Stoichiometric model of chlorine dioxide delignification of softwood kraft pulps with oxidant-reinforced extraction

BRIAN N. BROGDON

ABSTRACT: A generalized, steady-state model estimates bleaching delignification and/or chlorine dioxide consumption for sequences that employ oxidant-reinforced extraction. The model is based on Germgård's stoichiometric expression for the D_0E_1 sequence, which relates chlorine dioxide uptake to post-extracted kappa number. Germgård's integrated stoichiometric model was modified to normalize the extracted kappa number to the incoming kappa number. This mathematical transformation allows for various brownstocks and oxygen-delignified pulps with different kappa numbers to be modeled as a single curve whereby its shape is related to the stoichiometric parameter. From analyzing various softwood bleaching studies, it was determined that this stoichiometric parameter could be expressed as a simple function of oxidant-reinforced extraction conditions (e.g., extraction temperature and peroxide dosage). The generalized delignification model forecasts chlorine dioxide usage with small relative error from the experimental values, typically ±3% to ±10%. This model is relatively simple, with a minimum number of equation parameters to determined, and can be used with other steady-state brightening stage models to predict bleach usage.

Application: For mills that use elemental chlorine-free bleaching sequences that contain oxidant-reinforced extraction stages, the model can predict chlorine dioxide consumption during bleaching delignification of softwood kraft pulps. The model can also be applied to bleach plant optimizations, computer simulations, and process control strategies.

Various investigators have been scrutinizing the relationship between chlorine dioxide (ClO_2) consumption and residual lignin removal for more than 30 years [1–11]. This relationship is represented by mathematical models, which couple kinetic and stoichiometric expressions. The delignification models fall into two classes: (1) those that measure delignification in chlorine dioxide (D_0) and extraction (E_1) separately and (2) those that measure delignification across D_0E_1 sequence as a lumped value. Both approaches have their merits and weaknesses, as was noted in a recent review of multistage bleach sequence modeling [12]. An impediment to the first approach is the difficulty of delineating lignin removal caused by D_0 and the subsequent E_1. However, models of the first type can be adapted to incorporate the impact of oxidant-reinforced caustic extraction [4,5,10]. Delignification models that lump lignin removal across D_0 and extraction are much simpler to employ [1,2,11]. Nonetheless, such models as they are currently constructed cannot account for the effects of oxidant-reinforced caustic extraction, which are commonplace in most modern elemental chlorine–free (ECF) bleaching sequences.

An alternative technique for calculating chlorine dioxide uptake during bleaching delignification is the steady-state approach [12–16], which does not consider process dynamics and greatly simplifies the calculations. In many cases, this simplification will suffice for chemical dosage optimization. Several investigators [14–21] have used steady-state models to optimize chlorine dioxide dosages in brightening stages. Typical models of this type are based on a stoichiometric relationship of kappa number reduction for a given amount of bleach consumption.

Hart and Connell [14] developed an empirical steady-state model of D_0(EP) delignification for mixed U.S. southern pine with brownstock kappa nos. 12–33. The authors coupled their D_0(EP) delignification model to a stoichiometric D_1 brightening model to minimize total chlorine dioxide usage and maximize pulp yield for a given brightness target. The delignification model was based on constant extraction conditions, a restriction in the experimental design that reduced the number of tests conducted and simplified the delignification model. However, this limitation did not allow for adjusting oxidant-reinforced extraction, which can supplement delignification and assist with bleach sequence optimization [3,13,15,16].

Brogdon [15] examined the bleaching data of Basta et al. [16] and developed a statistical, steady-state delignification model of D_0(EO) and D_0(EOP) sequences to explore the impact of oxidant-reinforced extraction conditions. The author's model, when coupled with brightening models of D_1 or $D_1E_2D_2$, could predict optimized chemical dosages in the D stages while adjusting oxidant-reinforced extraction conditions. That modeling approach was used earlier by van Lierop and coworkers [17] to investigate the impact of high-temper-

ature (EO) stages on extracted kappa number. Unfortunately, the delignification models of these studies were limited to one brownstock kappa number, which did not allow for simultaneous optimization of kraft pulping and bleaching, such as that of the Hart and Connell study [15].

A steady-state delignification model that includes variable brownstock or post-oxygen kappa number entering D_0 and adjustable oxidant-reinforced extraction conditions would be a very useful tool in pulp mill optimization. The primary focus of this paper is to re-examine the stoichiometric model developed by Germgård [1] for D_0E_1 delignification of softwoods and incorporate the effects of oxidant-reinforced extraction into this model.

GENERALIZED BLEACHING DELIGNIFICATION MODEL FOR D_0E_1

Germgård's original D_0E_1 delignification model, which related chlorine dioxide consumption to the amount of delignification after extraction, was of the following form (Eq. [1]):

$$\frac{d[ClO_2]}{d[Kappa]} = -A[Kappa]^{-m} \quad (1)$$

where [Kappa] is the extracted kappa number, $[ClO_2]$ is the percentage of chlorine dioxide (on pulp) consumed in the D_0, A is the stoichiometric parameter, and m is an exponent. This differential form of Eq. (1) can be expressed in its integrated form as Eq. (2):

