

Improved steady-state models for chlorine dioxide delignification sequences that include washer carryover effects

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ABSTRACT: In previous studies, generalized steady-state models were proposed to approximate the chlorine dioxide demand needed for the delignification of softwood and hardwood pulps, where the kappa number entering the bleach plant can fluctuate. However, these expressions neglect the effect of dissolved solids with the stock that originate from incomplete pulp washing. In this study, the original elemental chlorine-free (ECF) models are modified to include the effects of carryover from brownstock or post-oxygen washing. The stoichiometric bleach consumption from carryover, based on its composition, was calculated from various literature sources. The majority of the bleach demand (about 70%) results from the dissolved lignin contained in the brownstock carryover, with the remainder resulting from the inorganic sulfur constituents (e.g., sulfide and thiosulfate). When the effect of brownstock carryover was taken into account, the modified models accurately predicted the amount of chlorine dioxide consumed for a given delignification level (about $\pm 0.1\%$ chlorine dioxide) vs. actual bleach plant data. The improved models can be used to gauge the level of washer carryover entering the bleach plant if this parameter is not regularly monitored by the mill. Additionally, these modified expressions could be integrated into advanced process control strategies for ECF bleaching where the washer carryover or dissolved lignin entrainment is measured with online sensors.

Application: The modified steady-state models predict chlorine dioxide consumption needed for bleaching delignification for a variety of incoming kappa numbers and washer carryover levels. The models can be used for bleach plant optimizations, process control strategies, and computer simulations.

Most lignin removing processes used for pulp manufacturing, whether kraft pulping, oxygen (O_2), or chlorine dioxide delignification (D_0), can be divided into several steps. These steps include the mixing of chemicals and steam with the chips or pulp, the reactions in a reactor or tower, and the washing and removal of dissolved organics and spent reactants from the pulp [1-3]. Each of these steps influences the overall efficiency of the unit operation to delignify selectively while minimizing energy demands, chemical consumption, and environmental impacts [1-12]. Incomplete washing between coupled delignification operations, such as the kraft digester and the D_0 stage, will result in the carryover of dissolved solids into the bleach plant. Consequently, this will increase bleach consumption, as well as saltcake or make-up caustic demand in chemical recovery to balance the soda losses. However, minimizing carryover losses with extra wash water has to be judiciously balanced against the increased energy demand incurred when concentrating a more dilute black liquor stream sent to the evaporators [2,7-12].

Engineers often use numerical models to simulate various unit operations involved with bleach pulp production. Such models are very useful when optimizing unit opera-

tions individually or linked with one another [2-9,13-28]. Coupled models are particularly valuable to show how one operation in the mill, such as the bleach plant, directly affects other interconnected operations, such as the evaporators, digester, and recovery boiler, either in a positive or negative manner [2,13,27]. This can allow the process engineer to more effectively optimize the overall economic performance of the mill as a whole rather than sub-optimizing for gains in a given area that might be lost from negative consequences elsewhere [2].

Previous research developed generalized steady-state models to simulate bleaching stages that comprise elemental chlorine-free (ECF) sequences for softwood and hardwood pulps [23-26]. The new expressions are based on ECF laboratory data from the available literature and on earlier stoichiometric functions used to predict bleaching delignification and brightening [18-20,28]. Steady-state models of bleaching stages, such as the modified expressions, could be used for process control [22,29-34] and for balancing chlorine dioxide usage across multiple stages [3,13,18-20,30].

The new ECF delignification functions can handle a range of pre- D_0 kappa numbers, as well as variable

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oxidant-reinforced extraction conditions [23,24]. This allows the models to predict extracted kappa numbers or D_0 bleach demand. This feature of variable pre- D_0 kappa number can be used to evaluate how changes made at the kraft digester, either to increase pulp yield or production rates, affect chlorine dioxide consumption and pulp bleachability at the bleach plant [2,13]. In addition, this attribute provides flexibility in the model's capacity to analyze mill data, where there is some natural process variability in the kappa number entering the bleach plant [13,22,29,34].

One factor that has yet to be incorporated into the ECF delignification model is the effect of brownstock or post-oxygen washer carryover. This added feature would permit the user to evaluate how changes made to brownstock or post-oxygen washing operations affect chemical consumption during bleaching. Conversely, this component could be used to estimate the carryover from the pulp washers entering the bleach plant if this parameter is not regularly measured or monitored.

The objective of this paper is to propose generalized mathematical models for chlorine dioxide delignification that account for how carryover affects the predicted kappa number after extraction for a given D_0 bleach charge. Published data from the literature will be used to estimate the stoichiometric relationship of chlorine dioxide consumption to the amount of carryover contained in the pulp. The revised models will be validated with actual bleach plant data.

BACKGROUND

Washer carryover

Unbleached or oxygen-delignified pulp slurries exiting the pulp mill and entering the bleach plant will contain some dissolved materials. This dissolved material, or carryover, is typically comprised of inorganics that originated from the kraft cooking liquor. It also contains organics from the dissolved wood, such as degraded lignin and carbohydrates. Carryover arises from the incomplete removal and recovery of this material during pulp washing. Washer losses for most modern pulp mills range from 1% to 5% of the dissolved solids from the digester [7-12,35]. These losses are generally at the lower range for pulp mills producing bleached stocks. Carryover can be expressed as soda or saltcake loss (kilograms/ton pulp either as equivalent sodium oxide [Na_2O] or sodium sulfate [Na_2SO_4]), chemical oxygen demand (COD) (kilograms oxygen/ton pulp), wet or liquid kappa (kappa units/milliliter of pulp filtrate), total dissolved solids or black liquor solids (kilograms/ton pulp), or conductivity (millisiemens/centimeter [mS/cm]) [7-12,35-38]. Bleach mills typically monitor carryover by measuring conductivity or refractive index, either with online sensors or from washer samples. These measurements can be correlated to saltcake or dissolved solids losses. Washer

efficiencies may be assessed from samples taken occasionally from the washer lines, which are analyzed in the laboratory for COD, dissolved solid, or sodium levels.

Surveys conducted over the past two decades polled North American pulp mills on the levels of carryover entering the ECF bleaching processes [39-41]. Washed softwood brownstocks and oxygen-delignified pulps were reported to contain carryover contents ranging from 5 kg to 20 kg COD or saltcake per metric ton pulp. These surveys noted that the average values were 8-10 kg Na_2SO_4 or 8-15 kg COD per metric ton pulp for brownstocks, whereas values were 8-9 kg Na_2SO_4 or 8-11 kg COD per metric ton pulp for oxygen-delignified pulps. Hardwood brownstocks and oxygen-delignified pulps generally have similar saltcake or COD carryover statistics as their softwood counterparts.

