Revised steady-state model for chlorine dioxide brightening that considers extraction washer carryover effects

BRIAN N. BROGDON

ABSTRACT: In an earlier investigation, a generalized model was developed to simulate the first chlorine dioxide (ClO_2) brightening stage (D_1). That stoichiometric model accurately predicts pulp brightness values for given bleach charges and vice versa for laboratory softwood pulps. The equation parameters are dependent on the kappa number and brightness of the extracted pulp. In this study, the earlier model was refined to include the negative effects of extraction carryover to simulate more realistically a mill's D_1 stage. Extracted pulps that contain washer carryover were found to brighten as if the pulp had a kappa number equal to the sum of the extracted kappa and the kappa value of extraction dissolved solids. If this higher kappa (i.e., apparent or wet kappa) is used in place of the extracted kappa with the D_1 model, the equations suitably predicted the bleached brightness for a given bleach charge. The modified expressions were used to quantify the amount of carryover and to calculate carryover bleach consumption for a softwood D_0(EOP)D_1 fiber line. The mill's washed pulps were found to have carryover levels of 1.4 kappa units, which was consuming 48% of the total D_1 bleach charge. Additional analyses revealed that extraction carryover consumes 2.5-4.6 kg ClO_2/ton pulp per kappa unit of carryover when bleaching a pulp to 78% to 84% ISO.

Application: This revised model forecasts pulp brightness for extracted softwood kraft pulps for a variety of chlorine dioxide, extracted kappa, and washer carryover levels. It can be used to analyze bleach plant data to determine extraction washer carryover and bleach consumption caused by this material. Other applications include bleach plant optimizations, process control strategies, and computer simulations.

Multistage bleach plants consist of different oxidation stages, which further delignify, brighten, and remove dirt and shives from the brownstock or oxygen delignified pulp [1-5]. These stages are comprised of mixers, towers, and washers. Removal of dissolved materials and spent reactants during washing is important because these components can interfere with a subsequent bleaching stage [1,3-5].

Surveys [6,7] of Canadian mills in the 1990s and 2000s indicated that most bleach plants use vacuum drum washers after the extraction stage of chlorine dioxide (ClO_2) delignification sequences. Washer carryover at these mills [7], expressed as chemical oxygen demand (COD), usually ranged from 3 kg to 17 kg COD/ton pulp, with the mode being ~ 12 kg COD/ton pulp. These levels of carryover contribute an additional 0.5-3.5 kappa units to the extracted pulp that entered the D_1 stage (where a kappa unit [1 mL of 0.1 N potassium permanganate ($KMnO_4$)/g pulp] of extraction dissolved solids corresponds to ~4.8 kg COD/ton pulp [8,9]).

Several bleach plant audits [10-12] have identified extraction carryover as a contributing factor to excessive D_1 bleach consumption. Steelreath and co-workers [10] examined the kappa numbers of discharged pulp mats from the (EOP) drum washer. Kappa numbers were measured on the mats with its surrounding filtrate included (i.e., "wet kappa" or "unwashed kappa"). These values were then compared with the kappa of the mat after laboratory washing. The investigators [10] reported that the (EOP) pulp mat contained 2.1 kappa units of extraction effluent. This amount of entrainment was estimated to consume ~40% of the total D_1 bleach charge (~4 kg ClO_2/ton pulp). Similarly, Pryke and Nylen [11] reported that poor drum washing was contributing ~5 kappa units of (EOP) carryover with the pulp, which was expending ~10 kg ClO_2/ton pulp in the mill's D_1 stage. Lunn [12] disclosed that filtrate entrainment with an (EOP) pulp from an atmospheric diffusion washer was as high as 5.4 kappa units when the dilution factor was very low. With the drum washer studies [10,12], the investigators discovered that discharge consistencies from pulp washers were much less than 15%, which was attributed to insufficient vacuum pressure across the cylinder's filter.

Most bleach plants do not routinely track interstage washing carryover. Lunn [12] illustrated some common problems of auditing bleach plant washers and calculating their efficiencies. Additionally, Earl and Schofield [7] demonstrated that higher equivalent displacement ratio (EDR) values do not always equate to cleaner pulp mats leaving the extraction drum washer. Their analysis of bleach plant surveys revealed that mills using hot water on one or more of the top shower bars had half the extraction carryover going into D_1 versus those using cleaner bleach filtrates (i.e., ~6 versus ~13 kg COD/ton pulp). Recent reports [13-16] have demonstrated the ability of in-line sensors to monitor dissolved lignin with washed pulps. Such sensors are used to monitor washer carryover entering the oxygen delignification (O) or chlorine dioxide delignification (D_0) stage.