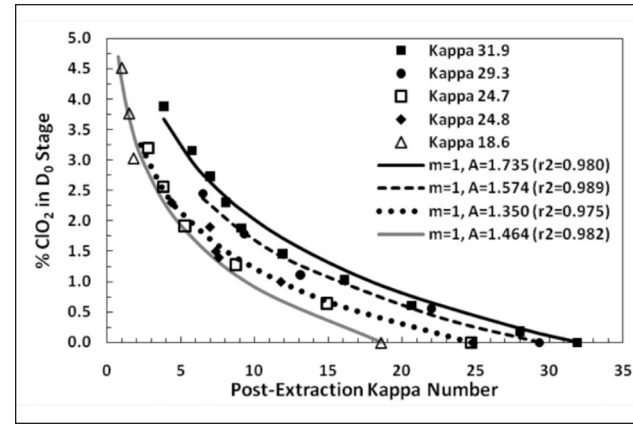
$$[ClO_2] = \begin{cases} -A \bullet \ln\left(\dfrac{[Kappa]}{[Kappa_0]}\right) & \text{for } m = 1 \\ -\dfrac{A}{1-m} \bullet \left([Kappa]^{1-m} - [Kappa_0]^{1-m}\right) & \text{for } m > 1 \end{cases} \quad (2)$$

where $[Kappa_0]$ is the pulp's pre-D_0 kappa number. Germgård observed that m has a value of ~1 for D_0E_1 delignification of softwood brownstocks and a value of ~1.5 for oxygen-delignified softwood pulps. The author suggested that A was significantly affected by the chloride and hydrogen ion concentration in the D_0-stage, was not affected greatly by the temperature or consistency of the D_0-stage, and was mildly affected by the temperature and hydroxyl ion concentration of the E_1-stage.

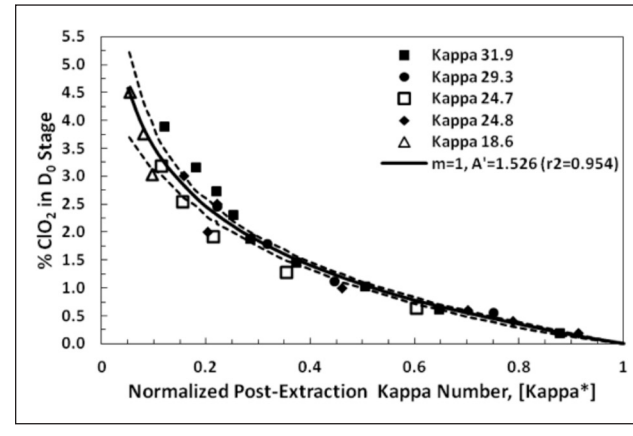
Data from various D_0E_1 delignification studies [3,22–25], where the extracted kappa numbers were measured at various chlorine dioxide dosages, were analyzed by using Eq. (2). **Figure 1** illustrates the fitted curves to the individual data sets (i.e., entering brownstock kappa number) to Eq. (2) where m = 1. The value of A varies from 1.35 to 1.74 for the individual data sets with a coefficient of correlation (r^2) value of ≥0.97. Germgård's original stoichiometric model represents the D_0E_1 delignification data from the scientific literature reasonably well.

Histed and coworkers [26] proposed that the amount of bleaching delignification from chlorine dioxide substitution (i.e., [CD]) and extraction (E_1 or [EO]) for a given charge of bleach could be generalized for various brownstock kappa numbers. These investigators observed that the bleach consumed by a 20–55 kappa brownstock, at ≥0.15 kappa factor (KF), could be expressed by a linear function if the data were plotted as the fraction brownstock kappa remaining in extracted pulp. Histed et al. suggested, in a later study [22], that a similar approach could be used for 100% chlorine dioxide delignification for D_0E_1 and D_0(EO) for a 31.9 kappa brownstock.

The data from Fig. 1 were reanalyzed by plotting the chlorine dioxide consumed in the D_0 stage in terms of the fraction of brownstock kappa remaining after E_1 (**Fig. 2**). The collective D_0E_1 data, when expressed in the normalized kappa (i.e., $[Kappa^*] = [Kappa]/[Kappa_0]$), were observed to follow a single generalized curve (Eq. [3]):



1. Chlorine dioxide consumption (as ClO_2 on pulp) in the D_0 stage to the post-extraction delignification (~70°C E_1) for softwood kraft pulps with different pre-D_0 kappa numbers (i.e., [$Kappa_0$]). Data fitted to Eq. (2). Source data for brownstocks with [$Kappa_0$] of 31.9 [22], 29.3 [23], 24.7 [24], 24.8 [3], and 18.6 [25].



2. Chlorine dioxide consumption (as ClO_2 on pulp) in the D_0 stage to the normalized post-extraction kappa number (i.e., [Kappa*] = [Kappa]/[$Kappa_0$]) with different pre-D_0 kappa numbers (i.e., [$Kappa_0$]). Data are from the D_0E_1 sequence (~70°C E_1) fitted to Eq. (3). Dotted lines represent ~95% probability interval in predicted ClO_2 consumed. Source data for softwood brownstocks with [$Kappa_0$] of 31.9 [22], 29.3 [23], 24.7 [24], 24.8 [3], and 18.6 [25].