Chlorine dioxide consumption from washer carryover constituents

Before ECF bleaching, the industrial rule of thumb was that 1-1.5 kg of active chlorine was consumed for every kilogram of carryover, expressed as equivalent Na_2SO_4 , entering the chlorination stage [7,8,42,43]. Post-oxygen washer carryover, when measured as COD, had been reported by several investigators to expend an additional 0.5-0.8 kg of active chlorine for every kilogram of COD that comes into chlorination [43-46]. **Table I** lists some values on the stoichiometry of chlorine dioxide uptake by pulp washer carryover into the D_0 stage [9,11,27,41,45,47-51]. These values were either obtained from the literature or calculated from literature data. In general, washer carryover tends to consume about 20% more chlorine than chlorine dioxide when compared on an active chlorine basis.

There is some variability in the reported values of chlorine dioxide consumption caused by washer carryover. Part of the scatter is related to how the carryover is quantified, whether it is kilograms of equivalent saltcake, COD, or dissolved solids. The relationship between the various characterization methods for carryover varies depending on pulp yield and wood species (**Table II**) and the composition of the kraft cooking liquor. The COD values reported are approximated using literature methods [52,53] and are comparable to reported observations [54-56]. The main components in the black liquor carryover contributing to bleach consumption in the D_0 stage are the dissolved kraft lignin, sodium sulfide, sodium thiosulfate, and sodium sulfite (**Table III**).

Typically, 60% to 70% of the dissolved solids are composed of degraded wood components, whereas the balance contains various inorganic species. Dissolved lignin accounts for ~30% of the total dissolved solids (Table II). Much of the other dissolved wood organics (Table III), arising from the degraded carbohydrates, besides hexenuronic acid [57], have been demonstrated by Viirimaa

Source	Value	Units	Comments
Connell and Carmichael [41]	0.15 to 0.23	kg ClO ₂ /kg COD	Brownstocks
Pryke [47]	0.30	kg ClO ₂ /kg Na ₂ SO ₄	Softwood brownstock; calculated from 0.8 kg active Cl ₂ /kg Na ₂ SO ₄ value for ClO ₂
	0.13	kg ClO ₂ /kg soda (Na ₂ O)	Calculated from Na ₂ SO ₄ value using 2.29 Na ₂ O/Na ₂ SO ₄ ratio
	0.18 to 0.20	kg ClO ₂ /kg dissolved solids (DS)	Estimated from Na ₂ SO ₄ value using 1.5 to 1.7 DS/Na ₂ SO ₄ ratio
Compton [9]	0.17	kg ClO ₂ /kg DS	Brownstocks
Lunn [45]	0.23	kg ClO ₂ /kg COD	Calculated from 0.6 kg active Cl ₂ /kg COD value for D ₀ from Lunn's literature survey.
Turner et al. [11]	0.15 to 0.19	kg ClO ₂ /kg DS	Calculated from 0.4 to 0.5 kg active Cl ₂ /kg DS value for D ₀ and (DC) delignification
Brunner [27]	0.16	kg ClO ₂ /kg COD	Calculated from data for ~17-kappa softwood and hardwood brownstocks
Barroca et al. [48]	0.19	kg ClO ₂ /kg COD	Eucalyptus brownstock; calculated from 3.5 to 21 kg COD/ton data
Miller and Lennon [49]	0.13 to 0.16	kg ClO ₂ /kg COD	Post-O ₂ softwood; calculated from the data and compared to a similar post-O ₂ softwood bleaching study that examined different D ₀ ClO ₂ charges[50]
Maples et al. [51]	0.096 to 0.16	kg ClO ₂ /kg DS	Post-O ₂ softwood and hardwood; calculated from overall bleach sequence (mill data)

I. Chlorine dioxide (ClO₂) consumption in the D₀ stage caused from brownstock and post-oxygen washer carryover, either reported or calculated from literature bleaching data (COD = chemical oxygen demand).

Yield	Kappa	Black Liquor (per kg brownstock)				Ratios			
		Dissolved Solids (DS) (kg)	COD (kg)	Saltcake Equivalent (kg)	Lignin (kg)	COD/DS	DS/ Saltcake	COD/ Saltcake	Lignin/DS
Mixed Softwoods (Southern United States)									
47.4	30	1.88	1.66	1.23	0.579	0.880	1.52	1.34	0.308
46.5	27	1.91	1.71	1.21	0.596	0.898	1.57	1.41	0.313
45.5	24	1.94	1.78	1.19	0.615	0.918	1.64	1.50	0.317
44.3	21	1.98	1.86	1.15	0.637	0.941	1.71	1.61	0.322
Mixed Hardwoods (Southern United States)									
49.0	18	1.71	1.51	1.12	0.484	0.883	1.53	1.35	0.283
47.6	16	1.75	1.59	1.09	0.500	0.907	1.62	1.46	0.285
46.1	14	1.80	1.68	1.05	0.517	0.933	1.71	1.60	0.287
44.6	12	1.85	1.77	1.02	0.535	0.955	1.82	1.74	0.289

II. Approximated values for softwood and hardwood black liquor carryover that cover a range of brownstock yields and kappa numbers. (COD values are estimated from black liquor constituents and appropriate COD multiplication factors [52,53] for each component. COD values are comparable to literature reports [54-56]).

Data Source	Value	Units	Comments
Dissolved Organics			
Virrimaa et al. [58]	0.40	kg ClO ₂ /kg kraft lignin	Kraft lignin; calculated from the data and compared to a similar softwood bleaching study [50] that examined different D ₀ ClO ₂ charges
	0.29	kg ClO ₂ /kg oxidized lignin	Isolated O ₂ kraft lignin; calculated from the data and compared to a similar softwood bleaching study [50] that examined different D ₀ ClO ₂ charges
	~0	kg ClO ₂ /kg alkali-degraded carbohydrates	Addition of about 10 kg/ton pulp of glycolic acid, glucose, or succinic acid to D ₀ stage did not have a noticeable effect on bleaching delignification
Inorganic Sulfur Species			
Masschelein [60] and Pan et al. [61]	0.82 - 0.86	kg ClO ₂ /kg Na ₂ S	Sources indicate that sulfides are oxidized to elemental sulfur or thiosulfate along with sulfate; Pan et al. [61] indicated that only 40% of ClO ₂ is fully reduced to chloride
Masschelein [60]	0.21	kg ClO ₂ /kg Na ₂ SO ₃	Oxidation of sulfite to sulfate and reduction of ClO ₂ to chloride
Ferweda [62]	0.42	kg ClO ₂ /kg Na ₂ S ₂ O ₃	Oxidation of thiosulfate to sulfate and reduction of ClO ₂ to chloride

III. Calculated chlorine dioxide uptake in the D₀ stage caused from individual components in washer carryover.

et al. [58] to contribute negligibly to bleach uptake during chlorine dioxide delignification of a 14.2-kappa softwood. These investigators showed that the addition of 0.53% kraft lignin to this pulp caused the post-D₀E₁ kappa to increase from 4.3 to 5.1. This shift corresponds to a bleach uptake of 0.40 kg chlorine dioxide per kilogram lignin when compared to a similar ECF bleaching study [50], which examined various chlorine dioxide charges. From this value, we can calculate a stoichiometric value of 0.11-0.13 kg chlorine dioxide per kilogram of total dissolved solids (on a weighted basis) (Table II). This assumes that the lignin is the only contributing factor. These figures, however, are about 30% lower than the values listed in Table I from the literature. The difference is likely related to the bleach neutralization reactions that occur with the inorganic species.

