

Generalized steady-state stoichiometric models for chlorine dioxide brightening stages for softwood kraft pulps

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ABSTRACT: A generalized, steady-state model is proposed for predicting brightness and/or bleach consumption during chlorine dioxide brightening (D_1 and D_2) of softwood pulps treated with chlorine dioxide delignification sequences. The model is adapted from the D_1 hardwood model of McDonough and co-workers, which related chlorine dioxide consumption to brightness gains with three tunable parameters. Literature data from various elemental chlorine-free bleaching studies were analyzed to find generalized relationships for the models' parameters. Data analysis revealed that the ultimate brightness limits for both D_1 and D_2 models, at excessively high bleach charges, were approximately 92% ISO. Another parameter for the D_1 model was found to be a linear function of extracted kappa number, whereas for the D_2 model, the parameter was a linear function of post- D_1 brightness. The third equation parameter for the D_1 and D_2 models was found to be a function of the other two parameters and the entering brightness value. The generalized brightening models predict D_1 brightness to $\pm 1\%$ ISO units and D_2 brightness to $\pm 0.3\%$ ISO units for a given bleach charge consumed. These relatively simple brightening models, which have a minimum number of equation parameters, can be used in conjunction with other bleaching delignification models to simulate bleach consumption for a given ECF sequence.

Application: Process engineers can use the modified stoichiometric models to optimize chemical usage and troubleshoot problems in the bleach plant.

Chlorine dioxide consumption contributes significantly to the bleaching costs of softwoods [1–7]. Most modern-day bleach plants use chlorine dioxide to both delignify and brighten brownstocks and oxygen-delignified pulps [8,9]. Proper proportioning of chlorine dioxide for delignification (D_0) and brightening (D_1 and D_2 [if used]) is crucial for minimizing bleaching costs [2,4–7,10]. Overuse of chlorine dioxide in the D_0 stage, unlike in the past with chlorine for chlorination [6,10,11], affords minimum bleach savings for brightening while marginally reducing the extracted kappa number [1–6,10]. Numerical models, which can simulate multistage bleach sequences based upon various variable inputs and constraints [2–7,10,12–23], can aid process engineers with optimizing chemical usage and with troubleshooting in the bleach plant.

Several researchers have developed steady-state models for the various D stages of elemental chlorine-free (ECF) bleach sequences [2,4,6,16–24]. In some studies, these stoichiometric equations have been used to mathematically quantify how changes made at the kraft digester affect the brightening response of the resulting pulp (i.e., bleachability) [16–21]. In other studies, the equations have been used to determine the optimum chlorine dioxide dosages for D_0 and D_1 (or $D_1E_2D_2$) [2,4,6,17–22]. The mathematical simplicity of these stoichiometric models allows them to be easily implemented into a spreadsheet software program.

These models, however, have the drawback of limited applicability beyond their original experimental constructs. Brogdon [4,6] developed a statistical response surface model for various three- and a five-stage ECF sequences for a 24-kappa softwood brownstock. Unfortunately, the author's model was limited to this one brownstock (which was based upon the laboratory data of Basta et al. [25]). Hart and Connell [3] improved upon the McDonough et al. [17–20] bleach response model to predict the chlorine dioxide consumption for an ECF sequence. Their model handled a range of brownstock kappa numbers and chlorine dioxide charges in the D_0 and the D_1 stages to predict postbleached brightness. However, that model was limited to the $D_0(EP)D_1$ sequence with fixed (EP) conditions (i.e., a single peroxide charge [3,6]). The brightening response models of McDonough and others [16–21] can predict bleach consumption for D_1 or D_1 and D_2 for specific kraft pulps. Nonetheless, the equation parameters of the model have to be determined and tuned predicated upon the conditions used during kraft pulping and bleaching delignification [16–21,26].

The primary goal of this paper is to present a more encompassing mathematical model for chlorine dioxide brightening that predicts pulp brightness for a given bleach charge and vice versa. Previous work [23,24] has been successful for developing generalized expressions for chlorine dioxide delignification coupled with oxidant-reinforced extraction; these

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expressions can handle a range of pre-D₀ kappa numbers, as well as variable oxidant-reinforced extraction conditions.

LITERATURE DATA ANALYSIS OF SOFTWOODS

Published softwood bleaching data from various studies [2,16,17,25,27–31] were reanalyzed to obtain stoichiometric brightness expressions. The partial bleach sequence prior to chlorine dioxide brightening is given in **Table I**. The brightness vs. chlorine dioxide consumption data were fitted to selected mathematical models using the statistical curve-fitting program WinCurveFit (v. 1.1.6, Kevin Raner Software; Mt. Waverly, Victoria, Australia). The software program employed a quasi-Newton method (Davidon-Fletcher-Powell al-

gorithm) for minimizing the lack-of-fit for the nonlinear and linear regressions. The 95% confidence intervals [CI] of the mathematical expressions were calculated from the program's computed standard errors of regression for the equation parameters multiplied by the appropriate t-statistic (Student's t distribution, two-tail).