Bleaching Study	Kraft Pulp Type	Kappa No.	D_0 Stage Conditions	Extraction Stage	
				Common Conditions	Oxidant Reinforcement
Histed et al. [22]	Unbleached spruce, pine, and balsam mix	31.9	0.18%–3.88% ClO_2, 2.6% consistency, 30°C– 60°C, pH 3	2% NaOH, 11% consistency, 70°C	E_1 none (EO) 0.34 MPa O_2
Brogdon [23]	Unbleached U.S. southern pine mix	29.3	0.56%–2.45% ClO_2, 3% consistency, 45°C, pH 2.1–2.5	0.81%–3.54% NaOH, 10% consistency, 70°C	E_1 none
Chirat et al. [24]	Unbleached softwood	24.7	0.64%–3.00% ClO_2, 10% consistency, 70°C, pH 2.7	3% NaOH, 10% consistency, 70°C	E_1 none
Mothra et al. [3]	Unbleached softwood	24.8	Similar to Chirat et al. [24]	Similar to Chirat et al. [24]	E_1 none
Rapson and Anderson [25]	Unbleached spruce	18.6	2.3%–6.0% ClO_2, 6% consistency, 70°C, pH 2.4	3% NaOH, 12% consistency, 60°C	E_1 none
Reeve and Weishar [28]	Unbleached pine, spruce, and fir mix	34.0	1.29%–3.88% ClO_2, 8% consistency, 50°C, pH ~2	2.4%–3.2% NaOH, 8% consistency, 70°C	(EO) 0.14 MPa O_2
Reeve and Weishar [28]	Unbleached pines mix	15.0	0.57%–1.71% ClO_2, 8% consistency, 50°C, pH ~2	1.7%–2.5 % NaOH, 8% consistency, 70°C	(EO) 0.14 MPa O_2
Reeve and Weishar [28]	O_2-delignified pine, spruce, and fir mix	16.0	0.61%–1.83% ClO_2, 8% consistency, 50°C, pH ~2	1.7%–2.5 % NaOH, 8% consistency, 70°C	(EO) 0.14 MPa O_2
Reeve and Weishar [28]	O_2-delignified southern pines	18.0	0.68%–2.05% ClO_2, 8% consistency, 50°C, pH ~2	1.7%–2.5 % NaOH, 8% consistency, 70°C	(EO) 0.14 MPa O_2
van Lierop et al. [27]	Unbleached softwood	24.1	0.92%–2.02% ClO_2, 3.5% consistency, 50°C, pH 2.2–3.3	1.6% NaOH, 10% consistency, 70°C–110°C	(EO) 0.15 MPa O_2
van Lierop et al. [13]	Unbleached spruce, pine, and fir mix	31.4	1.79%–3.22 % ClO_2, 3.5% consistency, 50°C, pH 2–3	2.25% NaOH, 10% consistency, 70°C–90°C	(EO) 0.15 MPa O_2 (EOP) 0%–1% H_2O_2
Tessier and Savoie [6]	Unbleached softwood	32.3	1.88%–2.70% ClO_2, 3.1% consistency, 40°C, pH 3	1.5%–2.5% NaOH, 10% consistency, 77°C	(EO) 0.60 MPa O_2 (EOP) 0 - 0.5% H_2O_2
Malinen et al. [29]	O_2-delignified softwood	19.3	0.59%–1.76% ClO_2, 3% consistency, 50°C, pH 2–4	2% NaOH, 10% consistency, 80°C	(EO) 0.5% O_2 (EOP) 0 - 0.4% H_2O_2
Basta et al. [16]	Unbleached U.S. southern pines mix	24.0	0.91%–2.10% ClO_2, 3.5% consistency, 40°C–50°C, pH 2–3	~1.5% NaOH, 10% consistency, 70-90°C	(EO) 0.22 MPa O_2 (EOP) 0%–1% H_2O_2
Hart and Connell [14]	Unbleached U.S. southern pines mix	16.0–33.6	0.61%–4.33% ClO_2, 9% consistency, 57°C	End pH ~10.5, 9% consistency, 85°C	(EP) 0.3% H_2O_2

I. Bleaching conditions reported for D_0-stage and various extraction stages (E_1, [EO], [EP] or [EOP]) for various literature studies from which data were analyzed.

$$[ClO_2] = \begin{cases} -A' \bullet \ln\left(\dfrac{[Kappa^*]}{[Kappa_0^*]}\right) \\ -\dfrac{A'}{1-m} \bullet ([Kappa^*]^{1-m} - [Kappa_0^*]^{1-m}) \end{cases} \quad (3)$$

in which the terms [*Kappa*] and [$Kappa_0$] in Eq. (2) were replaced with the normalized [*Kappa**] and [$Kappa_0$*], respectively, and *A'* is the corresponding stoichiometric parameter. The value of [$Kappa_0$*] is defined as unity (i.e., [$Kappa_0$]/[$Kappa_0$] = 1). The best-fit curve is for $m = 1$ and $A' = 1.526$ with an r^2 value of 0.954. The generalized curve for brownstock kappa nos. 19–32 is a little less accurate at predicting the chlorine dioxide consumption of the D_0E_1 sequence than the individual curves of Fig. 1. The dotted lines in Fig. 2 represent ~95% variability in the predicted chlorine dioxide consumed if one assumes the ~95% probability interval in the measured kappa number. Most of the literature data are within the variance of model (Eq. [3]) given the associated uncertainty in the kappa number measurement. The generalized model is more appealing than Eq. (2) because it represents D_0E_1 delignification over a wide range of brownstock kappa numbers with the fewest D_0E_1 parameter values to be determined.

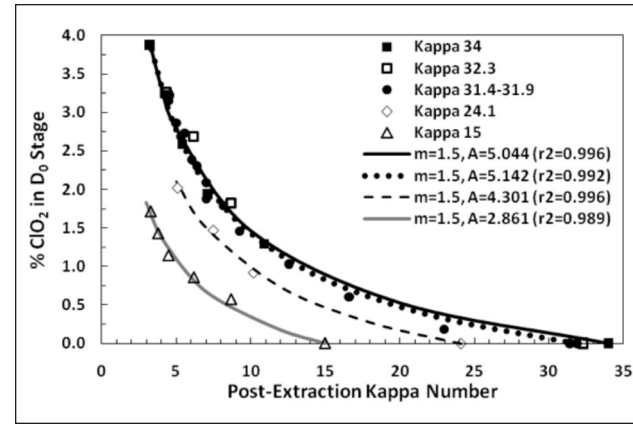
Literature data analysis

Data from various chlorine dioxide delignification studies, which used E_1, (EO), (EP) or (EOP), were analyzed. The conditions reported in these studies are given in **Table I**. The delignification data were fitted to either Eq. (2) or Eq. (3) using the statistical program WinCurveFit (Kevin Raner Software, version 1.1.6). The nonlinear, curve fitting program employed a quasi-Newton method (Davidon-Fletcher-Powell algorithm) for minimizing the lack of fit. Linear regression analysis of the stoichiometric parameter, *A'*, for various extraction temperature and peroxide charges was performed with Minitab version 15.1 (Minitab; State College, PA, USA).