The goal of this work was to evaluate some simple mathematical equations to model the chlorine dioxide brightening (D_1) of softwoods, which includes extraction washer carryover. A generalized steady-state model of the D_1 stage [17], which is a modification of an earlier literature model for hardwoods [18,19], was used as a starting point. Laboratory D_1 bleaching data from the literature [20], which examined progressively washed pulps after extraction, was scrutinized to modify the earlier D_1 model [17]. Afterward, the revised model was used to analyze actual mill data for a softwood D_0(EOP)D_1 sequence.

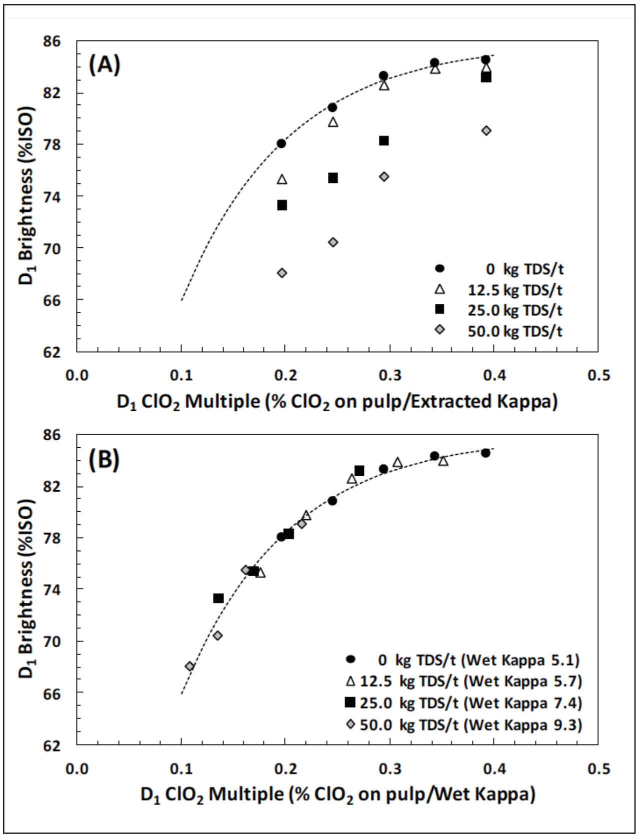
LITERATURE DATA ANALYSIS

Bleaching data from the literature [20] were re-analyzed to obtain brightness expressions for the D_1 stage. Brightness development versus bleach consumption data were fitted to equations using the statistical curve-fitting program WinCurveFit (Kevin Raner Software, version 1.1.6) [17]. The statistical software used a quasi-Newton method (Davidon-Fletcher-Powell algorithm) for minimizing the lack-of-fit for the nonlinear and linear regressions. The 95% confidence intervals for each fitted parameter were calculated from the program's computed standard errors for that parameter multiplied by the pertinent t-statistic (Student's t distribution, two-tail).

INCORPORATING WASHER CARRYOVER INTO CLO_2 BRIGHTENING MODEL

Initial literature data analysis

Pattyson and co-workers [20] explored the D_1 bleaching of a Canadian softwood delignified by (CD)E_1 sequence. The well-washed pulp had a kappa of 5.1 and a brightness of ~33% ISO. The authors examined E_1 carryover levels of 0 kg, 12.5 kg, 25 kg, and 50 kg total dissolved solids (TDS) per ton of pulp into the D_1. The authors' data are plotted in **Fig. 1A** in terms of the D_1 charge multiple, which ratios the chlorine dioxide consumed during brightening to the pulp's extracted kappa number [11,18,19]. The pulps that contained progressively higher levels of E_1 dissolved solids yielded lower D_1 brightness values for the same bleach charge. Alternatively, **Table I** displays how the various carryover levels increased the amount of bleach needed to obtain a given brightness (i.e., 79% ISO).



1. Brightness response in the D_1 versus the chlorine dioxide multiple for various E_1 washer carryover levels: (A) data plotted with chlorine dioxide multiple calculated using the well-washed E_1 kappa number and (B) data plotted with chlorine dioxide multiple calculated from the estimated E_1 "wet kappa" values of Table I. Data from Pattyson and co-workers [20] for northern Ontario softwood treated with (CD)E_1 before D_1.

