to the same equilibrium constraints as the ion exchange process, (2) include precipitates as solids attached to fiber but assume the reaction kinetics are slow on the washing time

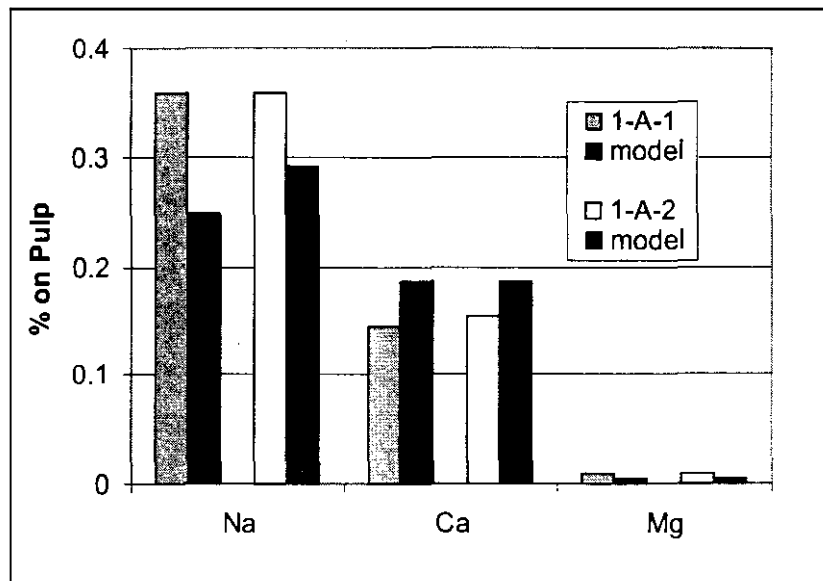


Figure 5. Trace metal concentrations for two cases modeling the softwood extraction stage washer.

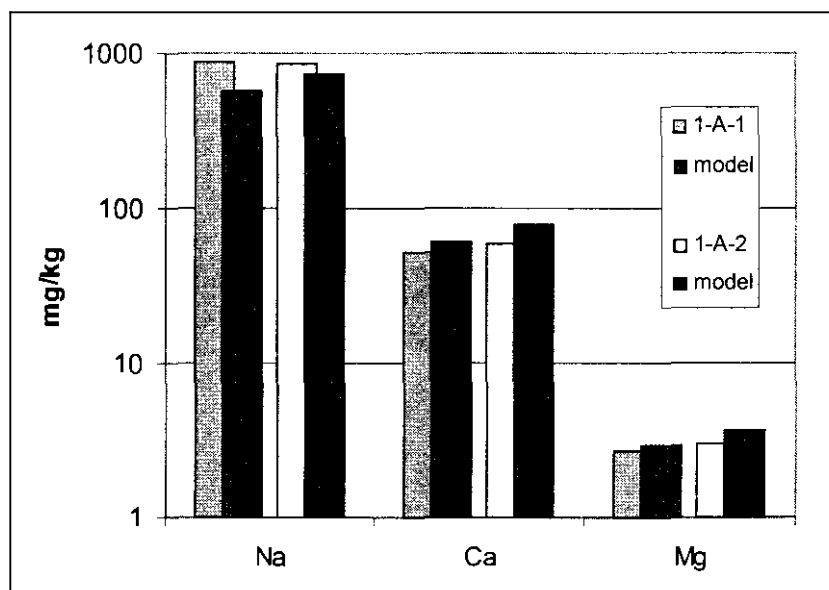


Figure 6. The filtrate data for the softwood extraction stage washer.

scale and therefore should be excluded from the equilibrium calculation, or (3) ignore the precipitation and treating all calcium as soluble. The cases where calcium carbonate was considered attached to fiber but subject to equilibrium conditions gave high mat calcium and low filtrate calcium concentrations in both the softwood and hardwood models. The cases where precipitation was ignored and all calcium was considered soluble gave low mat concentrations and generally high filtrate concentrations for the hardwood models, but still gave high mat concentrations and also high filtrate concentrations for the softwood models. The softwood case is physically impossible and an indication of other errors in sampling, analysis or the model. The hardwood case appears to be more accurate and suggests the tentative conclusion that calcium carbonate precipitates in the vat are not necessarily entrained in the fibers and are subject to a washing efficiency in vat dewatering and mat washing. This efficiency appears to change with conditions.

