

Impact of dissolved lignin in oxygen delignification and chlorine dioxide stages

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ABSTRACT: While carryover of dissolved lignin between stages in the pulp mill fiber line is a well-known problem, it is still typically seen only as a minor disturbance factor or bias in the control of oxygen (O_2) delignification and bleaching stages. The present study, however, reveals that it plays a larger role than anticipated, and that it should be properly analyzed in order to correctly control the process stages. This is especially important for the O_2 and D_0 stages as the lignin content is still high in these positions. The results of the study show that dissolved lignin carried over between stages may have a significant impact on the bleaching chemical consumption and, indirectly, on the pulp quality.

Mill investigations have shown very large variations in the dissolved lignin content in the pulp before the oxygen delignification stage and before the D_0 stage that have significantly influenced the bleaching chemical demand and, subsequently, the degree of delignification. In order to develop a better understanding of the mechanisms of the dissolved lignin's reactions, laboratory O_2 and D_0 experiments with controlled levels of dissolved lignin were conducted. It was anticipated that a better feedforward control could be achieved using an online dissolved lignin measurement, and results from mill trials are presented. Chlorine dioxide laboratory experiments using different levels of carryover (i.e., different dissolved lignin contents) were conducted. It was concluded that the filtrate kappa number provides a relevant measure of the bleach demand due to the dissolved lignin and that, subsequently, the combined fiber and filtrate kappa number provides an appropriate measure for optimum feedforward control of the stages. Mill results support these findings, which show that the chemical consumption is reduced significantly using the total kappa number. The post-D or post-DE kappa number feedback control can most probably be eliminated by using this technology.

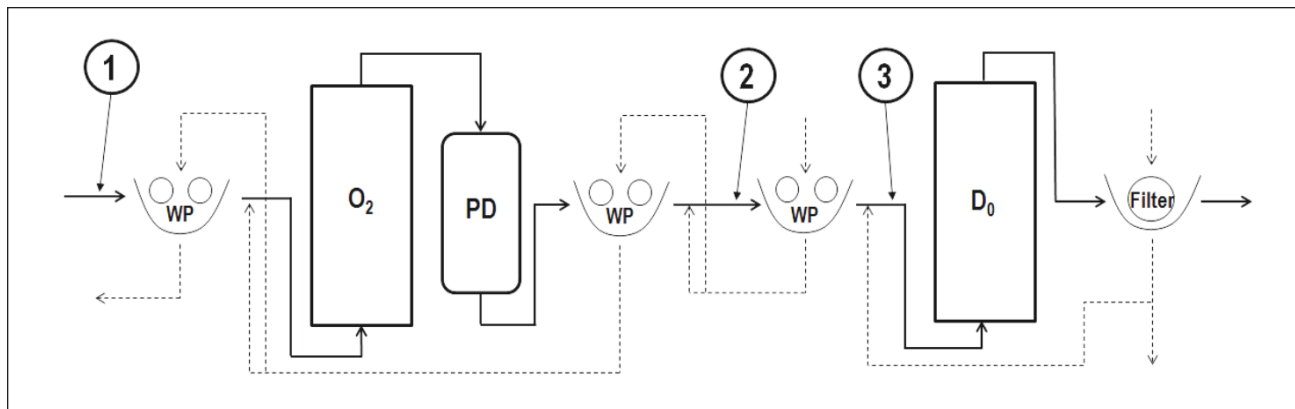
Application: By using a feed forward control based on pre- D_0 bleach load, mills can avoid over- and under-charging of chlorine dioxide, resulting in lower chemical costs and better pulp uniformity.

A chemical pulp mill is a complex process, and it is an inevitable challenge to optimally operate it so that the highest productivity and profitability is achieved. Process optimization requires a shift of the control target levels closer to the critical limits, which in turn demands proper measurements of key process and product parameters. In addition to the basic, though critical, process parameters such as flow, temperature, pressure, pH, and pulp consistency, the only pulp property that has typically been used to control the critical delignification is the lignin content of the pulp fibers, expressed as kappa number. Some mills still use manual laboratory testing for fiber kappa number, but most mills today use automatic multi-point kappa analyzers. While multi-point kappa analyzers, with a central measuring unit connected to several sampling points, have historically been used, single point kappa analyzers have been successfully introduced to the industry in the last few years. These analyzers offer better control opportunities due to their high measuring frequency, while at the

same time providing a less complex technical solution that supports lower maintenance, as well as high uptime and availability for automatic control.

While the fiber kappa number is indeed a critical parameter, recent research [1] has revealed that the carryover of dissolved lignin from cooking and oxygen (O_2) delignification can be very high and that, even more importantly, it often varies significantly with time. For instance, data from several mill installations of in-line continuous measurement of dissolved lignin shows that the variability of the dissolved lignin carryover into a D_0 stage, expressed as filtrate kappa number, may even exceed the variability of the fiber kappa number in many cases. The present study has investigated the impact of the dissolved lignin on the degree of delignification in oxygen and chlorine dioxide (ClO_2) stages, as well as the relationship between the filtrate kappa number measurement and the total chlorine dioxide demand.

