

Extension of a steady-state chlorine dioxide brightening model for Z-ECF bleaching of softwood kraft pulps

BRIAN N. BROGDON AND LUCIAN A. LUCIA

ABSTRACT: Earlier studies developed a steady-state model to predict the brightness and/or bleach consumption during the chlorine dioxide brightening (D_1) of softwood pulps produced by conventional elemental-chlorine-free (ECF) sequences. This model relates the chlorine dioxide consumed to the brightness gains predicated upon an asymptotic D_1 brightness limit, an incoming D_1 pulp brightness, and an equation parameter (β_{11}). The current investigation examines the application of this model to ECF sequences that use ozone delignification (Z-ECF). Literature D_1 data from various Z-ECF bleaching studies, which investigated OZ, OD_0/Z , and OZ/D_0 delignification, were fitted to the model. The β_{11} parameter was found to be linearly correlated to the entering kappa number. Interestingly, this linear relationship was found to be identical to the relationships observed when modeling the D_1 stage for conventional ECF and chlorine-based bleach sequences. Subtle differences in D_1 brightening response in the model among the various bleach sequences are reflected by incoming pulp brightness (at the same kappa number). The current model is used to illustrate how alterations to Z-ECF delignification affect D_1 brightening and chlorine dioxide consumption.

Application: The steady-state model for the first chlorine dioxide brightening stage predicts the brightness for ECF bleaching sequences that utilize ozone for delignification. Other applications of the model include bleach plant optimizations, computer simulations, and/or process control strategies.

Advances made in the mid-1990s with high-shear mixers and high-consistency reactor designs that homogeneously disperse ozone gas with the pulp led to the commercialization of medium- and high-consistency ozone (Z) stages. Ozone, like chlorine dioxide, can delignify brownstocks and oxygen-delignified pulps. Unlike chlorine dioxide delignification (D_0), Z stages indiscriminately attack the carbohydrates if high ozone charges are applied ($\geq 1\%$ on pulp). These undesired reactions, if left unchecked, lead to unacceptable reductions in pulp viscosity and strength. Hence, kappa number reductions across a Z stage are normally limited to 2.5–7 units to assuage cellulose degradation. Additional kappa reductions, typically 1 to 3 units, can be attained if the post-Z pulps are extracted with caustic (e.g., E or (EOP)).

In 2018, roughly thirty fiber lines worldwide utilized ozone to bleach ten million metric tons/year of oxygen-delignified pulp [1,2]. Most of these bleach plants integrated the Z stage into elemental chlorine-free (ECF) sequences. In these ozone-based ECF-light or Z-ECF sequences, ozone replaces part or all of the chlorine dioxide dedicated to delignification in the D_0 stage [3–8]. Commercial examples include $Z/(EOP)D(PO)$, $Z/D_0(EOP)D_1$, and D_0Z/ED_1D_2 , where the slash denotes no interstage washing [9]. Replacing a single D_0 stage with Z, D_0Z , or Z/D_0 can reduce overall ECF bleaching costs, effluent loadings (for example, absorbable organic halogen [AOX] and color), and pulp extractive levels. These Z-ECF sequences are frequently used

to produce dissolving pulp grades (e.g., viscose) where the final pulp viscosity can be fine-tuned.

The bleaching literature reports that Z-ECF sequences can brighten oxygen-delignified softwood and hardwood kraft pulps to full brightness (86% to 90% ISO) when using chlorine dioxide and/or pressurized peroxide brightening stages (i.e., D_1 and (PO)) [2–8,10–16]. Usually, these investigations fixed the chemical charges for the individual stages when bleaching oxygen-delignified softwood kraft pulps. Relatively few studies explicitly report how ozone-delignified pulps brighten in a D_1 stage when the chlorine dioxide charge and/or the entering kappa number are varied [17–21]. Such information is useful when operating and optimizing Z-ECF sequences.

Prior works [21–23] have focused on individual bleach stage models for conventional ECF bleach sequences. Such models predict the delignification and brightening responses of kraft pulps. These expressions can be used to calculate bleach consumption, as well as interstage brightness levels and/or kappa numbers, for various bleach plant inputs and constraints (e.g., entering bleach plant kappa number, extraction stage conditions, etc.). A goal of the current study is to present a simple D_1 brightening model to estimate the post- D_1 brightness of softwood kraft pulps that have been delignified by ozone or ozone and chlorine dioxide. Another objective is to compare the similarities and differences of the D_1 brightening model with Z-ECF sequences to chlorine-based and conventional ECF sequences.

DATA ANALYSIS

Chlorine dioxide brightening data were acquired from several sources that delignified softwood kraft pulps by Z-ECF [17-19,24], conventional ECF [25-31], and chlorine-based partial sequences [32-34]. These studies systematically examined how chlorine dioxide dosage, incoming pulp kappa number, and entering pulp brightness affected post-D₁ brightness. As with the other modeling studies [21-23], older source data that reported brightness as GE or El-rephro units for laboratory handsheets were converted to ISO units using the nomographs of Reeve [35].

In the first part of this investigation, selected Z-ECF data sets [17] were fitted to the D₁ model to determine all three equation parameters [21-23]. Nonlinear regression analyses were performed using CurveExpert Professional software (Daniel G. Hyams, version 2.6.5; Madison, AL, USA). This software employed a Levenberg-Marquardt (LM) algorithm to minimize the lack-of-fit. The parameter values, in addition to their standard errors and 95% confidence intervals, were calculated by the program for each data set. An analysis of variance (ANOVA) with the partial *F* test was conducted to determine if one of the D₁ model parameters, the asymptotic brightness, could be directly calculated from the optical properties of the pulp instead of being regressed. Statistical hypothesis testing used a significance level (α) of 0.05.

Later in this investigation, additional Z-ECF data sets [18,19,24] were fit by the D₁ model to determine the pre-D₁ brightness and the β_{11} equation parameter values; in these cases, the asymptotic brightness parameter was directly computed from pulp properties. Subsequently, the regressed β_{11} values were then linearly correlated versus the entering D₁ kappa numbers for the various data sets. Similar analyses were also conducted with conventional ECF and chlorine-based data sets [25-34]. Analysis of covariance (ANCOVA) [36,37] was performed on these linear correlations results to determine if there were any significant statistical differences (at $\alpha = 0.05$) among Z-ECF, conventional ECF, and chlorine-based delignification partial sequences. Before initiating the ANCOVA, an ANOVA was executed to confirm the homogeneity of slopes, which is a prerequisite for the ANCOVA. These statistical analyses were done using JMP Pro software (SAS Institute Inc., version 15.1.0; Carry, NC, USA).