MODELING FIRST CHLORINE DIOXIDE BRIGHTENING STAGE

Initial attempts were made to develop a brightening model that was similar to an earlier stoichiometric model for chlorine bleaching delignification [23]. Data taken from several D₁ brightening studies [2,17,27] were analyzed by plotting the

Bleaching Study	Kraft Pulp Type	Kappa No.	Bleaching Delignification		D ₁ Conditions	E ₂	D ₂ Conditions
			Sequence	Conditions			
Brogdon and Lucia [27]	Black spruce (<i>Picea mariana</i>) Conventional pulping	25.0	D ₀ E; D ₀ (EO); D ₀ (EP); D ₀ (EOP)	0.20 KF D ₀ ; 0.5% H ₂ O ₂ in (EP) or (EOP)	0%–4.0% ClO ₂ ; ~4 pH	—	—
McDonough [16]	Loblolly pine (<i>Pinus taeda</i>) Conventional pulping	28.0	D ₀ (EO)	0.19 KF D ₀ ; 70°C (EO)	0%–1.2% ClO ₂ ; ~4 pH	Yes	0%–0.8% ClO ₂ ; ~4 pH
McDonough [16]	Loblolly pine (<i>P. taeda</i>) Conventional pulping	18.5	D ₀ (EO)	0.19 KF D ₀ ; 70°C (EO)	0%–1.2% ClO ₂ ; ~4 pH	Yes	0%–0.8% ClO ₂ ; ~4 pH
McDonough [16]	Loblolly pine (<i>P. taeda</i>) Modified kraft	14.5	D ₀ (EO)	0.19 KF D ₀ ; 70°C (EO)	0%–1.2% ClO ₂ ; ~4 pH	Yes	0%–0.8% ClO ₂ ; ~4 pH
McDonough et al. [17]	Southern U.S. pines 4,000 H-factor Conventional pulping	15.7	D ₀ (EO)	0.20 KF D ₀ ; 70°C (EO)	0%–1.6% ClO ₂ ; ~4 pH	Yes	0%–0.9% ClO ₂ ; ~4 pH
McDonough et al. [17]	Southern U.S. pines 2,100 H-factor Conventional pulping	14.6	D ₀ (EO)	0.20 KF D ₀ ; 70°C (EO)	0%–1.6% ClO ₂ ; ~4 pH	Yes	0%–0.9% ClO ₂ ; ~4 pH
McDonough et al. [17]	Southern U.S. pines 1,570 H-factor Conventional pulping	26.3	D ₀ (EO)	0.20 KF D ₀ ; 70°C (EO)	0%–1.6% ClO ₂ ; ~4 pH	Yes	0%–0.9% ClO ₂ ; ~4 pH
McDonough et al. [17]	Southern U.S. pines 760 H-factor Conventional pulping	28.3	D ₀ (EO)	0.20 KF D ₀ ; 70°C (EO)	0%–1.6% ClO ₂ ; ~4 pH	Yes	0%–0.9% ClO ₂ ; ~4 pH
Annergren et al. [28]	Scandinavian softwoods (mill produced)	35.4	D ₀ (EO)	0.14 to 0.30 KF D ₀ ; 70°C (EO)	0%–2.5% ClO ₂	--	--
Basta et al. [25]	Southern U.S. pines Conventional pulping	24.0	D ₀ (EO)	0.14 to 0.23 KF D ₀ ; 90°C (EO)	0%–1.4% ClO ₂ ; ~4 pH	Yes	0%–0.95% ClO ₂ ; ~ 4 pH
Suess et al. [29,30]	Oxygen-delignified softwood (mill produced)	10.0	D ₀ E; D ₀ (EO); D ₀ (EP); D ₀ (EOP)	0.25 KF D ₀ ; 75–90°C extrac- tion; 0.25% H ₂ O ₂ in (EOP)	0%–0.76% ClO ₂	--	--
Runge [31]	Loblolly pine (<i>P. taeda</i>) Conventional pulping	30.4	D ₀ E; D ₀ (EO); D ₀ (EP); D ₀ (EOP)	0.20 KF D ₀ ; 0.5% H ₂ O ₂ in (EP) or (EOP)	0.75% ClO ₂	Yes	0%–0.8% ClO ₂ ; ~4 pH
Hart and Connell [2]	Southern U.S. pine mix Modified kraft	13.5, 17.1, 25.4, and 32.6	D ₀ (EP)	0.05 to 0.40 KF D ₀ ; 0.6% H ₂ O ₂ in (EP)	0%–3.0% ClO ₂ ; ~4 pH	--	--

I. Elemental chlorine-free bleaching conditions reported for the various literature studies.

fraction of chromophores remaining after the D_1 vs. the D_1 stage charge multiple, m_1 . This multiple ratios the chlorine dioxide consumed in the D_1 stage to the pulp's extracted kappa number. This normalizes the amount of bleach consumed for variations in the post-extraction kappa number; several investigators [7,21,26] have used this charge multiple to compare brightening curves for a given bleach demand. The amount of chromophores in the pulp, denoted as the absorption coefficient (k), is calculated from the pulp's brightness by the Kubelka-Munk remission function [6], as in Eq. (1):

$$\frac{k}{s} = \frac{(1 - \frac{\text{Brightness}}{100})^2}{2(\frac{\text{Brightness}}{100})} \quad (1)$$

where s is the light scattering coefficient. The fraction of chromophores remaining, denoted as k^* , is derived by dividing the calculated k/s value from the D_1 brightness by the initial k/s value. The initial k/s value is determined from the post-extracted brightness. It is known that chemical pulp bleaching does not affect the light-scattering coefficient [6], so the light-scattering term drops out when calculating k^* .

Plots of k^* vs. m_1 are shown in **Fig. 1**, which yielded a stoichiometric curve. The curve was modeled using an expression derived from the D_0 (EO) delignification model [23], as in Eq. (2):

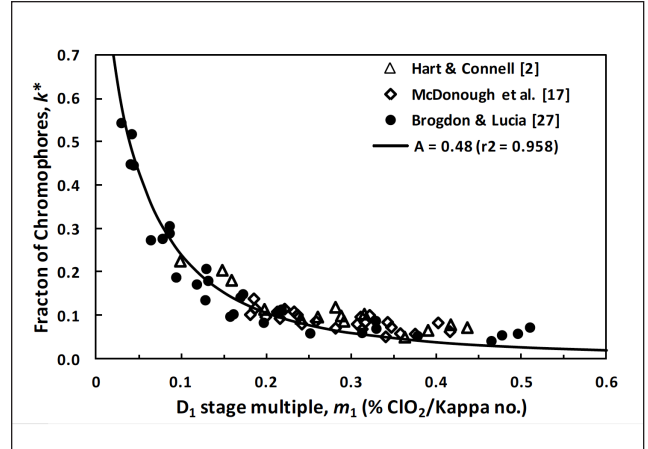
$$k^* = \frac{1}{(\frac{m_1}{2A} + 1)^2} \quad (2)$$

where A is the stoichiometric parameter of the D_1 stage. Equation (2) has its origins from the integrated stoichiometric expressions of Teder and Tormund [33] for the D_1 stage. Predicted brightness values calculated from Eq. (2) significantly deviated from the experimental values by $\pm 1.0\%$ to $\pm 4.0\%$ ISO units. Additional work with Eq. (2) was abandoned due to the model's shortcomings to accurately predict D_1 brightness. However, Eq. (2) can be used as a crude first approximation of the chlorine dioxide uptake for D_1 stages for a given brightness target.