Results for the mat on the softwood washer are provided in Figure 5. Two cases are shown representing separate sets of samples. As stated above, the fit was better assuming the calcium in the washer vat was soluble and was very poor when the equilibrium model was run assuming an attached or entrained precipitate. The model underestimates the sodium in the mat by about 20%, and overestimates the calcium in the mat by about 20%. Error on magnesium is a little higher, about 40%. The accuracy of the filtrate data is similar. Note for filtrates, the ordinate is displayed as a log scale (Figure 6).

Results for the washer mat and filtrate data on the hardwood line are provided in Figures 7 and 8. In this case, the model with calcium carbonate precipitation in the vat and the model without calcium carbonate precipitation are both shown. The actual data is between the two scenarios. Without precipitation the model underestimates the calcium concentration by about 35%, and with precipitation, it overestimates the calcium mat concentration by about 35%. Filtrates show the opposite effect. It should be noted that the error with magnesium is much larger for the two hardwood sample sets. This may be due to the precipitation of magnesium hydroxide at the higher vat pH of the hardwood extraction stage.

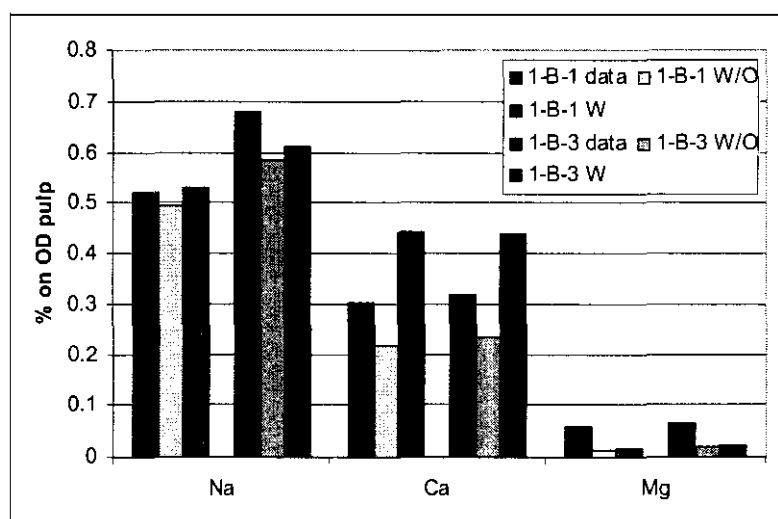


Figure 7. Mat concentrations on the hardwood extraction stage washer. Both cases - with and without calcium carbonate precipitation in the vat are shown.

Precipitation: Before extending the interpretation of the modeling results to a discussion of the scale prediction at the mill, it is of value to reflect on the overall accuracy of the modeling effort and on the precipitation processes that appear to be present in the mill. The precipitation processes of most concern to the Covington mill relate to calcium. Extraction stages are most prone to calcium carbonate scales but the mill also reports calcium oxalate deposits on these washers. The model has "predicted the mat and filtrate calcium concentration to within about a 20% error in most cases.

Although still not ideal, this is reasonably close for a mill process, is within the normal variation observed in a mill, and is acceptable error in calculating

precipitation. This is particularly true in the case of calcium oxalate where the variation in the reported solubility product exceeds the 20 % in the equilibrium model by a large margin.¹⁹ Precipitation processes involve very dilute solutions and an insoluble reactant or product. Mass transfer, diffusion and supersaturation all affect the rate of the precipitation process. For oxalate, the solubility product determined after 10 minutes is an order of magnitude larger than the solubility product determined after 24 hours.¹⁹ Because of these issues, an equilibrium calculation cannot really predict that scale will occur, or even that a nonscaling precipitation process will occur. All it can really determine is that a precipitation process is possible.