An optimum operation of the oxygen delignification stage, as well as the chlorine dioxide stages, is critical for the perfor-



1. A schematic flow diagram showing the sampling positions, marked 1-3, at the kraft pulp mill. The solid lines represent the pulp stream and the dotted lines denote filtrate streams.

mance of the pulp mill, and the findings presented in the current study show that an improved fiber line process control can be achieved by accounting for the variations in the dissolved lignin carryover. Subsequently this can be transferred into reduced overall chemical costs, higher yield and selectivity, improved pulp uniformity, and minimized off-specification pulp production.

EXPERIMENTAL

Laboratory oxygen delignification and chlorine dioxide bleaching experiments were conducted on softwood kraft pulp samples and the corresponding filtrates, which were collected at a Swedish pulp mill. The sampling positions are depicted in the schematic process diagram in **Fig. 1**.

The oxygen delignification experiments were conducted in autoclaves with conditions according to **Table I**. A pulp sample with cooking kappa number 28 was used. The pulp sample was thoroughly washed and varying amounts of pulp filtrate containing dissolved lignin were added to simulate different carryover levels. The filtrate was separated from a 4.5% consistency pulp sample taken before a wash press prior the oxygen stage; position 1 in Fig. 1. The filtrate additions corresponded to filtrate kappa numbers ranging from 0 to 10.1 (per mL filtrate). The NaOH charge in the oxygen stage was 2%, and some alkali was contributed by the filtrate additions.

The chlorine dioxide (D_0) bleaching experiments were conducted in sealed polyethylene bags that were immersed in a water bath at 50°C. The retention time was 50 min in most experiments. The pulp consistency was 10%, and the kappa

Dry pulp, g	100
Pulp consistency, %	10
Temperature, °C	90
Reaction time, min	120
Oxygen pressure, bar	5
NaOH charge, %	2

I. Conditions used in the O_2 delignification experiments.

Dry pulp, g	30
Pulp consistency, %	10
Temperature, °C	50
Reaction time, min	5–50*
Kappa factor**	0.05–0.30
Start pH	2–2.5
* 50 min was used, except for investigation of the kinetics.	
** Calculated on total kappa number	

II. Conditions used in the ClO_2 bleaching experiments.

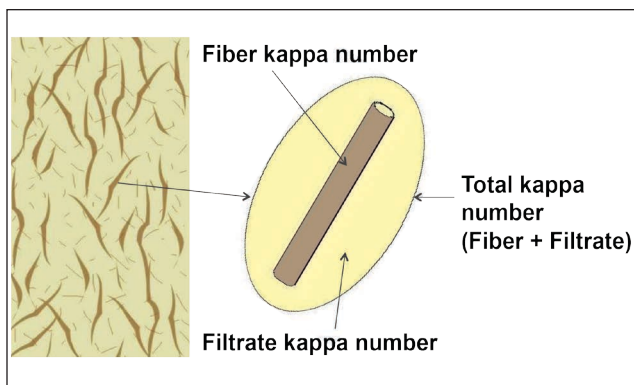
factor calculated on total kappa number varied between 0.05 and 0.30 (i.e., active chlorine charge per total kappa number; see definition that follows). The samples used in the experiments consisted of well-washed pulp samples and pulp samples containing dissolved lignin. Filtrate samples (i.e., without fibers) were also subjected to chlorine dioxide bleaching. The bleaching conditions are summarized in **Table II**.

For chlorine dioxide bleaching, according to the results of the present study, the total kappa number of a pulp slurry corresponds to the sum of the fiber kappa number and the filtrate kappa number, as schematically illustrated in **Fig. 2**. The kappa number of the fibers was determined on well-washed fibers according to the ISO 302 method “Pulps — Determination of Kappa number.” The same method was also applied for determination of the filtrate kappa number, using a certain volume of the filtrate. The filtrate kappa number was thus determined per mL of filtrate, but could subsequently be recalculated to pulp fiber basis by taking into account the pulp consistency, with the resulting filtrate kappa number “per g fiber.”

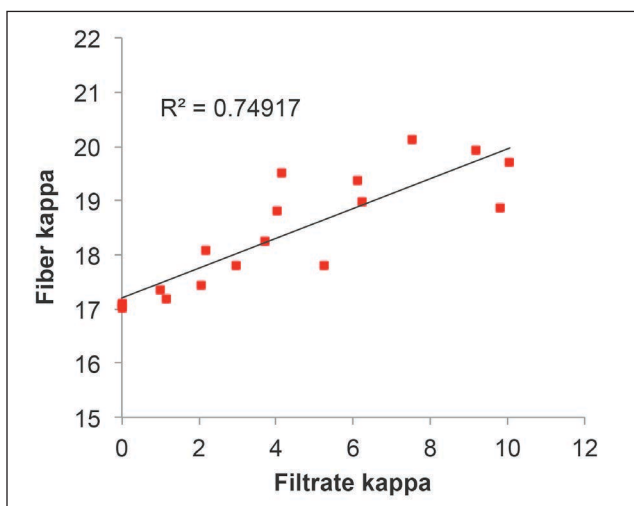
RESULTS AND DISCUSSION

Impact from dissolved lignin in oxygen delignification

According to, e.g. [2,3], recirculated “oxidized” filtrate from post- O_2 washing is less harmful to the delignification efficiency than “non-oxidized” carryover originating from