RESULTS

Chlorine dioxide brightening model

Over the past several years, a simple steady-state model of the D₁ stage has been developed and used to predict the chlorine dioxide needed to reach a brightness target for kraft pulps that have been delignified by conventional ECF partial sequences, such as D₀(EOP) and OD₀(EO) [21-23]. The post-D₁ pulp brightness, y_1 (% ISO), is a function of the chlorine dioxide consumed, x_1 (as % ClO₂ on pulp):

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

The equation has three parameters that characterize the brightening response: asymptotic D₁ brightness limit (c_{01}), starting pulp brightness (B_E , % ISO), and β_{11} (% ISO%·ClO₂). Brightness versus bleach consumption data for a given pulp can be fitted to Eq. 1 by nonlinear regression to simultaneously determine B_E , c_{01} , and β_{11} .

Earlier analyses [21-23] with softwood and hardwood bleaching data revealed that c_{01} can be directly computed using the optical properties of the pulp and the Kubelka-Munk remission function. This function relates pulp brightness to the optical properties of light scattering (s) and light absorption (k) coefficients of the pulp:

$$\text{Brightness (\%)} = 100 \left(1 + \frac{k}{s} - \sqrt{2 \frac{k}{s} + \left(\frac{k}{s} \right)^2} \right) \quad (2)$$

Chemical pulp bleaching reduces k by eliminating chromophores while leaving s unaffected. Teder and Tormund [38] ascertained an asymptotic light scattering coefficient (k_∞) value of about 0.10 m²/kg (at 457 nm) for chlorine dioxide brightening kinetics. Interestingly, this limiting k_∞ is close to the value reported by Middleton and Scallan [39] for lignin-free cellulosic fibers. **Table I** lists computed c_{01} values for an assortment of softwood species based on the s values of softwoods [19,20,40] and the k_∞ value of 0.10 m²/kg. Most softwood pulps have c_{01} values between 92.0% and 92.5% ISO. These values closely correspond to the observed upper limit of bleached brightness of softwood kraft pulps bleached by ECF sequences [21,28,41-44].

Initial tests to determine D₁ model's asymptotic brightness

Gupta and Eckert [17] examined the OZED and OZD bleaching of Douglas fir kraft pulp to approximately 80% to 90% ISO brightness. The investigators took an oxygen-delignified pulp and delignified it using Z or ZE at various ozone dosages. Subsequently, the resulting pulps were treated in a D₁ brightening stage using a range of bleach charges. Select data sets from their study (pre-D₁ brightness from about 45% to 77% ISO) were fitted to Eq. 1 (**Table II** and **Fig. 1**). The regressed c_{01} values varied and had no discernible correlation to the entering D₁ brightness. The directly computed c_{01} values from Eq. 2 (i.e., 92.1% ISO) were within the 95% confidence intervals of the regressed c_{01} values.

Next, curve fitting was performed on the data sets of **Table II** where c_{01} was fixed at the computed 92.1% ISO value. The results are presented in **Table III** and **Fig. 1**. This reduced model fitted the D₁ brightening data reasonably well, with a small increase in standard errors of the

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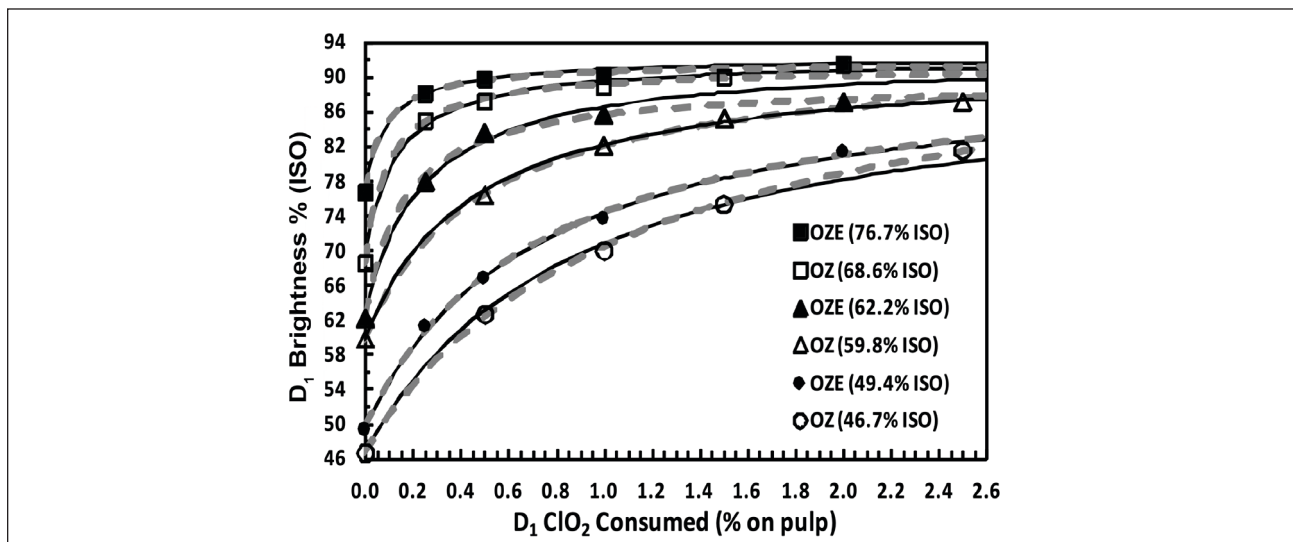
Pulp	Unbeaten Pulp Light Scattering Coefficient (s)	Estimated Asymptotic D_1 Brightness (c_{01})
Black spruce [40]	31.6 m ² /kg	92.4% ISO
Douglas fir [40]	29.7 m ² /kg	92.1% ISO
Loblolly pine [40]	29.0 m ² /kg	92.0% ISO
Scandinavian Scots pine [19,20]	34.8 m ² /kg	92.7% ISO
Southern U.S. mixed softwoods [40]	29.1 m ² /kg	92.0% ISO
West Coast Canadian mixed softwoods [40]	29.4 m ² /kg	92.1% ISO
Central Canadian mixed softwoods [40]	33.2 m ² /kg	92.5% ISO
Scandinavian mixed softwoods [40]	31.6 m ² /kg	92.3% ISO

I. Directly computed c_{01} values of softwood kraft pulps with the Kubelka-Munk remission function (Eq. 2) using $k_{\infty} = 0.10$ m²/kg and appropriate s values of unbeaten pulps.

Bleaching Delignification	Brightness Entering D_1 Stage, % ISO	Nonlinear Regression Results of Full Model					
		SE of Model, % ISO	B_{E_r} , % ISO	β_{11}	c_{01r} , % ISO	SE of c_{01r} , % ISO	95% CI of c_{01r} , % ISO
OZE	49.4	0.76	49.6	31.2	92.3	2.2	±9.4
OZE	62.2	0.79	62.2	4.56	89.6	0.97	±4.2
OZE	76.7	0.37	76.7	1.21	91.7	0.38	±1.6
OZ	46.7	0.45	46.8	56.3	96.6	1.6	±7.0
OZ	59.8	0.41	59.8	16.3	93.0	0.79	±3.4
OZ	68.6	0.32	68.6	2.20	91.1	0.36	±1.6

O = oxygen; Z = ozone; E = alkaline extraction.

