Optimization of elemental chlorine-free bleaching for a softwood kraft pulp – part 1: impact of oxidative extraction on chlorine dioxide stoichiometry

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ABSTRACT: The present investigation meticulously analyzes how oxidative alkaline extraction can be augmented through process changes, and how these augmentations can be leveraged to optimize chlorine dioxide usage with elemental chlorine-free (ECF) sequences for a conventional softwood kraft pulp. Bleaching data from Basta and co-workers (1992 TAPPI Pulping Conference) are re-examined and re-interpreted in this study. We determined that ~60% to 65% of the overall ClO_2 charge should be applied in the D_0-stage. Peroxide addition to an (EOP) can replace 0.6 to 2.5 Kg. ClO_2 per Kg H_2O_2. Boosting the (EO) temperature to 80°C is equivalent to a 70°C (EOP) with 0.25% to 0.30% H_2O_2,whereas a 90°C (EO) is equivalent to 0.50% – 0.75% H_2O_2 in a 70°C (EOP). The stoichiometric bleaching data from this study can guide decision-making for lowering chemical usage and minimize costs to reach target brightness levels with three- and five-stage sequences.

Application: The presented findings show how alkaline extraction variables, such as temperature and/or peroxide inclusion, affect overall chlorine dioxide consumption and distribution for various bleach sequences. Operators, engineers, and scientists can use this stoichiometric data to best decide how to allocate chemical charges to achieve brightness targets while minimizing costs.

Many elemental chlorine-free (ECF) bleaching studies have focused on kraft pulping modifications [1-3], oxygen delignification [3-6], and balancing chlorine dioxide (ClO_2) charges in bleaching stages as methods to lower total ClO_2 consumption [4-11] while maximizing bleached pulp yield. If pulping and/or oxygen delignification selectively removes more lignin prior to bleaching, then it displaces a portion of the ClO_2 that would have otherwise been consumed by this unbleached lignin. Balancing the amount of ClO_2 used in delignification (D_0) and brightening stages (D_1, D_2) helps eliminate wasted oxidant consumption in ineffective kappa number reduction or chromophore removal.

A factor largely ignored in ECF bleaching is the potential of first caustic extraction stage. It is generally assumed that the conclusions drawn from earlier chlorination and extraction optimization studies [12-27] are equally applicable to today's ECF bleaching. Caustic extraction is often viewed as an integrated extension of the previous oxidation stage, whereby oxidized lignin is just neutralized, solubilized, and removed from the fiber with no notable reactions occurring. Another reason why extraction has been neglected is the complexity associated with various bleaching sequences. The number of experiments geometrically increases when one considers how extraction variables affect bleach sequence optimization. This added complexity makes full-blown laboratory optimization studies highly laborious, tedious, and costly to conduct. Hence, most bleach studies hold the extraction stage variables constant in order to simplify the experimental design.

Caustic extraction has played a pivotal role in low-cost bleaching ever since its introduction almost a century ago to augment single-stage hypochlorite bleaching [13]. Oxidative reinforcement with oxygen, peroxide, or their combinations are known to lower the extracted kappa number by 1 to 3 units (versus an E-stage) at a given kappa factor for chlorinated (C) or chlorine dioxide substituted ((CD) or (DC)) treated pulps [15,17]. Oxygen-reinforced extraction (i.e., (EO)) has been widely accepted as the baseline for extraction performance due to low chemical and capital costs to implement into an existing bleach plant. Peroxide addition to an (EO)-stage (i.e., (EOP)) can further drop the extracted kappa number by ~0.5 or more units at a given kappa factor, or can reduce the applied kappa factor in the C or (CD) up to 0.03 units [15,17,18].

Recently, several softwood studies have been published that have re-examined how modified alkaline extraction processes affect ECF bleaching [19-26,28-30]. Van Lierop and co-workers [21, 22] investigated very aggressive (EO) and (EPO) stages, which utilize high extraction temperatures (90°C – 110°C) and/or high peroxide dosages (≥1%). Their work suggested that a 30-min, high-temperature (110°C), oxygen-pressurized pre-retention tube followed by atmospheric extraction at 90°C was more economically effective than utilizing high peroxide dosages in the (EPO)-stage, either

at moderate or high temperatures (85°C to 110°C). Süss and co-workers [20] examined $D_0(EO)D_1P$ and $D_0(EOP)D_1P$ bleaching at typical commercial extraction conditions (75°C to 90°C). Their work implied that 90°C (EO)-stage requires similar levels of ClO_2 in D_1 to reach 86% to 88% ISO brightness as 75°C (EOP)-stage. However, the 90°C (EOP)-stage with 0.25% H_2O_2 reduced the ClO_2 requirements in the D_1 by ~0.4% ClO_2 on softwood pulp. Van Lierop et al. noted that very high temperature (EO) extraction results in higher COD releases (~10 Kg/T higher from 70°C to 110°C); Süss and co-workers [20] suggested this increase in COD translates to a bleach yield loss (i.e., shrinkage) of ~1%. Bleach yield losses of ~0.75% units are known when boosting the E1-stage temperature by Δ 40°C (i.e., 40°C to 80°C) [16].

