Factors contributing to calcium oxalate scale at the Simpson Tacoma Kraft mill

DOUGLAS W. REID AND MATTHEW L. HINCK

ABSTRACT: Simpson Tacoma Kraft Company's bleached kraft pulp mill in Tacoma, Washington, USA, experienced severe calcium oxalate scaling in the D0 stage washer and bleach plant sewer heat exchanger. After removing the calcium oxalate, the mill implemented two process changes to contend with the calcium oxalate: pH control in the D0 stage and a partial re-opening of the counter-current washing strategy. A study was undertaken to determine the relative impact of washing strategy and D0 stage pH on calcium oxalate formation. Extensive testing performed at the mill was used to tune a computer model of the bleach plant. Various operating strategies were simulated and the data were compared to published kraft bleaching filtrate solubility data. We determined that strict countercurrent washing did not cause the calcium oxalate scale outbreak. D0 stage pH also had minimal impact on calcium oxalate precipitation in the washer. It was a factor in the sewer heat exchanger where temperatures are lower. These results allowed the mill to run strict countercurrent washing with more confidence and save 8.6 m^3/air dried metric tons (150 L/min) of hot water in the bleach plant. The mill has also been able to shorten the list of potential causes of the scale outbreak and believes that good pH control is the key to sustainable operation.

Application: Mills with calcium oxalate scale can use the approach described in this paper to help solve their scale problem.

Simpson Paper Company owns and operates an integrated 1300 air dried metric tons (ADMT)/day kraft mill (Simpson Tacoma Kraft) in Tacoma, Washington, USA. The mill started up in 1928 and produces white top and natural linerboard, white and kraft papers and unbleached kraft pulp. Extensive modernization projects at the mill since 1986 have included the addition of a new power boiler, new bleach plant, new washer line, modernization of recaust operations, new old corrugated container (OCC) fiber plant, and modernization of the mill's largest paper machine. The first major project was the construction of a 500 ADMT/day bleach plant, in which softwood kraft pulp (kappa 26-28) is bleached to 84% ISO brightness using a DEopD sequence. The bleach plant has Beloit Rauma pressure washers on all three stages, and has employed strict countercurrent washing since 1992.

The bleach plant had not experienced any type of scale problems while elemental chlorine was still being used in the process. When the mill started running elemental chlorine free (ECF) bleaching campaigns in 1997 and 1998, however, scale problems began to appear. The mill first thought the scaling problems were an anomaly. The presence of scaling was irregular and would appear and disappear randomly. However, in October of 1999, the mill had a severe outbreak of calcium oxalate (CaC_2O_4) scale deposits on the drum, doctor board, and upper and lower wash ponds of the D0 washer. The D0 washer was so severely plugged that filtrate would not drain through the washer wire. Poor drainage on the washer resulted in high chemical consumption and lost production. At the peak of the problem, the bleach plant had to be shut down as often as once every three days to hydroblast scale from the washer. Scaling also occurred in the bleach plant heat recovery system, which uses D0 filtrate to heat fresh water destined for the D1 stage washer.

Two conditions were identified as the most likely causes of the scale:

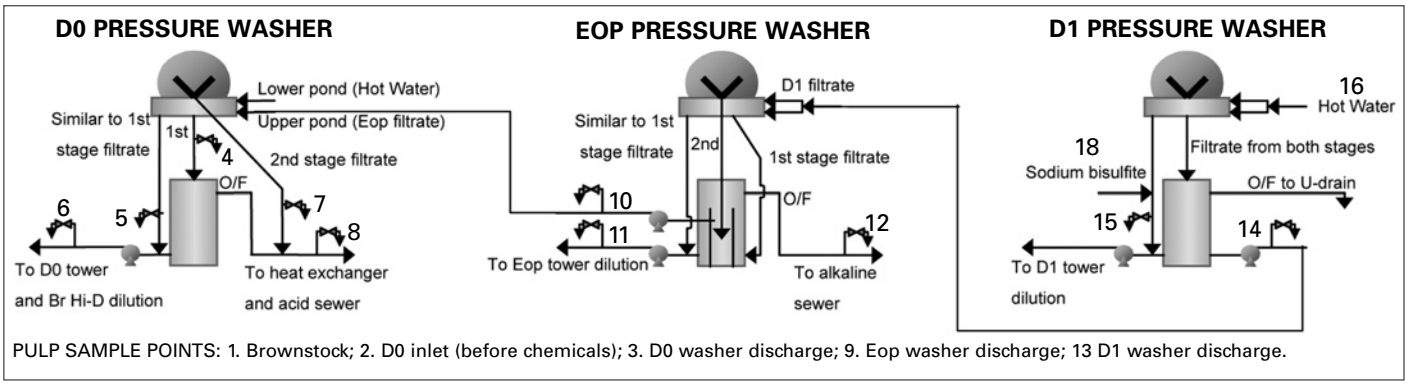
1. D0 stage pH had increased from about 2.5 when the mill was using elemental chlorine to about 4.0 - 4.5 with 100% chlorine dioxide.
2. The strict countercurrent washing strategy in the bleach plant utilized water efficiently, but allowed a smaller purge of process contaminants compared to open washing sequences.

