A mathematical model for chlorine dioxide delignification

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ABSTRACT

A kinetic model for 100% chlorine dioxide delignification was developed based on experimental data. The model predicts kappa number, brightness, and chlorine dioxide consumption after the first bleaching tower. In addition, we found that the relationship between the chlorine consumption and the kappa number decrease was linear and independent of the unbleached pulp kappa number. We also developed a relationship between brightness and kappa number after the first bleaching stage. The model can easily be inverted to calculate the required kappa factor to reach a brightness or kappa setpoint after the first bleaching stage, making it particularly suitable for developing model-based control strategies.

Application:

The data and kinetic model presented in this paper can be used by bleach plant operators to calculate the chlorine dioxide charge needed to reach the desired kappa number or brightness at the outlet of the D0 stage from the tower temperature and residence time.

THE BLEACH PLANT IS AT THE END of the pulping process and represents the last chance to improve pulp quality before it is shipped to customers. Increased chemical costs, tighter customer demand, and tougher environmental regulations are all incentives for better bleach plant control. Traditional bleach plant control systems seem to be approaching a plateau in their effectiveness and investment return. However, new control tools and sensors have emerged that can help us deal with long transport delays and nonlinearities that characterize bleach plants. In recent years, advanced bleach plant control schemes based on material tracking, kappa number, and residual and brightness measurements have been developed. Mathematical models based on our knowledge of the bleaching process can be used to calculate the control moves from the predicted product properties and process characteristics. Control moves will then be more effective in reducing variations and in improving the process efficiency.

As more pulp mills are switching to 100% chlorine dioxide in the first bleaching stage, there is a need for an accurate and robust kinetic model that can be used for process optimization and/or control. This paper presents such a kinetic model for chlorine dioxide delignification, which is used in a model-based control strategy for a bleach plant located in western Canada. From the incoming kappa number measurement, chlorine dioxide charge, and tower residence time, the model predicts the kappa number, brightness, and residuals after the first bleaching tower.

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DEFINITIONS

At the mill discussed in this paper, the first bleaching stage is a 100% chlorine dioxide delignification stage and will be referred to as the D0 stage. The kappa number after the D0 stage will be referred to as Dkappa. Similarly, the brightness after the D0 stage will be referred to as Dbrightness. The kappa factor (Kf), also known as active chlorine multiple (ACM), is defined as the total available chlorine (TAC) divided by the kappa number:

$$Kf = TAC/\text{kappa number} \quad (1)$$

where

$$TAC = 2.63 \times \%ClO_2 \text{ (wt.\% on o.d. pulp)} \quad (2)$$

Finally, the chemical residual is the amount of chlorine dioxide (ClO_2) that remains in the pulp filtrate on a weight percent basis on ovendry (o.d.) pulp. Inversely, the ClO_2 consumption is the amount of chemical consumed on a weight percent basis on ovendry pulp.

KINETIC STUDY OF THE CHLORINE DIOXIDE DELIGNIFICATION REACTION

Chlorine dioxide oxidizes the aromatic units of lignin. Reactions of chlorine dioxide are very complicated, because it is degraded into other chlorine compounds and the rates of side reactions are not fully known.

There are two main methods for obtaining experimental data and studying bleaching reaction kinetics. The first method is called the *constant condition method.* As the name implies, the concentration of the active bleaching chemicals is held constant throughout the reaction. This method has the following advantages:

- No assumption as to the stoichiometry is required.
- The effect of each chemical can be studied separately.
- Mathematical kinetic models are easy to obtain.

However, this method might yield inaccurate reaction rates, since it does not represent industrial conditions, where the bleaching chemi-

Dry pulp, g	300
Sample time, min	0.25, 1.33, 2.5, 4, 7, 10, 15, 30, 50, 75
Consistency, %	3.1
Mixing time before sampling, s	5
pH after chemical injection	3.0

I. Experimental conditions of chlorination

cals are first mixed with the pulp and then are consumed as the reaction proceeds into the bleaching tower. The second method is the *differential method,* in which the bleaching conditions approach those of an industrial bleaching tower. We have used the second approach and tried to reproduce industrial conditions as closely as possible. In the following, we discuss the experimental conditions and the procedure used for the study.

Experimental conditions and procedure

Three pulp samples with different initial unbleached kappa numbers were taken from the decker. Initial kappa numbers between 29.0 and 32.3 were selected to cover the typical range of variation recorded at the mill. For each pulp, we have measured the Dkappa, Dbrightness, and ClO_2 consumption as a function of time (15 seconds and 1.33, 2.5, 4, 7, 10, 15, 30, 50, and 75 min) at two different temperatures (40 and 50°C) and at different ClO_2 charges (kappa factors between 0.15 and 0.23).

Sulfuric acid was added before the ClO_2 injection to obtain a pH near 3.0 after the chlorine dioxide addition. The experiments were performed in a reactor especially designed so that pulp and liquor samples can be taken during the chlorination reaction. A special sampling device is used to take about 10 g of pulp and about 250 mL of filtrate from the reactor without losing any ClO_2, which is very volatile. The pulp sample is placed into a beaker containing cold deionized water bubbled with SO_2 to stop the reaction.