Sodium sulfide, sodium thiosulfate, and sodium sulfite roughly comprise 13%, 22%, and 10% of the total inorganics, respectively, found in spent kraft liquor [59]. Each of these inorganic sulfur species react with chlorine dioxide (Table III). Based on these stoichiometric values [60-62], we can estimate that the inorganic portion of the brownstock carryover will neutralize 0.07-0.09 kg of chlorine dioxide per kilogram of total dissolved solids. When these calculations are added to the earlier values computed for lignin alone, the overall carryover has a bleach uptake of 0.18-0.22 kg chlorine dioxide per kilogram of dissolved solids. This approximation is close to the stoichiometric

values listed in Table I from the literature for dissolved solids of brownstock carryover.

The carryover emanating from oxygen delignification differs from kraft digester carryover [35,46,54-56]. Approximately 50% to 80% of the dissolved material arising from oxygen delignification is comprised of organics. Normally, the COD/dissolved solids ratio of this material ranges from 0.6 kg to 0.8 kg COD/kilogram dissolved solids [35,46,54]. It is comprised of 30% to 40% oxidized kraft lignin and 20% to 40% carbohydrates. Viirima et al. [58] examined the addition of 0.53% oxygen-treated kraft lignin to a softwood pulp before D₀E₁ delignification. The investigators saw the extracted kappa number rise from 4.3 to 4.8. This increase in extracted kappa, similar to the previous case with kraft lignin, suggests that 0.29 kg of chlorine dioxide is consumed for every kilogram of oxygen-treated lignin. From this value, we arrive at a stoichiometric bleach uptake of 0.087-0.11 kg chlorine dioxide per kilogram dissolved solids from the oxidized lignin alone (~0.11-0.18 kg ClO₂/kg COD). These values are relatively close to the values listed in Table I for post-oxygen carryover. Somewhat higher stoichiometric values than the ones listed in Table I might be explained by the sodium thiosulfate content in the inorganic dissolved solids. This dissolved solid comes from the oxidized white liquor, which is often used as the alkali for oxygen delignification [46,63,64]. As shown for brownstock carryover, sodium thiosulfate can contribute to the overall bleach demand.

Kinetic modeling of bleach consumption from washer carryover

Relatively few studies have incorporated the effects of washer carryover into bleach sequence models. Barroca et al. [48] developed a kinetic model of the D₀ stage for treating eucalypt pulps with various levels of brownstock carryover. The investigators noted that chlorine dioxide reacts very rapidly with the dissolved solids in the carryover and the bound lignin in the pulp fibers. The study showed that the depletion of chlorine dioxide caused by the carryover occurs in the fast reaction phase, which lasts for the first 15 s. Gu and Edwards developed a reaction network kinetic model for the D₀ stage [15-17]. Their model is based on 15 rate expressions, which included the reactions of chlorine dioxide with various components found in the carryover. Chlorine dioxide reacts very rapidly with the dissolved lignin—almost as quickly as the fiber-bound lignin.

The kinetic models can simulate the influence of carryover on D₀ bleach consumption. However, these kinetic models generally require the aid of specialized software programs to compute because the differential equations are coupled with other kinetic expressions, which must be solved simultaneously by numerical methods to determine the total bleach consumption. A simpler approach to simulate an ECF delignification sequence is to use steady-state models [3,13,18-20,23-26], which can be easily calculated in a spreadsheet program.

INCORPORATING CARRYOVER EFFECTS INTO THE STEADY-STATE MODEL

Previous generalized steady-state models

In earlier works [23,24], generalized steady-state expressions were developed to predict the amount of bleach consumed to obtain a targeted extracted kappa number, and vice versa. The models can simulate various chlorine dioxide delignification sequences, such as D₀(EO), D₀(EOP), etc. These models can manage a wide range of kappa numbers entering the D₀ stage and as a range of extraction stage conditions. The expressions for softwood and hardwood kraft pulps are Eqs. (1) and (2), respectively:

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

$$[Kappa^*] = 1 - \frac{1}{n} \cdot \ln\left(\frac{[ClO_2] + 2.77 \cdot e^{-n}}{2.77 \cdot e^{-n}}\right) \quad (2)$$

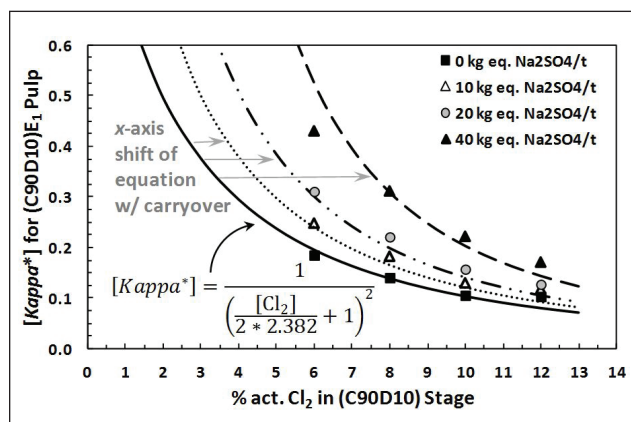
where A and n are stoichiometric coefficients for softwood and hardwood pulps, respectively, $[ClO_2]$ is the chlorine dioxide charge (% ClO_2 on pulp), and $[Kappa^*]$ is the normalized extracted kappa number. This term, $[Kappa^*]$, is defined as:

$$[Kappa^*] = \frac{[Kappa]}{[Kappa_0]} \quad (3)$$

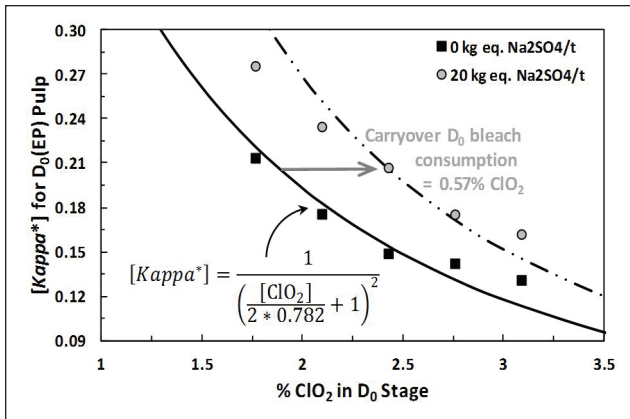
where $[Kappa_0]$ is the kappa number of the pulp entering the D₀ stage and $[Kappa]$ is the extracted kappa number. The values of A and n can be determined via curve fitting of experimental bleaching data and tend to be linear functions of extraction conditions (i.e., extraction temperature and peroxide charge [23,24]). Both A and n are positive and non-zero.