II. Determination of all three parameters of Eq. 1 from the nonlinear regression of the Gupta and Eckert data [17] with predicted brightness standard error (SE) and 95% confidence interval (CI) for c_{01} . Coefficients of determination (R^2) for the various regressions were 0.997 or higher.



1. Nonlinear regression of D_1 data sets (symbols) of the Gupta and Eckert study [17] to Eq. 1. Dotted lines denote simultaneous regression of c_{01} , B_{E_r} and β_{11} (Full Model; Table I). Solid lines denote simultaneous regression values of B_{E_r} and β_{11} (Reduced Model; Table II), while c_{01} held at 92.1% ISO.

Bleaching Delignification	Brightness Entering D ₁ Stage, % ISO	Nonlinear Regression Results of Full Model					
		SE of Model, % ISO	B_{E_r} % ISO	SE of B_{E_r} % ISO	β_{11}	SE of β_{11} , % ISO	R^2
OZE	49.4	0.62	49.6	0.58	30.7	1.2	0.998
OZE	62.2	1.33	62.3	0.85	7.04	0.85	0.987
OZE	76.7	0.36	76.7	0.36	1.44	0.13	0.997
OZ	46.7	0.92	46.5	0.90	40.1	1.9	0.996
OZ	59.8	0.43	59.8	0.42	14.5	0.5	0.999
OZ	68.6	0.55	68.6	0.55	2.89	0.23	0.997

O = oxygen; Z = ozone; E = alkaline extraction.

III. Determination of B_{E_r} and β_{11} parameters of Eq. 1 from the nonlinear regression of the Gupta and Eckert data [17] with standard error (SE) values (where c_{01} computed by Eq. 2 and fixed at 92.1% ISO during regression).

Bleaching Delignification	Brightness Entering D ₁ Stage, % ISO	Computed F_0 Ratio	Critical F	p -Value	Accepted Model
OZE	49.4	0.00905	18.5	0.933	Reduced Model (H_0)
OZE	62.2	6.44	18.5	0.127	Reduced Model (H_0)
OZE	76.7	0.937	18.5	0.435	Reduced Model (H_0)
OZ	46.7	10.8	18.5	0.0815	Reduced Model (H_0)
OZ	59.8	1.23	18.5	0.383	Reduced Model (H_0)
OZ	68.6	6.97	18.5	0.118	Reduced Model (H_0)

O = oxygen; Z = ozone; E = alkaline extraction.

IV. Analysis of variance for the Full Model (regression of all three parameters) vs. Reduced Model (regression of B_{E_r} and β_{11} while c_{01} held at 92.1% ISO). Inferences are based on a 95% confidence level ($\alpha = 0.05$) to determine if the reduced model adequately represents the Gupta and Eckert data [17].

predicted brightness versus the full model. The reduced model was compared to the full model using the ANOVA and the partial F test (Table IV). Insufficient statistical evidence indicated that the null hypothesis could not be rejected at the 95% confidence level. Hence, the c_{01} parameter of Eq. 1 can be directly computed from the pulp's optical properties.

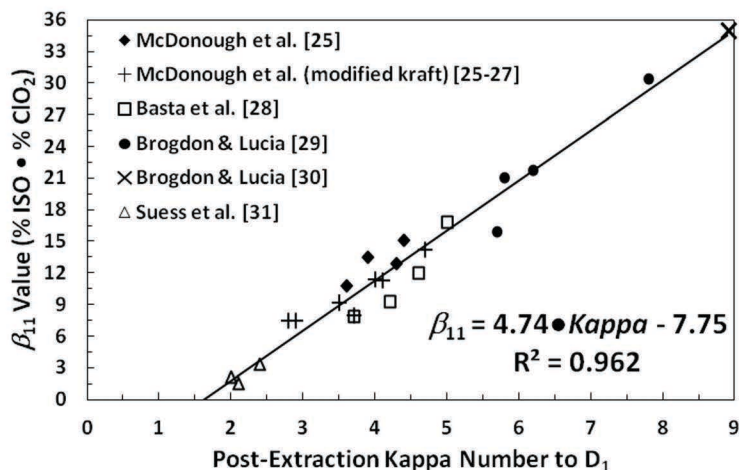
Subsequent tests correlating D_1 model parameter to entering kappa number

Prior D_1 curve fitting of conventional ECF data to Eq. 1, where c_{01} was calculated from Eq. 2, showed correlations between the regressed β_{11} values and the entering D_1 pulp properties [21]. Individual linear relationships are observed between the pre- D_1 brightness and the regressed β_{11} value for various softwood pulps when delignified by conventional ECF sequences. Unfortunately, there was no universal expression found where there were a common slope and y -intercept. Nonetheless, when entering D_1 kappa numbers were regressed against β_{11} , a generalized expression was obtained for the various pulps [21]. The data from this earlier study, along with additional β_{11} values computed from other D_1 bleaching data with modified kraft pulps

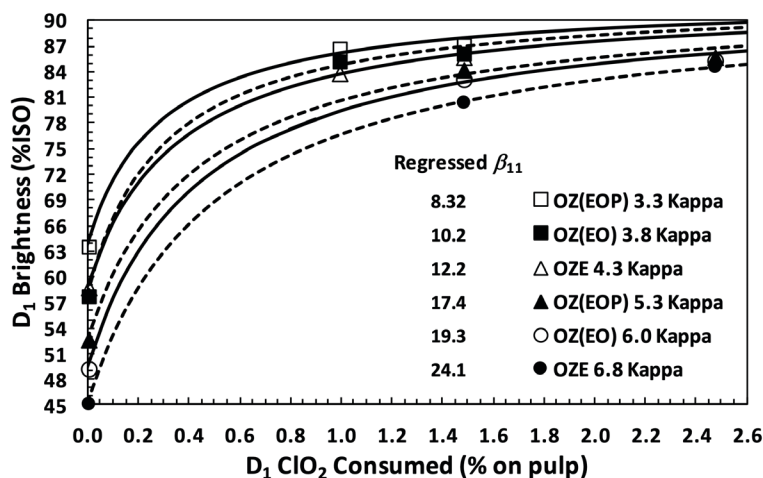
delignified by conventional ECF partial sequences, are presented in Fig. 2. When the kappa number correlation for calculating β_{11} is used with Eq. 1, the model predicts D_1 brightness values with a standard error (SE) of 0.99% ISO points.