2. Schematic illustration of fiber, filtrate, and total kappa number, respectively.

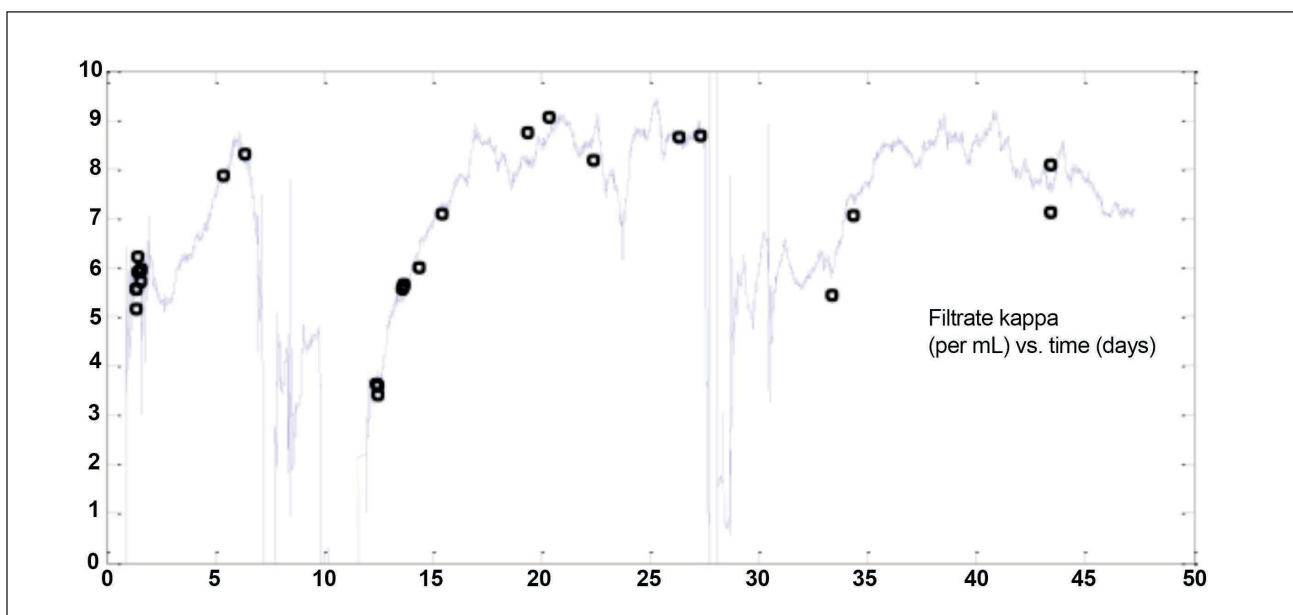


3. Fiber kappa number after oxygen stage vs. filtrate kappa number in the pulp prior to the oxygen stage (per mL filtrate).

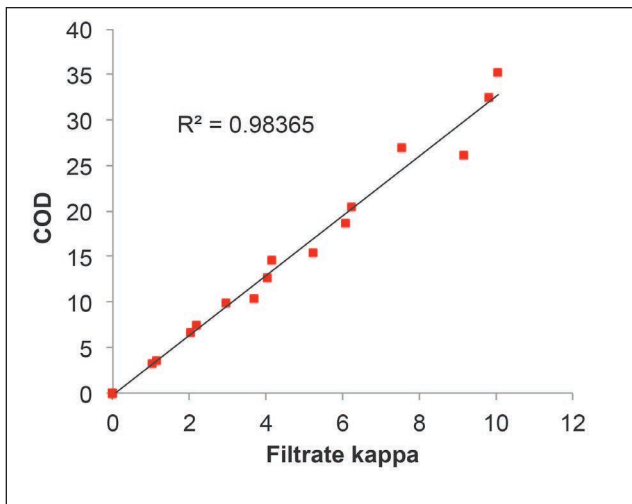
the cooking stage. Laboratory experiments were therefore conducted in order to further investigate how varying black liquor carryover influences the delignification reactions in the oxygen stage. As described in the Experimental section, the filtrate used to achieve various carryover/COD levels in the present study was taken before the wash press prior to oxygen delignification (Fig. 1). Consequently, this filtrate will not be fully representative of the actual conditions in the O₂ feed. However, these conditions were used in order to achieve a large range of carryover levels. Further investigations exclusively using recirculated “oxidized” filtrate are planned to understand the relative impact of the two types and to resolve the impact to the alkali contribution from the filtrates.