Modeling ECF delignification with washer carryover

Laboratory bleaching data from various sources [42,47,65-67] were analyzed to assess the repercussions of washer carryover on the steady-state ECF delignification models. The first example is from the investigation conducted by Reeve [42] on a softwood brownstock. Although the Reeve study examined the chlorination sequence, (C90 D10)E₁, it is the only study that examined multiple levels of washer carryover. The data without any carryover were fitted to Eq. (1) using the $[Cl_2]$ term, expressed as percent active chlorine on pulp, in place of the $[ClO_2]$ term. The results are plotted in Fig. 1, along with the carryover data expressed as kilograms Na_2SO_4 /ton pulp. The fitted curve for the well-washed pulp is horizontally translated to the right when carryover is included with the brownstock. The magnitude of this displacement is directly proportional to the amount of carryover. In this particular case, the stoichiometric constant is 0.105% active chlorine per kilogram Na_2SO_4 /ton pulp (i.e., 1.05 kg active Cl_2 /kg Na_2SO_4), which is close to Reeve's calculated values of ~0.15% active chlorine per kilogram Na_2SO_4 /ton pulp [42].



1. Bleach consumption (as percent active chlorine on pulp) in the (C90 D10) stage versus the normalized (C90 D10)E₁ kappa number, $[Kappa^*]$ (Eq. [3]). Data are from the laboratory study of Reeve [42], which used a 32.7-kappa softwood brownstock. Well-washed data fitted to Eq. (1) where the percent active chlorine charge, $[Cl_2]$, was substituted for $[ClO_2]$. The data for the pulps with different levels of black liquor carryover can be modeled with the same equation with an x-axis translation correction.



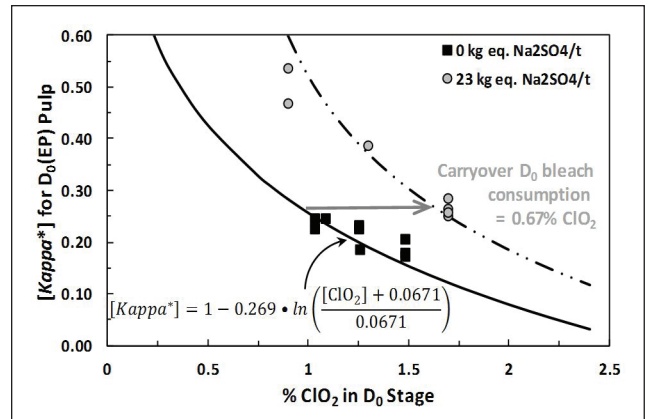
2. ClO_2 consumption (as % ClO_2 on pulp) in the D_0 stage versus the normalized $D_0(\text{EP})$ kappa number, $[\text{Kappa}^*]$ (Eq. [3]). Data are from the $D_0(\text{EP})$ laboratory study of Pryke [47], which used a 29-kappa softwood brownstock. Well-washed data fitted to Eq. (1). The data for the brownstock with black liquor carryover can be modeled with the same equation with an appropriate horizontal displacement correction.

The next laboratory data set is from a University of Toronto study [47]. The study examined the $D_0(\text{EP})$ delignification of a softwood brownstock with and without black liquor carryover. Equation (1) was used to analyze the data. **Figure 2** shows the results. Again, the fitted function for the well-washed pulp could model the pulp with black liquor entrainment when the appropriate horizontal translation is taken into account. The amount of chlorine dioxide consumed by the 20 kg Na_2SO_4 /ton pulp carryover, which is the horizontal displacement, was approximately 0.57%. This yielded a stoichiometric bleach coefficient of 0.029% chlorine dioxide per kilogram Na_2SO_4 /ton pulp (0.29 kg ClO_2 /kg Na_2SO_4).

The third example is from several ECF delignification surveys [64–66] with a mixed hardwood brownstock that came from the same pulp mill. In one of the studies [65,66], the hardwood brownstock was well washed. In the other investigation [67], the brownstock included the mill's typical brownstock carryover (~23 kg Na_2SO_4 /ton pulp or ~35 kg COD/ton pulp [68]). The data from these laboratory studies were evaluated with the hardwood model, Eq. (2). **Figure 3** shows that the fitted curve for the well-washed pulp was translated to the right by ~0.67% chlorine dioxide for the pulp that contained the entrained black liquor. This indicated that the stoichiometric coefficient of the hardwood carryover was 0.029% chlorine dioxide per kilogram Na_2SO_4 /ton pulp (0.29 kg ClO_2 /kg Na_2SO_4) when expressed as saltcake loss, or 0.019% chlorine dioxide per kilogram COD (0.19 ClO_2 /kg COD) when expressed as COD.

Modification of the ECF steady-state models

The previous analyses suggest that the influence of carryover on bleach consumption can be approximated with simple modifications to Eqs. (1) and (2) for softwoods and hard-



3. ClO_2 consumption in the D_0 stage versus the normalized $D_0(\text{EP})$ kappa number, $[\text{Kappa}^*]$. Data taken from $D_0(\text{EP})$ laboratory studies [65–67], which used a 15-kappa mixed-hardwood brownstock from the same mill. Well-washed data fitted to Eq. (2). Data for the hardwood brownstock with black liquor carryover can be modeled with the same expression with an appropriate x-axis translation term. Black liquor carryover was ~23 kg Na_2SO_4 /ton pulp (~35 kg COD/ton pulp) [67,68].

woods, respectively. The approximation includes the horizontal displacement caused by the bleach consumption of the carryover, $\gamma \cdot [\text{C.O.}]$, into the original expressions:

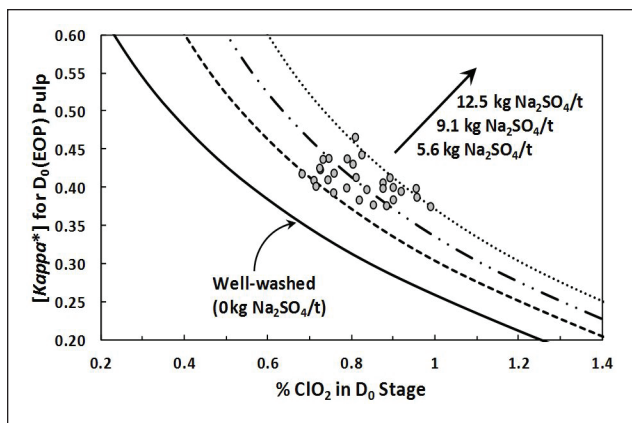
$$[\text{Kappa}^*] = \frac{1}{\left(\frac{[\text{ClO}_2] - \gamma \cdot [\text{C.O.}]}{2A} + 1\right)^2} \quad (4)$$

$$[\text{Kappa}^*] = 1 - \frac{1}{n} \cdot \ln\left(\frac{[\text{ClO}_2] - \gamma \cdot [\text{C.O.}] + 2.77 \cdot e^{-n}}{2.77 \cdot e^{-n}}\right) \quad (5)$$