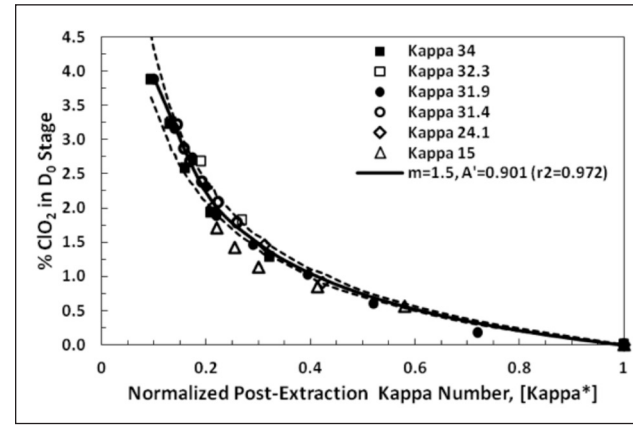
The calculated variability in chlorine dioxide consumption by the mathematical model was determined by propagation of error technique [30]. This analysis used the uncertainty in the kappa number measurement, which was set to be ± twice the standard deviation. Kappa number measurements typically have a standard deviation of ~0.20–0.40 units over the kappa no. 2–25 range [23,31]. It was assumed that the standard deviation was ±0.24 units. Twice the standard deviation was used to approximate ~95% probability interval of the kappa number, which should yield ~95% probability range for the chlorine dioxide consumed when the propagation of error analysis was applied to the mathematical model.

GENERALIZED BLEACHING DELIGNIFICATION MODEL FOR D_0(EO)

Data from various D_0(EO) delignification studies of softwoods, where the extracted kappa number was measured at various ClO_2 dosages were examined [6,13,22,27,28]. The data sets were initially analyzed individually using Eq. (2) and



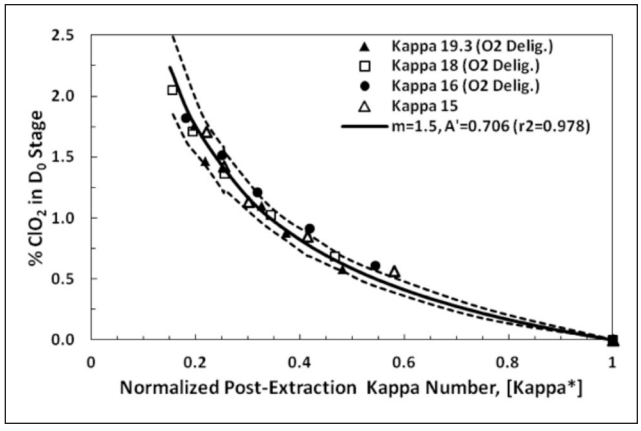
3. Chlorine dioxide consumption (as ClO_2 on pulp) in the D_0 stage to the amount delignification (after 70°C [EO]) for softwood kraft pulps with different pre-D_0 kappa numbers (i.e., [$Kappa_0$]). Data fitted to Eq. (2). Source data for softwood brownstocks with [$Kappa_0$] of 34 [28], 32.3 [6], 31.9 [22], 31.4 [13], 24.1 [27], and 15 [28].



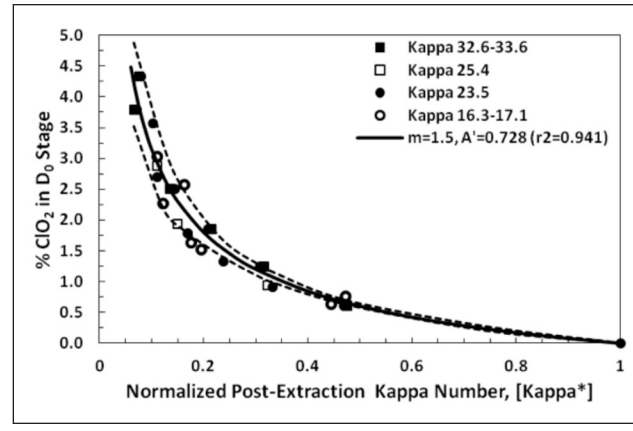
4. Chlorine dioxide consumption (as ClO_2 on pulp) in the D_0 stage to the normalized post-(EO) kappa number (i.e., [Kappa*] = [Kappa]/[$Kappa_0$]) with different pre-D_0 kappa numbers (i.e., [$Kappa_0$]). Data are from the D_0(EO) sequence (~70°C [EO]) fitted to Eq. (3). Dotted lines represent ~95% probability interval in predicted ClO_2 consumed. Source data for softwood brownstocks with [$Kappa_0$] of 34 [28], 32.3 [6], 31.9 [22], 31.4 [13], 24.1 [27], and 15 [28].

are plotted in **Fig. 3**. The value for *m* was determined to be ~1.5, and the value of *A* ranged from 2.86 to 5.53 for brownstock kappa nos. 15–35. Equation (2) represents each of the data sets very well, as is illustrated by the high coefficient of correlation ($r^2 > 0.98$). The chlorine dioxide stoichiometry of the D_0(EO) sequence of unbleached softwoods seems to follow what Germgård observed for the D_0E_1 sequence for oxygen-delignified softwoods where $m = 1.5$.