McDonough et al. [17] suggested a simple mathematical relationship between the amounts of chlorine dioxide consumed (x_1) in D_1 to the post- D_1 brightness (y_1), as in Eq. (3):

$$y_1 = b_{01} + b_{11}(1 - e^{-b_{21}x_1}) \quad (3)$$

where b_{01} is the post-extraction stage brightness, b_{11} is the maximum brightness increase achieved in D_1 , and b_{21} is the brightening response index of the D_1 stage. The quantity $b_{01} + b_{11}$ denotes the asymptotic brightness of the D_1 stage. The brightening response index characterizes how rapidly D_1 brightening approaches the asymptotic brightness based



1. Stoichiometric bleach consumption (% on pulp) for the D_1 stage to the fraction of chromophores remaining after extraction, k^* , for various chlorine dioxide delignified pulps. Data from the various studies were fitted to Eq. (2). Refer to Table I for details of the chlorine dioxide delignified pulps.

upon the amount of bleach consumed. One limitation of Eq. (3) is determining the brightness ceiling value ($b_{01} + b_{11}$). McDonough and others [17–20] ascertained the asymptotic value by treating D_0 (EO)- or OD_0 (EO)-delignified pulps with a maximum D_1 chlorine dioxide charge of 1.6%–1.8% (on pulp as chlorine dioxide). However, Brogdon and Lucia [27], Hart and Connell [2], Parthasarthy et al. [32], and Annergren et al. [28] have reported additional D_1 brightness gains of 1.0%–3.0% ISO units when chlorine dioxide charges were above 1.8%. McDonough et al. [26], in a later D_1 -stage study, noted the difficulties with calculating well-defined brightness ceilings for red oak kraft pulps. The authors proposed an alternative D_1 brightness model (Eq. [4]):

$$y_1 = c_{01} - \frac{c_{11}}{m_1 + c_{21}} \quad (4)$$

The constant c_{01} denotes the asymptotic brightness of the D_1 stage, whereas the constants c_{11} and c_{21} determine the brightening response for a given chlorine dioxide charge multiple. The value of c_{11}/c_{21} represents the maximum brightness gain in the D_1 stage relative to the entering pulp brightness (i.e., post-extracted brightness). Thus, the quantity of $c_{01} - c_{11}/c_{21}$ is fixed by the brightness of the post-extracted pulp. The chlorine dioxide charge multiple, m_1 , of Eq. (4) can be replaced with the chlorine dioxide consumed (x_1) in D_1 (Eq. [5]):

$$y_1 = c_{01} - \frac{\beta_{11}}{x_1 + \beta_{21}} \quad (5)$$

where the equation parameters β_{11} and β_{21} are analogous to c_{11} and c_{21} but are based upon x_1 .

The D_1 bleaching data from McDonough et al. [17] were

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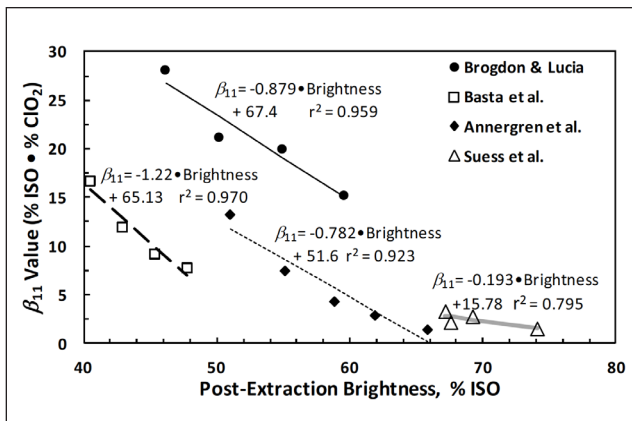
fitted to Eq. (5). Values of the D_1 brightness ceiling, c_{01} , are shown in **Table II**. The brightness ceiling values are close to the ultimate brightness limit of approximately 92% ISO that is generally reported for kraft pulps brightened with chlorine dioxide [28,34–39]. A similar analysis was performed with the D_1 data sets from Brogdon and Lucia [27], Annergren et al. [28], Basta et al. [25], and Suess and others [29,30]. These analyses also yielded a c_{01} value of approximately 92% ISO

brightness, regardless of the D_0 kappa factor (KF) used, the pre- D_0 kappa number, or the extraction stage conditions. These observations suggested that Eq. (5) could be simplified to two tunable equation parameters, β_{11} and β_{21} .