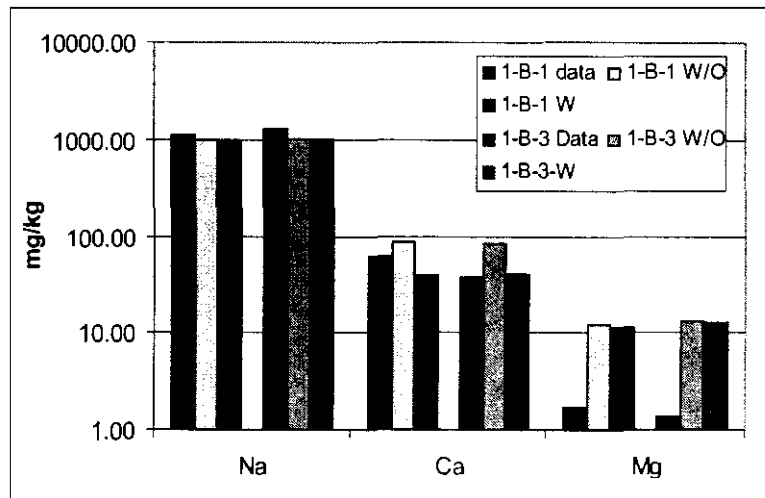


Figure 8. Filtrate concentrations on the hardwood washer. The graph displays the model results with and without the assumption of calcium carbonate precipitation in the vat.

The goal in the equilibrium modeling is to be able to determine where scale formation is possible and a probability of the likelihood it will occur. To accomplish this, the equilibrium calculation determines the maximum potential concentration of calcium (or barium) in a particular process stream. In this case, maximum potential concentration is total calcium less the amount bound to wood pulp. This value is multiplied by the divalent oxalate and carbonate concentrations (with all concentrations adjusted for activities) and the product divided by the solubility product. The log of this value is used as the scale predictor. A value of 1 indicates that the possible concentrations will exceed the solubility product by a factor of 10. This is still below the level of supersaturation observed for calcium carbonate formation under conditions that model kraft pulping.³ A log factor of about 2 is considered to be a pretty likely indicator that scale problems will occur. Note that once precipitation or scale has started, supersaturation is no longer a factor but inhibition due to oils, fats, and other substances common within the process can still impede the rate at which the scale accumulates.

Although the error in calcium concentrations is judged to be minor relative to the error in "predicting" precipitation, the error in estimating pH is also critical to the prediction. Both oxalate and carbonate are bases and react with acid to form hydrogen oxalate and bicarbonate, neither of which is considered to participate directly in the precipitation process. The equilibrium model has not matched the observed pH changes accurately. For the lab case, the measured mat pH was between 3.35 on the top layer, and 5.75 on the bottom layer. The model predicted a pH range from 2.9 to 3.1. This type of error is critical since the estimated free divalent oxalate concentration is reduced by about 90% by this error. For the mill models, the final mat pH was measured at about 9, but the estimated mat pH was around 3.0. At a pH of 9, calcium carbonate is reasonably stable and will not dissolve to any appreciable extent. At a pH of 3, only about 10% of the oxalate remains. At this point, the nature of the proton mass balance error is not completely understood, but the mass balance does not currently account for the buffering capacity of the carbonate

and oxalate. With the mill samples, these concentrations are large enough to account for the observed error in the analysis.

There are some features of the model scale predictions that are very useful – even with the large pH errors. Model results for the change in the supersaturation index of the three common mineral scales are shown in Figure 9. The value in the graph are the values for the filtrate in the bottom increment layer of the model since this is the filtrate in contact with the washer wire and entering the filtrate tank.

The model predicts calcium carbonate in the vat and shows that the probability of oxalate formation under the vat conditions is very low. Recall that calcium carbonate had been removed from the pine washer vat several days before the first set of samples were collected. There is no pH error in the calculations of the equilibrium in the vat.