Experiment no.	Initial K number	Initial kappa	ClO_2 charge, % on o.d. pulp	Kappa factor	Temperature, °C
1	19.3	29.0	1.88	0.17	40
2	19.3	29.0	2.21	0.20	40
3	19.3	29.0	2.54	0.23	40
4	19.3	29.0	1.88	0.17	50
5	19.3	29.0	2.21	0.20	50
6	19.3	29.0	2.54	0.23	50
7	21.2	31.0	2.00	0.17	40
8	21.2	31.0	2.35	0.20	40
9	21.2	31.0	2.70	0.23	40
10	21.2	31.0	2.00	0.17	50
11	21.2	31.0	2.35	0.20	50
12	21.2	31.0	2.70	0.23	50
13	21.9	32.3	1.88	0.15	40
14	21.9	32.3	2.35	0.19	40
15	21.9	32.3	2.70	0.22	40
16	21.9	32.3	1.88	0.15	50
17	21.9	32.3	2.35	0.19	50
18	21.9	32.3	2.70	0.22	50
19*	21.2	31.0	2.35	0.20	45
20*	21.2	31.0	2.35	0.20	45
21*	21.2	31.0	2.35	0.20	45
22*	21.2	31.0	2.35	0.20	45

*Replica

II. Experimental design

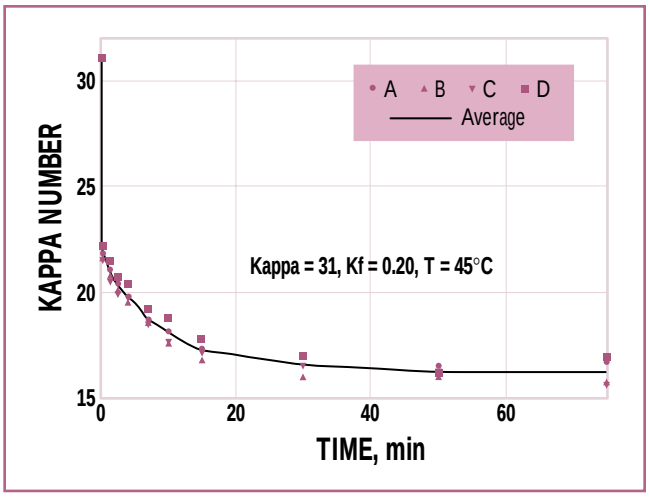
Then the pulp is washed with 6 L of cold deionized water before measuring kappa number and brightness according to CPPA standard procedures. **Tables I and II** summarize the experimental conditions and the experimental design.

Experimental results

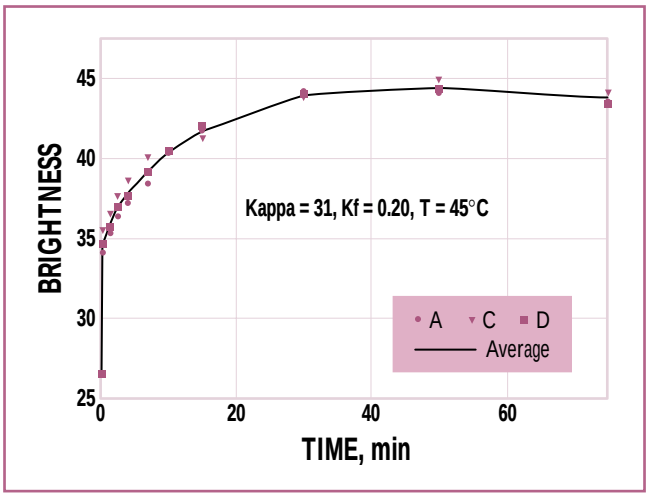
Reproducibility. Four experiments (Nos. 19 to 22) have been conducted at the same operating conditions (unbleached kappa number = 31.0, kappa factor = 0.20, and temperature = 45°C) over a period of 3 weeks to check the degree of reproducibility of the equipment and the procedure. The data obtained for kappa number, brightness, and chlorine dioxide consumption are shown in **Figs. 1–3**. The reproducibility is excellent, and calculations based on the four sets of experimental data showed a standard deviation of less than 3%.

It is important to note that brightness reversion occurs when all the chlorine dioxide is consumed. For these experiments, the reversion happens around 50 min, when the ClO_2 consumption is completed (Fig. 3), and it can be seen that brightness decreases (Fig. 2). This phenomenon has been observed with some of the experiments we have conducted at low chlorine dioxide charges, leading to a rapid consumption of all the chemical. For this reason, it is a common practice in the industry to maintain some residuals of chlorine dioxide after the first bleaching tower to avoid brightness reversion.

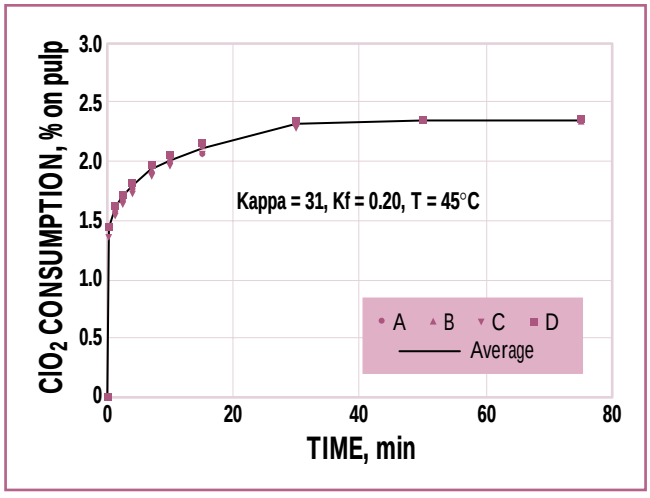
Kinetics of the chlorine dioxide delignification reaction. **Figures 4–12** show the experimental results we have obtained for kappa number, brightness, and chlorine dioxide consumption as a function of time. The effect of kappa factor and temperature for the pulps at three different kappa numbers has been investi-