Plots as in Fig. 1A generally yield a singular trend for kraft pulps that have varying extracted kappa numbers. Using the chlorine dioxide multiple tends to normalize the bleach consumed relative to kappa differences of the pulp [10,11,18,19]. It was hypothesized that the previously mentioned pulps with carryover would bleach like a pulp that has a higher extracted kappa. This higher E_1 kappa would include the kappa contri-

E_1 Carryover Level, kg TDS/ton pulp	% ClO_2 (on pulp)	D_1 Charge Multiple, % ClO_2/E_1 kappa	Carryover-to-Well-Washed Ratio	Estimated Wet Kappa No.	Recalculated D_1 Charge Multiple, % ClO_2/wet kappa
0	1.08	0.21	1.00	5.1	0.21
12.5	1.20	0.24	1.11	5.7	0.21
25	1.57	0.31	1.45	7.4	0.21
50	1.98	0.39	1.83	9.3	0.21

I. Calculated D_1 bleach consumption to reach 79% ISO brightness and wet kappa numbers of E_1 pulps with carryover. Bleach consumption estimated from Fig. 1A data. Data from Pattyson and co-workers [20] for northern Ontario softwood treated with (CD)E_1 before D_1 (E_1 kappa 5.1 and brightness 33% ISO). (TDS = total dissolved solids.)

butions from the pulp and its surrounding filtrate with E_1 dissolved solids (i.e., "wet kappa" or "apparent kappa"). Wet kappa values were estimated for each of the E_1 carryover levels in Table I relative to the increased bleach consumption of the well-washed pulp. Figure 1A data are re-plotted in Fig. 1B using a revised chlorine dioxide multiple based on the wet kappa values of Table I. The bleaching responses of E_1 pulps with entrained dissolved solids are similar to that exhibited by the well-washed pulp when using the wet kappa values. Similar observations are noted when examining the summarized mill data and wet kappa values from the Steelreath et al. [10] and Pryke and Nylen [11] studies. These findings lend support to the previously mentioned hypothesis. In this particular case, each kilogram of E_1 total dissolved solids per ton of pulp appeared to increase the extracted pulp kappa by 0.088 units.

Assessing the generalized steady-state model

Previously, a generalized steady-state expression for softwood pulps was developed to calculate bleach consumption to reach a target brightness level in the D_1 and vice versa [17]. The model is a variant of an equation proposed by McDonough et al. [18,19] to mathematically quantify the bleachability of hardwood pulps. The modified expression is given as:

$$y_1 = c_{01} - \frac{\beta_{11}}{x_1 + \frac{\beta_{11}}{c_{01} - B_E}} \tag{1}$$

where y_1 is the post-D_1 brightness (% ISO), c_{01} is the asymptotic D_1 brightness limit (% ISO), x_1 is the chlorine dioxide consumed (% on oven dry pulp), B_E is the post-extraction brightness (% ISO), and β_{11} is an equation parameter that is fitted to the bleaching data. The modeling study [17] examined the laboratory data from various elemental chlorine-free (ECF) bleaching sequences, and determined that c_{01} was a constant value of 92% ISO. The β_{11} parameter was also found to be a function of the extracted kappa number ($Kappa_E$) of the pulp entering the D_1:

$$\beta_{11} = 4.535 * Kappa_E - 7.434 \tag{2}$$

The Pattyson et al. data [20] were initially regressed to Eq. (1). The purpose of this test was to evaluate if E_1 dissolved solids affected the c_{01} parameter. **Table II** lists the fitted c_{01} values and their associated 95% confidence intervals (CIs). Calculated CI ranges for all the regressed c_{01} values included 92% ISO asymptotic limit. From this result, it was determined that E_1 dissolved solids do not affect the pulp's c_{01} parameter, and that 92% ISO is a reasonable c_{01} estimate.

A second regression was performed on the data using Eq. (1). **Table III** presents the regressed β_{11} and B_E values where c_{01} was fixed at 92% ISO. This analysis revealed that the starting B_E value was unaffected by the amount of E_1 solids entering D_1. On the other hand, the fitted β_{11} was influenced by the level of extraction carryover. The Pattyson et al. data [20] are plotted in **Fig. 2** and compared with the predictions from Eq. (1) using the fitted parameters of Table III. Forecasted brightness values at a given bleach charge were reasonably close to the laboratory measurements, generally within ±0.5 units for the well-washed pulps and ±0.8 units for the partially washed pulps. These differences are within the CI ranges reported for D_1 stage repeatability in the laboratory [17,22].