These recent investigations have stirred interest in the role of (EO) and (EOP) for ECF optimization. Is it more practical to use $H2O_2$ and/or steam in extraction versus ClO_2 in the D-stages? One item lacking in the previously mentioned studies is how these extraction variables affect global ClO_2 balancing in $D_0(EOP)D_1$ and $D_0(EOP)D_1E_2D_2$ bleaching to a given brightness target. Van Lierop et al. [21] focused on the final post-extraction kappa number as the gage for optimization with (EO) versus (EPO). They assumed that a given brightness increase in the D_1 would require the same amount of ClO_2 for a given post-extraction kappa. The authors conducted a few D_1 experiments at a single ClO_2 charge (i.e., 0.8%) to test their assumption. Their tests were carried out with pulps treated with very high D_0 kappa factors (0.27 KF). However, these conditions may be at the asymptotic limits of both bleaching delignification and brightness (i.e., brightness ceiling), which may skew the overall conclusions drawn by the authors.

The overall objective of our studies is to rigorously examine how ClO_2 dosages in the delignification and brightening stage interact with (EO) stage variables, such as H_2O_2 dosage and reaction temperature, and how these interactions work in concert with each other to affect bleaching efficiency and cost. In this paper, we will first focus on interactions and ClO_2 stoichiometry, while a second study to be published later will examine bleach cost minimization. We will re-analyze the extensive bleaching data presented by Basta and co-workers [30] on a Southern softwood kraft pulp with the $D_0(EOP)D_1E_2D_2$ sequence. Although Basta et al. [30] did not expound upon chemical consumption and cost minimization, their study contains a wealth of information demonstrating how extraction stage variables impact overall ClO_2 allocation in D-stages of ECF sequences.

RESULTS AND DISCUSSION

Methodology

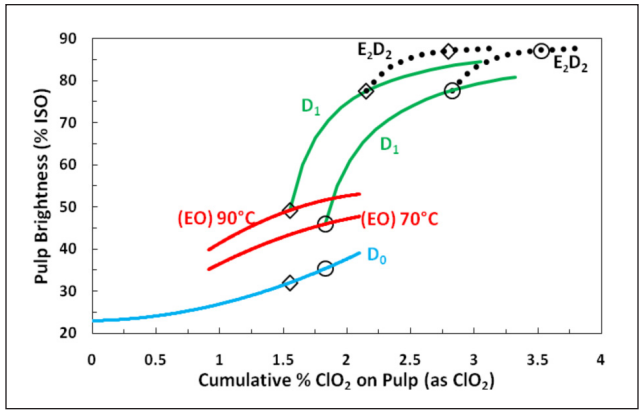
This investigation re-analyzes and re-interprets the ECF bleaching data of Basta and co-workers [30]. The details from their experimental bleaching experiments are described here.

In the experiments, a conventional U.S. Southern pine kraft pulp was used, which had a kappa number of 24, SCAN intrinsic viscosity of 1052 dm^3/Kg (~27.8 mP•s, TAPPI T-230), and brightness of 23% ISO. **Table 1** summarizes the conditions of each stage. The first caustic extraction stage, (EO) or (EOP), employed a 1.5-L rotating autoclave with an oxygen pressure of 0.22 MPa (~32 psig) [30-32]. The % NaOH used in the first extraction was estimated from the total % NaOH used in bleaching (~2.4%) since the authors [30] did not disclose this information. The D_1-stages were conducted at various times to result in a small ClO_2 residual (~1% to 2% of the overall charge) at various times; D_2 stages were conducted at various times to result in a slightly higher ClO_2 residual (~4% of the overall charge). Caustic or sulfuric acid was added prior to ClO_2 addition to reach these optimum pH targets.

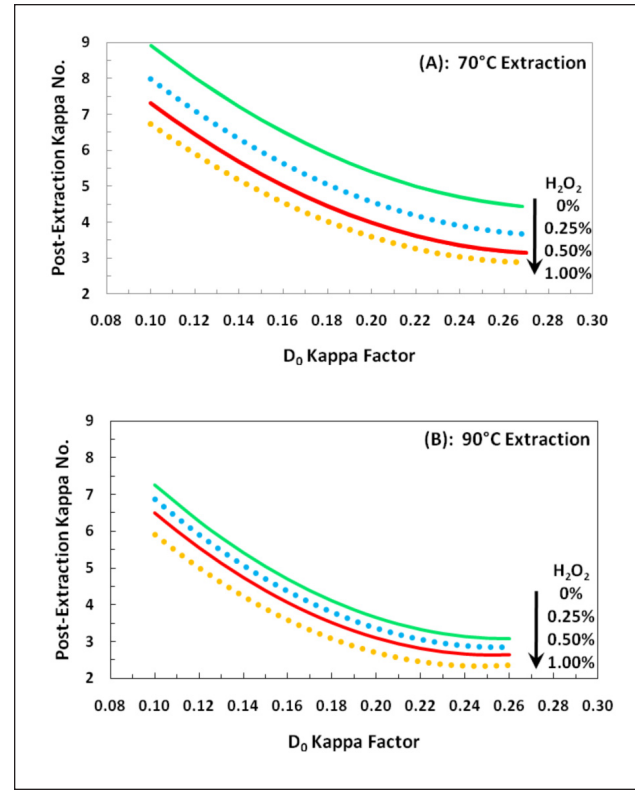
The nomographs presented by Basta et al. [30] for delignification and brightness development were based on >200 bleaching experiments yielding >3000 data points. This graphical information was re-analyzed by statistical regression in our present study. Post-extraction kappa numbers were determined to be a function of D0 kappa factor (KF), extraction H_2O_2 dosage, and extraction temperature, similar to the reports of van Lierop et al. [21]. Post-D_1 brightness levels were ascertained to be a function of post-extraction kappa number