The resulting fiber kappa numbers after the oxygen delignification experiments are plotted vs. the filtrate kappa number in the pulp prior to the oxygen stage (Fig. 3). The data points are somewhat scattered, but it is still evident that there is quite a significant negative impact on the delignification from the carryover, as in a 2–3 kappa number unit increase over the studied range. The size of the filtrate addition was chosen to cover the actual filtrate kappa number range determined using an in-line dissolved lignin transmitter (Fig. 4). Figure 4 shows a 47-day representative trend, and it is evident that the sensor signal correlated well with the manual reference samples. According to Fig. 5, the filtrate kappa number and COD of the liquor phase are linearly correlated as expected, and it can be seen that filtrate kappa number 10 (i.e., per mL filtrate) corresponds to ~32 g/L COD for this filtrate. At 10% pulp consistency, this filtrate corresponds to 90 kappa units (i.e., per g fiber) or ~300 kg COD per ton of pulp.

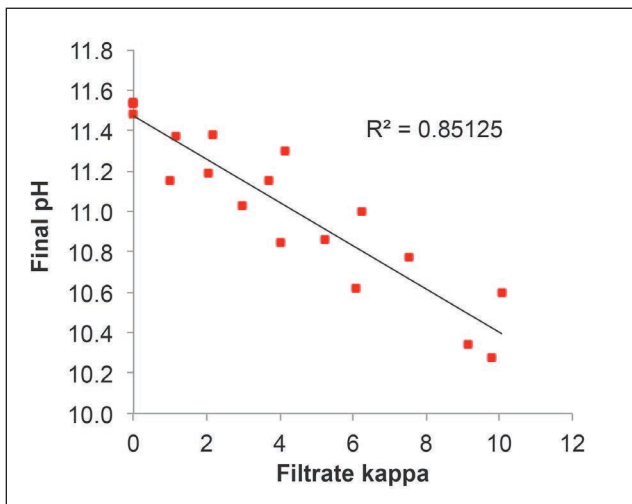
The filtrate pH was determined (at room temperature)



4. Filtrate kappa number trend over 47 days using an in-line dissolved lignin transmitter in the pulp mill. The circles denote laboratory reference samples.



5. Chemical oxygen demand (COD, g/L) prior to oxygen stage vs. filtrate kappa number (per mL filtrate) prior to oxygen stage.



6. Final pH (at room temperature) after oxygen stage vs. filtrate kappa number (per mL filtrate) prior to oxygen stage.

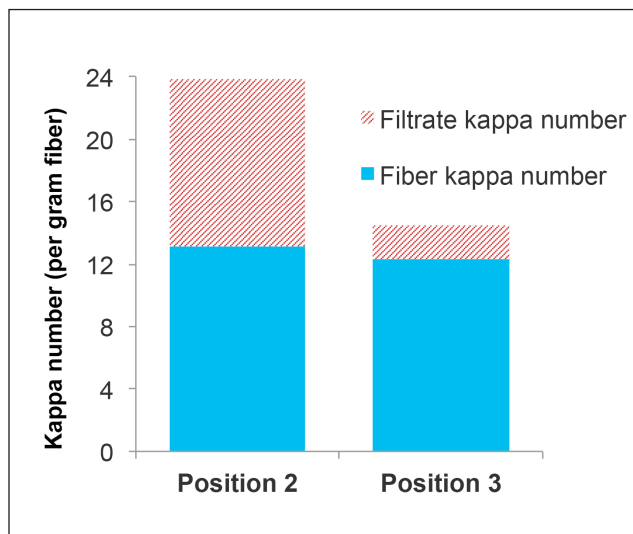
after the laboratory oxygen delignification experiments, and **Fig. 6** shows that the dissolved lignin consumed a significant amount of alkali, thus explaining the poor delignification observed for high filtrate kappa number levels in Fig. 3. It is also reasonable that oxygen will be consumed more rapidly in these laboratory experiments in the case of high dissolved lignin concentration. The results indicate that the dissolved lignin concentration, in case of any variability, should be accounted for in the control of an oxygen delignification stage to compensate for its alkali consumption at least. In most mills, a feedback loop using post-O₂ kappa number is employed. However, given that changes in the carryover may be large, sudden, and frequent, a control using a feedforward element that includes the filtrate kappa number will likely better keep the desired degree of kappa number targets, and also subsequently provide better preconditions for the operation of the bleach plant.