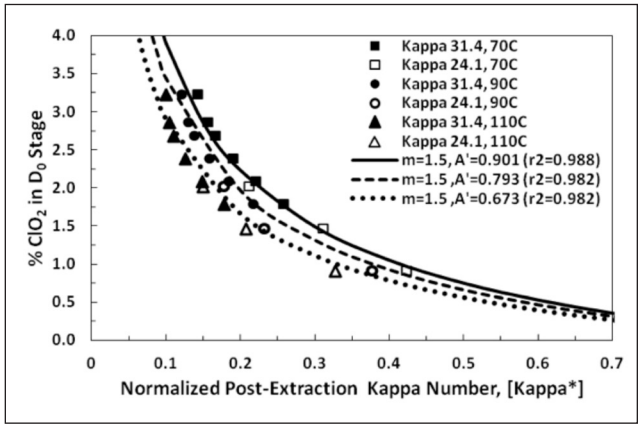
The various D_0(EO) data sets were then evaluated using Eq. (3) by converting the [*Kappa*] values to their normalized values. This transformation collapsed the family of curves in Fig. 3 to a singular trend, as shown in **Fig. 4** for [$Kappa_0$] between 24 and 35. This trend can be represented by Eq. (3)



5. Chlorine dioxide consumption (as ClO_2 on pulp) in the D_0 stage to the normalized post-(EO) kappa number (i.e., [Kappa] = [Kappa]/[$Kappa_0$]) with different pre-D_0 kappa numbers (i.e., [$Kappa_0$]). Data are from the D_0(EO) sequence (70°C [EO]) fitted to Eq. (3). Dotted lines represent ~95% probability interval in predicted ClO_2 consumed. Source data for softwood pulps with [$Kappa_0$] of 19.3 [29], 18 [28], 16 [28], and 15 [28].*



7. Chlorine dioxide consumption (as ClO_2 on pulp) in the D_0 stage to the normalized post-(EP) kappa number (i.e., [Kappa] = [Kappa]/[$Kappa_0$]) with different pre-D_0 kappa numbers (i.e., [$Kappa_0$]). Data are from the D_0(EP) sequence (85°C and 0.3% H_2O_2 [EP]) fitted to Eq. (3). Dotted lines represent ~95% probability interval in predicted ClO_2 consumed. Source data from reference [14].*



6. Chlorine dioxide consumption (as ClO_2 on pulp) in the D_0 stage to the normalized post-extraction kappa number (i.e., [Kappa] = [Kappa]/[$Kappa_0$]) with different pre-D_0 kappa numbers (i.e., [$Kappa_0$]) and (EO) temperatures. Data fitted to Eq. (3). Source data for softwood brownstocks with [$Kappa_0$] of 31.4 [13] and 24.1 [27].*

when m is set to 1.5 and A' is set to 0.901 with an $r^2 > 0.97$. The predicted chlorine dioxide consumption, as modeled by Eq. (3), is relatively good, considering the error generally associated with the kappa number measurement. Chlorine dioxide uptake of the lower kappa number pulps (<20) forecasted by the model with A' =0.901 is less accurate with values overpredicted by 15%–20%. The lower kappa number softwoods (15–19) [28], either unbleached or oxygen-delignified, are better represented as a collective by the generalized form of Eq. (2) when m is 1.5 and A' is 0.706 ($r^2 > 0.97$), as shown in **Fig. 5**.

A second set of D_0(EO) delignification data, from the studies of van Lierop et al. [13,27], was examined to see the impact of (EO) extraction temperature on the generalized D_0(EO) delignification model. The data from these studies, which investigated (EO) reaction temperatures of 70°C, 90°C, and 110°C for two different softwood brownstocks, were replotted in **Fig. 6** using the normalized [*Kappa**]. Increasing the extraction temperature affects the value of the stoichiometric parameter (A') of Eq. (3) in a linear fashion. These values decrease from 0.901 at 70°C to 0.673 at 110°C, and the value of m remains constant at 1.5. The generalized model fits van Lierop et al. data [13,27] well with an $r^2 > 0.98$; predicted ClO_2 consumed in D_0 has relative errors of ±5% of the experimental values. The effect of higher (EO)-stage extraction temperature on ClO_2 consumption of the D_0(EO) sequence can be modeled with Eq. (3) with the stoichiometric parameter (A'); the value of A' decreases by ~6% for a Δ10°C increment in (EO) temperature, relative to 70°C.

GENERALIZED BLEACHING DELIGNIFICATION MODEL FOR D_0(EP)

The D_0(EP) delignification data of Hart and Connell [14] for various ClO_2 charges in the D_0-stage and for various brownstock kappa nos. (16–34) were analyzed using the generalized model (Eq. [3]). **Figure 7** illustrates the D_0(EP) delignification data when expressed in terms of [*Kappa**]. In this instance, the values of m and A' were determined to be 1.5 and 0.728, respectively. The fitted model showed an r^2 of 0.941. The predicted ClO_2 usage of D_0(EP) sequence (at a fixed peroxide level of 0.3% on pulp) was within ±10% of the actual experimental data (i.e., relative error) for [$Kappa_0$] of 23–35. The predictions of the model for the lowest kappa no. range (16–17) showed a higher relative error of ±15%. If the uncertainty in the kappa number measurement (as denoted by the dotted lines of Fig. 7) is considered, then these differences in experimental and model values are relatively close.

GENERALIZED BLEACHING DELIGNIFICATION MODEL FOR D_0(EOP)

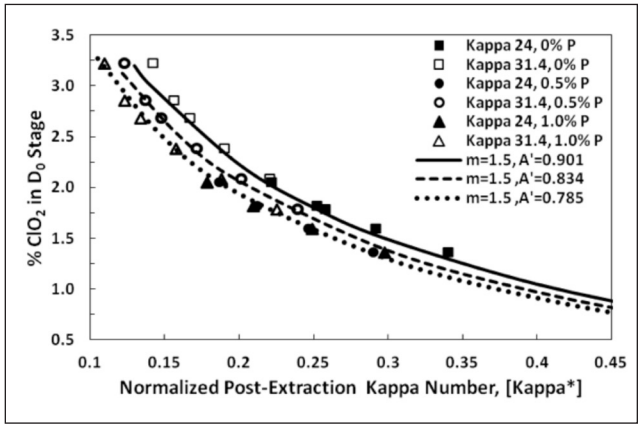
Unlike the previous bleaching delignification instances, there are limited raw data in the published literature regarding the D_0(EOP) treatment of different softwood brownstocks whereby chlorine dioxide, peroxide, and extraction temperature have been systematically varied. However, a few studies have reported the above delignification variables in graphical form, from statistical response surface models for softwood brownstocks of kappa 31.4 [13] and 24 [15,16]. These data sets for various ClO_2 charges for fixed values for extraction conditions (i.e., peroxide charge and extraction temperature) were plotted in terms of [*Kappa**] and fitted to Eq. (3), as shown in **Figs. 8** and **9**. The fitted model shows that for a value of m = 1.5, the value of A' varies linearly in accordance to peroxide charge and temperature used during (EOP) stage. The value of A', relative to that of (EO) stage of identical temperature, appears to decrease by 1.5% for each 0.1% increment of peroxide charge. Equation (4) expresses how the stoichiometric parameter of Eq. (3) is influenced by the conditions in the (EO) or (EOP):