Modifying the generalized steady-state model

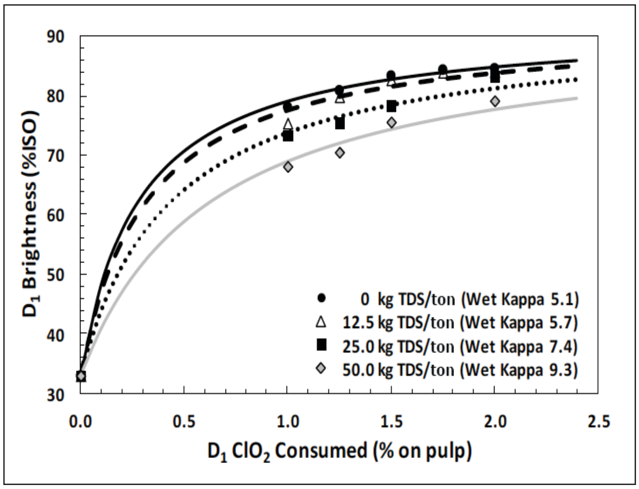
The above regression analyses revealed that Eq. (1) could rea-

E_1 Carryover Level, kg TDS/ton pulp	Eq. (1) – R^2	Eq. (1) – Asymptotic Brightness, c_{01}	Standard Error of c_{01}	95% CI of c_{01}
0	0.999	94.3% ISO	±1.6% ISO	±5.1% ISO
12.5	0.996	98.4% ISO	±3.4% ISO	±10.8% ISO
25	0.997	99.7% ISO	±3.8% ISO	±16.4% ISO
50	0.997	102.4% ISO	±6.1% ISO	±26.1% ISO

II. Calculated D_1 brightness ceiling values, c_{01}, of Eq. (1) from the curve fitting of Pattyson et al. data [20] with their associated 95% confidence intervals (CIs) and coefficient of correlations (R^2).

E_1 Carryover Level, kg TDS/ton pulp	Eq. (1) – R^2	β_{11}	Standard Error of β_{11}	95% CI of β_{11}	B_E	Standard Error of B_E	95% CI of B_E
0	0.999	16.9	±0.6	±1.6	33.0% ISO	±0.6% ISO	±1.8% ISO
12.5	0.996	19.3	±1.3	±3.6	33.0% ISO	±1.4% ISO	±3.8% ISO
25	0.997	26.4	±1.6	±5.1	33.0% ISO	±1.3% ISO	±4.2% ISO
50	0.995	37.9	±2.3	±7.2	32.9% ISO	±1.5% ISO	±4.7% ISO

III. Calculated β_{11} and B_E (extracted brightness) values of Eq. (1) from the curve fitting of Pattyson et al. data [20] with their associated 95% confidence intervals (CIs) and coefficient of correlations (R^2). Nonlinear regressions were performed with c_{01} = 92% ISO.



2. Predicted brightness values from the D_1 model (Eq. [1], various lines) fitted to experimental data (symbols) from Pattyson et al. [30] with various levels of extraction carryover (C.O.). Equation (1) parameter values listed in Table III were used (with c_{01} = 92% ISO).

sonably represent the D_1 bleaching response of well-washed and partially washed pulps after caustic extraction if β_{11} can be determined. These analyses also showed that changes in E_1 dissolved solids entering the D_1 resulted in a proportional change to the model's β_{11} parameter. One kilogram of E_1 total dissolved solids carryover per ton of pulp caused the β_{11} parameter to increase by 0.44 ± 0.13 units (where ± is the 95% CI). This implies that Eq. (2) could be modified to include how different carryover levels affect the β_{11} value:

$$\beta_{11} = 4.535 * Kappa_E + 0.44 * C.O._{TDS} - 7.434 \qquad (3)$$

where $C.O._{TDS}$ denotes extraction carryover expressed as kg TDS/ton pulp. An alternative method for quantifying how extraction carryover affected β_{11} is to consider the pulp mat's "wet kappa" number (denoted as *Apparent Kappa*). An examination of the data in Tables I and III suggested that the wet kappa of the pulp mat and the β_{11} value were linearly related, and had a relationship as expressed as Eq. (2) (with an R^2 = 0.983):

$$\beta_{11} = 4.535 * Apparent\ Kappa - 7.434 \qquad (4)$$

The *Apparent Kappa* of Eq. (4) can be the "wet kappa" value measured on the pulp mat leaving the extraction washer, or it can be determined as the sum of kappa number contribution from the well-washed extracted pulp ($Kappa_E$) and the associated extraction stage carryover ($Kappa_{C.O.}$), expressed as kappa units (on pulp):