Impact from dissolved lignin in chlorine dioxide bleaching

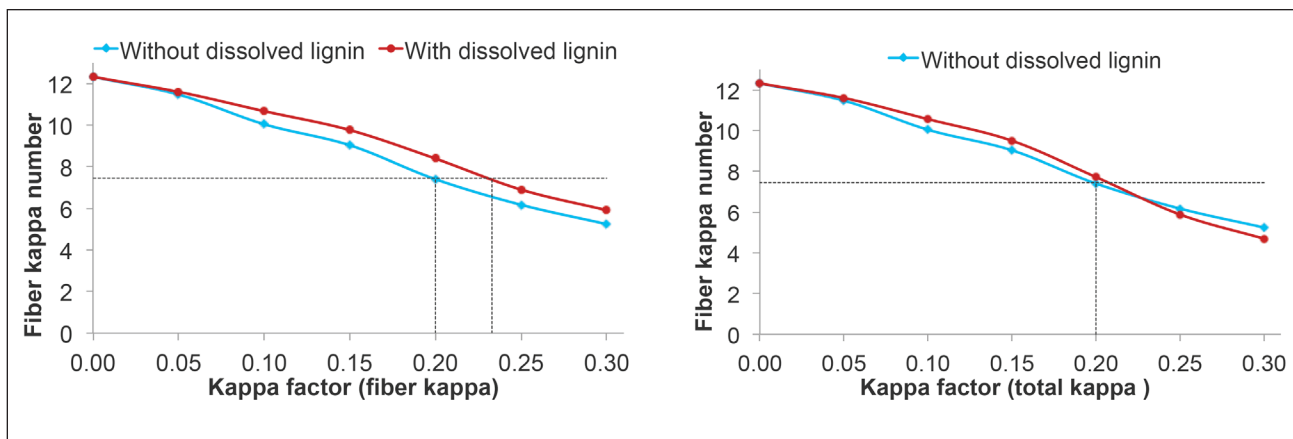
In order to determine the chlorine dioxide demand due to reactions with the dissolved lignin content, laboratory bleaching experiments were conducted using pulp samples with and without dissolved lignin. **Figure 7** shows the fiber and filtrate kappa numbers for the two pulp samples at 10% pulp consistency. It can be seen that the filtrate kappa contribution for the sample from position 2 is approximately 75% of the fiber kappa number and correspondingly 17% for position 3.

The results from laboratory bleaching of the pulp sample from position 3, with and without dissolved lignin present, are shown in **Fig. 8**. It can be seen that the fiber kappa number reduction is influenced by the dissolved lignin content in the surrounding filtrate. As a comparison, the dotted line at kappa factor 0.20 resulted in a kappa number of 7.4 for the case without dissolved lignin present (i.e., using well-washed pulp), while a kappa factor of approximately 0.23 was required to achieve the same kappa number for the case with dissolved lignin present (i.e., using unwashed pulp), which corresponds to 15% more ClO₂. Consequently, the additional chlorine dioxide required to achieve the same kappa number level for the two cases is approximately proportional to the filtrate kappa contribution, which was 17% of the fiber kappa number according to earlier. In Figure 8 (right), the kappa factor was calculated based on the total kappa number (i.e., the fiber kappa number plus the kappa number of the filtrate). As expected, the kappa numbers for the two cases, with and without dissolved lignin, are quite similar. Thus, the results suggest that the additional ClO₂ charge needed for the dissolved lignin is proportional to the additional amount of lignin in the filtrate (i.e., filtrate kappa number).

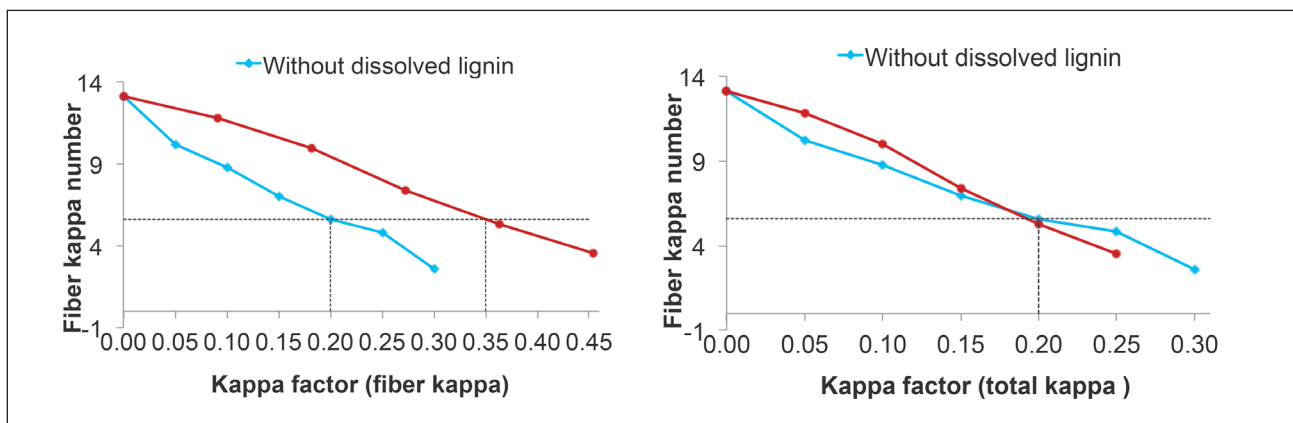
While the results presented in Fig. 8 provide a rather good indication with respect to the impact of the dissolved lignin relative to its chlorine dioxide demand, it could be argued that



7. Fiber and filtrate kappa numbers of the pulp samples used in the study.



8. Fiber kappa number vs. kappa factor for well-washed pulp and unwashed pulp, respectively, from position 3. The kappa factor was calculated based on fiber kappa number (left) or on total kappa number (right).