$$A' = 1.294 - 0.00560 \bullet T - 0.122 \bullet P \qquad (4)$$

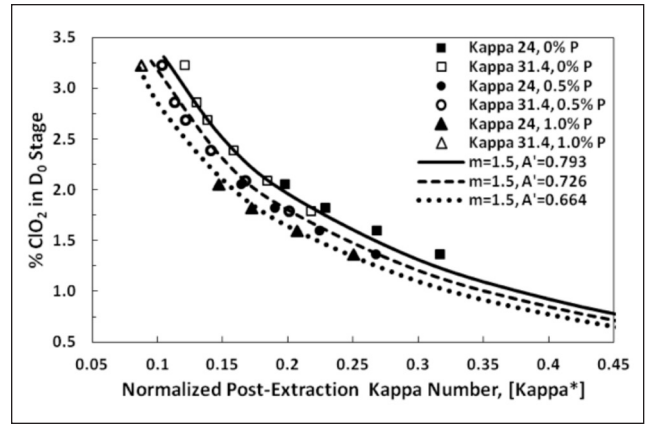
where T is the extraction temperature (in °C) and P is the percentage of peroxide used in (EOP). The generalized model seems to follow the graphical data from the two studies reasonably well; predicted ClO_2 consumption had a relative error of ±3.5% from the experimental data.

DISCUSSION

The generalized, steady-state models for D_0(EO), D_0(EOP), and D_0(EP) delignification, which are modified (and integrated) from Germgård's original stoichiometric D_0E_1 model [1], seem to reasonably predict ClO_2 uptake to obtain a targeted post-extracted kappa number. These modifications extend the utility of the original stoichiometric model to envisage the impact of oxidant-reinforced extraction conditions, such as extraction temperature and peroxide charge, as well as the pre-D_0 kappa number.



8. Chlorine dioxide consumption (as ClO_2 on pulp) in the D_0 stage to the normalized post-(EOP) kappa number (i.e., [Kappa*] = [Kappa]/[$Kappa_0$]) with different pre-D_0 kappa numbers (i.e., [$Kappa_0$]) and (EOP) peroxide levels (at 70°C). Data fitted to Eq. (3). Source data for softwood brownstocks with [$Kappa_0$] of 24 [15,16] and 31.4 [13].



9. Chlorine dioxide consumption (as ClO_2 on pulp) in the D_0 stage to the normalized post-(EOP) kappa number (i.e., [Kappa*] = [Kappa]/[$Kappa_0$]) with different pre-D_0 kappa numbers (i.e., [$Kappa_0$]) and (EOP) peroxide levels (at 90°C). Data fitted to Eq. (3). Source data for softwood brownstocks with [$Kappa_0$] of 24 [15,16], and 31.4 [13].

Analysis of various bleaching delignification data for simple extraction (E_1 stage) and oxidant-reinforced extraction—(EO), (EP), and (EOP)—differ in their model's exponential value m. This exponent increases from unity for the D_0E_1 model to ~1.5 for the D_0(EO), D_0(EOP), and D_0(EP) models. In this work, the value of m was set at 1.5 for the oxidant-reinforced extraction stages to be able to compare the influence of extraction conditions on the stoichiometric parameter, A'. The best-fit curves for Eq. (3) generally show the value of m to be between 1.5 and 1.6; however, in the instances examined in this study, m set to 1.5 was within the uncertainty calculated for that variable.

Another curious observation from the literature data analysis is the impact of the softwood kappa number entering into the D_0 stage. Most of the modeling done in this study was for softwood pulps with kappa nos. between 20 and 35. The value of A' for the generalized model (Eq. [3]) seems to be unaffected by the entering kappa number for this kappa range. However, the value of A' seemed to shift to lower values for pulps with kappa nos. between 15 and 19 (Fig. 4 versus Fig. 5). That may reflect significant differences in how the residual lignin of low-kappa softwoods responds to chlorine dioxide delignification. Another possible explanation is that the lower kappa number pulps (<20) contain a greater proportion of hexenuronic acids (HexAs) to residual lignin than the higher-kappa-number pulps and this proportional shift affects chlorine dioxide stoichiometry.

Some of the model trends used to develop the D_0(EOP) delignification model for higher-kappa brownstocks might be applicable to the lower kappa number range, such as that

D_0 Stage % ClO_2 Experimental	% H_2O_2 in Extraction	Kappa No.	[Kappa*]	Bleaching Celignification Model Predicted % ClO_2 Consumption	Relative Error from Experimental
0	NA	19.3	1	0	-
0.59	0	9.3	0.481	0.59 (±0.06)	~0.0%
0.88	0	7.2	0.373	0.85 (±0.08)	-3.9%
1.10	0	6.3	0.326	1.00 (±0.10)	-9.5%
1.47	0	4.2	0.218	1.52 (±0.18)	+3.5%
1.76	0	3.8	0.197	1.66 (±0.20)	-5.5%
0.59	0.4	8.6	0.446	0.62 (±0.06)	+5.9%
0.88	0.4	7.1	0.368	0.81 (±0.08)	-8.1%
1.10	0.4	5.8	0.301	1.03 (±0.05)	-6.6%
1.76	0.4	3.0	0.155	1.91 (±0.26)	+8.9%
1.10	0.2	5.9	0.306	1.04 (±0.10)	-5.4%
1.76	0.2	3.2	0.166	1.87 (±0.24)	+6.5%