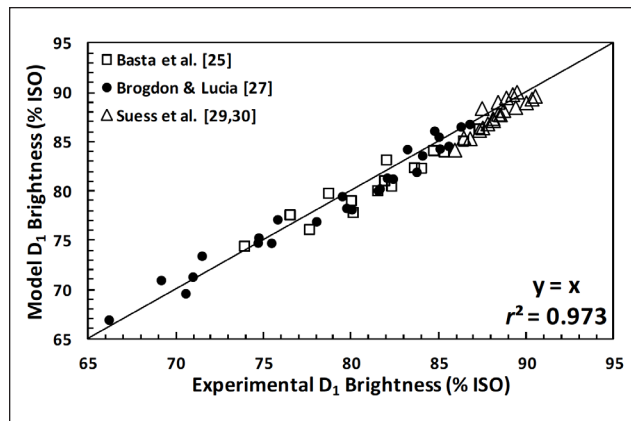
Data from various D_1 bleaching investigations [2,17,25,27–30] were explored. These investigations examined several chlorine dioxide charges in the D_1 stage and reported post-extraction brightness and/or post-extraction kappa number

Data Source	Pulp Kappa No.	Bleaching Delignification	Extracted		Model D_1 Brightness Ceiling of c_{01} (% ISO)	Standard Error of c_{01} (% ISO)	95% CI of c_{01} (% ISO)
			Kappa No.	Brightness (% ISO)			
McDonough et al. [17]	15.7	$D_0(\text{EO}); 0.20 \text{ KF}$	3.9	48.2	95.1	± 3.2	Not calculated
McDonough et al. [17]	14.6	$D_0(\text{EO}); 0.20 \text{ KF}$	3.6	53.4	90.5	± 5.7	Not calculated
McDonough et al. [17]	26.3	$D_0(\text{EO}); 0.20 \text{ KF}$	4.4	50.6	86.6	± 0.7	Not calculated
McDonough et al. [17]	28.3	$D_0(\text{EO}); 0.20 \text{ KF}$	4.0	53.7	90.6	± 5.1	Not calculated
Annergren et al. [28]	35.4	$D_0(\text{EO}); 0.14 \text{ KF}$	Not reported	51.0	87.0	± 0.4	± 1.6
Annergren et al. [28]	35.4	$D_0(\text{EO}); 0.18 \text{ KF}$	Not reported	55.1	89.3	± 0.7	± 2.8
Annergren et al. [28]	35.4	$D_0(\text{EO}); 0.22 \text{ KF}$	Not reported	58.8	90.7	± 0.3	± 1.2
Annergren et al. [28]	35.4	$D_0(\text{EO}); 0.26 \text{ KF}$	Not reported	61.9	92.0	± 0.5	± 2.3
Annergren et al. [28]	35.4	$D_0(\text{EO}); 0.30 \text{ KF}$	Not reported	65.8	92.7	± 0.3	± 0.9
Brogdon and Lucia [27]	25.0	$D_0E_1; 0.20 \text{ KF}$	7.8	46.2	92.8	± 1.6	± 3.9
Brogdon and Lucia [27]	25.0	$D_0(\text{EO}); 0.20 \text{ KF}$	6.2	50.2	93.2	± 2.2	± 5.6
Brogdon and Lucia [27]	25.0	$D_0(\text{EP}); 0.20 \text{ KF};$	5.8	54.9	95.0	± 1.6	± 4.1
Brogdon and Lucia [27]	25.0	$D_0(\text{EOP}); 0.20 \text{ KF};$	5.7	59.6	91.9	± 0.8	± 2.1
Basta et al. [25]	24.0	$D_0(\text{EO}); 0.15 \text{ KF};$	5.0	40.6	90.0	± 0.5	± 2.4
Basta et al. [25]	24.0	$D_0(\text{EO}); 0.175 \text{ KF};$	4.6	42.9	91.2	± 0.3	± 1.5
Basta et al. [25]	24.0	$D_0(\text{EO}); 0.20 \text{ KF};$	4.2	45.3	92.0	± 0.5	± 1.0
Basta et al. [25]	24.0	$D_0(\text{EO}); 0.225 \text{ KF};$	3.7	47.8	92.5	± 0.3	± 1.2
Suess et al. [29,30]	10.0	$D_0E_1; 0.25 \text{ KF}$	2.6	67.2	90.9	± 0.1	± 0.3
Suess et al. [29,30]	10.0	$D_0(\text{EO}); 0.25 \text{ KF};$	2.0	69.3	92.0	± 0.2	± 0.6
Suess et al. [29,30]	10.0	$D_0(\text{EO}); 0.25 \text{ KF};$	2.4	67.6	91.8	± 0.4	± 1.1
Suess et al. [29,30]	10.0	$D_0(\text{EOP}); 0.25 \text{ KF};$	2.1	74.2	93.5	± 0.4	± 1.2

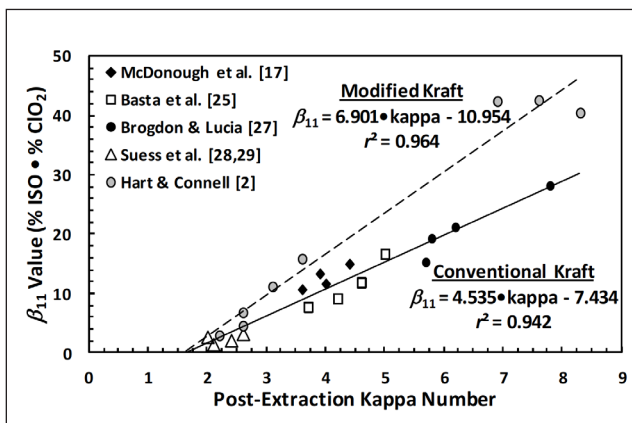
II. Calculated D_1 brightness ceiling values, c_{01} , of Eq. (5) from the curve fitting of various laboratory bleaching data sets with their associated 95% confidence intervals (CI).