9. Fiber kappa number vs. kappa factor for well-washed pulp and unwashed pulp, respectively, from position 2. The kappa factor was calculated based on fiber kappa number (left) or on total kappa number (right).

the differences, or similarities, are close to the inevitable uncertainties in such experiments. Therefore, pulp from position 2 was used in further bleaching experiments, because this pulp contained much more dissolved lignin (Fig. 7) and would thus provide greater significance to the conclusions.

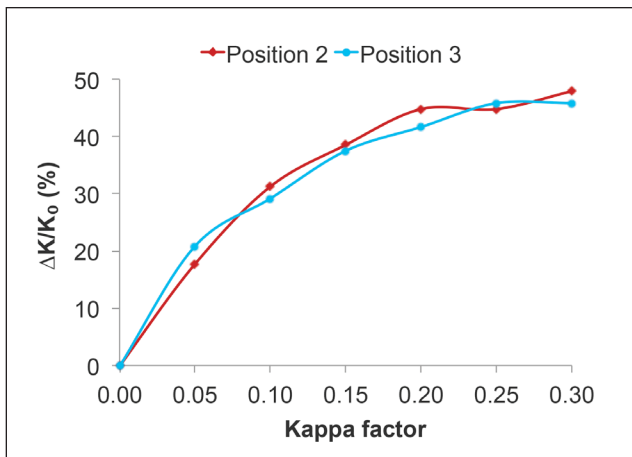
Figure 9 shows the results from the bleaching experiments using pulp from position 2, organized in the same way as for pulp from position 3 in Figure 8. In this case, the additional ClO_2 demand was approximately 75% higher for the unwashed pulp (kappa factor 0.35 vs. 0.20), which is again proportional to the contribution of the filtrate kappa number relative to the fiber kappa number. It is evident that the required ClO_2 charge is proportional to the total kappa number (i.e., the total bleach load), which is the sum of the fiber kappa number and the filtrate kappa number.

It can be seen in Figs. 8-9 (right hand diagrams) that the experiments with dissolved lignin present resulted in slightly higher fiber kappa number (compared to the experiments without dissolved lignin) for kappa factors up to approximately 0.2, while slightly lower fiber kappa numbers were achieved for higher kappa factors. These differences may be within the statistical uncertainty of the experiments including analyses,

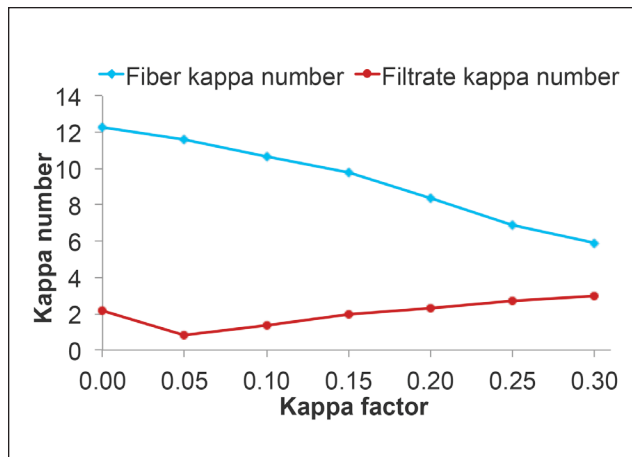
but they still indicate that when the ClO_2 charge is low, a larger share of it is consumed by the dissolved lignin rather than the fibers, possibly due to its higher accessibility or differences in reaction rate. Another observation comparing Figures 8 and 9 is that the fiber kappa number reductions over the complete kappa factor range are different (i.e., their bleachability is different). The samples had been taken at different times and were therefore not identical, and although the differences were relatively large, the results cannot be explained in another way.

Filtrates separated from the pulp samples were bleached (i.e., without fibers present) in further experiments in order to compare them. Filtrate in position 2 will have a relatively high contribution from carryover from the O_2 delignification stage, whereas filtrate from position 3 will have a relatively high contribution from recirculated post- D_0 washing filtrate due to the dilution after the press before the D_0 stage. Chlorine dioxide was charged in proportion to the respective filtrate kappa number up to kappa factor 0.30. Since the kappa number levels are quite different for the two filtrates (10.7 vs. 2.2), the relative kappa reduction is plotted vs. the kappa factor in **Fig. 10**, which shows that the two filtrates respond