II. Stoichiometric ClO_2 consumption (% ClO_2 on pulp) in the D_0 stage to the normalized post-extraction kappa number (i.e., [Kappa*] = [Kappa]/[$Kappa_0$]) for an oxygen-delignified softwood pulp ([$Kappa_0$] = 19.3) [29] for 80°C (EO) or (EOP). Model calculations based on Eq. (3) with m = 1.5 and A' value calculated from Fig. 5, with corrections for extraction temperature and peroxide addition. The ~95% probability interval in predicted ClO_2 consumption is given by the ± values.

reported by Malien et al. [30] for a 19.3 kappa oxygen-delignified softwood. In this study, the authors used (EO) and (EOP) stages at 80°C with peroxide dosages between 0% and 0.4%. If the *A'* value from Fig. 5 of 0.706 for 70°C (EO) are used and adjustments are made for relative impact of temperature and peroxide, then the value of *A'* for Eq. (3) can be roughly calculated, as Table II illustrates. In this instance, the value of *A'* for the D_0(EO) at 80°C should be around 0.664, based on a ~6% decrease in *A'* for each for a Δ10°C increment in (EO) temperature, relative to 70°C. Similar estimations of *A'* can be made for the 80°C D_0(EOP) by using the rough estimation of an incremental 1.5% reduction in A' for D0(EO) for each 0.1% unit of peroxide used in (EOP). **Table II** shows the forecasted ClO_2 usage in D_0 for 80°C extraction stages, (EO) and (EOP). The relative errors in ClO_2 values from the model are well within the uncertainty of the kappa number measurement.

Of note, however, D_0(EP) or D_0(EOP) delignification can be adversely affected by excessive peroxide decomposition caused by transition metal ions and/or very high extraction temperatures (>100°C). The above generalized D_0(EOP) model is based on published data where peroxide stabilizers, such as magnesium sulfate ($MgSO_4$) or chelants, were used and extraction temperatures were <100°C. This steady-state model does not take into account peroxide decomposition, so it may under predict ClO_2 usage for a targeted extracted kappa number or over predict extraction delignification at a targeted ClO_2 charge.

The generalized delignification model of this study can be used to predict post-D_0(EO) or post-D_0(EOP) kappa numbers for a given chlorine dioxide charge by using the inverse function of Eq. (3) for m >1 (Eq. [5]):

$$[Kappa^*] = \frac{1}{\left(\frac{(m-1)*[ClO_2]}{A'}+1\right)^{1/(m-1)}} \quad (5)$$

and in the instance of m = 1.5, Eq. (5) becomes Eq. (6):

$$[Kappa^*] = \frac{1}{\left(\frac{[ClO_2]}{2A'}+1\right)^{2}} \quad (6)$$

The post-extraction kappa number is easily obtained by multiplying Eq. (5) or Eq. (6) by the softwood kappa number (i.e., [$Kappa_0$]) entering into the D_0 stage.

The generalized bleaching delignification models presented in this study could be used in conjunction with other steady-state models for chlorine dioxide brightening [14,15,17–21] for estimating bleach sequence ClO_2 consumption and optimization. The delignification model can estimate the impact of variations in brownstock kappa number, as well as oxidant-reinforced extraction conditions, on ClO_2 usage or post-extraction kappa. An attractive feature of these models is the minimum number of equation parameters to be determined and tuned.

CONCLUSIONS

A generalized, steady-state model was developed for estimating bleaching delignification and/or chlorine dioxide consumption for sequences that use oxidant-reinforced extraction. The model is a modified and integrated version of Germgård's stoichiometric model relating post-extracted kappa number reduction to ClO_2 uptake for the D_0E_1 sequence. Data from various softwood studies, which have used D_0(EO), D_0(EP), and D_0(EOP), were analyzed. It was observed that when the post-extracted kappa number was normalized, the Germgård stoichiometric model could be simplified so that bleaching delignification can be represented by a single curve for a range of incoming kappa numbers into the D_0 stage. The shape of this curve is characterized by the stoichiometric parameter, *A'*, which was found to be a simple function of oxidant-reinforced extraction conditions (e.g., extraction temperature and peroxide dosage). Low-kappa-number softwoods (15–20), such as those produced from oxygen delignification or modified kraft pulping, could be modeled as a group similar to brownstocks with kappa nos. between 24 and 35.

Predicted ClO_2 consumption for D_0(EO), D_0(EP), and D_0(EOP) sequence for given target post-extraction kappa numbers are reasonably accurate, with relative errors of ±3% to ±10% of reported laboratory experiments and r^2 values >0.94. This generalized, steady-state model is relatively simple and has minimum number of equation parameters to be determined. The model has potential for use in combination with other steady-state brightening models to predict bleach sequence bleach usage and aid in bleach sequence optimization.