Similarly, the chlorine dioxide brightening data obtained from the Z-ECF studies of Lindholm [19] and Brown et al. [18] were fitted to Eq. 1. In these cases, the c_{01} for the oxygen-delignified kraft pulps were directly computed from Eq. 2 for the Scandinavian Scots pine and the Southern U.S. mixed softwood (Table I). Selected data sets from the Lindholm study [19] and the respective curve fits are illustrated in Fig. 3. The β_{11} values obtained from the nonlinear regression were subsequently compared to pulps' kappa numbers entering the D_1 stage. This plot is shown in Fig. 4. Similar to conventional ECF, the regressed β_{11} values for Z-ECF pulps were linearly correlated to the incoming D_1 kappa number.

The Z-ECF data from Gupta and Eckert [17] were not included in this analysis since the authors did not disclose post-Z or post-E kappa number measurements. The Lindholm investigation [19] examined how extraction stage conditions (e.g., OZE and OZ(EOP)), interstage washing (i.e.,



2. Regressed β_{11} vs. post-extracted kappa no. for conventional ECF bleaching sequences performed on various softwood kraft pulps (from previous D_1 modeling study [21] denoted with geometric symbols). Additional data denoted with + and × calculated from new data sets with the current modeling study.

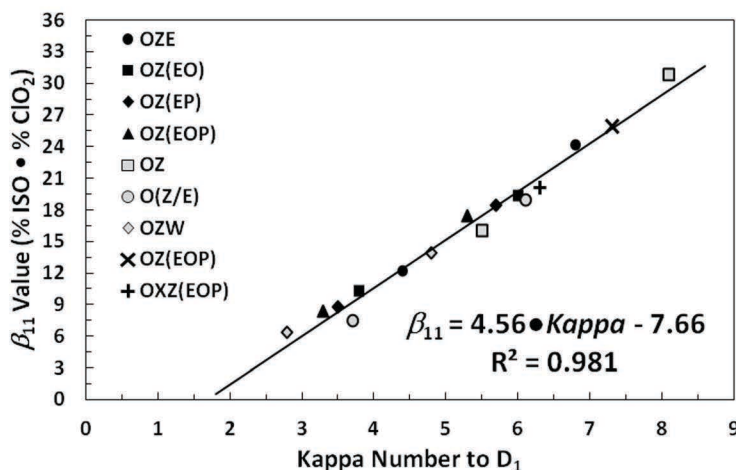


3. Nonlinear regression of selected D_1 data sets (symbols) of the Lindholm study [17] with Scots pine to Eq. 1. Values of B_E and β_{11} determined from nonlinear regression analysis while holding c_{01} at 92.7% ISO. Curved lines (solid for unfilled symbols and dotted for filled symbols) denote the model's predicted brightness as chlorine dioxide consumption increases.

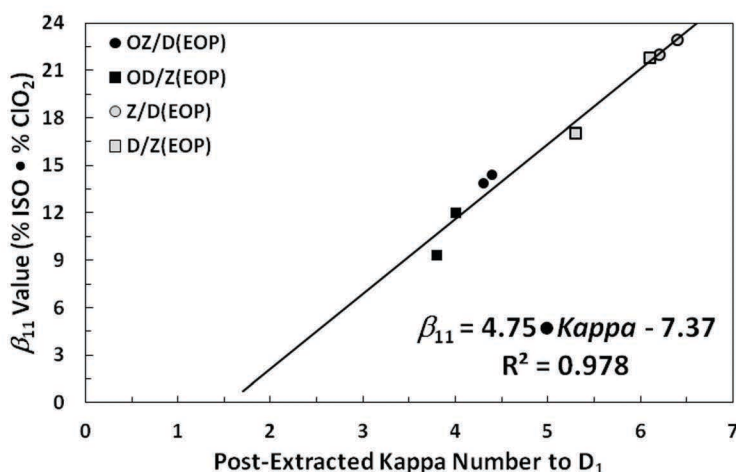
O(Z/E) vs. OZE), and wash stage insertion (i.e., OZ vs. OZW) affected D_1 stage brightness development with a Scots pine pulp delignified by the OZ partial sequence. The Brown et al. study [18] investigated how a Southern U.S. mixed softwood pulp brightened in a D_1 stage when delignified by OZ(EOP) partial sequence that included xylanase (X). Brightness predictions from the fitted D_1 stage model, where the β_{11} value was calculated from the kappa number, were good for the Z-ECF data sets (SE of 0.94% ISO points).

Most softwood bleach plants that operate Z-ECF sequences today use ozone to displace part of the chlorine dioxide utilized for delignification, such as with the OZ/ D_0 (EOP) or OD₀Z/E partial sequence [2-8,12,13]. Ozone substitution with Z/ D_0 , where the medium consistency pulp is mixed and reacted with ozone in a retention tube (1 to 2 min), then

degassed, and finally mixed with chlorine dioxide and reacted in a tower without interstage washing, has similarities to chlorination with chlorine dioxide substitution (i.e., (CD) or (DC)) [2,3,12-16,32]. Most published bleaching studies of the 1990s investigated how Z/ D_0 differed from D_0 /Z with regards to delignification and how much chlorine dioxide can be replaced by ozone [12-16]. Almost none reported the D_1 brightening responses of these pulps to different chlorine dioxide charges. McDonough and Turner [24] presented results from an unpublished D_1 bleaching study conducted on a Southern U.S. softwood kraft pulp. This pulp was treated with Z/ D_0 (EOP), OZ/ D_0 (EOP), D_0 /Z(EOP), or OD₀/Z(EOP) where 50% of the chlorine dioxide charge was substituted with ozone (on an active chlorine basis). The data from this D_1 study were fitted to Eq. 1 to determine β_{11} and B_E while



4. Regressed β_{11} vs. entering kappa number to D_1 stage for Z-ECF bleaching (with OZ delignification) of various softwood kraft pulps. Geometric symbols denote regressed β_{11} calculated from the Lindholm data [19] with Scots pine. Additional β_{11} denoted by + and x calculated from the Brown et al. data [18] with Southern U.S. mixed softwoods. Stages denoted with W and X represent water wash and xylanase stage, respectively; the slash symbol denotes no interstage washing [9].



5. Regressed β_{11} vs. kappa number to D_1 stage for Z-ECF bleaching (with Z/D_0 or D_0/Z delignification) performed on unbleached or oxygen-delignified Southern U.S. softwood pulps. Regressed β_{11} from the McDonough and Turner data [24]. The slash symbol denotes no interstage washing [9].

c_{01} was held at 92.0% ISO (Table I). A generalized linear relationship was observed from the regressed β_{11} values and the extracted kappa number (**Fig. 5**). The slope and y-intercept of this linear correlation were remarkably close to those obtained from conventional ECF and Z-ECF without D_0 . Forecasted brightness values from Eq. 1 where the β_{11} value was computed from the kappa number were quite good (SE of 0.90% ISO points).