Stage Conditions	D_0	(EO) or (EOP)	D_1	E_2	D_2
Consistency, %	3.5	10	10	10	10
Temperature, °C	40 – 50	70 – 90	70	70	70
Time, min	30 – 60	60	variable	60	variable
Kappa factor (KF)	0.10 – 0.23	–	–	–	–
ClO_2, % on pulp	0.91 – 2.10	–	0.50 – 1.50	–	0.20 – 0.95
O_2 pressure, MPa	–	0.22	–	–	–
H_2O_2, % on pulp	–	0 – 1	3.0	–	–
NaOH, % on pulp	–	~1.5	variable	~0.5	variable
H_2SO_4, % on pulp	variable	–	variable	–	variable
End pH	~3	~11	~3	~11	~4

I. Conditions for $D_0(EO)D_1E_2D_2$ and $D_0(EOP)D_1E_2D_2$ employed by Basta et al. for 24 kappa Southern pine kraft pulp



1. Brightness versus culumative % ClO_2 used in the D-stages for $D_0(EO)D_1E_2D_2$ for 24-kappa pine pulp. Symbols (○, ◊) denote brightness developent during bleaching at various points during the sequence. Increasing (EO) temperature reduced total cumulative % ClO_2 by ~0.7% ClO_2 to reach 87% ISO brightness. Curves were calculated from regression model based on Basta et al. data [30].



2. Impact of D_0 kappa factor and H_2O_2 reinforcement in the (EO) or (EOP) on post-extraction kappa number for 24-kappa pine kraft pulp. Extractions were at (a) 70°C and (b) 90°C. Curves were calculated from regression model based on Basta et al. data [30].

and D_1 ClO_2 charge, whereas post-D_2 brightness levels were found to be a function of D_1-stage brightness and D_2 ClO_2 charge. The statistical regressions developed from the Basta et al. [30] graphical data had a sample coefficient of multiple determinations (i.e., r^2) values ranging from 0.992 to 0.998, indicating the veracity of these regressions to model the data. Plotted total ClO_2 curves for three- or five-stage sequences employing various (EO)- or (EOP)-stage conditions were created together with the above regression models using the Excel® Solver routine (Microsoft, 2007) to minimize the overall ClO_2 charge at a targeted final brightness.

Overview of bleach sequence optimization

Each individual stage in a bleach sequence contributes to the overall brightness development, as **Fig. 1** shows. (The curves for each stage were generated from the regression models and the D_0 and (EO) brightness data reported by Basta et al. [30].) Conditions employed in an earlier stage affect future brightness development in subsequent stages. Correct proportioning of ClO_2 across the bleach sequence maximizes the brightness gains, while minimizing the global ClO_2 charge. An 87% ISO brightness softwood kraft pulp can be achieved by utilizing 1.83% ClO_2 in the D_0 (0.20 KF), 1.00% ClO_2 in D_1, and 0.70% in D_2 with a 70°C (EO)-stage, as denoted by circles (○) in Fig. 1. Increasing the (EO) temperature from 70°C to 90°C boosts the D_0(EO) brightness by ~5% ISO at a given D_0 kappa factor. Augmenting the (EO) temperature reduces overall sequence ClO_2 usage. For example, an 87% ISO brightness pulp can be produced with 1.55% ClO_2 in the D_0 (0.17 KF), 0.60% ClO_2 in D_1, and 0.65% in D_2, as the diamonds (◊) in Fig. 1 illustrate. This decreases the total ClO_2 from 3.53% to 2.80% on pulp.

Basta et al. [30] did not disclose D_0(EOP) brightness data for various H_2O_2 charges or reaction temperatures. However, comparisons of (EO) versus (EOP) at various H_2O_2 charges and reaction temperatures can be done by examining the post-extraction kappa numbers, and how this parameter impacts brightness gains in D_1 and $D_1E_2D_2$ at various ClO_2 charges. Post-extraction kappa numbers have long been used to evaluate bleaching delignification, as well as to prognosticate future ClO_2 consumption [6,11].

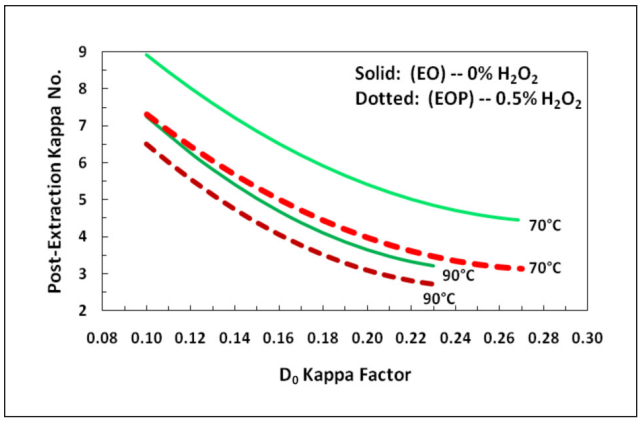
D_0(EO) versus D_0(EOP)

Figure 2 illustrates the delignification profile of the 24-kappa softwood pulp when treated with D_0(EO) and D_0(EOP) at various KF, H_2O_2 levels, and extraction temperatures. **Table II** gives the amount of ClO_2 in D_0 displaced by H_2O_2 inclusion in (EOP).