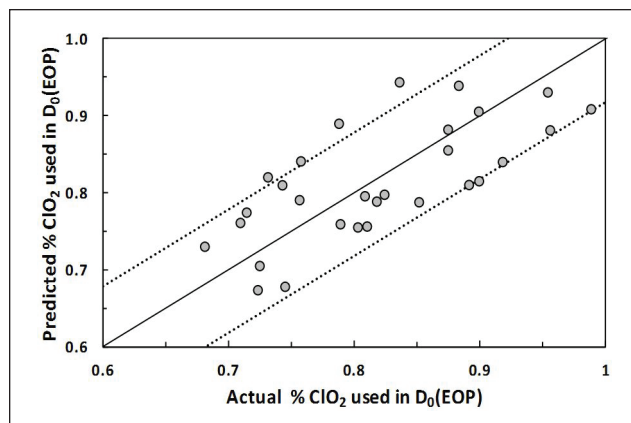
where $[\text{C.O.}]$ is the washer carryover entering the D_0 stage and γ is the stoichiometric coefficient for this material. The units of these terms can vary, depending on how the carryover is expressed, but the product of the terms is percent chlorine dioxide. Equations (4) and (5) assume that the contribution of D_0 stage washer carryover into the extraction stage is negligible. Literature reports [69,70] note that a moderate level of D_0 filtrate carryover into the extraction stage has an insignificant effect on the pulp's kappa number exiting extraction. Equations (4) and (5) should be valid for $[\text{Kappa}^*]$ values less than 0.45, which covers the industrial range of chlorine dioxide delignification sequences. Equations (4) and (5) are very simple mathematical approximations of the original expressions without the effect of washer carryover [23,24].

VALIDATION OF THE MODELS WITH MILL DATA

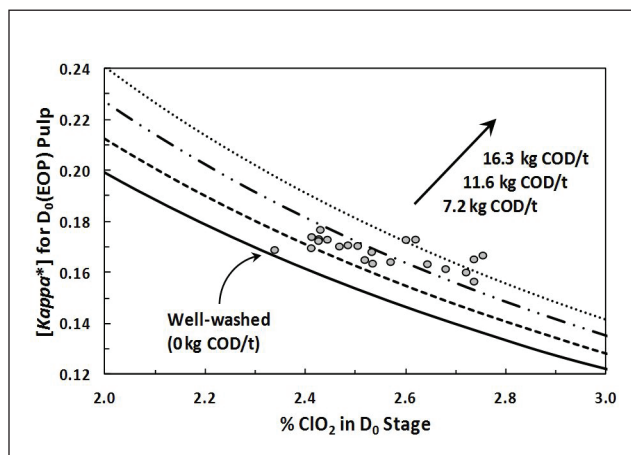
Bleach plant data for hardwood and softwood kraft pulps were obtained from two different sites to test the validity of the ECF delignification models that included carryover



4. Bleach plant data for chlorine dioxide consumption in the D_0 stage versus the normalized D_0 (EOP) kappa number, $[Kappa^*]$, for a southern U.S. hardwood brownstock. Plotted data are daily averages from a 4-week period where the brownstock kappa varied from 10.2 to 13.8 and washer losses varied from 5.6 kg to 12.5 kg Na_2SO_4 /ton pulp. The average carryover during the trial was 9.1 kg Na_2SO_4 /ton pulp. Data were fitted to (Eq. [5]), where $n = 3.7$ [24], which was based on average extraction stage conditions during the trial period; the carryover coefficient, γ , was calculated to be 0.03% ClO_2 per kg Na_2SO_4 /ton pulp.



5. Comparison of bleach plant data from Fig. 4 versus predicted chlorine dioxide consumption from the modified model, Eq. (5), where $n = 3.7$ and $\gamma = 0.03\%$ ClO_2 per kg Na_2SO_4 /ton pulp. The dotted lines represent $\pm 0.08\%$ ClO_2 difference of the model's prediction from the actual mill data.



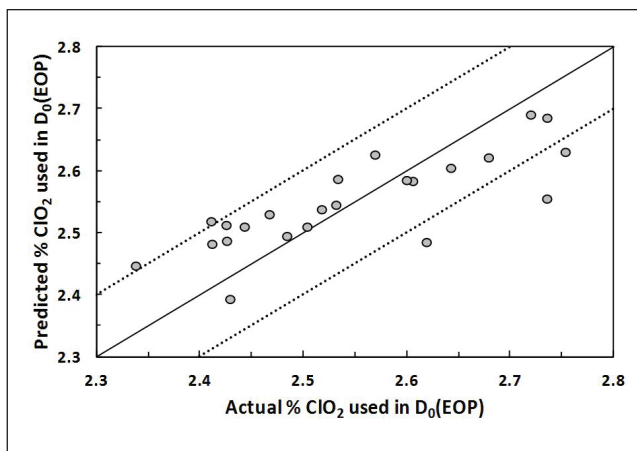
6. Bleach plant data for ClO_2 consumption in the D_0 stage versus the normalized D_0 (EOP) kappa number, $[Kappa^*]$, for a Jack pine brownstock. Plotted data are daily averages from a 3-week period where the brownstock kappa varied from 27.4 to 32.6 and washer losses varied from 7.2 kg to 16.3 kg COD/ton pulp. The average carryover during the trial was 11.6 kg COD/ton. Data were fitted to Eq. (4), where $A = 0.80$ [23], which was based on average extraction stage conditions during the trial period; the carryover coefficient, γ , was calculated to be 0.02% ClO_2 per kg COD/ton pulp.

effects. Both mills used a D_0 (EOP) delignification sequence. Daily averages of the brownstock kappa number, extracted kappa number, chlorine dioxide charge, and brownstock decker carryover were collected over a 3-4 week period. The hardwood fiber line used a mixture of southern U.S. hardwood chips, which were delignified to a kappa of 12. The average decker carryover into the bleach plant was 9.1 kg Na_2SO_4 /ton pulp during this period. The softwood mill primarily used Jack pine (*Pinus banksiana*), which was pulped to 30 kappa. The decker losses averaged 11.6 kg COD/ton pulp during this period. Values for A and n parameters of the softwood and hardwood D_0 (EOP) delignification models were estimated from published relationships [23,24], and were based on average temperature and peroxide dosage used during the data collection period at each mill.