These conditions clearly exceed the solubility product for calcium carbonate formation with a supersaturation index of 2.5 to 3.5, depending on the case. The model also “predicts” that the calcium carbonate will become less stable and conditions become more favorable for calcium oxalate formation. At very low shower flows, the supersaturation index for calcium carbonate drops below zero, indicating that it no longer exceeds the solubility product, but the index for calcium oxalate rises from near zero to 1.2 suggesting that precipitation is probable. This is what is observed in the mill, the scale that forms in the vats is calcium carbonate, but the scale on the wires, and in the repulper and filtrate tank has been calcium oxalate.

It is necessary to interpret the “prediction” within the framework of the hydrogen ion error. The final mat pH observed is much higher than predicted by the model. This does not change the trend. The drop in pH due to the low pH shower water still reduces the probability of lime scale formation. The mat pH around 10 means that less than 50% of the carbonate is in the active divalent form. The model allows an interesting analysis of the conditions in the vat. If calcium carbonate precipitation is not activated, the model also predicts that calcium oxalate exceeds the solubility product with a supersaturation index around 1.4. This is the case for both the hardwood and softwood samples. The carbonate in the vat suppresses the calcium concentration to the point that oxalate precipitation is unlikely, but when this constraint is removed by the drop in pH, oxalate precipitation is favored. The use of D_1 stage filtrate for wash water presents the mill with a very delicate balancing act to avoid scale problems. The acid filtrate reduces the concentration of free carbonate and in doing so, increases the probability of drifting into calcium oxalate forming conditions. Since the D_1 stage has periodic calcium oxalate scale problems, it has to be assumed that it is close to the saturation conditions. At a pH of 2-3, 90% of the oxalate is in the hydrogen oxalate form. As this filtrate moves through the mat, the pH rises, increasing the concentration of free oxalate and also increases the probability of calcium oxalate precipitation.

This raises the question of how the mill can avoid scale problems in these washers. Although these scenarios have not been run, obvious options are to replace the E stage shower water with mill water or paper machine white water. The mill water option - assuming low calcium and a neutral pH – will have less of an impact on mat pH. This improves the stability of the carbonate and under these conditions the oxalate anions should wash out somewhat harmlessly. However, the process will continue to carry a high loading of calcium into the final bleach stage and will not reduce the probability for scale problems in D_1 . If too much oxalate remains in the pulp, the drop in pH in

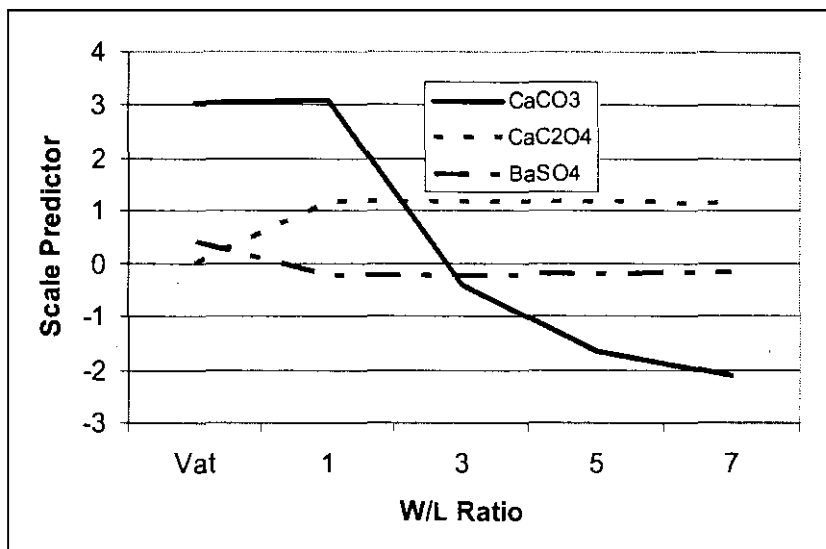


Figure 9. Supersaturation index from the model for the softwood washer.