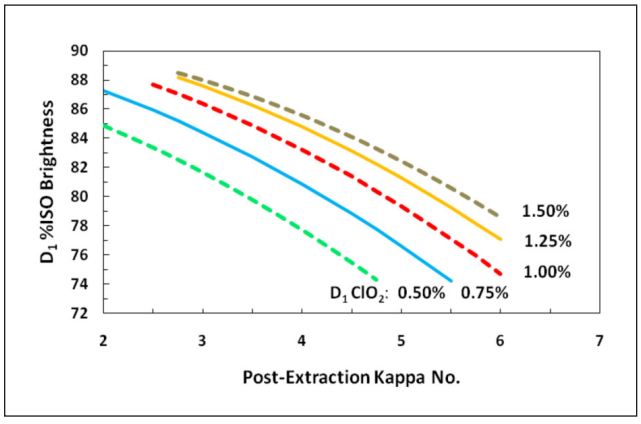
The amount of ClO_2 replaced by H_2O_2 varies in accor-

% H_2O_2 in (EOP)	% ClO_2 replaced (D_0)		
	70°C (EOP)	80°C (EOP)	90°C (EOP)
0.1	~0.22	~0.11	~0.10
0.2	~0.36	~0.19	~0.17
0.3	~0.47	~0.26	~0.22
0.5	~0.63	~0.37	~0.32

II. ClO_2 replaced by H_2O_2 in (EOP) in the D_0(EOP) to reach post-extraction kappa numbers of 3 to 5.



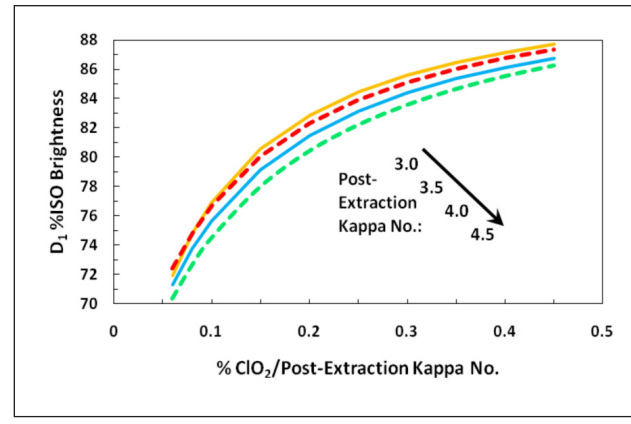
3. Comparison of 70°C and 90°C extractions for (EO) and (EOP). Curves were calculated from regression model based on Basta et al. data [30].



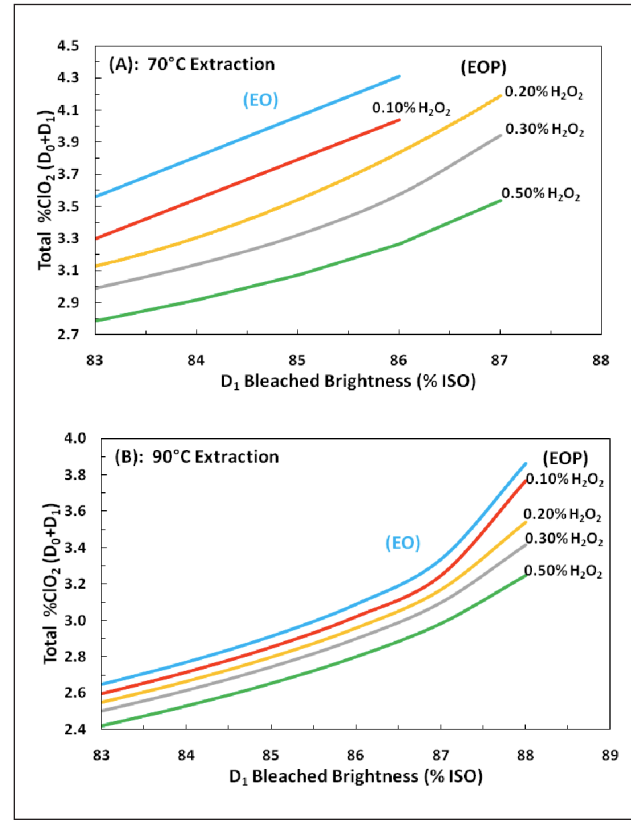
4. D_1 brightness response as a function of post-extraction kappa number and D_1 ClO_2 charge (as ClO_2). Curves were calculated from regression model based on Basta et al. data [30].

dance with extraction temperature when comparisons are made to a given extracted kappa number. Somewhat analogous results were observed when we re-examined the data of van Lierop et al. [21]. On a theoretical basis of oxidation equivalences, one kilogram of H_2O_2 should yield similar potential as ~0.79 kilograms of ClO_2. An (EOP) stage operated at 70°C and 0.5% H_2O_2 or less exhibits higher ClO_2 displacement than is predicted on oxidation equivalences. Values of ClO_2/H_2O_2 from Table II range from 1.25 to 2.20. These values are close to one kilogram H_2O_2 in the E_2-stage replacing two kilograms ClO_2 in brightening D-stages [14,15,18,30]. Raising the (EOP) temperature to 80°C or 90°C lowers the ClO_2/H_2O_2 ratio closer to the theoretical oxidation equivalence of these two oxidants.