$$Apparent\ Kappa = Kappa_E + Kappa_{C.O.} \qquad (5)$$

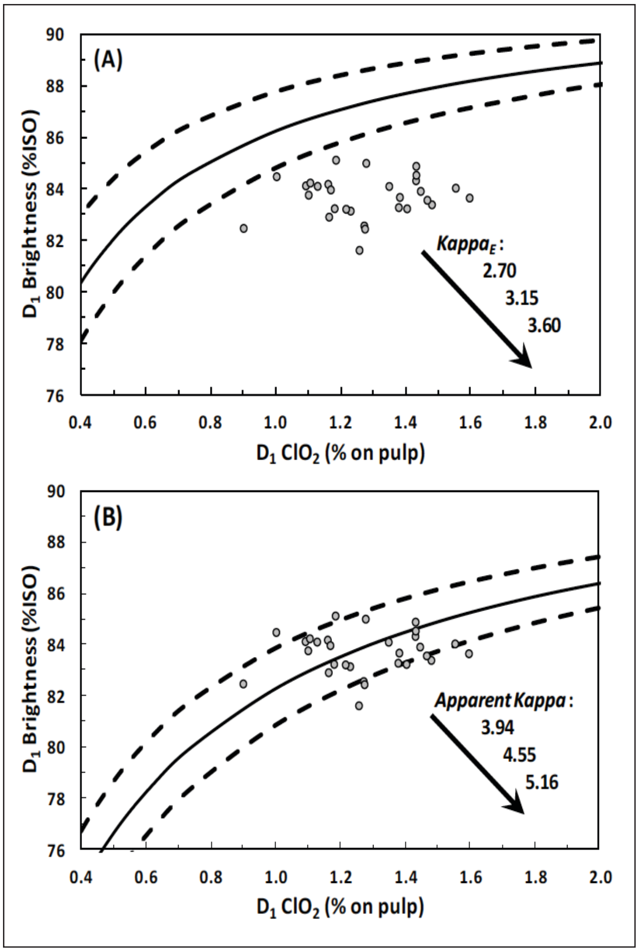
USING THE MODIFIED MODEL WITH MILL DATA

The modified model was used to analyze actual bleach plant data. Daily averages of process data were acquired over a 1-month period from a softwood kraft mill. This mill bleaches a brownstock, which is produced from a southern U.S. pine mixture, to an 84% ISO target using the D_0(EOP)D_1 sequence. **Table IV** summarizes the pertinent bleach plant conditions during this 1-month data collection. A small bleach residual (~0.1 g to 0.2 g ClO_2/L) was observed at the end of the D_1 stage. The mill uses a wash press between the (EOP) and the D_1 stage. The amount of (EOP) carryover is not regularly monitored with this fiber line; however, occasional washer audits performed by the mill have documented values of 13 kg to 17 kg TDS/ton pulp.

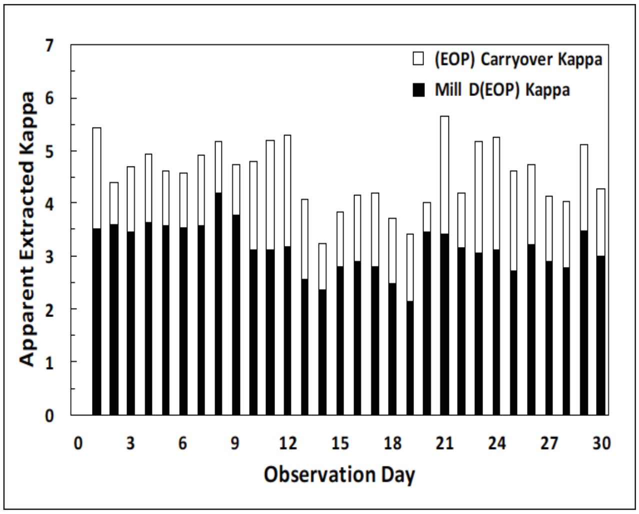
Daily bleach charges (x_1) and extracted kappa numbers ($Kappa_E$) were used as inputs into Eqs. (1), (4), and (5), with the B_E value of Table IV. In the initial calculations, the pulp was assumed to be well-washed and the extraction carryover was assumed to be negligible (i.e., $Kappa_{C.O.}$ = 0). Predicted brightness values were 2.4 to 4.4 points higher than the measured D_1 brightness (**Fig. 3A**). This preliminary assessment suggested that (EOP) carryover was not negligible. Equations (1), (4), and (5) were used again with the mill data. In this scenario, the model inputs were the mill's D_1 brightness (y_1), the ex-