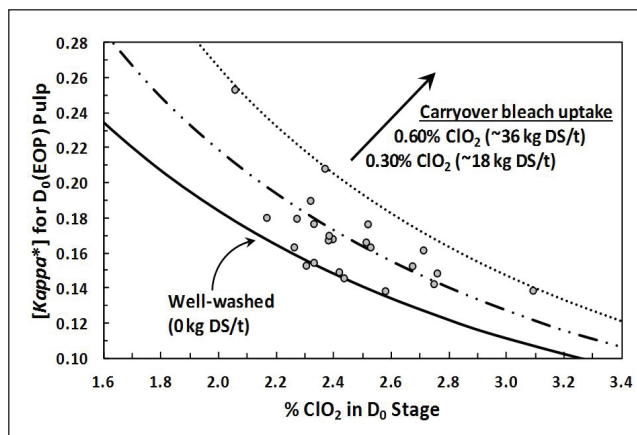
Figure 4 compares the hardwood ECF delignification model that excluded washer carryover (Eq. [2]) with the mill data where the brownstock contained black liquor entrainment. The model predicted a lower chlorine dioxide consumption for a given $[Kappa^*]$ value versus the actual mill data. The difference between actual and predicted bleach uptake averaged 0.27% (2.7 kg ClO_2 /ton pulp). If the washer carryover data is considered using the modified model (Eq. [5]) and the carryover coefficient, γ , is determined, the modified model forecasts the actual mill values well, generally to within $\pm 0.08\%$ chlorine dioxide (**Fig. 5**). In this particular case, the carryover coefficient was determined to be 0.030% chlorine dioxide per kilogram Na_2SO_4 /ton pulp (0.3 kg ClO_2 /kg Na_2SO_4).

The D_0 (EOP) data from the Jack pine pulp mill were

plotted in **Fig. 6** and assessed against the softwood model (Eq. [1]), which excluded the decker carryover. Like the previous hardwood example, the softwood model forecasted a lower bleach demand at a given $[Kappa^*]$ value than the observed mill values. The average difference between the model and the mill data was 0.23% (2.3 kg ClO_2 /ton pulp). The brownstock carryover data from the trial period were evaluated using the modified softwood delignification model (Eq. [4]) and the carryover coefficient was determined. When the carryover data were taken into account, the predicted bleach consumption from the modified model matches very closely to the mill data, generally within



7. Comparison of bleach plant data from Fig. 6 versus predicted ClO_2 consumption from the modified model, Eq. (4), where $A = 0.80$ and $\gamma = 0.02\%$ ClO_2 per kg COD/ton pulp. The dotted lines represent $\pm 0.1\%$ ClO_2 difference of the model's prediction from the actual mill data.



8. Bleach plant data for ClO_2 consumption (as % ClO_2 on pulp) in the D_0 stage versus the normalized $D_0(\text{EOP})$ kappa number, $[\text{Kappa}^*]$, for a southern U.S. softwood brownstock. Plotted data are daily averages from a 3-week period where the brownstock kappa varied from 25.5 to 30.2. In this case, data on the brownstock carryover was not known. The amount of bleach consumption from black liquor entrainment was estimated from Eq. (4) where $[\text{C.O.}] = 0$ (i.e., well washed) and $A = 0.75$ [23] (which was based on average extraction stage conditions during the trial period). Average bleach consumption from washer carryover was 0.30% ClO_2 .

$\pm 0.1\%$ (Fig. 7). The value of γ for this case study was 0.020% chlorine dioxide per kilogram COD/ton pulp.

In both mill cases, the calculated γ values for bleach consumption from the model fitting were close to the values listed in Table I. The average amount of lignin carryover for the hardwood was 0.47% on pulp (4.7 kg lignin/ton pulp) and for the softwood was 0.40% on pulp (4.0 kg lignin/ton pulp). These estimates were predicated on the earlier observation that $\sim 70\%$ of the bleach consumption caused from brownstock carryover is directly attributable

to the dissolved lignin. It can also be deduced that approximately one-third of the applied chlorine dioxide in the hardwood D_0 stage is consumed by the carryover. On the other hand, only about 10% of the D_0 bleach is consumed by the carryover for the softwood brownstock.

DISCUSSION

The modified steady-state models for softwood and hardwood ECF delignification (Eqs. [4] and [5]), respectively) seem to predict the mill's bleach demand reasonably, generally within 0.1% chlorine dioxide, to reach a targeted extracted kappa number for typical washer carryover levels. Thus, these expressions can be used if the carryover coefficient (γ) is known or can be calculated from historical washer carryover data. Alternatively, γ can be selected from the values listed in Table I.

Another method for determining γ is to compare the mill data to the theoretical well-washed curve (i.e., $[\text{C.O.}] = 0$). Figure 8, for example, is a plot of the chlorine dioxide consumption versus the $[\text{Kappa}^*]$ for a mixed softwood $D_0(\text{EOP})$ bleach sequence at a southern U.S. mill. The daily-averaged data were collected over a 3-week period where the brownstock kappa was ~ 27.5 and the $D_0(\text{EOP})$ kappa was 4.4 (i.e., overall period averages). In this particular case, the amount of brownstock carryover was unknown. However, the data show that the brownstock entering the bleach plant had a carryover bleach demand that averaged 0.30% chlorine dioxide on pulp. As noted earlier concerning bleach consumption of the components of brownstock carryover, dissolved lignin is discerned to account for $\sim 70\%$ of the total bleach uptake. Based on this observation, we can approximate that the mill's brownstock in Fig. 8 had $\sim 0.52\%$ dissolved kraft lignin, which equated to roughly 18 kg dissolved solids/ton pulp of washer carryover.

This analysis of this mill's fiber line revealed that the typical brownstock carryover increased the theoretical $D_0(\text{EOP})$ bleach demand by 13.5% . The amount of dissolved lignin entrainment resulted in an apparent brownstock kappa number that is 3.5 units higher (~ 31 kappa) if we use the standard kappa-to-lignin relationship (i.e., 1 kappa unit = 0.15% lignin on pulp). These results are somewhat similar to the Jack pine example given earlier. Variations in brownstock washer carryover have a much greater impact on bleach demand variability for hardwood versus softwood stocks. In these case studies, this observed effect is likely because of the lower kappa number of the hardwood pulp when compared to the softwood pulps. For the hardwood fiber line, the dissolved lignin entrainment would give the brownstock an apparent kappa number that is ~ 3 units higher than the measured value (i.e., 15 for the carryover stock versus 12 for the well-washed stock). In the mill cases examined in this study, daily averages were used to eliminate the residence time delay as the stock moves through the bleaching stages.

However, if the mean residence times are known for each stage at given production rates, then the modified ECF delignification models could be used to estimate the effects of washer carryover in real time. This could allow the models to be used in process control strategies for online chemical optimization [22,29-34]. Currently, some inline sensors are used for advanced bleach plant control that monitors dissolved lignin entrainment with pulps entering the D_0 stage and makes adjustments to bleach demand [33]. Such online data could be used with the refined ECF delignification models to improve bleach plant process control.

The results from this study indicate that organic and inorganic portions of washer carryover will exert an extra bleach demand during chlorine dioxide delignification. The bulk of this extra bleach demand is caused by the dissolved lignin entrainment. However, the bleach uptake from some dissolved sulfur species, which are found in black liquor, is not entirely negligible and may partly contribute to mill-to-mill variation in the observed stoichiometry for carryover. Additional research is needed to better estimate the contributions of the inorganics in washer carryover to chlorine dioxide consumption (e.g., the Virrimaa et al. [58] study that specifically examined the organic components).