Adjusting the (EO) temperature from 70°C to 80°C is approximately equivalent in bleaching delignification as 0.25 to 0.30% H_2O_2 in a 70°C (EOP). Likewise, an (EO) conducted at 90°C affords similar delignification levels at various D_0 kappa factors as 0.5% H_2O_2 (EOP) stage at 70°C (**Fig. 3**). Similar trends were observed when we re-examined the data disclosed by van Lierop et al. [21].



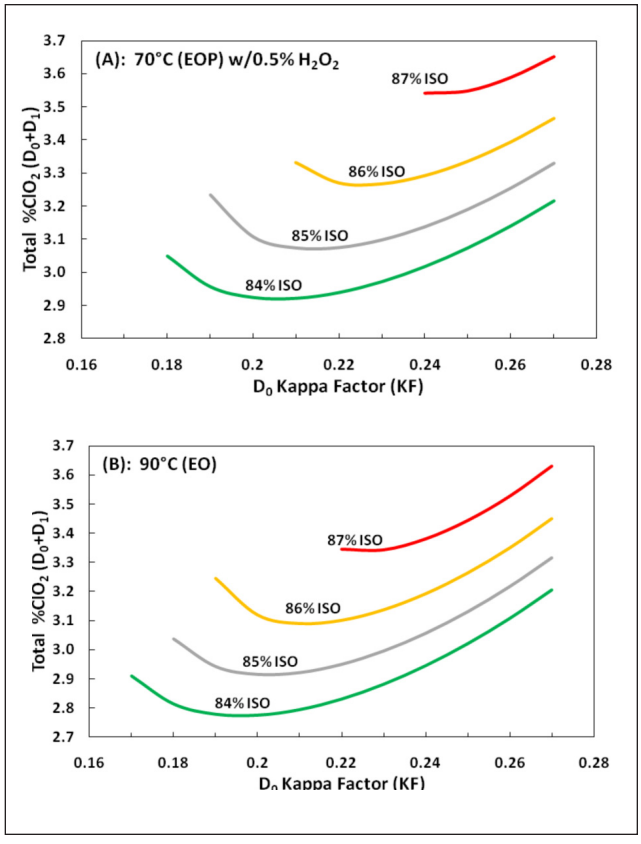
5. D_1 brightness response as a function of % ClO_2/post-extraction kappa number parameter.



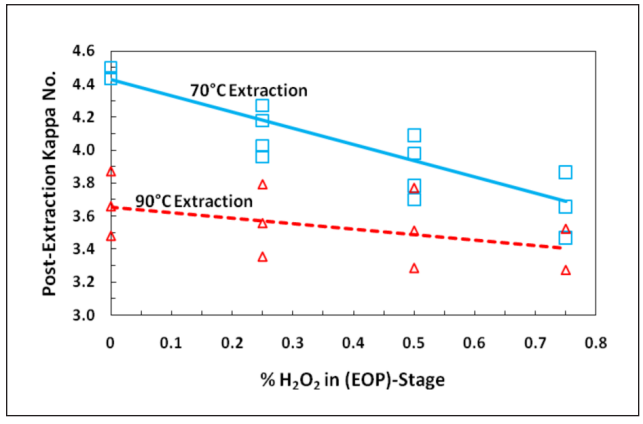
6. Minimized total % ClO_2 needed to reach target brightness for D_0(EO)D_1 and D_0(EOP)D_1 sequences. Extraction was performed at (a) 70°C and (b) 90°C.

D_1-stage brightening

Figure 4 represents the D_1 brightening as a function of post-extraction kappa number and D_1 ClO_2 charge. This information can be more succinctly expressed by normalizing the D_1 ClO_2 charges by entering the post-extraction kappa number (i.e., % ClO_2/extracted kappa number, **Fig. 5**) [6-8,11,33]. These normalized curves do not completely align on top of each other. The trends presented in Fig. 5 are similar to the plots published in scientific literature [8,33,34].



7. Effect of D_0 kappa factor on total % ClO_2 (D_0+D_1) for bleach brightness 84 to 87% ISO. (a) D_0(EOP)D_1 with 70°C (EOP) and 0.5% H_2O_2; and (b) D_0(EO)D_1 with 90°C (EO).



8. Post-extraction kappa number for 70°C and 90°C extractions at various H_2O_2 in (EOP) for D_0(EOP)D_1 bleaching to 84% ISO. The spread from the optimum post-extraction kappa represents 60% to 65% of the total ClO_2 applied in the D_0-stage.