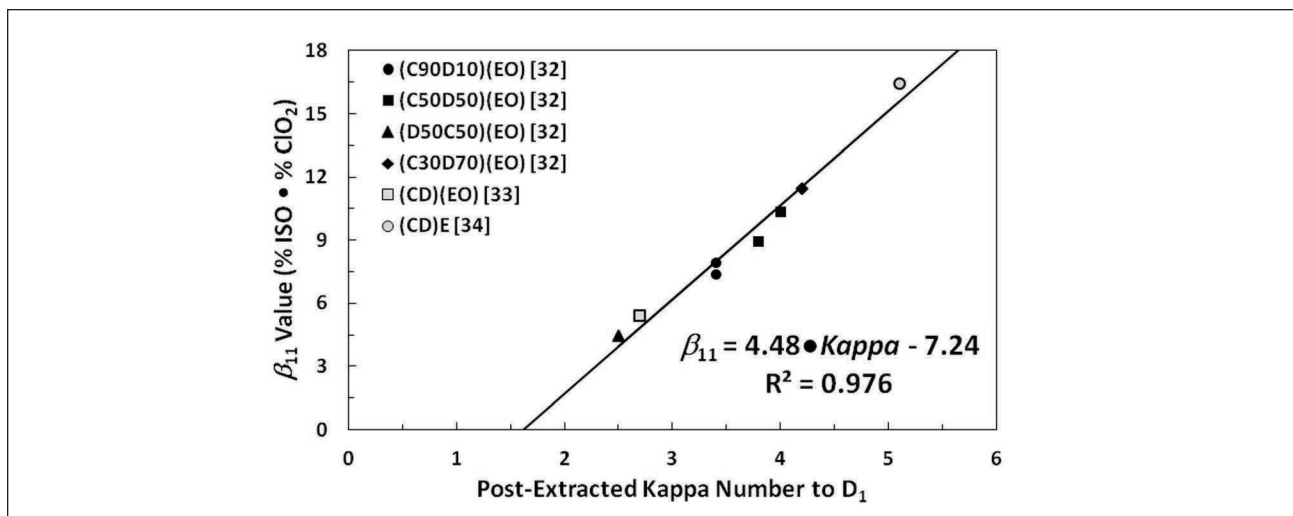
Comparisons of linear correlations of other bleach sequences to estimate D_1 model parameter

To investigate more fully how bleaching delignification impacts the D_1 brightening model, published D_1 laboratory data from Canadian softwood pulps delignified by (CD) and

(DC) stages [32–34] were also curve-fitted to Eq. 1 using a fixed c_{01} (Table I). Just as with conventional ECF and Z-ECF sequences, the chlorine-based sequences had a common linear expression relating the regressed β_{11} to the extracted kappa number (**Fig. 6**). Predicted brightness values from the D_1 model when the β_{11} value was calculated from the kappa number were very good (SE of 0.54% ISO points).

The individual linear correlations of regressed β_{11} to pre- D_1 kappa for conventional ECF, Z-ECF, and chlorine-based delignification sequences all yielded similar y-intercept and slope values (**Table V**). In most cases, the differences among the treatments' linear correlations are within their standard errors. An analysis of covariance (ANCOVA) was conducted to determine if these differences are significant.

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6. Regressed β_{11} vs. kappa number to D_1 stage for chlorine-based bleaching delignification (chlorination at different chlorine dioxide substitution levels) performed on Canadian mixed softwood pulps.

Bleaching Delignification Treatment	Slope			γ -Intercept			Standard Deviation (predicted β_{11})
	Estimate	SE	95% CI	Estimate	SE	95% CI	
Conventional ECF	4.74	0.20	±0.42	-7.75	0.93	±1.93	1.60
Z-ECF w/ OZ	4.56	0.17	±0.36	-7.66	0.92	±1.97	1.01
Z-ECF w/O ₃ substitution	4.75	0.29	±0.72	-7.37	1.52	±3.71	0.83
Chlorination w/ClO ₂ substitution	4.48	0.29	±0.70	-7.24	1.06	±2.60	0.63

V. Individual linear correlations of regressed β_{11} versus entering kappa number for various bleaching delignification treatments prior to the D_1 stage.

Source	Degrees of Freedom	Adjusted Sum of Squares	Adjusted Mean Square	Computed F_0 Ratio	Critical F	p-Value
Corrected model	7	2788.72*	398.39	248.64	2.21	<0.0001
Intercept	1	122.82	122.82	76.65	4.04	<0.0001
Treatment	3	0.11	0.037	0.023	2.80	0.9951
Kappa	1	919.02	919.02	573.57	4.04	<0.0001
Treatment × kappa interaction	3	0.99	0.33	0.21	2.80	0.8917
Error	48	76.91	1.60			
Total	56	13,458.93				
Corrected Total	55	2865.63				

*R² = 0.973 (Adjusted R² = 0.969).

VI. Analysis of variance for between-subject effects on the dependent variable (β_{11}) to test the homogeneity of slope values. Significant effects are based on a 95% confidence level (i.e., p-value ≤ 0.05).

Source		Degrees of Freedom	Adjusted Sum of Squares	Adjusted Mean Square	Computed F_0 Ratio	Critical F	p -Value
Model		4	2787.73	696.93	456.27	2.55	<0.0001
Treatment Kappa		3	10.58	3.53	2.31	2.79	0.0880
		1	2430.46	2430.46	1591.19	4.03	<0.0001
Error		51		77.90	1.53	77.90	1.53
Corrected Total		55	2865.63				
Term	Estimate	SE	Lower 95%	Upper 95%			
y-Intercept	-7.66	0.57	-8.79	-6.53			
Slope	4.67	0.12	4.44	4.91			
R ²	0.9728						
Adjusted R ²	0.9692						
Standard Deviation (predicted β_{11})	1.24						

VII. Analysis of covariance of β_{11} versus the entering kappa number for various bleaching delignification treatments prior to the D_1 stage (Table V). Statistical significance is based on a 95% confidence level (i.e., p -value ≤ 0.05).

In this statistical analysis, the regressed β_{11} is the dependent variable, the bleaching delignification treatment is an independent categorical variable, and the incoming kappa number is a continuous covariate. Prior to the ANCOVA, an ANOVA was performed with the covariate and the treatment to determine if there was an interaction between these two factors (**Table VI**); a significant interaction effect would signify that one or more of the slopes in Table V are different from one another. The ANOVA provided no statistical evidence for significant differences (i.e., $\alpha = 0.05$) among the slope values. Next, the ANCOVA was performed to resolve if distinctions among the treatment groups existed (i.e., different y -intercepts). Based on the ANCOVA evidence (**Table VII**), it was inferred that the differences among the bleaching delignification treatments are statistically insignificant at the 95% confidence interval. Hence, it was concluded from the ANOVA for homogeneous slopes (Table VI) and the ANCOVA for homogeneous y -intercepts (Table VII) that the individual linear relationships of Table V are coincidental with one another. The resulting linear expression in Table VII has tighter standard errors in the fitted slopes and y -intercept values.