LITERATURE CITED

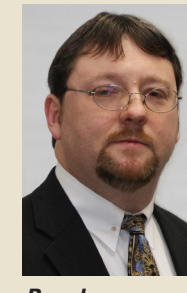
1. Germgård, U., *Svensk Papperstidn.* 85(6): R43(1982).
2. Germgård, U., Teder, A., and Tormund, D., *Nord. Pulp Pap Res. J.* 2(1): 16(1987).
3. Mortha, G., Lachenal, D., and Chirat, C., *Intl. Symp. Wood Pulping Chem., 11th*, ATIP (France), 2001, p. 447.
4. Jain, S., Mortha, G., and Christophe, C., *TAPPI J.* 8(11): 12(2009).
5. Lewis, J. R., "Modeling and control of the D_0(EOP) bleaching stages," Ph.D. dissertation, University of Washington, Seattle, WA, USA, 2009.
6. Tessier, P. and Savoie, M., *Can. J. Chem. Eng.* 75(2): 23(1997).
7. Saltin, G. and Edwards, L., *TAPPI Pulping Conf.*, TAPPI Press, Atlanta, 1993, p. 951.
8. Gu, Y. and Edwards, L., *TAPPI J.* 2(6): 19(2003).
9. Gu, Y. and Edwards, L., *TAPPI J.* 2(7): 3(2003).
10. Gu, Y. and Edwards, L., *TAPPI J.* 2(10): 3(2003).
11. Teder, A. and Tormund, D., *CPPA Trans. Tech. Sect.* 5(6): TR41(1980).
12. Brogdon, B.N. in *The Bleaching of Pulp* (P.W. Hart and A.W. Rudie, Eds.) 5th edn., TAPPI Press, Atlanta, 2012 (in press), Chap. 12.

ABOUT THE AUTHORS

Several publications have established mathematical relationships for time, chemical, and energy needed to bleach kraft pulps using ECF sequences. Steady-state models have received considerable attention for their simplicity and ease in implementing spreadsheet calculations. Often, such models are based upon stoichiometric relations between bleach consumption and kappa number or chromophore concentration.

When researching and writing the ECF bleach sequence modeling/optimization chapter for the upcoming *The Bleaching of Pulp* (5th edn.) from TAPPI Press, I discovered that there was little published on the stoichiometry for chlorine dioxide delignification. In the 1980s, Ulf Germgård proposed a mathematical expression relating the bleach consumed and the post-extracted kappa number. Unfortunately, the effects of oxidant-reinforced extraction were not included because that technology had not matured. This gap in our knowledge inspired the current work.

I wanted to demonstrate how a more generalized form of Germgård's stoichiometric model could be used to predict chlorine dioxide uptake and post-extraction kappa numbers. Model adjustments included some ideas proposed by Jack Histed and coworkers (1990) for chlorination. The new model works rather well for softwood brownstocks and oxygen-delignified pulps for D_0(EO), D_0(EP) and D_0(EOP) delignification sequences. A major advantage of this approach is the minimum number of equation parameters to be acquired and tuned.



Brogdon

Mills can use the findings to assist in their process optimization to lower overall production costs. The stoichiometric model also could be used in conjunction with existing bleaching kinetics to simulate the dynamics of a bleach sequence to process changes or to aid with process control schemes.

Several additional items could be investigated further. Can the approach be extended to hardwoods? Can the effects of black liquor carryover and chemical mixing be incorporated into the model? Can relationships be developed between post-extraction kappa numbers and brightness values for various oxidant-reinforced extraction conditions? The last point is needed if this work is coupled with existing steady-state models for ECF brightening stages.

Brogdon is senior consultant at FutureBridge Consulting & Training, Marietta, GA, USA. Email the author at Brian.Brogdon@gmail.com.

13. van Lierop, B., Faubert, M., Sacciadis, G., et al., *TAPPI Fall Tech. Conf.*, TAPPI Press, Atlanta, 2004, Conf. CD, Session 18-2.

14. Hart, P.W. and Connell, D., *TAPPI J.* 5(4): 23(2006).

15. Brogdon, B.N., *TAPPI J.* 9(8): 27(2010).

16. Basta, J., Andersson, L., Blom, C., et al., *TAPPI Pulping Conf.*, TAPPI Press, Atlanta, 1992, p. 547.

17. McDonough, T.J., *TAPPI Pulping Conf.*, TAPPI Press, Atlanta, 1996, p. 201.

18. McDonough, T.J., Rawat, N., and Turner, M., *Appita Annu. Gen. Conf. Proc.*, Appita, Melbourne, Australia,1997, p. 255.

19. McDonough, T.J., Krishnagopalan, G.A., Rawat, N., et al., *Intl. Symp. Wood Pulping Chem., 10th*, Yokohama, Japan, 1999, p. 269.

20. McDonough, T.J., Rawat, N. and Krishnagopalan, G.A., *Appita J.* 57(5): 381(2004).

21. McDonough, T.J., Uno, S., Rudie, A.W., et al., *TAPPI J.* 7(1): 4(2008).

22. Histed, J.A., Canovas, R.V., and Ruscitti, G., *TAPPI Pulping Conf.*, TAPPI Press, Atlanta, 1991, p. 697.

23. Brogdon, B.N. "The effect of ethanol media on chlorine dioxide and extraction stages for kraft pulp bleaching," Ph.D. dissertation, Institute of Paper Science and Technology, Atlanta, 1997.

24. Chirat, C., Lachenal, D., and Morthra, G., *TAPPI Pulping Conf. Proc.*, TAPPI Press, Atlanta, 2000, Conf. CD.

25. Rapson, W.H. and Bertil, C.B., *Intl. Pulp Bleaching Conf. Proc.*, CPPA, Montréal, QC, Canada, 1985, p. 227.

26. Histed, J.A., Canovas, R.V., and Ruscitti, G., *Tappi J.* 73(10): 201(1990).

27. van Lierop, B., Faubert, M.G., Labonté, S., et al., *PAPTAC Annu. Meet., 85th*, PAPTAC, Montréal, 1999, p. B133.

28. Reeve, D.W. and Weishar, K.M., *Bleach Plant Oper. Semin.*, TAPPI Press, Atlanta, 1991, p. 137.

29. Malinen, R., Rasimus, R., and Rantanen, T., *TAPPI Pulping Conf.*, TAPPI Press, Atlanta, 1993, p. 925.

30. Taylor, J.R. in *An Introduction to Error Analysis: The Study of Uncertainties in Physical Measurements* 2nd edn., University Science Books, Sausalito, CA, USA, 1997, Chap. 3.

31. Runge, T.M. and Ragauskas, A.J., *Holzforschung* 53(6): 623(1999).