D_0(EO)D_1 versus D_0(EOP)D_1

Total ClO_2 charges to achieve 83% to 88% ISO brightness were determined by balancing the amounts of ClO_2 employed in D_0 and D_1, in addition to manipulating H_2O_2 charges and temperatures in extraction (**Fig. 6**) utilizing the regression model and the spreadsheet Solver routine. A post-extraction kappa number of 4.5 or less is generally required to obtain ≥84% ISO in three stages. This makes it extremely difficult to obtain these brightness targets for pulps treated with a 70°C (EO)-stage (Fig. 2) unless >0.25 KF is used in the D_0. Application of H_2O_2 and/or higher temperatures in extraction can be utilized to obtain lower post-extraction kappa numbers at lower KF charges.

% H_2O_2 in (EOP)	Total % ClO_2 replaced (D_0 + D_1)		
	70°C (EOP)	80°C (EOP)	90°C (EOP)
0.1	~0.26	~0.12	~0.07
0.2	~0.48	~0.21	~0.13
0.3	~0.67	~0.30	~0.17
0.5	~0.92	~0.43	~0.27

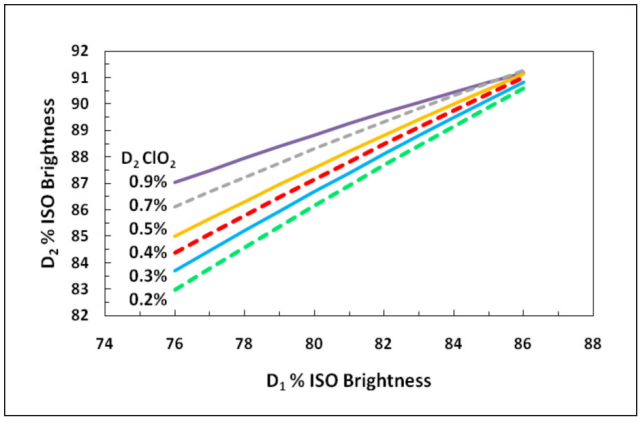
III. ClO_2 replaced by H_2O_2 in the D_0(EOP)D_1 sequence to reach 83% to 86% ISO brightness.

Bleaching Conditions	Bleach Sequence Extraction Stage		
	70°C (EO)	70°C (EOP)	70°C (EOP)
% ClO_2 in D_0 [KF]	2.37 [0.259]	1.79 [0.197]	2.00 [0.219]
% H_2O_2 in (EOP)	0	0.3	0.3
Post-extraction kappa no.	4.5	4.5	4.1
% ClO_2 in D_1	1.47	1.47	1.14
Total % ClO_2 used	3.84	3.26	3.14

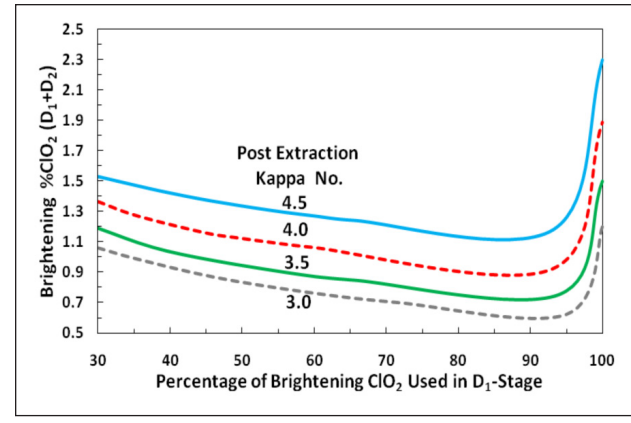
IV. Comparison of D_0(EO)D_1 to D_0(EOP)D_1 sequence to reach 84% ISO brightness. Optimization based on either reaching a target post-extraction kappa number or balancing ClO_2 charge between D_0 and D_1.

Typically, the optimized ClO_2 charges linearly increased for brightness levels of 83% to 86% ISO. The required ClO_2 rapidly escalates when the brightness targets are ≥86% ISO. This is due in part to the lower brightening efficiency of the D_1 stage as the % ClO_2/extraction kappa ratio rises above 0.35 to 0.40, coupled with the lower reductions in post-extraction kappa number when D_0 KF >0.22 is incrementally changed. Approximately 60% to 70%, and more specifically 61% to 66%, of the total ClO_2 needed to reach the brightness target should be employed in the D_0-stage (e.g., **Fig. 7**). This range for ClO_2in D_0 nominally results in a spread in the post-extraction kappa number of ±0.3 units from the calculated optimum value (**Fig. 8**).

The impact of H_2O_2 addition to extraction on the total ClO_2 needed in the three-stage bleach sequence is highly dependent upon the extraction temperature (**Table III**). One kilogram of H_2O_2 can roughly displace 2 to 2.5 Kg of ClO_2 at 70°C. However, this displacement ratio decreases by ~50% for each Δ 10°C increment in (EOP) temperature. Increasing the (EO) temperature from 70°C to 90°C yielded similar to 0.75% H_2O_2 in the 70°C (EOP) for reducing total ClO_2 usage. Likewise, an 80°C (EO) was comparable to a 70°C (EOP) employing 0.30% H_2O_2. The effectiveness of elevated (EO) temperatures to lower ClO_2 requirements, unlike H_2O_2 in (EOP), is approxi-



9. D_2 brightness response as a function of D_1 brightness and D_2 ClO_2 charge (as ClO_2). Curves were calculated from regression model based on Basta et al. data [30].



10. Amount of ClO_2 used in brightening (D_1+D_2) as a function of how much is applied in D_1 and post-extraction kappa number to reach 87% ISO brightness.