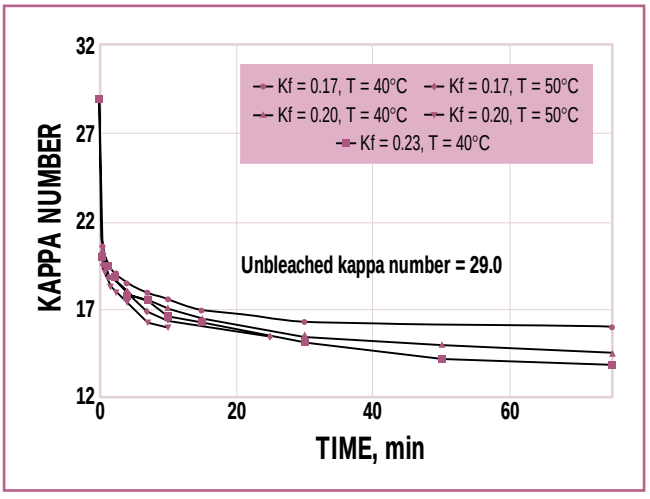
1. Kappa number vs. time



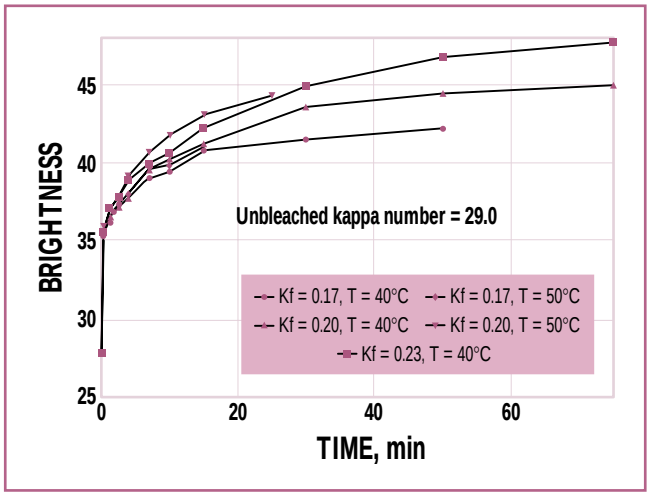
2. Brightness vs. time



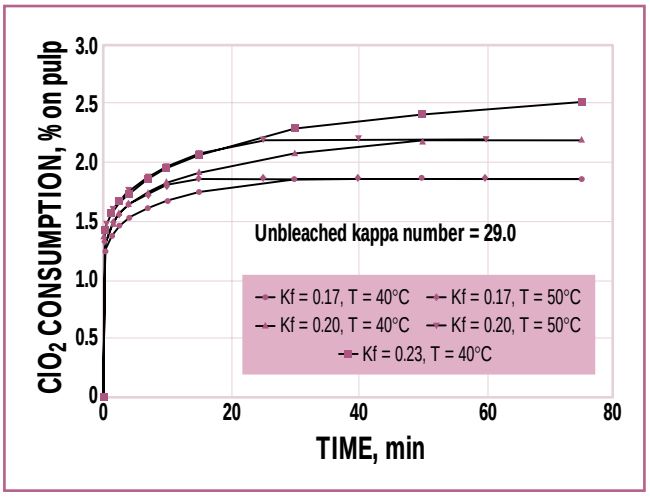
3. ClO_2 consumption vs. time



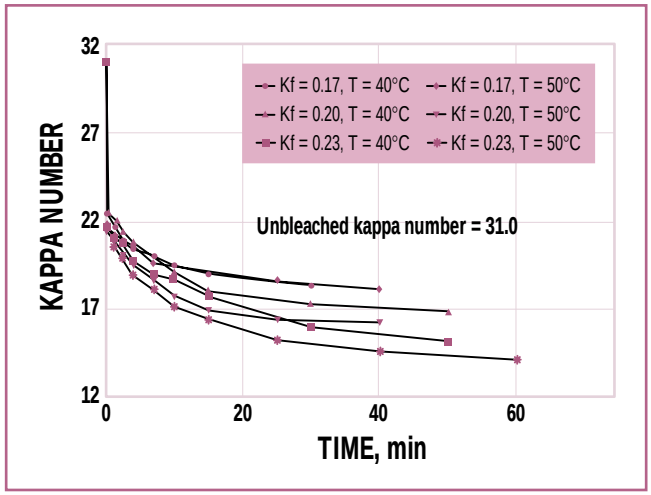
4. Kappa number vs. time



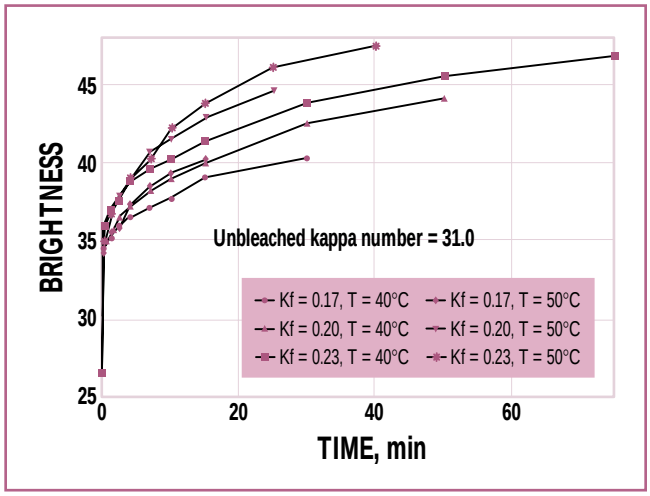
5. Brightness vs. time



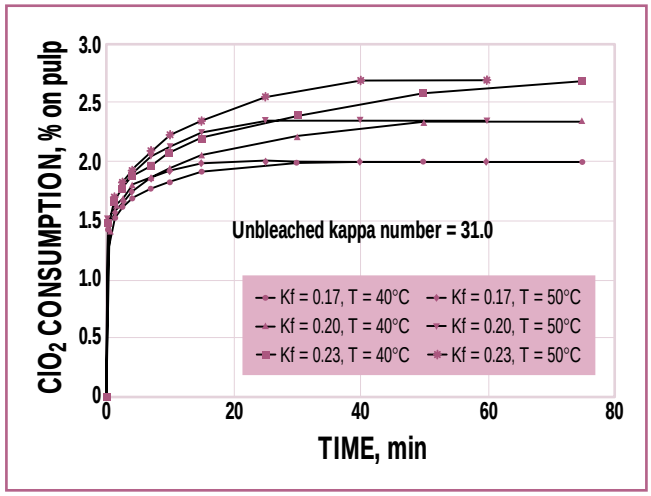
6. ClO_2 consumption vs. time



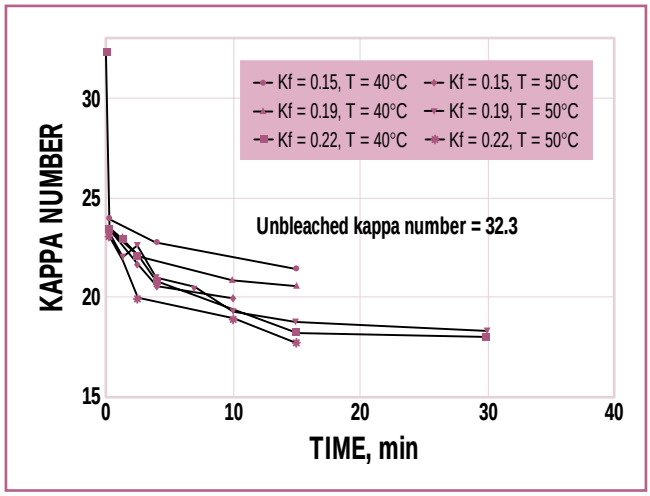
7. Kappa number vs. time



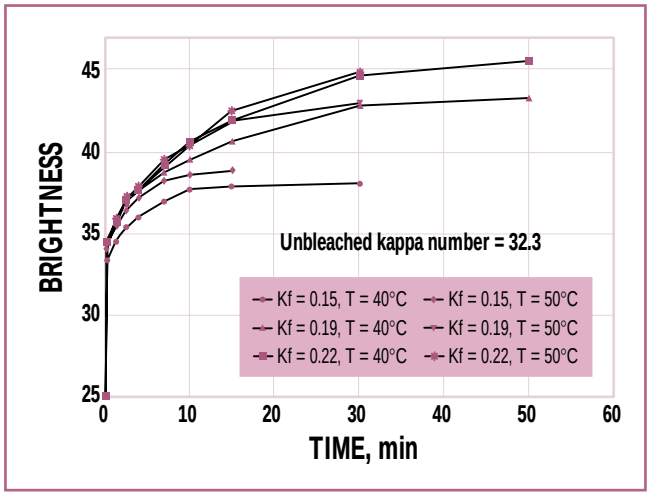
8. Brightness vs. time



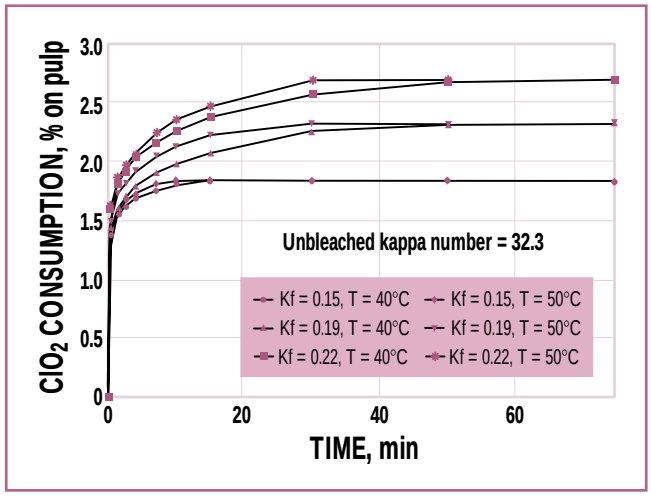
9. ClO_2 consumption vs. time



10. Kappa number vs. time



11. Brightness vs. time



12. ClO_2 consumption vs. time

gated. We have removed the experimental points where brightness reversion occurred. Several comments can be made on these figures:

- The chlorine dioxide delignification reaction seems to be a combination of a very fast reaction followed by a slow one. This can be related to the concept of "fast" and "slow" delignification reactions.
- It can take as much as 90 min for the reaction to be completed, depending on the experimental conditions.
- As expected, the reaction is faster at 50°C than at 40°C but reaches the same Dkappa number and Dbrightness at steady-state conditions for the same kappa factor at a given kappa number.
- The degree of delignification increases with increasing kappa factor and decreasing unbleached kappa number.
- There is an asymptote for both kappa number and brightness that is certainly linked to what is known as "floor lignin."

Effect of chlorine dioxide consumption on Dkappa number. **Figure 13** shows that the Dkappa number of the chlorinated pulp decreases linearly with increasing chlorine dioxide consumption. The three lines are parallel, meaning that the slopes of the curves remain the same for the three different pulps. The slope is –6.5 kappa number/ClO_2 consumed (% on o.d. pulp). In terms of available Cl_2, the slope becomes –2.5 kappa number/available Cl_2 consumed (% on o.d. pulp), which is also the value reported by Histed *et al. (1)* in their study on the effect of chlorine charge on delignification.