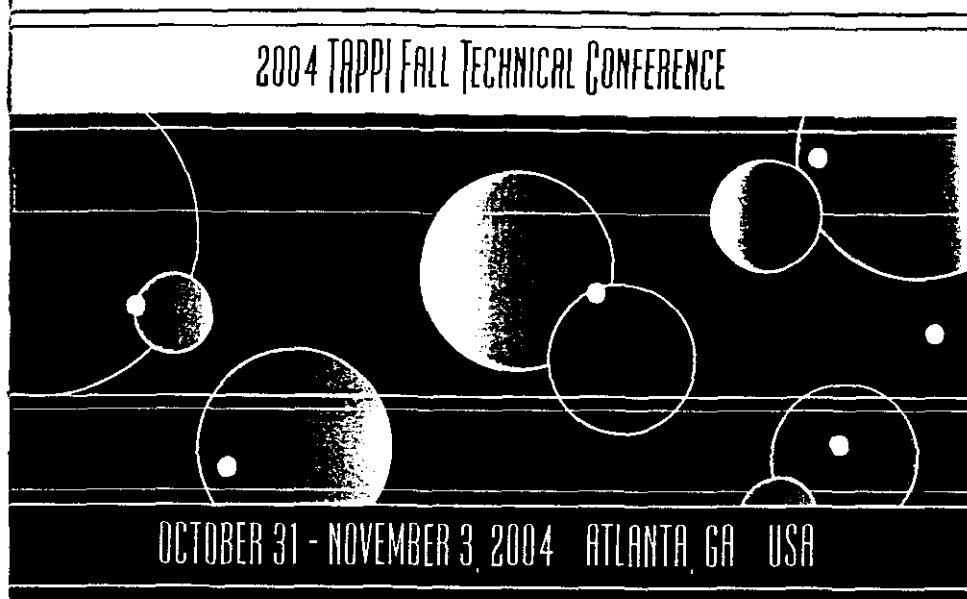
the ClO_2 stage will cause the calcium carbonate to dissolve and calcium oxalate precipitation early in the D_1 stage. It needs to be recognized that this is what is happening in the mill now. If the D_1 stage filtrate is shifted to the D_0 stage washer at the same time, it will improve the overall metals washing efficiency in the first stage which would reduce the scaling potential throughout the bleach line. An alternative is to use papermachine white water on the E stage washer. The Covington mill operates at a headbox pH near 5, but uses a carbonate containing coating. This results in a whitewater with high calcium concentration. These scenarios, and some alternative pH strategies will be evaluated before completion of the project.

Conclusions: A laboratory simulation of pulp washing has shown that calcium ions can be concentrated in the bottom side of the pulp mat by the ion exchange behavior of kraft pulp. This effect helps to explain the high frequency of mineral scale problems on bleach plant washers. To test whether the kinetics of the ion exchange needed to be considered in washer models, several experiments were carried out to determine how rapidly the process reached equilibrium. These results demonstrated that ion exchange of trace metals on wood pulp is very fast and is close to the equilibrium within 2.5 seconds. An Excel chemical and ion exchange equilibrium spreadsheet was linked to a 10 increment (layer) Excel finite element model of a washer mat and the combination used to mimic the laboratory experiment and evaluate trace metal behavior and scale potential in washing. The model matches the calcium concentration observed in laboratory washing experiments accurately. Although it fails to mimic the pH and trace metals changes observed in the top layer of the experiment exactly, it does predict the increase in trace metal concentration in the lower layers of the mat relative to the starting pulp. Using the model to estimate the mat and filtrate concentrations of trace metals in a mill, the model “predicts” the calcium concentration in these streams to within a 20% error. The model correctly predicts that calcium carbonate is the likely precipitate in the extraction stage washer vats, but calcium oxalate is likely to form on the wires and in the filtrate tank. This effort further demonstrates that trace metal management in bleach plants can be modeled using first principles methods and the industry has the fundamental knowledge needed to make this a useful tool for resolving scale problems in mills.

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