To solve the problem, the mill adjusted the D0 stage pH to 2.5 using sulfuric acid, and modified its washing strategy on the D0 washer. This washer has two stages, both of which normally use extraction filtrate. When the scale outbreak occurred, the mill put hot water on the first wash stage in an effort to purge contaminants from the process.

These measures were successful in preventing the scale problem from reoccurring, but it was unclear which change had the most impact and why. We undertook this study to determine the impact of D0 stage pH and washing strategy by determining the composition of various process streams and the solubility of calcium oxalate in those streams. By predicting where calcium oxalate may precipitate, and the conditions that lead to precipitation, the mill would be better able to combat this problem.

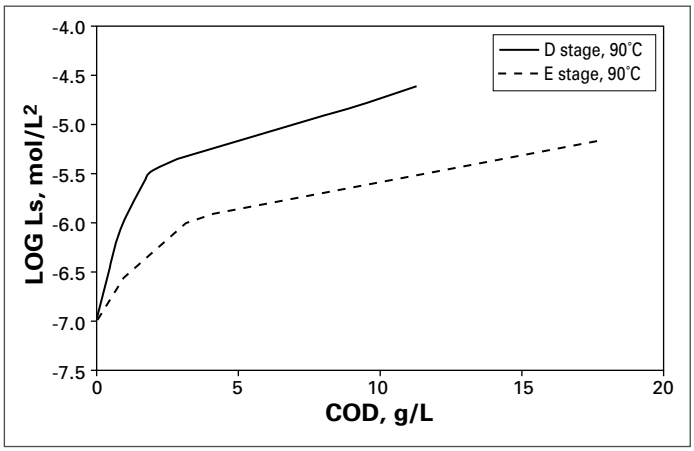
METHOD

A mass and energy balance was calculated using Eka Chemicals' proprietary BP Flow model. This is a computerized mass and energy balance built on a WinGEMS platform. Extensive sampling and testing was performed at the mill in November 1999 in order to tune the model to match Tacoma's operation. We collected flow, temperature, and chemical concentration data from the mill's log sheets and performed hand tests such as consistency and pH on samples collected at the mill. Samples were taken at 18 points throughout the bleach plant (**Fig. 1**) and tested for metals (Ba^{2+}, Ca^{2+}, Cu^{2+}, Fe^{2+}, Mg^{2+},

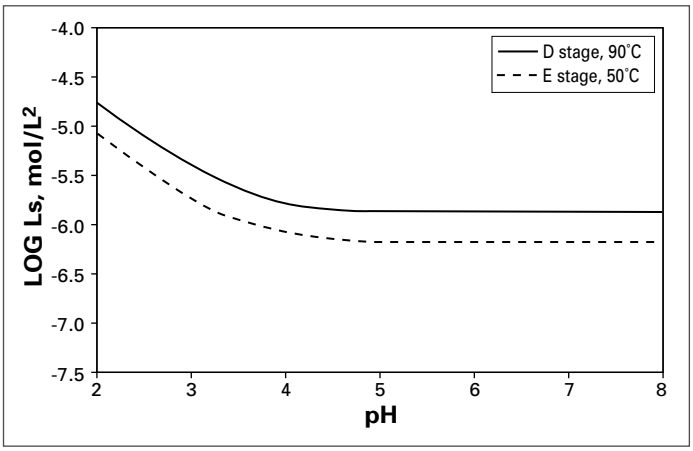


PULP SAMPLE POINTS: 1. Brownstock; 2. D0 inlet (before chemicals); 3. D0 washer discharge; 9. Eop washer discharge; 13 D1 washer discharge.