Range	Monthly Range	Monthly Average	Standard Deviation	Comments
Brownstock kappa no.	16.8 to 29.6	22.8	0.45	
D_0(EOP) kappa no.	2.14 to 4.18	3.17	0.45	
D_0(EOP) brightness, % ISO	–	55	–	Periodically monitored
(EOP) carryover, kg TDS/ton	13 to 17	–	–	Historical washer audits
D_1 ClO_2, % on pulp	0.90 to 1.60	1.25	0.18	
D_1 tower pH	4.7 to 6.0	5.3	0.4	
D_1 brightness, % ISO	81.6 to 85.8	83.8	0.9	

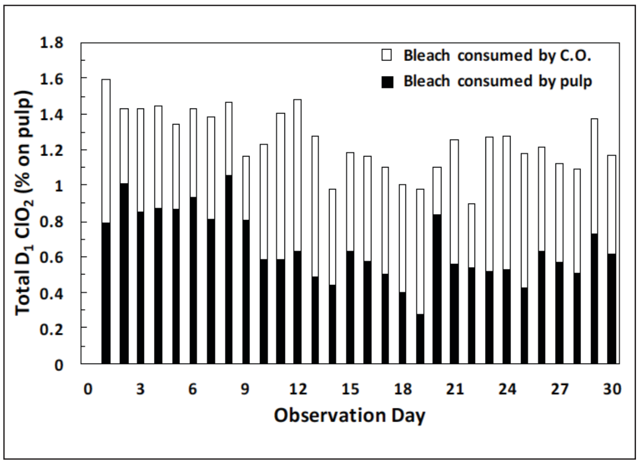
IV. Softwood bleach plant conditions during the data collection over a 1-month period.



3. Predicted brightness values of the modified D_1 model (lines) to the bleach plant data from D_0(EOP) fiber line. Plotted data (symbols) are daily averages during the 1-month period where the post-(EOP) kappa number was 3.15±0.45 (where ± is the standard deviation). Top graph (A) is the predicted brightness levels with the model where $Kappa_{C.O.}$ was set to zero. Bottom graph (B) is the predicted brightness levels with the model where Apparent Kappa was 4.55±0.60.



4. Post-(EOP) kappa numbers from mill data of Fig. 3 (black bars), calculated Apparent Kappa (black + white bars), and carryover kappa ($Kappa_{C.O.}$; white bars) from the modified D_1 model. The bleach plant averaged 1.4±0.6 kappa units of (EOP) washer carryover (where ± is the standard deviation).



5. Total chlorine dioxide consumption in D_1 from the mill data of Fig. 3 (black + white bars), and calculated chlorine dioxide consumption by the (EOP) pulp (black bars) and its associated carryover (white bar) from the data analysis of bleach plant data with modified D_1 model. The bleach plant averaged 6.0±1.5 kg/ton pulp of bleach consumption that was expended on (EOP) washer carryover.

tracted pulp's kappa number ($Kappa_E$), and the mill's bleach charge (x_1). The model was solved to determine the *Apparent Kappa* of the extracted pulp leaving the washer (Fig. 3B). The second analysis revealed that the *Apparent Kappa* during the month averaged 4.55±0.61 (where ± is the standard deviation) (**Fig. 3B**). This implied that the washed pulp contained 1.4 kappa units of (EOP) carryover (**Fig. 4**), or about 16.4 kg TDS/ton pulp (based on Eq. [3]). The calculated carryover average value is within the historical range reported by the mill (Table IV).

The results from these two analyses were compared to estimate the bleach consumption attributable to (EOP) carryover (**Fig. 5**). The comparisons revealed that approximately 6 kg ClO_2/ton pulp was being consumed by entrained dissolved solids that remained with the washed pulp. This represented roughly 48% of the total D_1 bleach charge that was being used unproductively.