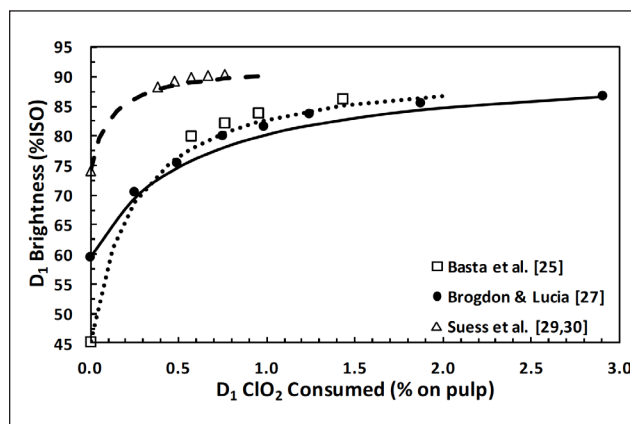
2. Linear trends of the β_{11} parameter of the D_1 brightness model (Eq. [5]) to the post-extracted brightness for selected D_1 brightening data sets. The β_{11} value is determined where the D_1 brightness ceiling, c_{01} , was set to 92% ISO. Refer to Table I for details of the chlorine dioxide delignified pulps.



4. Predicted brightness values from the D_1 model (Eq. [5]) vs. experimental brightness values reported for selected D_1 stage data at various chlorine dioxide charges. Refer to Table I for details of the chlorine dioxide delignified pulps.



3. Linear relationships of the β_{11} parameter of the D_1 brightness model (Eq. [5]) to the post-extracted kappa number for conventional and modified kraft pulps. The β_{11} value is determined where the D_1 brightness ceiling, c_{01} , was set to 92% ISO. Refer to Table I for details of the chlorine dioxide delignified pulps.



5. Predicted brightness values from the D_1 model (Eq. [5], various lines) compared to experimental data (various symbols) for selected D_1 bleaching studies.

values. The primary objective was to determine whether there was a relationship between the β_{11} value and the pulp's initial brightness or kappa number. The β_{11} value was determined with $c_{01} = 92\%$ ISO. **Figure 2** is a plot of β_{11} vs. post-extracted brightness. Linear regression of the data sets yielded various expressions that had relatively high coefficient of correlation values (r^2), which were >0.92 in most cases. No specific relationship was readily apparent that could explain the variation of the slopes and abscissa or ordinate intercept values among the data sets. However, a plot of β_{11} vs. the post-extracted kappa afforded a generalized linear relationship (**Fig. 3**) for conventional and modified kraft pulps. These relationships had a relatively high coefficient of variation values ($r^2 > 0.94$) over the range of extracted kappa numbers examined. The two types of kraft pulps had x -intercept values that approached approximately 1.6 kappa. Because β_{11} can be

calculated from the extraction kappa number of Fig. 3, the β_{21} value can be determined from the pulp's extracted brightness (i.e., post-extracted brightness = $92 - \beta_{11} / \beta_{21}$).

Figure 4 shows the predicted vs. the laboratory measured D_1 brightness values for the data sets from Brogdon and Lucia [27], Basta et al. [25] and Suess and others [29,30]. The brightness model (Eq. [5]) employed the parameters calculated from the post-extracted kappa and brightness values. **Figure 5** shows selected examples of D_1 brightness development vs. bleach consumed for the studies analyzed. The forecasted D_1 brightness was relatively close to the experimentally measured value, usually with $\pm 1.0\%$ ISO units. These differences in brightness are close to the variation observed with well-controlled laboratory studies [31,40,41], which can vary by $\pm 0.7\%$ ISO units (95% CI) for D_1 .

MODELING FINAL CHLORINE DIOXIDE BRIGHTENING STAGE

The original brightening model that McDonough [16] proposed was for the terminal D stage of a five-stage ECF se-

quence (i.e., D_2). Equation (6) shows this model, which is similar to Eq. (3) for the D_1 stage:

$$y_2 = b_{02} + b_{12}(1 - e^{-b_{22}x_2}) \quad (6)$$

where y_2 is the post- D_2 brightness, x_2 is the percentage of chlorine dioxide consumed in D_2 , b_{02} is the pre- D_2 stage brightness, b_{12} is the maximum brightness increase across D_2 , and b_{22} is the brightening response index. Likewise, the value of $b_{02} + b_{12}$ represents the upper brightness limit of the final stage. The b_{02} value is equated with the brightness exiting from D_1 or from D_1E_2 . Typically, the second extraction stage, E_2 , does not greatly affect the post- D_1 brightness unless the stage is reinforced with peroxide [25,38,42,43]. In later works, McDonough et al. [19,21,26] indicated that b_{12} and b_{22} parameters were either linear or quadratic functions of b_{02} . Equation (6) was successfully used by the authors to predict D_2 brightening when $\leq 1\%$ chlorine dioxide was consumed. Unfortunately, the expressions relating b_{12} and b_{22} to b_{02} are limited to softwood pulps treated with a fixed KF charge of 0.20 for D_0 (EO) or OD_0 (EO) sequences. In addition, the empirical functions relating these parameters are highly specific to the kraft pulping conditions employed by the authors in the study (e.g., altered liquor concentration profiles and/or effective alkali charge). These drawbacks restrict the generalization of Eq. (6).

To overcome some of these limitations for softwood pulps, a version of Eq. (5) was examined as a model for D_2 brightening (Eq. [7]):

$$y_2 = c_{02} - \frac{\beta_{12}}{x_2 + \beta_{22}} \quad (7)$$

where c_{02} is the D_2 brightness ceiling, and β_{12} and β_{22} are analogous to β_{11} and β_{21} , respectively, but are based upon x_2 .

Similarly, the quotient, β_{12}/β_{22} , represents the maximum brightness gain in D_2 relative to pulp's pre- D_2 brightness (i.e., post- D_1 brightness).