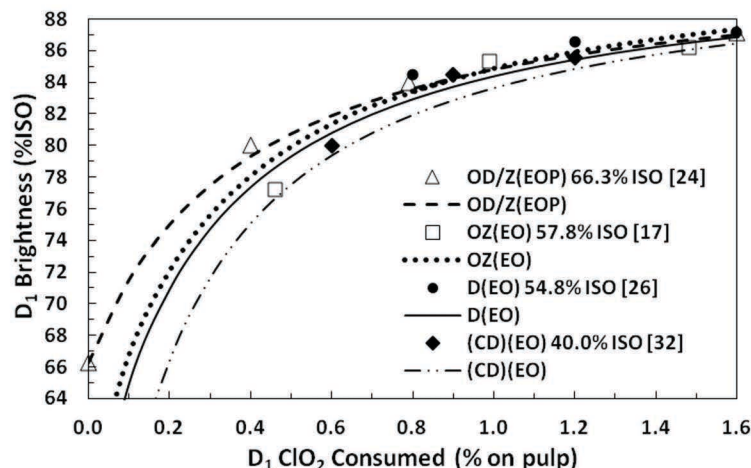
DISCUSSION

The generalized D_1 model (Eq. 1) developed for conventional ECF bleach sequences can predict D_1 stage brightness responses of oxygen-delignified softwood kraft pulps where a Z-stage has been used for additional delignification or displacement of chlorine dioxide in a D_0 stage. The asymptotic brightness parameter (c_{01}) can be estimated based upon the pulp's light scattering coefficient and the limiting light absorption coefficient (about 0.10 m²/kg).

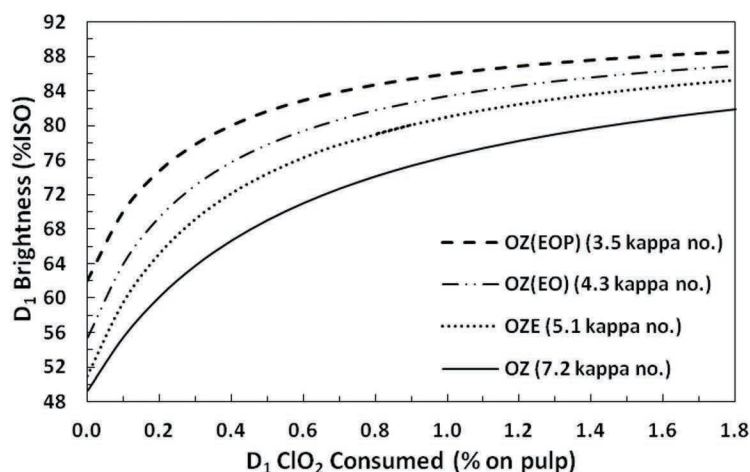
This limit is approximately 92% ISO for most softwood pulps [21,28,41-43]. The pre- D_1 pulp brightness can be used for the value of B_E . The β_{11} parameter determines the overall brightening response of the pulp. It can be calculated from the generalized relationship if the incoming kappa number is known:

$$\beta_{11} = 4.67(\text{pre-}D_1 \text{ Kappa No.}) - 7.66 \quad (3)$$

It was expected that the D_1 stage brightening response would be correlated to the incoming kappa number. This measured property has historically been used to gauge chlorine dioxide usage in brightening stages to reach a brightness target [28,41-43]. An interesting result obtained from this study is the singular linear relationship for β_{11} that holds for softwood pulps delignified by conventional ECF, Z-ECF, or chlorine-based partial sequences (Eq. 3). This finding was somewhat anticipated based on earlier work [23] with the model investigating extraction stage carryover. In that prior work, the old literature data of softwoods bleached by (CD)ED that had variable extraction carryover to D_1 was examined. It was observed that β_{11} versus pre- D_1 kappa relationships were nearly identical for conventional ECF and chlorine-based delignification sequences. The current modeling study suggests that the D_1 stage brightening responses are similar for pulps treated by different delignification sequences when compared at the same incoming kappa number. Subtle differences in the initial brightening response in the lower bleach charges (about <1% ClO₂ on pulp) are reflected by the incoming brightness parameter (B_E) of Eq. 1. This effect is illustrated in **Fig. 7** with the D_1 brightening of softwoods treated with



7. Comparisons of predicted D_1 bleaching responses of softwood kraft pulps (3.7 to 3.8 kappa number) treated with different bleaching delignification treatments. Symbols are the D_1 data from the literature studies [17,24,26,32]. Predictions from Eq. 1 with c_{01} calculated from the optical properties of the pulp (Eq. 2) and β_{11} calculated from Eq. 3. Predicted brightness values had a standard error of 1.1% ISO points.



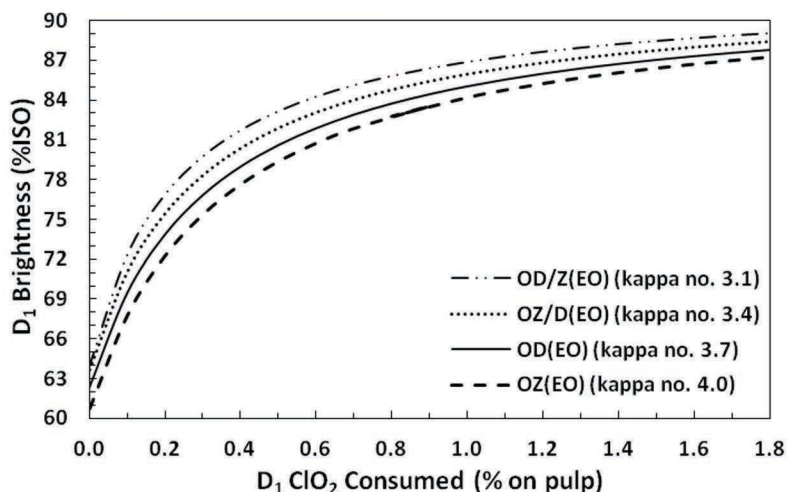
8. Model predictions for D_1 bleaching response of a Scots softwood pulp treated by various Z-ECF bleaching sequences. Incoming brightness and kappa numbers are based on data from Lindstrom [46], who investigated how alkaline extraction conditions affected OZ delignification. Predictions based on Eqs. 1–3.

different delignification sequences that have a common incoming kappa number.

The D_1 brightening model should provide reasonable predictions for Z-ECF sequences so long as the ingoing kappa number is 2 or higher. The D_1 stage brightening response of pulps with kappa numbers below 2 tends to resemble a terminal D_2 stage, such as with the D_0 (EOP) D_1 ED_2 sequence [22,28,41,45].