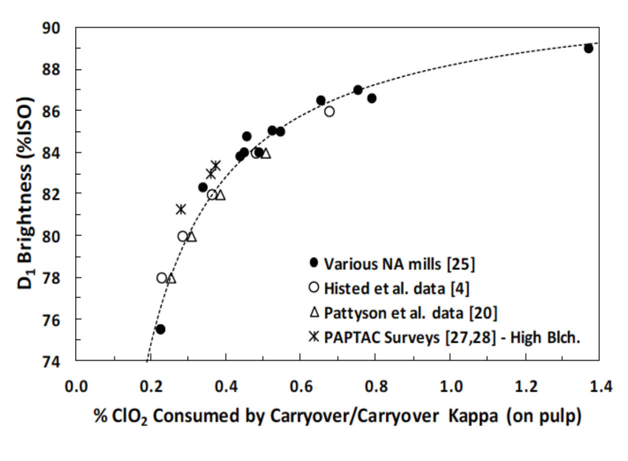
DISCUSSION

The revised model for the D_1 stage (Eqs. [1], [4], and [5]) can predict pulp brightness for laboratory and mill data if the extracted pulp's kappa number and brightness are known, as well as the bleach charge and the amount of extraction carryover. The brightening response of the partially washed pulp, which contains entrained dissolved solids, bleaches as if the pulp had a kappa number equal to the "wet kappa" value. This higher *Apparent Kappa* is the sum of contributions from the pulp and the entrained dissolved solids. The amended model generally over-predicts the D_1 brightness of the pulp at the mill if the extraction carryover is not considered and is not negligible. In these cases, the amount of carryover can be approximated by using different data inputs into the model. This presumes that other factors that influence brightness, such as chemical mixing, D_1 pH, and zero bleach residual have been eliminated.

The proposed model is based on several assumptions. It assumes that extraction carryover does not affect the B_E parameter, which is set to the extracted pulp brightness after extensive washing. Generally, the post-extraction brightness will decrease by 2.5 to 4.5 points for each unit increase in the pulp's extracted kappa number [18,23]. Results from the regression analysis (Table III) implied that the well-washed pulp brightness is a reasonable estimate of B_E, and that B_E is not significantly affected by increasing carryover levels. This carryover material is dissolved in the liquid layer that surrounds the pulp and is not physically bound to the fiber walls. Although this material contributes to the overall lower brightness of the aqueous slurry, it should not contribute to the pulp's brightness when it is made into laboratory handsheets. Laboratory standards for making handsheets for brightness measurements will wash out most dissolved materials contained in the pulp slurry (e.g., TAPPI Standard T 272 sp-12 "Forming handsheets for reflectance testing of pulp [sheet machine procedure]"). Additionally, extraction dissolved solids would not likely undergo condensation reactions that would physically re-attach them to the fiber during the D_1 stage.

Another underlying assumption is that the D_1 asymptotic brightness (c_{01}) is fixed at 92% ISO and that c_{01} is unaffected by the carryover level. The dissolved solids of the aqueous slurry are not expected to influence the c_{01} parameter. Previous modeling work [17] examined the nonlinear regression of published data to Eq. (1) and found that the c_{01} parameter was approximately 92% ISO for various softwood pulps. This limit was observed for a wide range of post-extraction kappa numbers (i.e., 2 to 8) after the D_0(EO) sequence. This asymptotic limit of 92% ISO was also noted in a kinetic study of chlorine dioxide bleaching of softwoods [21]. The initial regression analysis of literature data in this study (Table II) indicated that 92% ISO was a reasonable estimate of c_{01}, and that c_{01} was not significantly influenced by various carryover levels. Other D_1 stages models, such as the earlier model proposed by McDonough and co-workers [24], were also explored with the Pattyson et al. data [20]. Nonlinear regression analyses using this alternative model revealed that all the pulps from the study had statistically identical asymptotic brightness values.

A third assumption regards the relationship of the β_{11} parameter to the post-extraction kappa of the pulp (Eq. [2]), as well as to the extraction stage carryover level (Eq. [4]). Prior modeling work [17] found a linear correlation of the β_{11} to the post-extraction kappa (Eq. [2]) for a variety of softwood pulps delignified by ECF sequences. Subsequently, Eq. (2) has been found to represent the relationship of extracted



6. Calculated bleach consumption by extraction carryover, expressed as % ClO_2 (on pulp) per kappa unit of carryover, versus the brightness from D_1 stage for softwoods. Values determined with modified D_1 model using data from various sources [4,20,25,27,28].

kappa to β_{11} for softwood brownstocks delignified by chlorination or chlorine dioxide substitution [25]. Additionally, the "wet kappa" values from the Pattyson et al. [20] data exhibited the same relationship to β_{11} as seen with post-extraction kappa. These observations tend to substantiate the validity of Eqs. (2) and (4). Alternative linear correlations of the β_{11} parameter to extracted kappa or "wet kappa" could exist, particularly if the pH of D_1 stage is not optimized. Equations (3) and (4) are based on entrained dissolved solids derived from a simple extraction stage (E_1). Parming and co-workers examined the D_1 bleaching kinetics of extraction carryover [26]. The authors reported that E_1, (EO), and (EP) dissolved solids consume the same amount of chlorine dioxide. This implies that extraction stage conditions should not affect how carryover consumes bleach in D_1 so long as there is zero residual peroxide. Additional laboratory studies, like those performed by Pattyson et al. [20] and Histed et al.[4], are needed to further establish the linear relationship.