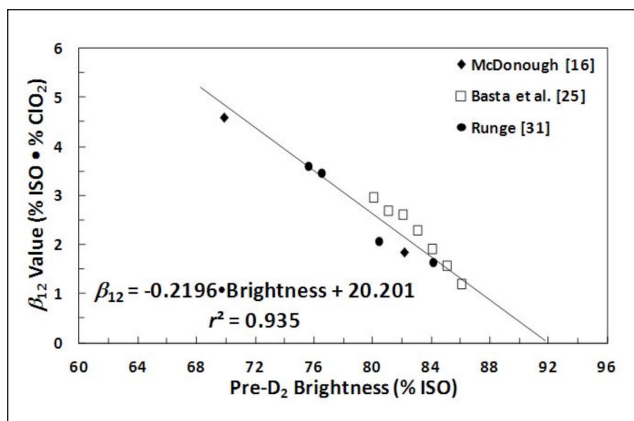
The experimental data from the D_2 bleaching studies of Basta et al. [25], Runge [31], and McDonough [16] were fitted to Eq. (7). The data sets had entering D_2 brightness values ranging from 70% to 85% ISO. The asymptotic D_2 brightness, like those earlier from the D_1 stage, afforded a value of approximately 92% ISO, which was within the estimated 95% CI of the nonlinear regression analyses (Table III). This suggested that c_{02} of Eq. (5) could be set to 92% ISO, regardless of prior ECF bleach sequence conditions.

The β_{12} parameter was then determined for the various D_2 data sets while c_{02} was fixed constant at 92% ISO. The value of β_{12} decreased linearly as the entering D_2 pulp brightness level increased (Fig. 6); the relationship had a relatively high coefficient of correlation ($r^2 > 0.93$). Another noteworthy observation from the β_{12} regression analysis was the abscissa intercept value, which was approximately 92% ISO. As the D_1 brightness (pre- D_2 brightness) approaches its asymptotic value, the β_{12} parameter for the D_2 stage model approaches zero. This observation is consistent with the maximum brightness ceiling obtainable with either a final D_2 stage or a final D_1 stage using the proposed brightening models (i.e., Eqs. [3] and [5]). The β_{22} parameter can be calculated from the entering brightness and the β_{12} parameter (i.e., pre- D_2 brightness = $92 - \beta_{12}/\beta_{22}$).

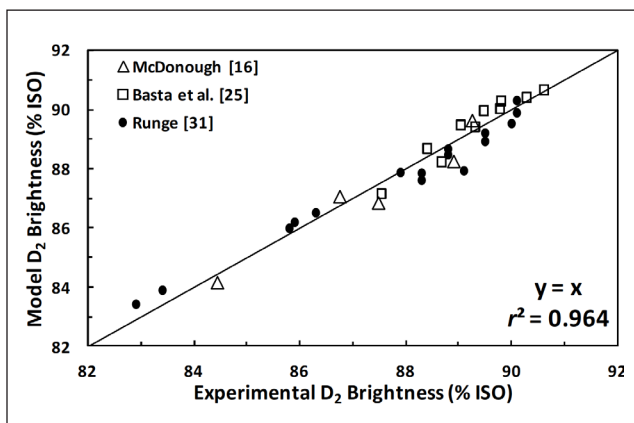
Figure 7 shows the predicted vs. experimentally measured D_2 brightness for the data sets from Runge [31], Basta et al. [25], and McDonough [16], where Eq. (7) used the incoming D_2 brightness value and the relationship in Fig. 6. Figure 8 shows selected examples of D_2 brightness development vs. chlorine dioxide consumed for the bleaching studies scrutinized. Forecasted D_2 brightness values were

Data Source	Pulp Kappa No.	Prior Bleaching	Pre- D_2 Brightness	Model D_2 Brightness Ceiling, c_{02} (% ISO)	Standard Error of c_{02} (% ISO)	95% CI of c_{02} (% ISO)
Runge [31]	30.4	$D_0E_1D_1E_2$	75.5	94.3	± 1.2	± 5.0
Runge [31]	30.4	D_0 (EO) D_1E_2	76.4	93.6	± 0.9	± 3.6
Runge [31]	30.4	D_0 (EP) D_1E_2	80.5	93.2	± 1.6	± 6.8
Runge [31]	30.4	D_0 (EOP) D_1E_2	84.1	91.8	± 0.5	± 2.4
Basta et al. [25]	24.0	D_0 (EO) D_1E_2	83.0	90.6	± 0.2	± 0.8
Basta et al. [25]	24.0	D_0 (EO) D_1E_2	85.0	91.3	± 0.3	± 1.0
McDonough [16]	28.0	D_0 (EO) D_1E_2	70.3	90.4	± 0.0	Not calculated
McDonough [16]	28.0	D_0 (EO) D_1E_2	81.4	90.1	± 0.9	Not calculated
McDonough [16]	18.5	D_0 (EO) D_1E_2	84.0	93.9	± 1.8	Not calculated
McDonough [16]	14.5	D_0 (EO) D_1E_2	84.8	91.2	± 0.3	Not calculated

III. Calculated D_2 brightness ceiling values, c_{02} , from curve fitting of various D_2 data to Eq. (7) with their associated 95% CI.



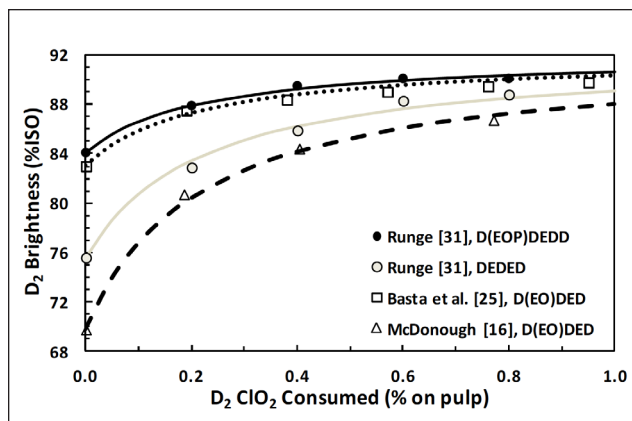
6. Linear relationship of the β_{12} parameter of the D_2 brightness model (Eq. [7]) to the pre- D_2 brightness value (i.e., post- D_1 brightness) for selected bleaching studies. The β_{12} value is determined where the D_2 brightness ceiling, c_{01} , was fixed at 92% ISO. Refer to Table I for details of the pre- D_2 pulps.