One drawback highlighted in the introduction of this manuscript is the dearth of published data regarding how ozone-delignified softwood pulps brighten in a D_1 stage for different Z-ECF sequences. The D_1 model can be used to estimate how modifications to Z-ECF sequences that affect the kappa and the brightness of the incoming pulp influ-

ence bleach consumption and brightness development in the D_1 stage. Examples of this are shown in **Fig. 8** and **Fig. 9**. In the first illustration, an OZ-delignified Scots pine pulp (with a kappa of 7.2 and brightness of 49.3% ISO) is treated with simple or oxidant-reinforced alkaline extraction. Using an E stage with the OZED lowers the kappa number by two units and uses 0.6% less chlorine dioxide to reach 80% ISO versus using the OZD. The model also predicts that post- D_1 brightness levels of 85% to 87% ISO are attainable if oxidant-reinforced alkaline extraction is used. In the second illustration, an oxygen-delignified Scandinavian softwood pulp is further delignified using D_0 , Z, D_0 /Z, or Z/ D_0 . Replacing half of the chlorine dioxide used in the D_0 of OD_0 (EO) D_1 with ozone (on a mass basis)



9. Model predictions for D₁ bleaching response of a Scandinavian mixed softwood pulp treated by various Z-ECF bleaching sequences. Incoming brightness and kappa numbers are based on data from Toven et al. [16], who investigated ozone substitution in the chlorine dioxide delignification. Predictions based on Eqs. 1–3.

with the OD₀/Z(EO)D₁ or OZ/D₀(EO)D₁ could reduce the chlorine dioxide needed in D₁ by 0.2% to 0.3% (on pulp) to reach 86% ISO. Conversely, replacing 50% of the ozone of the OZ(EO)D with chlorine dioxide (i.e., OD₀/Z(EO)D₁ or OZ/D₀(EO)D₁) could lower subsequent D₁ chlorine dioxide demand from 1.3% to 0.9% to reach 86% ISO. In this case, approximately 1.0 kg of O₃ can replace 1.7 kg of ClO₂, which nearly matches the theoretical replacement ratio.

CONCLUSIONS

A steady-state model of the chlorine dioxide brightening (D₁) stage has been developed and applied to conventional ECF, Z-ECF, and chlorine-based bleach sequences for softwood kraft pulps. This study focused on the application of the brightening model to softwood pulps delignified by OZ, OZ/D₀, and OD₀/Z that can predict the exit brightness or D₁ bleach consumption based on inputs of incoming pulp kappa number and brightness. The upper brightness constraint of the model can be calculated from the optical characteristics of the pulp, which is about 92% ISO for most softwood pulps. The incoming pulp brightness defines the initial brightening response of the pulp at low bleach charges. The overall D₁ brightening response parameter, β_{11} , is linearly correlated to the ingoing kappa number to the D₁. This linear correlation was found to be statistically unaffected by the bleaching delignification treatment, whether it is conventional ECF, Z-ECF, or chlorine-based partial sequence. Indeed, the model predicts similar bleaching responses of softwood kraft pulp delignified to the same kappa number by ECF, Z-ECF, or chlorine-based sequences, as observed from laboratory studies. The model can be used to illustrate how modifications to Z-ECF delignification consequently affect D₁ brightening and chlorine dioxide consumption. **TJ**

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LITERATURE CITED

- Hart, P.W., "Pulp bleaching," in *Kirk-Othmer Encyclopedia of Chemical Technology*, Online edn., John Wiley & Sons, Inc., Hoboken, NJ, 2019. <https://doi.org/10.1002/0471238961.1621121613030415.a01.pub3>.
- Metais, A. and Germer, E., *Paper360°* 13(4): 46(2018).
- Freeman, D., "Ozone delignification," in *The Bleaching of Pulp* (P.W. Hart and A.W. Rudie, Eds.) 5th edn., TAPPI Press, Peachtree Corners, GA, USA.
- van Lierop, B., Skothos, A., and Liebergott, N., "Ozone delignification," in *Pulp Bleaching: Principles and Practice* (C.W. Dence and D.W. Reeve, Eds.), TAPPI Press, Peachtree Corners, GA, 1996.
- Hostachy, J., *TAPPI J.* 9(8): 16(2010). <https://doi.org/10.32964/TJ9.8.16>.
- Metais, A. and Germer, E., *Paper360°* 11(2): 44(2016).
- Metais, A. and Germer, E., *Paper360°* 11(3): 52(2016).
- Metais, A., Hostachy, J.-C., and Van Wyk, B., *Paper360°* 8(5): 38(2013).
- TIP 0606-21, "Recommended pulp bleaching stage designation method," in *TAPPI Technical Information Papers*, TAPPI PRESS, Peachtree Corners, GA, 2015.
- Liebergott, N. and van Lierop, B., *Tappi* 64(6): 95(1981).
- Liebergott, N., van Lierop, B., and Kubes, G.J., *Ozone: Sci. Eng.* 4(3): 109(1982). <https://doi.org/10.1080/01919518208550950>.
- Fisher, S., Corbeil, S., and Sundar, M., "Strength preservation in ozone bleaching using (D/Z) or (Z/D) at low consistency," *TAPPI Pulping Conf.*, TAPPI Press, Peachtree Corners, GA, 1998, p. 1429.

13. Homer, G., Epiney, M., Muguet, M., et al., *Pulp Pap. Can.* 98(8): T269(1997).
14. Chirat, C. and Lachenal, D., *TAPPI J.* 80(9): 209(1997).
15. Chirat, C., Lachenal, D., Angelier, R., et al., *J. Pulp Pap. Sci.* 23(6): J289(1997).
16. Toven, K., Gellerstedt, G., Kleppe, P., et al., *J. Pulp Pap. Sci.* 28(9): J305(2002).
17. Gupta, M.K. and Eckert, R.C., "OZ prebleaching: Influence on viscosity and sheet strength," *TAPPI Oxygen Delignification Symp. Notes*, TAPPI Press, Peachtree Corners, GA, 1984, p. 133.
18. Brown, J., Cheek, M.C., Jameel, H., et al., *TAPPI J.* 77(11): 105(1994).
19. Lindholm, C.-A., *Nord. Pulp Pap. Res. J.* 9(1): 31(1994).
<https://doi.org/10.3183/npprj-1994-09-01-p031-036>.
20. Lindholm, C.-A., *J. Pulp Pap. Sci.* 16(6): J190(1990).
21. Brogdon, B.N., *TAPPI J.* 13(3): 17(2014).
<https://doi.org/10.32964/TJ12.2.17>.
22. Brogdon, B.N., *TAPPI J.* 16(5): 263(2017).
<https://doi.org/10.32964/TJ16.5.263>.
23. Brogdon, B.N., *TAPPI J.* 15(3): 178(2016).
<https://doi.org/10.32964/TJ15.3.178>.
24. McDonough, T. and Turner, M., "Partial replacement of ClO₂ by O₃ in the D₀ stage," unpublished data, Institute of Paper Science and Technology, Atlanta, GA, USA, 19-20 October 1999.
25. McDonough, T.J., Rawat, N., and Turner, M., *Appita Annu. Gen. Conf. Proc., 51st*, Melbourne, Appita, Macleod, Vic., Australia, 1997, p. 255.
26. McDonough, T.J., Krishnagopalan, G.A., Rawat, N., et al., *Int. Pulp Bleaching Conf.*, SPCI, Stockholm, 1998, p. 296.
27. McDonough, T.J., Krishnagopalan, G.A., Rawat, N., et al., *10th International Symposium of Wood and Pulping Chemistry*, Japan TAPPI, Tokyo, 1999, pp. 296-301.
28. Basta, J., Andersson, L., Blom, C., et al., *TAPPI Pulping Conf.*, TAPPI Press, Peachtree Corners, GA, 1992, p. 547.
29. Brogdon, B.N. and Lucia, L.A., *J. Wood Chem. Technol.* 25(3): 149(2005). <https://doi.org/10.1080/02773810500191716>.
30. Brogdon, B.N. and Lucia, L.A., *J. Wood Chem. Technol.* 25(3): 133(2005). <https://doi.org/10.1080/02773810500191690>.