The proposed model has been used to analyze other literature data [4,27,28] and data from different bleach plants [25]. These analyses are similar to the one presented earlier on mill data. The amount of chlorine dioxide consumed by the dissolved solids is not a constant value. It varies in accordance with the D_1 brightness target. **Figure 6** is a plot of the chlorine dioxide consumed per kappa unit of carryover versus the D_1 brightness. This entrained dissolved material consumes 2.5 kg to 4.6 kg ClO_2/ton pulp per kappa unit when bleaching to 78% to 84% ISO brightness. This bleach consumption by carryover increases extensively when bleaching to the 84% to 88% ISO range. Reported stoichiometric values for bleach uptake by carryover [29] are 0.22 kg to 0.40 kg ClO_2/kg TDS per ton of pulp (~2.5 kg to 4.5 kg ClO_2/ton pulp per kappa unit).

CONCLUSIONS

A revised model for the first chlorine dioxide brightening stage (D_1) was developed that more accurately represents bleach plant data for softwood pulps. The model incorporates the deteriorative effects of extraction washer carryover into D_1. Extracted pulps with entrained dissolved solids brighten as if the pulp had a kappa number equal to its extracted kappa plus the kappa of the carryover. The new model was used to analyze bleach plant data from a softwood fiber line that uses a D_0(EOP)D_1 sequence. Calculations were performed to determine the amount of extraction washer carryover (as kappa units) entering the D_1 and its associated bleach consumption. At this mill, the washer carryover level averaged 1.4 kappa units during the 1-month observation period, which was estimated to consume ~48% of the total chlorine dioxide charge applied. The chlorine dioxide uptake by extraction carryover stage is not a constant value; it varies in accordance to the D_1 brightness target. For example, extraction carryover consumes 0.25% to 0.46% chlorine dioxide on pulp per kappa unit of carryover when bleaching to 78% to 84% ISO. **TJ**

ACKNOWLEDGEMENTS

The author thanks Paul F. Earl for providing the presentation he gave summarizing the PAPTAC Bleaching Committee's 2004 survey of Canadian bleach plants [12]. In addition, the author gratefully acknowledges the laboratory data published in the Pattyson and co-workers study [20], which were used to revise the D_1 model. Portions of this work were presented in Session 3-3 at the 2015 TAPPI Pulping, Engineering, Environmental, Recycling, and Sustainability (PEERS) Conference in Atlanta, GA, USA, and at the PaperWeek Canada 2016 Conference in Montréal, QC (Bleaching Session II, Paper 1).

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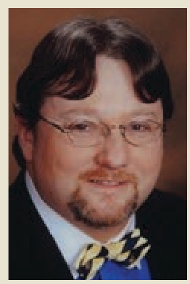
ABOUT THE AUTHORS

This work presents refinements to a generalized model for chlorine dioxide bleaching (D_1) that was recently proposed for softwood kraft pulps (see *TAPPI J*. 13[3]: 17[2014]). It was based on published laboratory data for extracted pulps that were well-washed before bleaching. The model did not consider how entrained dissolved organics from extraction affected the D_1 stage. Carryover can be a significant contributor to D_1 bleach demand, especially when one considers that most washers are overloaded in the bleach plant. Thus, the current objective was to modify the D_1 model to account for bleach uptake caused by washer carryover. This would then improve the model's accuracy to represent an actual bleach plant.

Limited data were found from the literature where the investigators examined how dissolved solids from extraction affected D_1 brightness and bleach consumption. The last studies that scrutinized this topic were published 30 to 40 years ago. Laboratory data from the University of Toronto and Great Lakes Forest Products investigation [20] were re-examined in this modeling study.

The most interesting discovery from the current study is how the extraction dissolved solids behaved like the residual lignin in the pulp that enters the D_1 stage. Extracted pulps with carryover exhibit a D_1 bleaching response that is related to their wet kappa number similar to that of well-washed pulps and their extracted kappa number. Based on this finding, the original model equations were easily modified to simulate the effects of extraction stage carryover.



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Most mills do not regularly monitor washer carryover entering the D_1 stage. Process engineers could use the modified model to analyze bleach plant data to estimate the amount of extraction carryover. With this information, additional calculations can be performed to determine how much chlorine dioxide is being consumed by brightening versus carryover reactions. The equations could be used with process control strategies for mills that have in-line sensors [13-16] that measure dissolved lignin or filtrate kappa on pulps exiting the extraction washer.

Future work will attempt to develop generalized D_1 stage models for hardwood pulps, similar to the ones developed for softwoods.

Brogdon is president/owner, Future Bridge Consulting Services LLC, Marietta, GA, USA. Email Brogdon at Brian.Brogdon@gmail.com.

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