Stoichiometry of the chlorine-dioxide delignification reaction. More important is the stoichiometry of the delignification reaction, i.e., the relationship between kappa number and chlorine dioxide consumption. **Figure 14** shows the decrease in Dkappa number (ΔDkappa number = initial kappa number–Dkappa number) as a function of chlorine dioxide consumed. The relationship is linear and independent of the kappa number of the unbleached pulp. The following relationship was found:

$$\Delta\text{Dkappa number} = 5.8 \times \text{ClO}_2 \text{ consumed (\% on o.d. pulp)} \quad (3)$$

In terms of available Cl_2, the previous relationship becomes:

$$\Delta\text{Dkappa number} = 2.2 \times \text{Cl}_2 \text{ consumed (\% on o.d. pulp)} \quad (4)$$

Histed *et al. (1)* have reported a value of 2.66 for the stoichiometry of the chlorine delignification reaction for commercial northeastern Canadian softwood mixtures of black spruce, jack pine, and balsam. Slightly different values are expected because of the formation of chlorate when chlorine dioxide is used.

Relationship between brightness and kappa number. Brightness and kappa number on washed pulp were measured on the pulp samples used during the chlorine dioxide kinetic study. The experimental data are shown in **Fig. 15**. As shown in this figure, there is a good linear relationship between brightness and kappa number. The following relationship was found between brightness and kappa number after the first stage:

$$\text{Dbrightness} = 20 + 1.66 \times \Delta\text{Dkappa number} \quad (5)$$

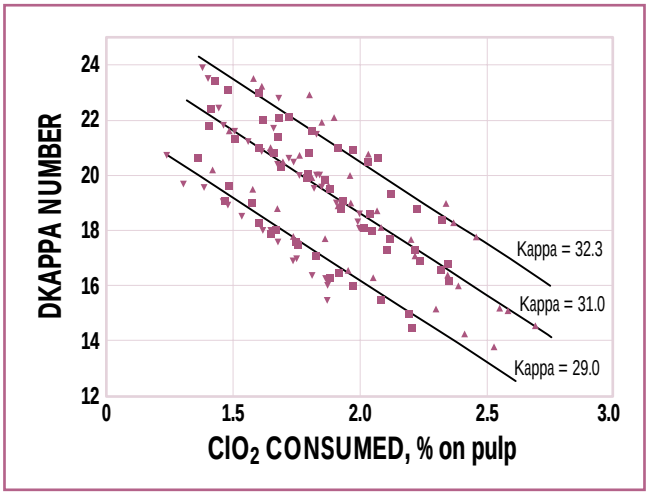
Modeling of the chlorine dioxide delignification reaction

On-line prediction of bleached pulp characteristics such as kappa number, brightness, and chemical residual for process control requires good mathematical models. Steady-state models, which are used in many bleach plant control strategies, assume that the tower residence time is long enough for the reaction to be completed. This assumption is rarely met in the industry, however, as most mills operate above the production rate the mill was originally designed for.

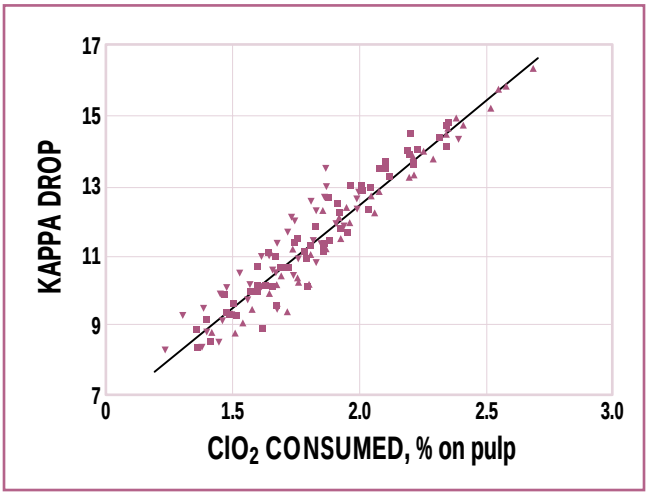
Research in the area of bleaching reaction kinetics has not caught up with the rapid changes we have seen in the past few years. Although many papers have been published on chlorine delignification with or without chlorine dioxide substitution, only a few papers in the literature are devoted to 100% chlorine dioxide delignification kinetics. Furthermore, the scientific community is still divided on how to explain the existence of "floor level" lignin. Two hypotheses have been proposed. The first one assumes that the reaction rate is limited by the formation of the so-called "immobilized chlorolignin" layer *(2).* The second assumes the formation of "blocking groups" during chlorination *(3).* Recent work by Ni *et al. (4, 5)* supports the second hypotheses and proposes a series of reactions that lead to the formation of these "blocking groups," namely trichlorolignin.

All the experimental results, including those presented in Figs. 1–12, indicate that the delignification in the first bleaching tower is the combination of a fast reaction followed by a slow reaction, and a few models have been proposed for chlorine dioxide delignification. The kinetic expression proposed by Germgard *et al. (6)* includes a term with the kappa number raised to the fifth power to fit the steep initial decrease in kappa during the first few minutes of reaction. A kappa number raised to a power higher than one or perhaps two is not realistic from a mechanistic point of view and makes the model extremely sensitive to kappa measurement errors when used for on-line predictions.