ABOUT THE AUTHORS

We wanted to ascertain if the simple D₁ brightness model, which was originally developed for conventional elemental chlorine-free (ECF) bleaching sequences with chlorine dioxide delignification (D₀), could accurately predict the D₁ brightness of softwood kraft pulps delignified by ozone (Z) or combinations of ozone and chlorine dioxide, such as Z/D₀ and D₀Z. There is limited literature data about how ozone-delignified pulps brighten in a D₁ stage if the incoming D₁ kappa number and/or the D₁ bleach charge are altered. If the D₁ model applies to ECF sequences that use a Z stage (for example, Z-ECF), then the model could provide approximations to answer what happens to bleached brightness when entering D₁ kappa number and/or bleach charge changes. This work is an extension of previous D₁ stage modeling work with softwoods bleached by conventional ECF bleaching sequences that were published in *TAPPI J.* 13(3): 17(2014) and *TAPPI J.* 15(3): 178(2016).

The challenge we encountered with this research is the limited amount of published laboratory data that systematically investigated how exiting D₁ brightness is affected by prior delignification treatment and entering D₁ pulp properties. We were able to locate a limited number of published studies from the 1980s and 1990s that methodically examined these factors. The information from these studies was used in our study to develop and test the D₁ brightness model for Z-ECF bleach sequences.

We were able to show that once the tuning parameters of the model could be calculated for Z-ECF bleach sequences based on incoming pulp properties, the resulting mathematical expression could predict post-D₁ brightness within acceptable limits.

One of the most interesting discoveries from our investigation was that one of the model's parameters (β_{11}) is correlated to the kappa number of the pulp entering the D₁ stage and that this correlation is the same for all softwoods, regardless of the delignification partial sequence used and whether it is conventional ECF, Z-ECF, or molecular chlorine-based sequences.

This generalization allows the D₁ model to apply to other softwood pulps treated with alternative delignification sequences.

Engineers and operators can use this simple model to predict how much chlorine dioxide is needed to obtain a post-D₁ brightness target should the entering D₁ kappa number change due to a process upset.

Alternatively, the model could be coupled with other steady-state models of other bleaching stages in a spreadsheet to optimize chemical usage in bleach sequences and to minimize bleaching costs.

Future work will attempt to develop generalized D₁ stage models for hardwood and eucalypt pulps for Z-ECF bleaching sequences.



Brogdon



Lucia

Brogdon is president at Future Bridge Consulting Services LLC, Marietta, GA, USA. Lucia is associate professor at North Carolina State University, Raleigh, NC, USA. Email Brogdon at brian.brogdon@gmail.com.

31. Suess, H.U. and Davies D., *Pulp Pap. Can.* 108(7/8): 41(2007).
32. Liebergott, N., van Lierop, B., Kovacs, T., et al., *TAPPI Pulping Conf.*, TAPPI Press, Peachtree Corners, GA, 1990, p. 429.
33. Histed, J., McCubbin, N., and Gleadow, P.L., "Water reuse and recycle," in *Pulp Bleaching: Principles and Practice* (C.W. Dence and D.W. Reeve, Eds.), TAPPI PRESS, Peachtree Corners, GA, 1996.
34. Pattysen, G., Rae, R.G., Reeve, D.W., et al., *Pulp Pap. Can.* 82(6): T212(1981).
35. Reeve, D.W., "Bleaching technology," in *Pulp and Paper Manufacture, Alkaline Pulping* (T.M. Grace, B. Leopold, E.W. Malcolm, et al., Eds.) Vol. 5, Joint Textbook Committee of the Paper Industry, TAPPI/CPPA, Peachtree Corners, GA/Montreal, QC, 1989.
36. Huitema, B.E., *The Analysis of Covariance and Alternatives*, 2nd edn., John Wiley & Sons Inc., Hoboken, NJ, USA, 2011.
37. Montgomery, D.C., Peck, E.A., and Vining, G.G., *Introduction to Linear Regression Analysis*, 5th edn., John Wiley & Sons Inc., Hoboken, 2012.
38. Teder, A. and Tormund, D., "Kinetics of chlorine dioxide bleaching," *Trans. Tech. Sect. CPPA* 3(2): 41(1977).
39. Middleton, S.R. and Scallan, A.M., *Nord. Pulp Pap. J.* 7(1): 22(1992).
<https://doi.org/10.3183/nppri-1992-07-01-p022-024>.
40. Nanko, H., Button, A., and Hillman, D., "Market pulp atlas," in *The World of Market Pulp* (C.E. Swann, Ed.) 3rd edn., WOMP LLC, Appleton, WI, USA, 2005.
41. Connell, D. and Carmichael, S., "Chlorine dioxide as a brightening agent," in *The Bleaching of Pulp* (P.W. Hart and A.W. Rudie, Eds.) 5th edn., TAPPI Press, Peachtree Corners, GA, 2012.
42. Germgård, U. and Karlsson, R.-M., *Pap. Puu* 66(11): 627(1984).
43. Germgård, U. and Karlsson, R.-M., *Pap. Puu* 67(11): 655(1985).
44. Rapson, W.H. and Anderson, C.B., *Int. Pulp Bleaching Conf.*, CPPA, Montreal, 1985, p. 227.
45. Ragnar, M., *Nord. Pulp Pap. Res. J.* 18(2): 162(2003).
<https://doi.org/10.3183/nppri-2003-18-02-p162-167>.
46. Lindholm, C.-A., *J. Pulp Pap. Sci.* 19(3): J108(1993).

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