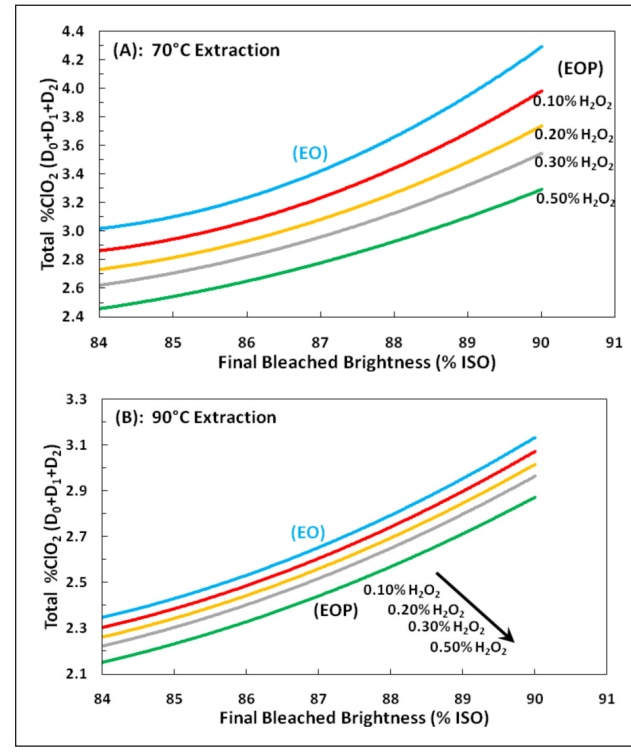
mately the same when examining pre-bleaching delignification versus the overall three-stage sequence performance.

Changes made to extraction conditions influenced the optimum post-extraction kappa number once the ClO_2 charges were balanced between the two D-stages. Figure 8 shows that for an 84% ISO brightness, increasing the H_2O_2 from 0% to 0.75% in the 70°C (EOP) caused the optimum post-extraction kappa to decrease from ~4.4 to 3.7. If the extraction temperature increased to 90°C, then applying higher H_2O_2 charges shifts the optimum post-extraction kappa from ~3.6 to 3.4. This observation is an important factor to consider with sequence optimization (**Table IV**). Many studies [7,8,21,22] focus comparisons on a fixed post-extraction kappa number instead of looking at how each stage interacts with each other when a perturbation is made to a given stage. Peroxide addition to extraction displaces ClO_2 in *both* D_0 and D_1. By looking at the overall sequence instead of totally focusing on a targeted post-extraction kappa, the full potential of the lowest ClO_2 charge can be realized for *both* delignification and decolorization.

$D_1E_2D_2$ brightening

An extended sequence allows for ClO_2 proportioning across D_1 and D_2 in order to more easily bleach higher post-extraction kappa number stocks (i.e., >4) to 86% to 90% ISO. **Figure 9** is the D_2 brightening as a function of D_1 brightness and ClO_2 charge (as ClO_2) in the D_2. A post-D_1 brightness of 76% ISO or higher is needed in order to reach a final bleached brightness of ~87% ISO.

The relative distribution of ClO_2 charges in the two brightening stages to reach 87% ISO are shown in **Figure 10**. The $D_1E_2D_2$ sequence lowers the amount of ClO_2 required to brighten the pre-bleached pulp by 45% to 50% when compared to a single D_1 stage. Approximately 75% to 90% of the ClO_2 used in brightening stages should be supplied to the D_1 stage for the lowest overall ClO_2. The optimum ClO_2 distribution appears independent of post-extraction kappa number. All of these findings correspond to the study of Axegård et al. [35].



11. Minimized total %ClO_2 needed to reach target brighness for D_0(EO)$D_1E_2D_2$ and D_0(EOP)$D_1E_2D_2$ sequences. Extraction was performed at (a) 70°C and (b) 90°C.

D_0(EO)$D_1E_2D_2$ versus D_0(EOP)$D_1E_2D_2$

An analysis similar to that performed for the three-stage bleach sequence was carried out examining the extended bleach sequence. Total ClO_2 charges to reach brightness targets of 84% to 90% ISO were minimized by balancing the amounts ClO_2 employed in D_0, D_1, and D_2, in addition to manipulating H_2O_2 charges and temperatures in extraction. **Figure 11** presents the results from these scenarios. In these analyses, the minimum charge in the D_2 stage was set to 0.2% ClO_2.

The minimized ClO_2 charges linearly increased, to some

% H_2O_2 in (EOP)	Total % ClO_2 replaced (D_0 + D_1 + D_2)		
	70°C (EOP)	80°C (EOP)	90°C (EOP)
0.1	~0.21	~0.08	~0.05
0.2	~0.38	~0.15	~0.10
0.3	~0.51	~0.21	~0.14
0.5	~0.70	~0.32	~0.22

V. ClO_2 replaced by H_2O_2 in the (EOP) in the D_0(EOP)$D_1E_2D_2$ sequence to reach 84% to 90% ISO brightness.

extent, as the brightness targets shifted from 84% to 90% ISO. The extended bleach sequence reduced the total ClO_2 needed to bleach to 84% to 87% ISO brightness by 15% to 25% when compared to the short three-stage sequence (≤ 86% ISO).