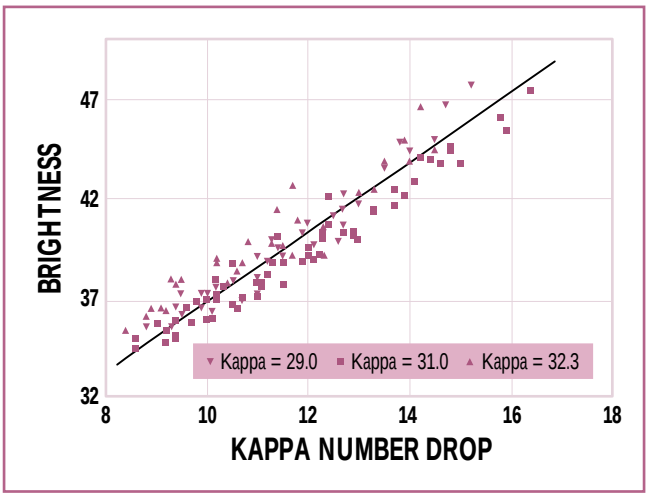
Saltin and Edwards *(7)* have developed a fairly detailed kinetic model for chlorine dioxide pre-



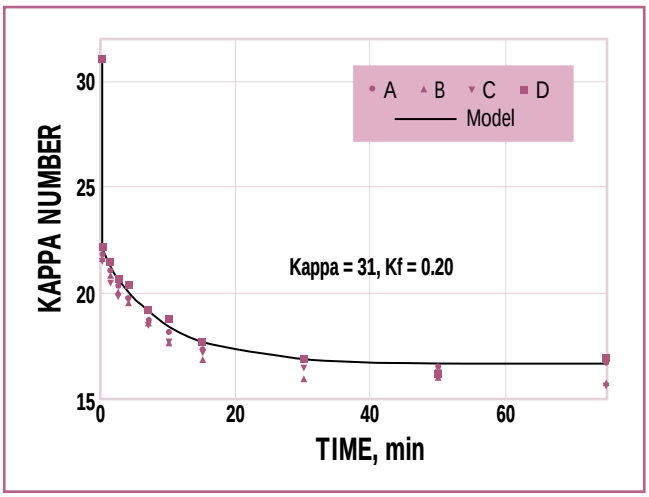
13. Dkappa number vs. ClO_2 consumed



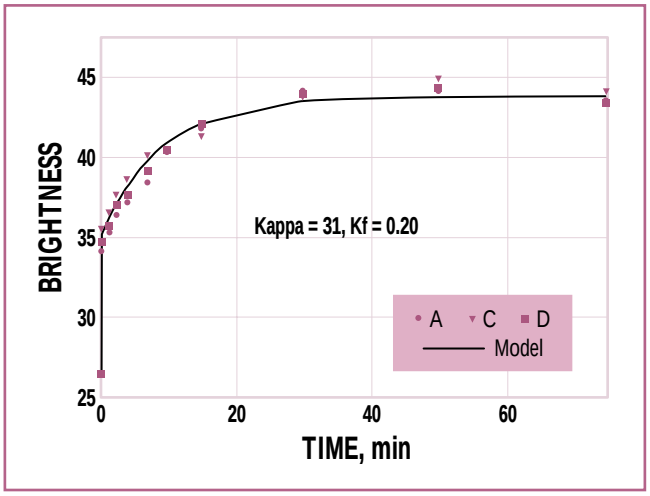
14. Kappa drop vs. ClO_2 consumed



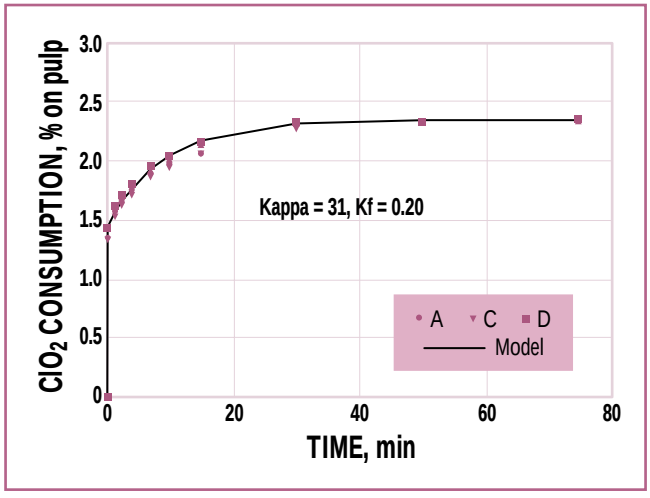
15. Brightness vs. kappa number drop



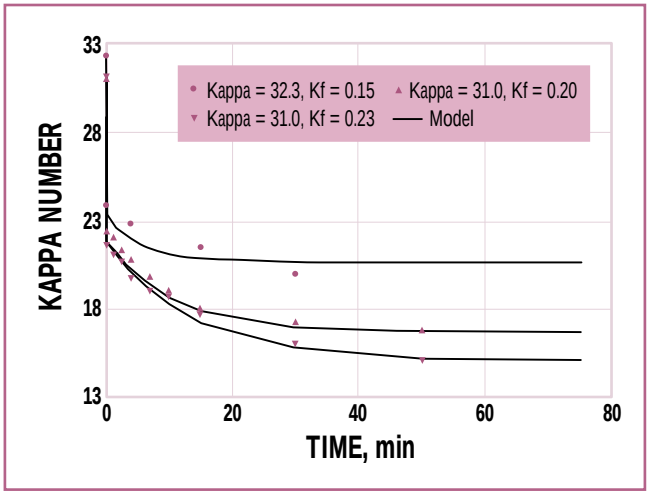
16. Experimental data and model prediction