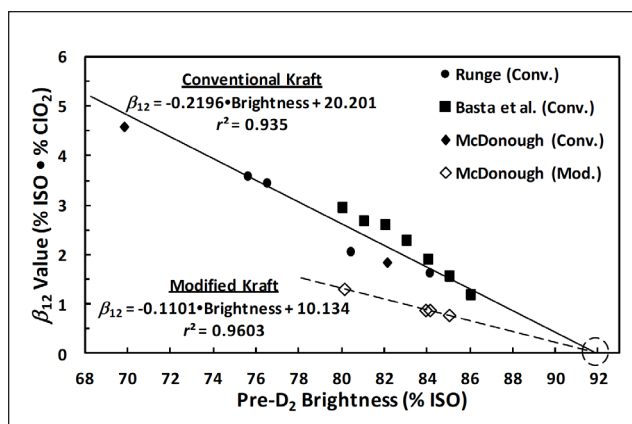
7. Predicted brightness values from the D_2 model (Eq. [7]) vs. experimental brightness values reported for selected D_2 stage data at various chlorine dioxide charges. Refer to Table I for details of the pre- D_2 pulps.

comparatively close to the experimentally measured values, typically within $\pm 0.4\%$ ISO units. This difference is within the experimental variation $\pm 1.0\%$ ISO units seen for laboratory D_2 studies (at the 95% CI) [31].

McDonough noted in his D_2 investigation [16] that kraft pulps produced by a modified kraft pulping process bleached differently than conventional kraft pulps. The D_2 bleaching data from the author's study were analyzed with Eq. (7) with c_{02} set at 92% ISO. When the β_{12} parameters were plotted against the corresponding pre- D_2 brightness values (Fig. 9), it yielded a linear relationship, similar to the relationship observed for conventional pulps. The slope shifted to -0.11% chlorine dioxide while the abscissa intercept remained constant at 92% ISO. This observation indicated that the β_{12} parameter can be affected by the conditions employed during kraft pulping. Thus, the D_2 brightening model (Eq. [7]) is congruent with the findings of McDonough [16].



8. Predicted brightness values from the D_2 model (Eq. [7], various lines) compared to experimental data (various symbols) for selected D_2 bleaching studies. Refer to Table I for details of the pre- D_2 pulps.



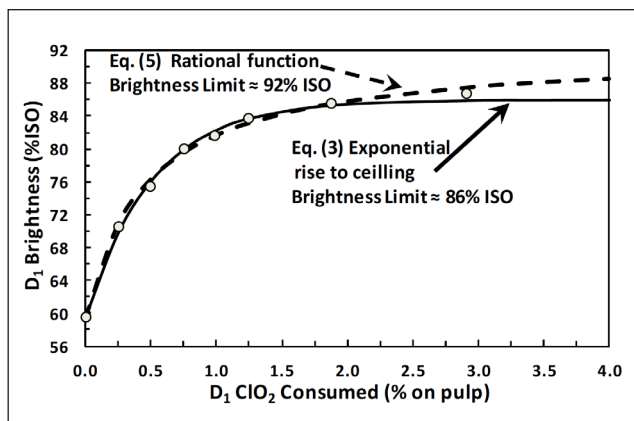
9. Comparison of conventional (solid symbols) vs. extended kraft (open symbols) cooks on the relationship of the β_{12} parameter of the D_2 brightness model (Eq. [7]) to the pre- D_2 brightness for selected bleaching studies. The β_{12} value is determined where the D_2 brightness ceiling, c_{01} , was fixed at 92% ISO. Refer to Table I for details of the pre- D_2 pulps.

DISCUSSION

Generalized steady-state models for D_1 and D_2 brightening, which were based on Eqs. (5) and (7), respectively, accurately forecasted brightness development for a given amount of chlorine dioxide consumed. Calculated brightness values with the D_1 model were usually within $\pm 0.5\%$ to $\pm 1.5\%$ ISO units of the actual value, whereas with the D_2 model, calculated values were within $\pm 0.1\%$ to $\pm 0.4\%$ ISO units. These models can be employed to calculate the amount of chlorine dioxide needed to reach a given brightness target by using their inverse function (Eq. [8]):

$$x_i = -\beta_{2i} + \frac{\beta_{1i}}{c_{0i} - y_i} \quad (8)$$

where the subscript index i is either 1 for the D_1 or 2 for the D_2 stage.



10. Comparison of the chlorine dioxide brightening models (Eqs. [3] and [5]). Both models accurately predict D_1 brightening for a given amount of chlorine dioxide consumed (approximately 0.5%–1.5% as commercially practiced). The models differ in their predicted brightness limit of the D_1 stage.

The analyses performed on the various D_1 and D_2 literature data indicated that both models have asymptotic brightness limits near 92% ISO. This limit held for a range of softwood pulps treated with various ECF bleach sequences. This observation differs from those presented by McDonough and others [16–21,26] using Eqs. (3) and (6) for D_1 and D_2 , respectively.

Brightening stages tend to show small but significant brightness gains, even at bleach levels >1.8% for D_1 and >0.8% for D_2 [2,25,27,28,32]. These high bleach dosages are normally well beyond what is commercially employed. However, the brightness ceiling parameter determined from the nonlinear regression fitting to Eqs. (3) or (6) is heavily influenced by experimental data [27] obtained at these extreme dosage levels (**Fig. 10**). This likely explains why it is difficult to find a generalized expression that relates the asymptotic brightness limit with Eqs. (3) or (6). The brightness ceiling of 92% ISO for the proposed models (Eqs. [5], [7], or [8]) follows from other bleaching studies as the upper limits for softwood treated with chlorine dioxide [28,34–38]. Also, this limit is near the asymptotic light absorption coefficient value ($k_\infty = 0.1 \text{ m}^2/\text{kg}$ [6,34]) reported for chlorine dioxide bleaching kinetics (approximately 92% ISO for softwood with $s \approx 25\text{--}35 \text{ m}^2/\text{kg}$ [44]; Eq. [1]). Setting the upper brightness limits to a fixed value eliminates it as a parameter to be tuned; it also has the extra benefit of circumscribing the other two parameter values of the brightening models.