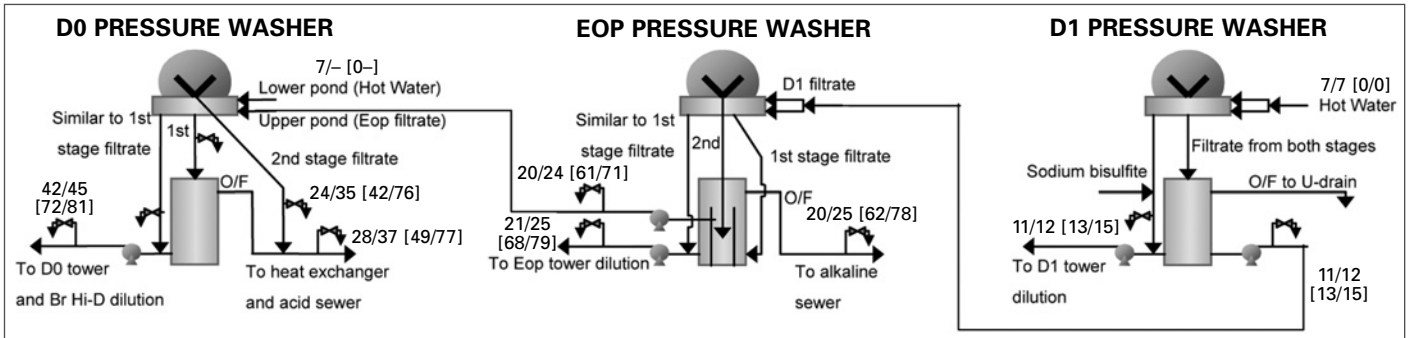
1. Sample points at the Simpson Tacoma Kraft mill.



2. Solubility of calcium oxalate in bleach plant filtrates as a function of COD, at pH 5 and 90°C (Ulmgren and Rådeström).



3. Solubility of calcium oxalate in D stage filtrate at 90°C and 50°C (Ulmgren and Rådeström).



PULP SAMPLE POINTS: 1. Brownstock 9/9 [5/5]; 2. D0 inlet (before chemicals) 29/31 [45/51]; 3. D0 washer discharge 21/28 [56/73]; 9. Eop washer discharge 13/15 [23/26]; 13 D1 washer discharge 8/8 [3/3].

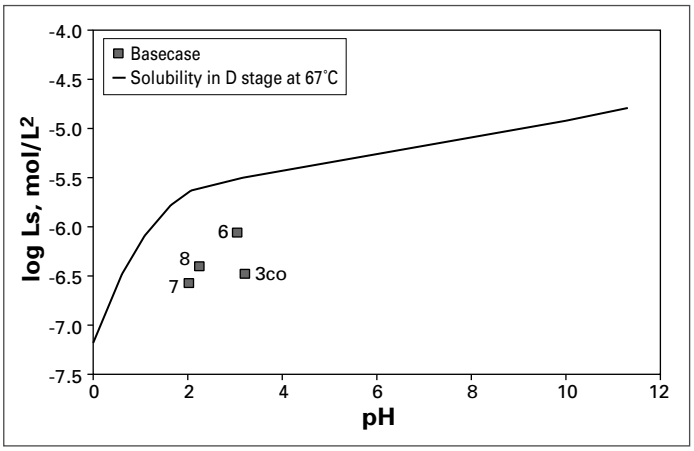
4. Calcium concentrations and oxalate concentrations (in brackets) for basecase (partially open washing) and strict countercurrent washing.

Mn^{2+}, K^+, Na^+) and anions (CO_3^{2-}, SO_4^{2-}, $C_2O_4^{2-}$). To minimize clutter, Fig. 1 does not show pulp streams and bleaching towers. During the sampling period, the mill was using hot water and Eop filtrate on the D0 washer and was not experiencing any calcium oxalate scale deposition.