CONCLUSIONS

Revised steady-state models have been developed for calculating chlorine dioxide consumption during ECF delignification sequences, where the softwood or hardwood pulps contain washer carryover. The stoichiometric bleach demand of the carryover varies depending on how the brownstock or post-oxygen washer losses are quantified (e.g., saltcake, COD, or dissolved solids). The majority of the bleach consumed by the carryover, approximately 70% for brownstock, is attributable to the dissolved lignin fraction. However, it was also discovered that a portion of the inorganic fraction could exert a small bleach demand, which is not negligible for brownstock carryover. Dissolved solids from post-oxygen washer losses consume less chlorine dioxide than those from brownstock washer losses. Analysis of various laboratory studies indicated that the original steady-state models could predict chlorine dioxide uptake of stocks containing carryover if the bleach demand of the dissolved solids is taken into account with an appropriate stoichiometric factor. The validity of these refined models were tested with mill data for softwood and hardwood brownstocks delignified by D_0 (EOP) sequence. The predicted bleach consumption from the new models closely followed the bleach plant data, generally within ± 1 kg chlorine dioxide on pulp. The chlorine dioxide delignification models could be used to estimate the bleach demand caused from washer carryover if this parameter is not closely monitored at the mill. These models could potentially be incorporated into advanced process control strategies for ECF bleaching where the washer car-

ryover or dissolved lignin entrainment is measured with online sensors.

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LITERATURE CITED

1. Reeve, D.W., in *Pulp Bleaching - Principles and Practice*, (C.W. Dence and D.W. Reeve, Eds.), TAPPI PRESS, Atlanta, GA, USA, 1996, pp. 3-24.
2. Hart, P.W., *TAPPI J.* 10(7): 37(2011).
3. Brogdon, B.N., in *The Bleaching of Pulp* (P.W. Hart and A.W. Rudie, Eds.) 5th edn., TAPPI PRESS, Atlanta, 2012, Chap. 12.
4. Brogdon, B.N., *TAPPI J.* 9(8): 27(2010).
5. Brogdon, B.N., *TAPPI J.* 9(9): 47(2010).
6. Brogdon, B.N., *TAPPI J.* 12(10): 33(2013)
7. Richardson, B., *Pulp Pap. Can.* 106(6): 43(2005).
8. Compton, R., *TAPPI Pulping Conf.*, TAPPI PRESS, Atlanta, 1997, p. 257.
9. Compton, R., "Brown stock washing economics," *TAPPI Brown Stock Washing Short Course*, 2005.
10. Shackford, L.D., *TAPPI Pulping Conf.*, TAPPI PRESS, Atlanta, 1997, p. 77.
11. Turner, P.A., Allen, L.H., Allen, S.L., et al., in *Pulp Bleaching: Principles and Practice* (C.W. Dence and D.W. Reeve, Eds.), TAPPI PRESS, Atlanta, 1996, pp. 569-596.
12. Santos, R.B. and Hart, P.W., *TAPPI J.* 13(1): 9(2014).
13. Hart, P.W. and Connell, D., *TAPPI J.* 5(4): 23(2006).
14. Wang, R.X., Tessier, P.J.-C., and Bennington, C.P.J., *AIChE J.* 41(12): 2603(1995).
15. Gu, Y. and Edwards, L., *TAPPI J.* 2(6): 19(2003).
16. Gu, Y. and Edwards, L., *TAPPI J.* 2(7): 3(2003).
17. Gu, Y. and Edwards, L., *TAPPI J.* 2(10): 3(2003).
18. McDonough, T.J., Rawat, N., and Krishnagopalan, G.A., *Appita J.* 57(5): 381(2004).
19. McDonough, T.J., Uno, S., Rudie, A.W., et al., *TAPPI J.* 7(1): 4(2008).
20. McDonough, T.J., Rawat, N., and Turner, M., *Appita Annu. Gen. Conf. Proc., 51st, Australian Pulp and Paper Industry Technical Association, Bundoora, Australia, 1997*, p. 255.
21. Jain, S., Mortha, G., and Christophe, C., *TAPPI J.* 8(11): 12(2009).

BLEACHING

22. Tessier, P., Savoie, M., and Pudlas, M., *TAPPI J.* 83(1): 139(2000).
23. Brogdon, B.N., *TAPPI J.* 11(3): 31(2012).
24. Brogdon, B.N., *TAPPI J.* 12(2): 17(2013).
25. Brogdon, B.N., *TAPPI J.* 13(2): 17(2014).
26. Brogdon, B.N., *TAPPI J.* 13(2): 29(2014).
27. Brunner, F.L., *TAPPI Pulping Conf.*, TAPPI PRESS, Atlanta, 1995, p. 725.
28. Germgård, U., *Sven. Papperstidn.* 85(6): R43(1982).
29. Tessier, P. and Savoie, M., *Pulp Pap. Can.* 103(7): 28(2002).
30. Dumont, G., Van Fleet, R., and Stewart, G., *Pulp Pap. Can.* 107(7/8): 55(2006).
31. Van Fleet, R.J., *Appita J.* 51(6): 412(1998).
32. Van Fleet, R., Morningred, D., Padasak, S., et al., *TAPPI PEERS Conf.*, TAPPI PRESS, Atlanta, 2012, Session 9-2, p. 224.
33. Lampela, K. and Erkkilä, N., *Pulp Pap. Can.* 100(9): 30(1999).
34. Ollila, M., Peltomäki, T., and Gomersall, T., *Can. Pulp Pap. Assoc., Tech. Sect., Prepr., Annu. Meet., 82nd.*, Canadian Pulp and Paper Association, Montreal, QC, Canada, 1996, p. A92.
35. Leddy, J.E., *Appita J.* 51(6): 408(1998).
36. Kopra, R., Helttunen, J., Tervola, P., et al., *Appita J.* 63(2): 131(2010).
37. Hise, R.G. and Hintz, H.L., *Tappi J.* 73(1): 185(1990).
38. Hise, R.G., Streisel, R.C., and Bills, A.M., *Tappi J.* 75(2): 57(1992).
39. Pryke, D.C. and Reeve, D.W., *TAPPI J.* 80(5): 153(1997).
40. Pryke, D.C. and Earl, P.F., "Softwood bleaching practices in Canada: analysis of the 2003 PAPTAC Bleaching Committee 'best practices' survey," *TAPPI Eng., Pulping Environ. Conf.*, TAPPI PRESS, Atlanta, 2005, Session 50-2.
41. Connell, D. and Carmichael, S., in *The Bleaching of Pulp* (P.W. Hart and A.W. Rudie, Eds.) 5th edn., TAPPI PRESS, Atlanta, 2012, Chap. 3.
42. Reeve, D.W., *Can. Pulp Pap. Assoc., Tech. Sect., Prepr., Annu. Meet., 70th*, Canadian Pulp and Paper Association, Montreal, 1984, p. A139.
43. Blomberg, L., Järvinen, R., Talka, E., et al., *TAPPI Pulping Conf.*, TAPPI PRESS, Atlanta, 1990, p. 217.
44. Stromberg, C.B., *Tappi J.* 74(10): 113(1991).
45. Lunn, R., *Pulp Pap. Can.* 102(3): 46(2001).
46. Miller, W.J. and Dixon, S.A., *TAPPI Bleach Plant Operations Semin.*, TAPPI PRESS, Atlanta, 1991, p. 87.
47. Pryke, D., "Delignification in the first stage of the bleach plant: principles and practice," *TAPPI Bleach Plant Operations Workshop*, TAPPI PRESS, 2007.
48. Barroca, M.J.M.C., Simões, R.M.S., and Castro, J.A.A.M., *Appita J.* 55(1): 60(2002).