The β_{11} value of Eq. (5) is generally a linear function of either the post-extraction brightness or kappa number. The extracted kappa number of the pulp yielded a linear expression (Fig. 3), whereas the extracted brightness typically yielded various linear expressions with different axis intercepts and slope values (Fig. 2). The β_{12} parameter is calculated from the extraction brightness and β_{11} value. The characteristic bleaching response in the D_1 stage is set by β_{11} and β_{21} , which in turn, is dependent upon the extracted kappa number and brightness. Thus, how a softwood kraft pulp responds to an

ECF delignification sequence in terms of extracted kappa number and brightness likely determines its chlorine dioxide response in the subsequent D_1 stage [45].

It is interesting to note the x-axis intercept value of Fig. 3 is approximately 1.6 for conventional and modified kraft pulps. This intercept is close to the limiting floor-level kappa number of approximately 1.5, which Chirat and co-workers [46] reported for the chlorine dioxide delignification of softwoods. Also, it appears that modifications made to the kraft pulping process will impact the linear function relating the β_{11} value to the extracted kappa number. In addition, the β_{11} value seems less sensitive to small changes in the extracted kappa numbers when in the range of 2–2.5 (Fig. 3). This observation fits with the conclusions of Ragnar [47], who noted that D_1 -stage brightness control with the post-extracted kappa becomes less responsive once the extracted kappa number drops below 2.5.

The β_{12} parameter of Eq. (7) is a linear function of the pre- D_2 brightness (i.e., post- D_1 brightness). The slope of this linear relationship is generally constant for conventional kraft pulps, but it can be affected by the pulping conditions. This observation with D_2 model (Eq. [7]) is in agreement with bleachability differences reported by McDonough and others [16–20]. The linear relationship between β_{12} and pre- D_2 brightness is consistent with the stage's brightness limit of 92% ISO, where the x-axis intercept is this asymptotic value. The characteristic bleaching response from the D_2 model is influenced by the entering brightness, which is linked to the extracted kappa number and the extracted brightness from the D_1 model, as well as the prior kraft pulping conditions.

An advantage of the proposed brightening models is the models' ability to predict bleaching responses to changes made during ECF bleaching delignification. However, to utilize this added functionality, mathematical expressions are needed that link bleaching delignification, such as the earlier study [23], to extracted brightness. A subsequent investigation [45] proposes some relationships that pair extracted kappa numbers to their extracted brightness values, which will allow for the coupling of ECF delignification and brightening models to simulate a steady-state bleach sequence.

CONCLUSIONS

Steady-state stoichiometric models for chlorine dioxide brightening stages were presented in this study. These models were based upon the D_1 hardwood model of McDonough et al. [26], which related brightness gains to bleach consumption with three equation parameters. Various ECF bleaching studies for softwoods were scrutinized to find generalized relationships to calculate the model parameters. It was observed that the ultimate brightness limit for the D_1 and D_2 models, which is one of the parameters, was 92% ISO. This limiting value matches the maximum brightness value seen with chlorine dioxide bleaching of softwood kraft pulps, as well as with fundamental chlorine dioxide bleaching kinetics. The second equation parameter for the D_1 model was

found to linearly vary with the extracted kappa number, whereas for the D₂ model, it linearly varied with the pre-D₂ (i.e., post-D₁) brightness. The final parameter was found to be a function of extracted brightness for the D₁ model, and pre-D₂ brightness for the D₂ model, in conjunction with the second parameter. Both models predict brightness gains for D₁ and D₂ stages to within $\pm 1.0\%$ and $\pm 0.3\%$ ISO units, respectively. These brightening models could potentially be used in combination with other steady-state delignification models to predict bleach-sequence bleach usage and aid in bleach-sequence optimization. **TJ**

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ABOUT THE AUTHORS

This work continues the series on steady-state models for elemental chlorine-free (ECF) bleach sequences (TAPPI J. 11[3]: 31[2012] and 12[2]: 17[2013]). The research was inspired when I was working on some chapters for *The Bleaching of Pulp* (5th edn.). These models have garnered significant interest for their simplicity, a feature that allows them to be easily employed in spreadsheet calculations. Such calculations can estimate optimum setpoints for bleach dosages in each stage for various scenarios, which can lower pulp manufacturing costs. The calculations also can assist with diagnosing bleach plant issues.

This work builds upon the research done by Ants Teder and Disa Tormund of STFI and by Tom McDonough and co-workers at IPST. An issue with the IPST brightening models was determining the equation parameters values. These parameters are influenced by the conditions employed during kraft pulping and bleaching delignification. This limits the generalization of the models unless the parameters are ascertained from a combined pulping and bleaching study.

I discovered, as I was examining published bleaching data, that one of the IPST brightening models, after some modifications, could be generalized for D₁ and D₂ stages. The most interesting findings was that the equation parameters were simple functions of the

pulp's kappa number and/or initial brightness entering the brightening stage, as well as a fixed brightness limit. This fixed limit corresponded to the residual chromophore limit reported in the kinetic study by Teder and Tormund. These observations attach physical meaning to the empirical equation parameters by connecting them to fundamental pulp properties. The modified models detect pulp bleachability differences caused by kraft digester conditions (e.g., modified pulping), which match the findings of McDonough and co-workers.

Additional work will develop relationships relating post-extraction kappa numbers to extracted brightness. Knowing this relationship will allow the coupling of the modified brightening models with the bleaching delignification models to simulate ECF sequences. Another issue to be investigated is whether the generalized models can be extended to model the brightening of hardwood pulps.



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