Solubility of calcium oxalate in bleach plant filtrate was determined from work done by Ulmgren and Rådeström [1]. In their work, filtrate samples from a variety of bleach stages were "spiked" with calcium and oxalate to determine the concentrations that would precipitate calcium oxalate. **Figure 2** shows the first of two interesting graphs from Ulmgren and Rådeström, which shows calcium oxalate solubility in D (chlorine dioxide) and E (extraction) stages. Calcium oxalate forms in the region above the curve, where the concentrations of oxalate and

SAMPLE POINT	DESCRIPTION
6	D0 washer - 1st stage filtrate
7	D0 washer - 2nd stage filtrate
8	D0 washer - 2nd stage filtrate
3co	D0 washer - liquor carryover with pulp

I. D0 stage sample points.



5. Solubility in D0 stage filtrates for basecase.

calcium ions are higher, but will not form below the curve where ion concentrations are lower. The curves were developed using actual mill filtrates and results were similar for different mills. COD (chemical oxygen demand) is the familiar test, which is related to the amount of organic material in a sample. Ls is the solubility product, equal to total calcium concentration multiplied by total oxalate concentration (Ls = $[Ca^{2+}]$ x $[C_2O_4^{2}]$).

Their second graph (**Fig. 3**) shows two interesting phenomena. First, higher temperature makes calcium oxalate more soluble. Second, lower pH makes calcium oxalate more soluble if pH < 5. Solubility is constant between pH 5 and 8, and calcium carbonate ($CaCO_3$) normally forms instead of calcium oxalate if pH > 8.

RESULTS AND DISCUSSION

Normal wash strategy vs. strict countercurrent washing

During sampling for the base case, the mill was using hot water and Eop filtrate on the D0 washer and was not experiencing any problems with calcium oxalate scale. We used data collected from the sampling to tune parameters in the model, so that it would match actual mill operation. Once tuned, the model was used to predict what would happen when strict countercurrent washing was employed. Overall, the base case model matches mill data very well, allowing accurate predictability from the model. **Figure 4** shows that strict countercurrent washing (using Eop filtrate only on the D0 washer) had the largest effect on concentrations of calcium and oxalate in D0 washer carryover and 2nd stage D0 washer filtrate. In each figure, the first number refers to concentration (mg/L) in the base case and the second number refers to concentration (mg/L) with strict countercurrent washing.

Figure 5 shows the solubility of D0 stage filtrates for the base case. The curve, based on Fig. 2, has been adjusted (using Fig. 3) to reflect actual temperatures at the mill. The curve also represents solubility at pH 5; i.e. the worst case scenario, so any filtrate with pH<5 will require higher calcium and oxalate concentrations than shown by this curve for precipitation to occur. **Table I** and **Fig. 6** describe the sample points shown on the graph. All filtrates are below the curve in Fig. 5, so no calcium oxalate precipitate will form. This agrees with the mill's experience.

Figure 7 shows the impact of switching the lower wash pond to Eop filtrate, i.e. running strict countercurrent washing. All points move closer to precipitation, but remain below the curve; therefore, calcium oxalate will not be formed.

Figure 7 also shows that high pH excursions in the D0 stage will not cause calcium oxalate scale because this curve already represents the worst case (pH 5) and no precipitation is indicated.

Based on these results, we concluded that strict countercurrent washing did not cause calcium oxalate scale to form, even at "worst case" pH levels. This indicates that something else, such as an abnormally high input of calcium or oxalate, or an abrupt change in temperature must have occurred.