ABOUT THE AUTHOR

This paper discusses further refinements to the steady-state models of chlorine dioxide delignification that were published a few years ago for softwood and hardwood pulps (*TAPPI J.* 11[3]: 31[2012] and 12[2]: 17[2013]). A factor that was not incorporated in the earlier works was the bleach expended by brownstock or oxygen delignification carryover. The impact of this dissolved material can be seen with actual bleach plant data, where the earlier models either over predict the delignification for a set bleach charge, or under predict the chlorine dioxide needed to achieve an extracted kappa number (e.g., Figs. 4 and 5). Thus, the goal was to amend the equations to improve their accuracy to represent mill data.

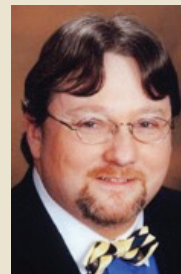
A challenge that I encountered was the limited amount of stoichiometric data for the reactions of chlorine dioxide with brownstock or oxygen delignification carryover. The last study that extensively examined this subject was a chlorination paper presented by Douglas Reeve at the 1984 CPPA conference [42]. This required me to investigate how each constituent of washer carryover contributes to the overall stoichiometric uptake. Some data were found in the literature that allowed me to approximate the relationships.

After the bleach stoichiometry was established, I discovered how easily carryover could be accounted for in the earlier steady-state models. The original equations were modified with a simple horizontal shift function to account for bleach uptake caused by

the carryover. These modifications improved the accuracy of the models to fit various bleach plant data where carryover levels were known. The new models could also be used to estimate the amount of washer carryover that enters the bleach plant if it is not monitored or known (e.g., Fig. 8).

Mills could use these models to forecast chlorine dioxide consumption needed for bleaching delignification for a variety of incoming kappa numbers and washer carryover levels. Other applications of the models include bleach plant optimizations and troubleshooting. The equations could be integrated into process control schemes, particularly for mills that have online monitors of carryover from the brownstock or oxygen delignification washers.

Future work will investigate how proposed models for chlorine dioxide brightening can be improved to fit actual bleach plant data by considering the carryover from the first extraction stage washer.



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49. Miller, W.J. and Lennon, V.E., *Pulp Washing '96 Conf. Proc.*, Canadian Pulp and Paper Association, Technical Section, Montreal, 1996, p. 37.
50. Reeve, D.W. and Weishar, K.M., *Bleach Plant Operations Semin.*, TAPPI PRESS, Atlanta, 1991, p. 137.
51. Maples, G.E., Ambady, R., Caron, J.R., et al., *TAPPI J.* 77(11): 71(1994).
52. Süss, H.U. and Kronis, J.D., *Breaking Pulp Yield Barrier Symp. Proc.*, TAPPI PRESS, Atlanta, 1998, p. 153.
53. Lenes, M., Hoel, H., and Bodén, L., *TAPPI J.* 84(4): 73(2001).
54. Greenwood, B.F., *Bleach Plant Operations Semin.*, TAPPI PRESS, Atlanta, 1991, p. 7.
55. Sankari, M., Ala-Kaila, K., Dahl, O., et al., *Nord. Pulp Pap. Res. J.* 19(2): 264(2004).
56. Allison, R.W., Suckling, I.D., and Sun, Y.P., "Dissolved solids entrainment in oxygen delignification: Effect of specific components," *Int. Pulp Bleaching Conf.*, Pulp and Paper Technical Association of Canada, Montreal, 2000, Session 2-3.
57. Vuorinen, T., Fagerström, P., Räsänen, E., et al., *J. Pulp Pap. Sci.* 25(5): 155(1999).
58. Viirima, M., Dahl, O., Niinimäki, J., et al., *Appita J.* 55(6): 484(2002).
59. Clayton, D., Easty, D., Einspahr, D., et al., in *Pulp and Paper Manufacture: Alkaline Pulping*, Vol. 5 (T.M. Grace, B. Leopold, E.W. Malcolm, et al., Eds.), Joint Textbook Committee of the Paper Industry, TAPPI/CPPA, Atlanta, 1989, pp. 15-22.
60. Masschelein, W.J., *Chlorine Dioxide Chemistry and Environmental Impact of Oxychlorine Compounds* (R.G. Rice, Ed.), Ann Arbor Science Publishers, Ann Arbor, Michigan, USA, 1979.
61. Pan, G.Y., Renard, J.J., and DeGraw, J.F., *TAPPI Pulping Conf.*, TAPPI PRESS, Atlanta, 1982, p. 365.
62. Ferweda, G., *Pulp Pap. Can.* 105(12): 63(2004).
63. Parthasarathy, V.R., *TAPPI J.* 80(10): 253(1997).
64. Mullen, T. and van Wyk, B., "Use of OWL(T) in the bleach plant will reduce caustic purchases and control white liquor chloride and potassium concentration," *African Pulp Pap. Week Conf. Proc.*, Technical Association of the Pulp and Paper Industry of South Africa (TAPPSA), Kloof, South Africa, 2002. Available [Online] http://www.tappsa.co.za/archive/APPW2002/Title/Use_of_OWL__T_/use_of_owl__t_.html <11Feb2015>.
65. Parthasarathy, V.R., Rudie, G.F., Detty, A.E., et al., *TAPPI Pulping Conf.*, TAPPI PRESS, Atlanta, 1993, p. 933.
66. Parthasarathy, V., Detty, A., and Steffy, J., "Elemental chlorine free and low chlorine bleaching of Chillicothe hardwood – Extending delignification and bleaching of hardwood pulps," *Internal Report No. 16,136*, Mead Central Research, Chillicothe, OH, USA, October 1993.
67. Connell, D., AkzoNobel-Eka Chemicals, unpublished results, 2012.
68. Hart, P.W., MeadWestvaco Corp., personal communications, 2012.
69. McDonough, T.J., Courchene, C.E., Shakel, A., et al., *Pulp Pap. Can.* 102(10): 46(2001).
70. McDonough, T.J., Baromès, J.-C., Carter, B.R., et al., *Environ. Conf.*, TAPPI PRESS, Atlanta, 1998, p. 85.



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