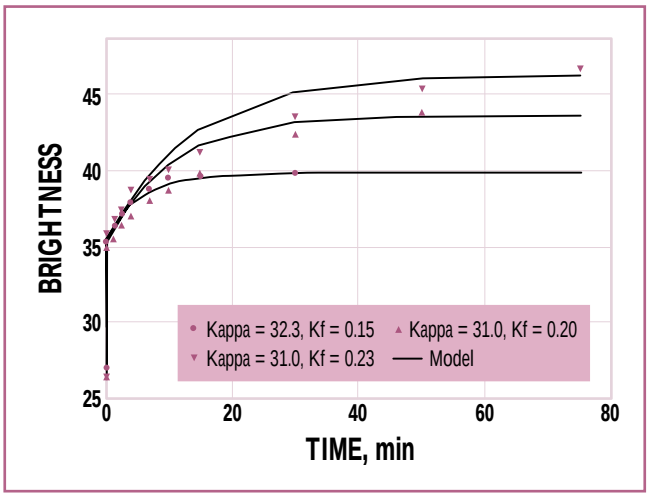
17. Experimental data and model prediction



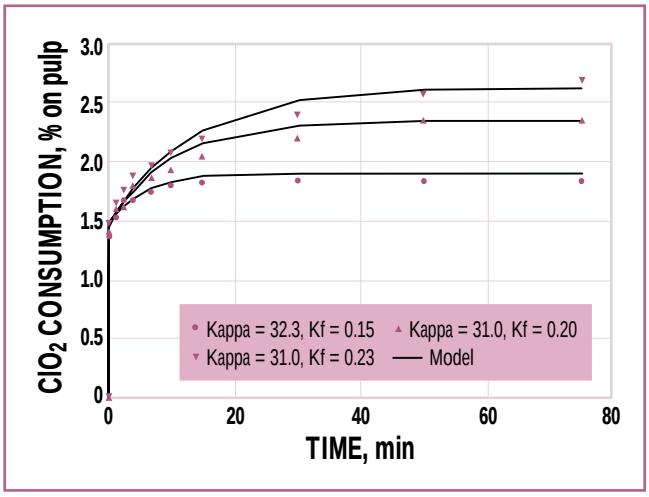
18. Experimental data and model prediction



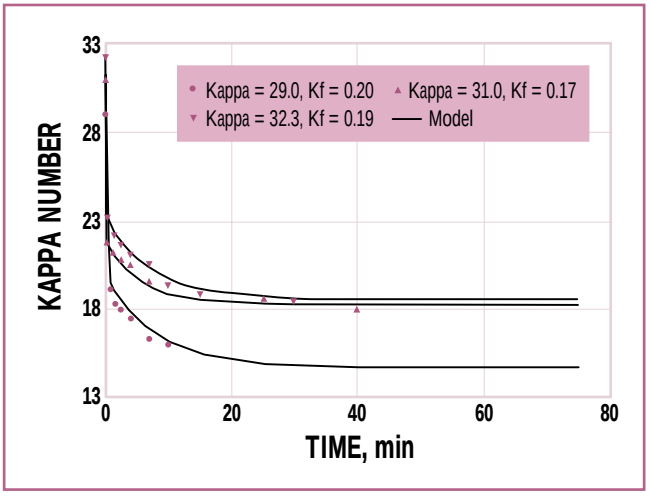
19. Experimental data and model prediction at 40°C



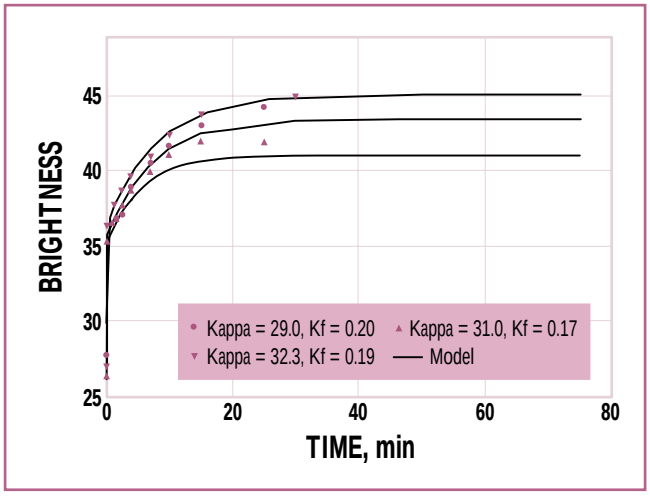
20. Experimental data and model prediction at 40°C



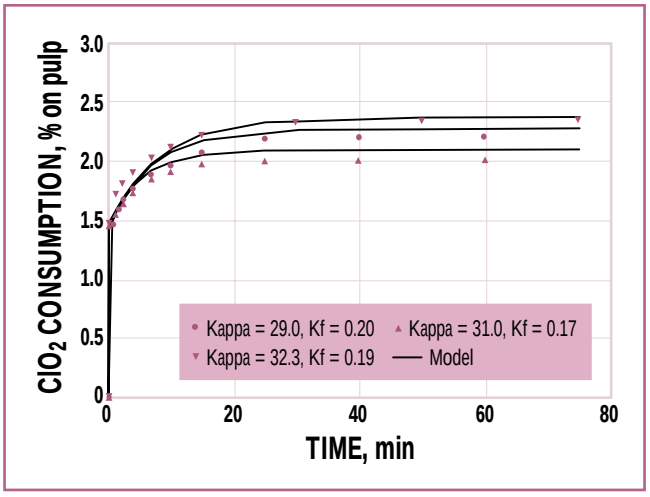
21. Experimental data and model prediction at 40°C



22. Experimental data and model prediction at 50°Cz



23. Experimental data and model prediction at 50°C



24. Experimental data and model prediction at 50°C

bleaching based on oxidation, substitution, and dissolution reactions that take place during bleaching. The proposed model is quite complex and requires many parameters. Such a detailed model is unfortunately too complex to be used in a model-based control strategy. As for the models used in commercial bleach plant control systems, they are based on polynomial regressions from mill data. The advantages of such empirical models lie in the simplicity of the calibration procedure. However, they are limited to the range of operating conditions on which they have been calibrated and are not based on the physical and chemical phenomena of the bleaching process.