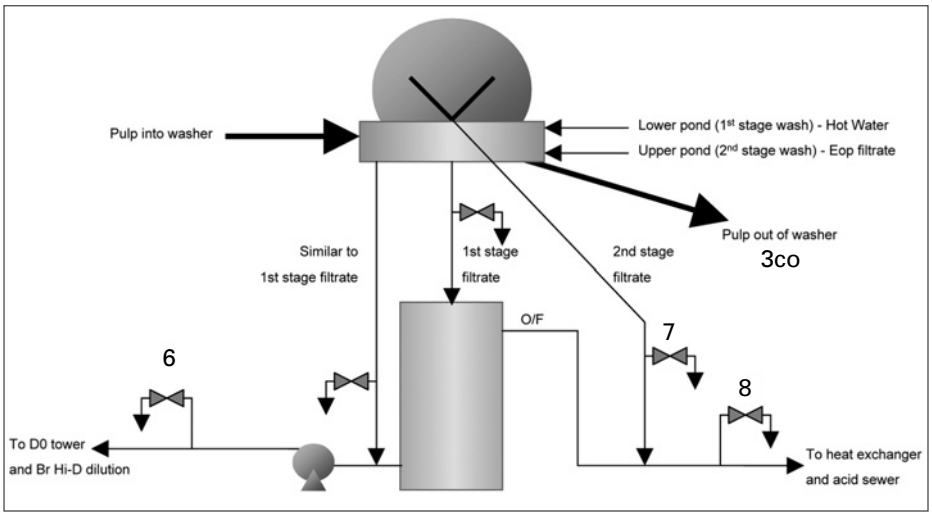
Applicability of solubility curves to Simpson Tacoma

One byproduct of the mill's washing strategy is very low flow in the alkaline sewer. In fact, with strict countercurrent washing it is possible to use all Eop filtrate on the D0 washer and reduce the alkaline sewer flow to zero. The mill's acid sewer essentially serves as a mixture of a typical mill's acid and alkaline sewers.

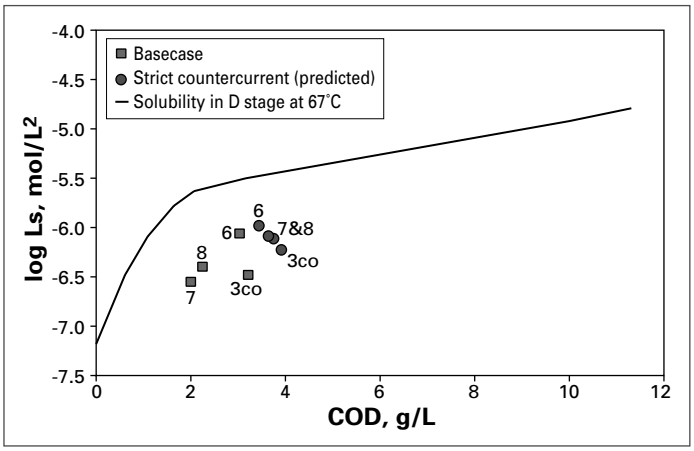
With this in mind, filtrate from the D0 washer probably behaves more like a mixture of D0 and Eop filtrate than a typical D0 filtrate. If the acid sewer is truly a mixture of D0 and Eop filtrates, then Ulmgren and Rådeström's solubility curve for D filtrate will not be applicable. To account for the mixture of D0 and Eop filtrates, calcium oxalate solubility has been estimated by averaging Ulmgren and Rådeström's curves (**Fig. 8**). All data from the mill falls underneath the "average" curve (**Fig. 9**) so this confirms that strict countercurrent washing and/or pH excursions did not cause calcium oxalate to precipitate.

Other causes of calcium oxalate scale

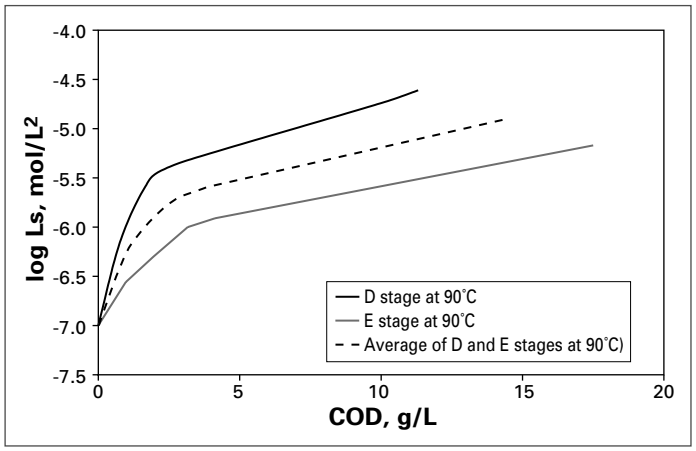
It appears that neither strict countercurrent washing nor pH excursions caused the scale outbreak, so other possibilities