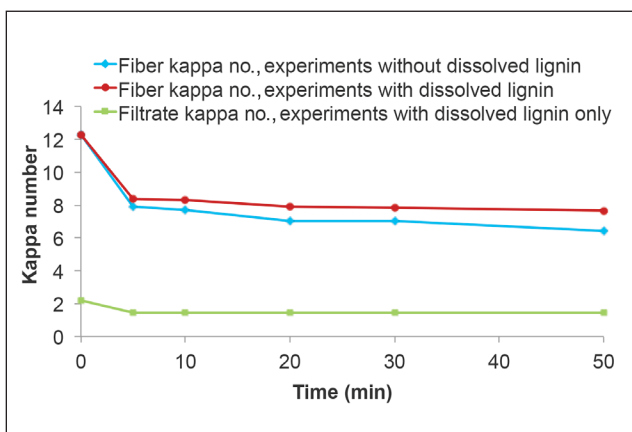
BLEACHING



10. Relative filtrate kappa number reduction vs. kappa factor for filtrate samples from position 2 and 3, respectively.



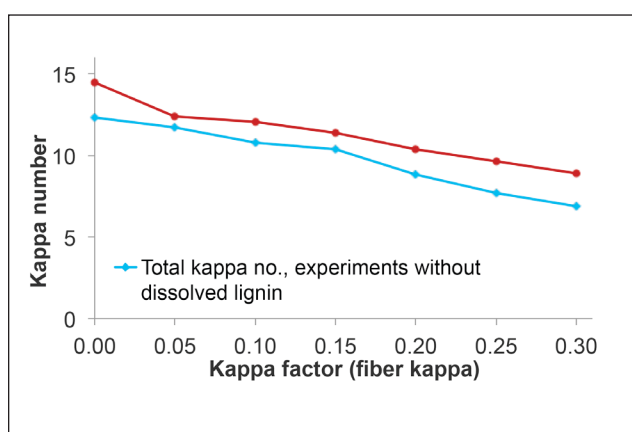
12. Fiber and residual filtrate kappa numbers for unwashed pulp vs. kappa factor calculated on total kappa number.



11. Kappa number vs. time for pulp samples (with and without dissolved lignin) and a filtrate sample, all from position 3.

very similarly to the bleaching. This indicates that the filtrate kappa number is an appropriate measure of the bleach demand of the filtrate, irrespective of being recirculated post-D₀ filtrate or not.

Previous research such as [4-6] states that most of the ClO₂ consumption and the kappa reduction takes place within the first 5 min. In order to verify this and to compare the different samples, the reaction time was varied from 5-50 min in another set of experiments. The following samples were bleached: (i) a well washed pulp sample from position 3, (ii) an unwashed pulp sample from position 3, and (iii) a filtrate separated from the pulp sample from position 3. The kappa factor was 0.20 and based on fiber kappa number for the two pulp samples and on the filtrate kappa number for the filtrate sample. According to **Fig. 11**, as shown in earlier studies, the majority of the kappa number reduction occurred readily for all samples, and virtually all reduction took place during the first 5 min. It can be noted that relative kappa reduction at 5 min was actually very similar for the pulp and filtrate sample — approximately 30% for the current conditions. It should also be noted that the kappa number for the filtrate



13. Total kappa number vs. kappa factor for well-washed pulp and unwashed pulp, respectively, from position 3. The kappa factor was calculated based on total kappa number.

sample has the same unit “Kappa number (per gram fiber)” as do the pulp samples; the filtrate kappa number as determined on a per mL filtrate basis can still be recalculated to a per gram fiber basis assuming a particular pulp consistency (i.e., 10% in these experiments).

Another interesting observation was made when studying the residual kappa number level of the resulting bleaching filtrate. **Figure 12** plots the fiber kappa number from the experiments using the unwashed pulp from position 3 again, supplemented this time by the kappa number of the resulting bleaching filtrate. It can be seen that the filtrate kappa number was lower than the initial value below kappa factor 0.20 with a minimum of 0.8 at kappa factor 0.05. This supports the observation that, at low kappa factors, the fiber kappa number decreases less when more dissolved lignin is present, even though using kappa factors based on the total kappa number. Furthermore, the contribution of the filtrate kappa number was actually very significant compared to the residual fiber kappa number towards the high end of the kappa factor range. Consequently, according to **Fig. 13**, the result-

	Mill A, Hardwood	Mill B, Softwood	Mill C, Softwood
ClO ₂	7	11	8
NaOH	7	13	10

III. Chemical savings (%) for three mills.

ing total kappa number (i.e., the combined fiber and filtrate kappa numbers) is even more affected by the influence of the dissolved lignin compared with Fig. 8 (left) showing the fiber kappa number only. The lignin dissolved from the fibers appears only partially degraded and remains available for further degradation reactions in the filtrate, as well as subsequent consumption of chlorine dioxide, if recirculated.