For control purposes, the prediction model should be simple but accurate and robust. Computation time and memory space should be kept at a reasonable level to avoid additional burden on the mill distributed control system (DCS) or host computer. The model must take into account varying conditions, such as residence time (which depends on the production rate), temperature, chemical charge, incoming kappa number for the prediction of kappa number, brightness, and chemical residual or chemical consumption after the tower. Instead of using a series of reaction rates to represent both slow and fast reactions as in Ackert's approach *(8)* and to reduce the number of parameters to be fitted from the experimental data, we have decided to use a simpler model.

The experimental curves that we have presented here clearly indicate that the time responses of kappa number, brightness, and ClO_2 consumption are made up of a nearly instantaneous response followed by an exponential or power-type response. The fast response corresponds to the chlorine substitution of the unchlorinated lignin monomers, which is completed within a few seconds, and to the chlorine substitution of the monochlorolignin monomers. To represent such a behavior, we have decided to use the following mathematical expressions to fit the experimental data:

$$\text{Dkappa(t)} = \text{unbleached kappa} - K_0 - K_k(1 - \exp^{-t/\tau_k}) \quad (6)$$

$$\text{Dbrightness(t)} = \text{inital brightness} + B_0 + K_b(1 - \exp^{-t/\tau_b}) \quad (7)$$

$$ClO_2 \text{ consumption(t)} = C_0 + K_c(1 - \exp^{-t/\tau_c}) \quad (8)$$

where K_0, B_0, and C_0 are the changes in kappa number, brightness, and chemical consumption as measured at 15 seconds, respectively; K_k, K_b, and K_c are the static gains for kappa number, brightness, and ClO_2 consumption, respectively; and τ_k, τ_b, and τ_c are the time constants.

Based on the physics of the process, the time constants should be the same for the three equations at a given temperature, since the time constants represent the speed of the phenomena. They are, however, functions of the chemical charge (or kappa factor) and temperature. Secondly, the static gains K_k, K_b, and K_c are not independent because of the relationships that exist between kappa number and brightness, and kappa number and ClO_2 consumption, as previously discussed (Figs. 13 and 14, Eqs. 3 and 6). The relationships between these static gains are:

$$K_b = 1.66\, K_k \quad (9)$$

$$K_c = K_k/5.8 \quad (10)$$

Calibration and validation

Basically, only five coefficients need to be fitted: K_0, B_0, C_0, K_k, and the time constant, τ. The initial drop in kappa and initial gain in brightness and ClO_2 consumption can be easily determined from the instantaneous responses we have observed on the experimental curves. We have found values of 9 for K_0, 8.5 for B_0, and 1.45% for C_0. A least-squares optimization technique was used to estimate the static gain K_k and the time constant τ as functions of temperature and kappa factor. The values of these parameters depend on the wood species and are mill specific.

The final proposed model thus becomes:

$$\text{Dkappa(t)} = \text{unbleached kappa} - 9 - K_k(1 - \exp^{-t/\tau}) \quad (11)$$

$$\text{Dbrightness(t)} = \text{initial brightness} + 8.5 + 1.66K_k(1 - \exp^{-t/\tau}) \quad (12)$$

$$ClO_2 \text{ consumption(t)} = 1.45 + K_k/5.8(1 - \exp^{-t/\tau}) \quad (13)$$

The comparison between the model predictions and the experimental data is shown in **Figs. 16–24**. First, we show the model predictions for the four duplicates at 45°C. The agreement is excellent and within the experimental error (Figs. 16–18). For an unbleached kappa number of 31 and a kappa factor of 0.20 at 45°C, the reaction is basically completed within 45 min. Then we show the model predictions at 40°C (Figs. 19–21) and at 50°C (Figs. 22–24) for different unbleached kappa numbers and kappa factors that cover the typical mill operating conditions. As one can see, the model predictions are quite good. At high unbleached kappa numbers and low kappa factors, the reaction is completed after 30 min since all the chlorine dioxide is quickly consumed. However, at low unbleached kappa factors and high kappa factors, significant drops in Dkappa number and gains in Dbrightness can still be achieved after 40 min.

KEYWORDS
Bleaching, brightness, chemical consumption, chlorine dioxide, chlorine number, delignification, experimental design, kappa number, mathematical models, reaction kinetics.

CONCLUSIONS

We have developed a model for the chlorine dioxide delignification reaction. The model predicts the kappa number, brightness, and ClO_2 consumption after the D0 stage from the unbleached kappa number, reaction time and temperature, and kappa factor. The model is simple enough to be used in a model-based control strategy. Only two parameters need to be fitted from either mill data or lab data.

A relationship has been found between kappa and brightness after the first bleaching tower. This relationship is important, as it allows switching from kappa number control in the D0 stage to brightness control in the EOP stage that follows the D0 stage. **TJ**

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