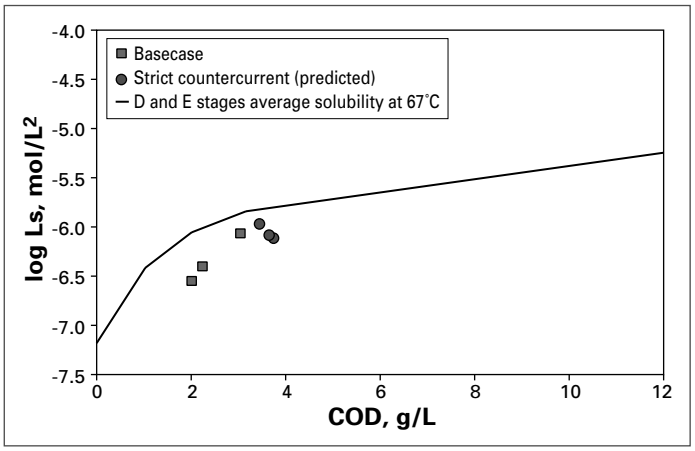
6. D0 stage sample points.



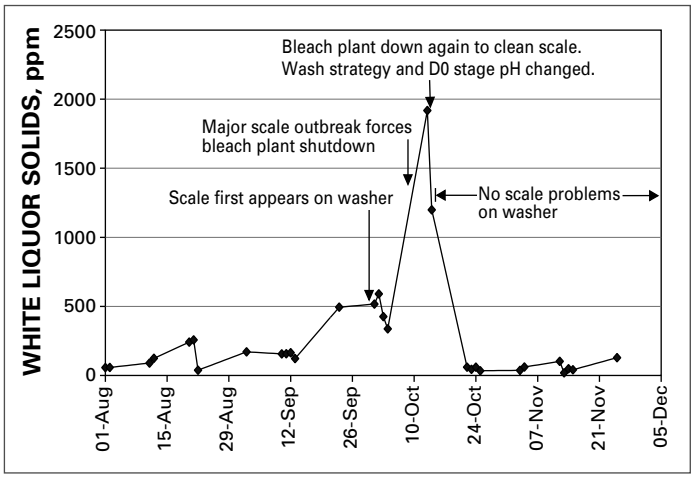
7. Solubility in D0 stage filtrates for basecase (partially open washing) and strict countercurrent washing.



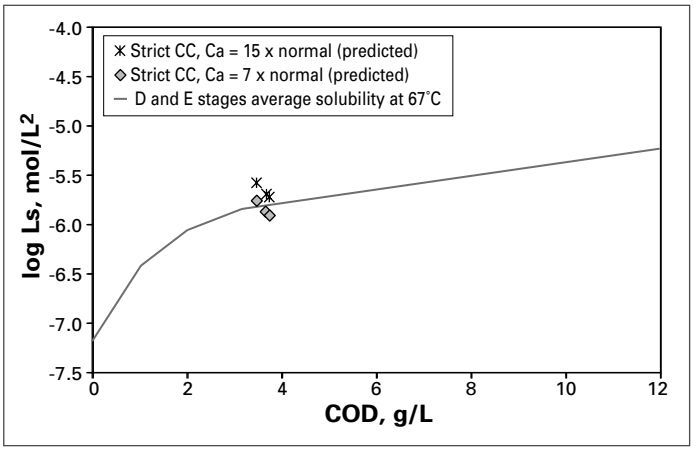
8. Average calcium oxalate solubility in a mixture of D and E stage filtrates.



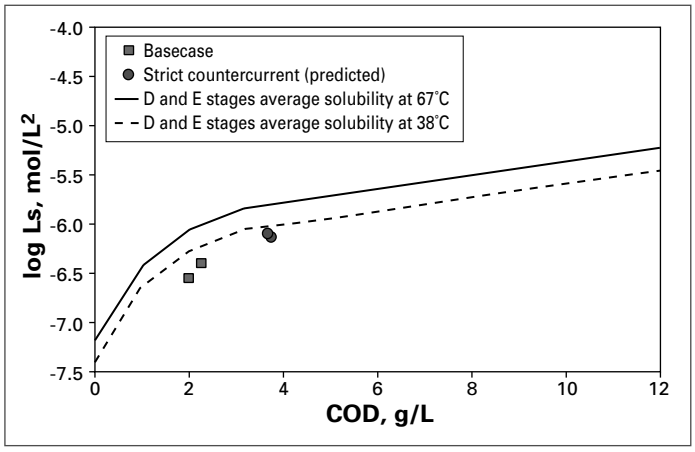
9. Mill data and average solubility in a mixture of D and E stage filtrates.