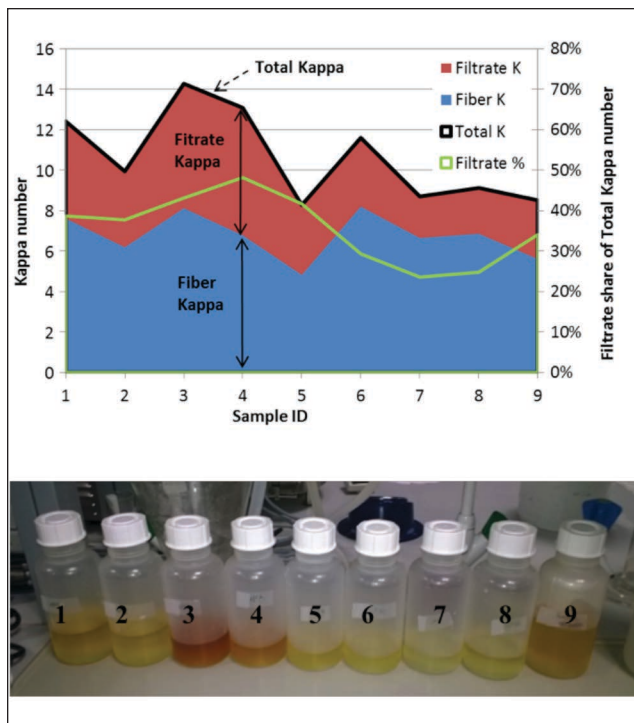
The present findings support the recent development in the industry to apply a control scheme based on measurement of the total kappa number prior to chlorine dioxide bleaching stages, in particular the D₀ stage. Such measurement can be done in line with one single sensor directly providing the total kappa number, or with two separate sensors for fiber and filtrate kappa number, which can be combined to provide the total kappa number. With the latter solution, the filtrate kappa number can be differentiated from the fiber kappa number. This provides the possibility to account for the variability in the carryover and to also optimize upstream washing operations. Consequently, a proposed state-of-the-

art D₀ process control strategy moves away from the conventional compensated brightness control and instead uses a feed forward control strategy based on the total kappa number. This has proven to be very effective in saving bleaching chemicals, and reductions of 7%–13% in chlorine dioxide and sodium hydroxide are reported for three typical installations (Table III).

Thus, in the suggested control scheme, the ClO₂ charge is primarily feed forward controlled based on pre-D₀ bleach load (before ClO₂ addition) measurement, and the typical slow post D₀ or EOP brightness or kappa number feedback becomes less active. In addition, a feedback trim from residual measurement at the post ClO₂ mixer may be used as a corrective gap action controller. Figure 14 shows mill data from a successful installation of a sensor for in-line measurement of total bleach load (i.e., total kappa number) at a North American pulp mill. It can be seen that the absolute variability of the filtrate kappa number was actually larger than that of the fiber kappa number. The filtrate share of the total kappa number in this case was 20%–50%. Again, using a feed-forward control based on the total kappa number provides a means for reaching desired process targets and thus lower bleaching cost and achieving more uniform pulp quality.

CONCLUSIONS

- Dissolved lignin can be successfully determined in the pulp slurry using novel in-line sensor technology that can be used for state-of-the-art optimization of fiber line operations with respect to chemical consumption, pulp evenness, and environmental impact.
- Several mill installations in oxygen delignification and chlorine dioxide stages have revealed that the concentration of dissolved lignin typically varies considerably.
- The results indicate that oxygen delignification control can be optimized based on feed forward information using the dissolved lignin content.
- The dissolved lignin carryover entering a D₀ stage consumes chlorine dioxide, and the filtrate kappa number is representative for the chlorine dioxide demand due to the dissolved lignin.
- The total kappa number or “total bleach load” (i.e., the sum of the fiber and filtrate kappa numbers for a pulp sample) is an adequate parameter to optimize the ClO₂ in a D₀ stage. The filtrate’s contribution to the total kappa number is typically significant, 10%–50% in the studied cases, and it has furthermore shown a high relative variability.
- Over- and undercharging of chlorine dioxide can be avoided using the proposed control concept, resulting in lower chemical cost and better pulp uniformity. Furthermore, indirect environmental improvements are plausible.
- The significance of the dissolved lignin carryover’s impact on the bleaching efficiency points to the importance of proper measurement and control of pulp washing performance, which in turn can be optimized using the accurate and continuous signal achieved from the new in-line sensors. **TJ**



14. Upper: Mill data showing (left axis) fiber, filtrate, and total kappa number as determined with laboratory samples, and (right axis) the corresponding share of the filtrate vs. total kappa number. Lower: Photograph of the mill sample filtrates from the upper figure.

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ABOUT THE AUTHORS

The international pulp and paper industry is under heavy pressure to reduce costs and reduce pollution loads, and the consumption of bleaching chemicals is one parameter that must be controlled better in the future. Bleaching chemicals are typically overcharged today to compensate for carryover in the filtrate streams, and proper process control could reduce the chemical demand.

There are surprisingly few studies that have been performed where the effect of carryover to the bleach plant is investigated thoroughly, so the present research specifically studied the influence of carryover in the D_0 stage.

The biggest challenge with our study was to obtain uniform bleaching, especially at short reaction times. This was addressed by thoroughly mixing the chemicals with the pulp prior to the bleaching stage.

The most interesting result of our study was that lignin dissolved from the fibers is only partially degraded and therefore remains available for further degradation reactions in the filtrate. This leads to

continued consumption of chlorine dioxide if the filtrate is recycled, which is commonly done in modern pulp mills.

By using a feed forward control based on pre- D_0 bleach load, it will be easier for mills to avoid over- and undercharging of chlorine dioxide, resulting in lower chemical costs and better pulp uniformity. Further investigations are planned where the impact of carryover on the oxygen stage is more carefully examined.

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