10. White liquor solids at the mill during 1999.

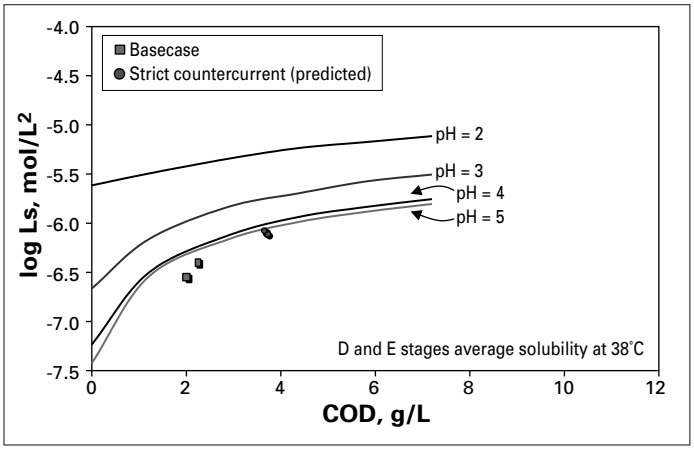


11. Solubility with high calcium concentration entering bleach plant (7x and 15x normal level).

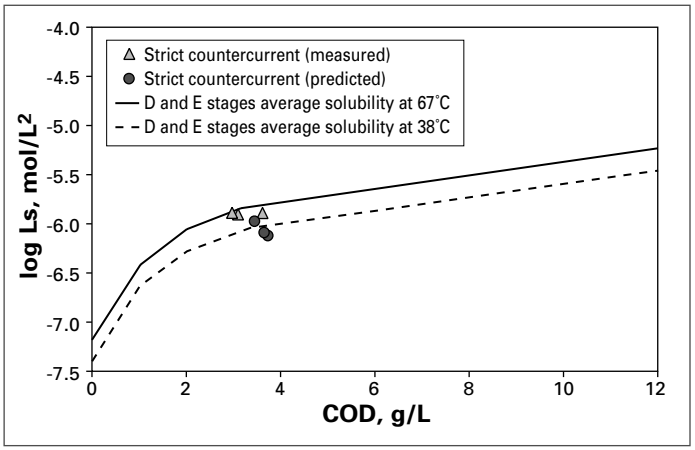


12. Solubility in the mill's bleach plant heat exchanger.

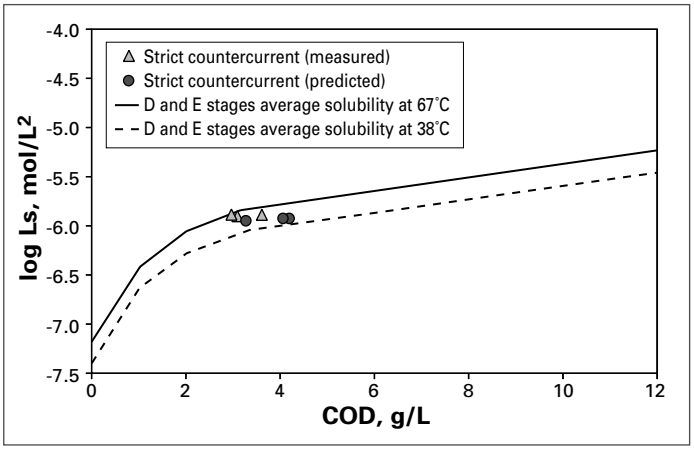
must be considered. Historical data shows that the mill experienced problems with white liquor clarification during the scale outbreak. **Figure 10** shows that lime mud concentration measured in the white liquor increased from 60 ppm in September to a high of 1900 ppm in mid-October (a 30 fold increase) and then decreased to normal levels by late October. An increase in lime mud concentration to 30 times the normal value would have a similar impact on the amount of calcium carried over into the bleach plant. **Figure 11** shows that calcium concentration in brownstock carryover only needs to increase by a factor of seven in order for calcium oxalate to precipitate in the first stage of the D0 washer. If calcium concentration in brownstock carryover increases by a factor of 15, then calcium oxalate will also precipitate in the second stage of the D0 washer. In addi-



13. Effect of pH on calcium oxalate solubility in bleach plant heat exchanger.



14. Comparison of measured and predicted results.



15. Comparison of measured results and modified prediction.

tion, the timing of the high lime mud carryover in white liquor coincides with the outbreak of calcium oxalate scale in the bleach plant.

With this additional information, we identified high calcium concentration due to lime mud carryover as the sole cause of the scale outbreak. This appears to be the correct explanation because the mill has since gone back to strict countercurrent washing in the bleach plant without experiencing any calcium oxalate scale in the D0 washer.

Bleach plant heat exchanger

Scale is still a problem in the bleach plant heat exchanger if D0 filtrate pH gets too high. This occurs because filtrate temperature drops to 38°C in the heat exchanger, making calcium oxalate less soluble.

Figure 12 indicates that, with strict countercurrent washing, filtrate used in the bleach plant heat exchanger is very close to precipitation (under worst case pH conditions). This explains why D0 stage pH has such a significant effect on scale in the heat exchanger. Lower pH raises the curve as shown in **Fig. 13**, making calcium oxalate more soluble. Conversely, high pH excursions lower the curve and make scale more likely.

Although fouling occurs once every 2 months on average, the cost of cleaning and maintaining the heat exchanger is greatly offset by the amount of energy recovered (~ 8800 kW).

Measured vs. predicted results

Further sampling was conducted at the mill in March 2001 when the mill was running strict countercurrent washing. **Figure 14** shows that the measured values are quite close to the values predicted by the model (data points correspond to sample points 6, 7, and 8). Discrepancies are mainly due to differences in operating conditions between the two periods (higher production rate, lower dilution factor, and lower COD carryover into the bleach plant in March 2001). When these differences are taken into account, all the predicted values move above the 38°C solubility curve, as shown in **Fig. 15**.

CONCLUSIONS

1. Strict countercurrent washing did not cause calcium oxalate scale deposits on the D0 washer. Subsequent mill operation with strict countercurrent washing confirms this.
2. pH excursions in the D0 stage did not cause calcium oxalate scale on the washer. However, they can cause calcium oxalate to precipitate in the bleach plant heat exchanger due to lower filtrate temperature in the heat exchanger.
3. It is likely that the calcium oxalate scale outbreak in the D0 washer was caused by high lime mud carryover in the mill's white liquor.
4. The solubility curves developed by Ulmgren and Rådeström appear to accurately predict scaling tendency in an operating bleached kraft mill, as long as the curves are adjusted to reflect actual mill conditions.
5. Computer modelling can be used to accurately predict concentrations of non-process elements in kraft bleach plants. **TJ**

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1. Ulmgren, P., Rådeström, R., "Calcium oxalate in bleach plant filtrates," Proceedings of 1997 TAPPI Minimum Effluent Mills Symposium, TAPPI PRESS, Atlanta, Georgia, USA, pp. 51-62.

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INSIGHTS FROM THE AUTHORS

We undertook this study in response to severe operational problems and financial losses caused by scale outbreaks at the mill. It was critical to prevent a reoccurrence.

This paper builds on work done by Ulmgren and Rådeström at STFI by applying their results on calcium oxalate solubility to solve a real-world problem. It also complements previous work that Eka and others have done in the area of computer modelling of NPE's (non-process elements) in bleached kraft mills.

The most difficult aspect of this research was to adjust the solubility curves to represent actual process conditions at the mill. We resolved that through interpolation and using our judgement. A further step might be to develop similar solubility curves for other scales such as barium sulfate and calcium carbonate.

Reid is senior process engineer, Eka Chemicals, Marietta, Georgia, USA; Hinck is fiberline manager, Simpson Tacoma Kraft, Tacoma, Washington, USA; email Reid at doug.reid@ekachemicals.com or Hinck at mhinck@simpson.com

Reid

Hinck