As a rule, 58% to 64% of the total ClO_2 charged should be applied in the D_0-stage, with the remainder split across the D_1- and D_2-stages. This range of ClO_2 in the D_0 charge affords a spread in the post-extraction kappa number of ±0.2-0.3 units from the optimum value. This was analogous to what was seen in the three-stage bleach sequence analysis (e.g., Figs. 7 and 8). Approximately 25% to 35% of the total ClO_2 charged should be applied in the D_1 stage, with the lower brightness targets requiring 25% to 30% and the higher brightness targets requiring 30% to 35%. The % ClO_2/extraction kappa values for these D_1 ClO_2 dosages vary from 0.15 to 0.30, which is generally the optimum range for D_1 brightening. All of these results appear in accord with other published studies balancing ClO_2 across the D-stages [7,8,33,35].

Peroxide addition in 70°C (EOP) stages displaces 1.3 to 1.8 Kg of ClO_2 per Kg H_2O_2 (**Table V**), which is somewhat lower than that seen for the three-stage bleach sequence (**Table IV**). Increasing the (EOP) temperature to 80°C lowers the replacement efficiency of H_2O_2 by 60% to levels near the predicted theoretical value (~0.79 ClO_2/H_2O_2). The effect of peroxide to lower ClO_2 requirements in 90°C (EOP) stages is approximately the same for both the three- and five-stage bleach sequence. Conducting an 80°C (EO)-stage yielded similar results as 0.30% H_2O_2 in a 70°C (EOP), whereas a 90°C (EO)-stage is equivalent to 0.50% H_2O_2 in a 70°C (EOP).

Balancing ClO_2 charges between D_0, D_1, and D_2 while modifying extraction variables affects the optimum post-extraction kappa number. The trends for the five-stage sequence are similar to those for the three-stage sequence (Fig. 8). The efficiency of H_2O_2 to replace ClO_2 (i.e., <90°C extraction) tends to be much greater, considering the overall bleach sequence than is perceived by strictly comparing to a targeted post-extraction kappa (**Table VI**).

Impacts on pulp properties

Basta et al. [30] disclosed limited data on how (EO) or (EOP) conditions affected final bleached pulp viscosity or strength. Viscosities of ~18.4 to 21.1 mPa•s (881 to 939 dm³/Kg SCAN intrinsic viscosity) were noted for 90% ISO pulps that utilized

Bleaching Conditions	Bleach Sequence Extraction Stage		
	70°C (EO)	70°C (EOP)	70°C (EOP)
% ClO_2 in D_0 [KF]	2.31 [0.253]	1.77 [0.194]	2.11 [0.231]
% H_2O_2 in (EOP)	0	0.3	0.3
Post-extraction kappa no.	4.6	4.6	3.9
% ClO_2 in D_1	1.42	1.42	1.24
% ClO_2 in D_2	0.59	0.59	0.20
Total %ClO_2 used	4.32	3.78	3.56

VI. Comparison of D_0(EO)$D_1E_2D_2$ to D_0(EOP)$D_1E_2D_2$ sequence to reach 90% ISO brightness. Optimization based on either reaching a target post-extraction kappa number or balancing ClO_2 charges between the three D-stages.

0.17 to 0.23 KF in the D_0 and 0% to 0.7% H_2O_2 in the 90°C (EOP). The bulk of the pulp viscosity loss, ~Δ4.9 mPa•s units (~Δ80 dm³/Kg units), occurs during the D_0(EO) or D_0(EOP) treatment. Peroxide addition to (EO) can results in some additional viscosity losses [29]. However, these (EO) or (EOP) viscosity losses can be offset by the addition of Mg-salts or bleach stabilizers [19-21,23,28]. Van Lierop et al. [21,22] noted that pulps treated by D_0(EO) or D_0(EOP) at various H_2O_2 charges and extraction temperatures exhibited almost identical tensile-tear strength curves as the untreated softwood brownstock. Dillner et al. [28] reported analogous strength findings. Thus, employing higher extraction temperatures and/or H_2O_2 addition does not result in lower final pulp strength, so long as excessive H_2O_2 decomposition is assuaged [19-21,23,28].

General discussion

The results of our study clearly illustrate the interactions of various bleaching stages with each other in three- and five-stage bleach sequences, particularly when varying the conditions of the first extraction stage to optimize bleaching. Combinations of higher extraction temperature and H_2O_2 reinforcement are not synergistic, or even additive in their individual abilities to affect total ClO_2 usage.

The potential of H_2O_2 to replace ClO_2 is variable and is strongly dependent on the reaction temperature of the extraction stage, as well as the amount of H_2O_2 applied. This observation makes equating H_2O_2 in terms of active chlorine or oxidation equivalents (OXE) misleading. Ragnar [29] and Renders et al. [36] have arrived at similar conclusions of utilizing such normalizing benchmarks for equating H_2O_2 efficiency. Many studies make mill-to-mill comparisons of ECF bleach sequences by incorporation of H_2O_2 as part of the total active chlorine applied in a given ECF bleach sequence (i.e., total

sequence kappa factor (SKF))[7,8,34]. Such evaluations may unduly skew the conclusions drawn, unless the extraction conditions for each bleached fiber line are nearly identical.

Several factors likely contribute to the variability of ClO_2 replacement by H_2O_2. Extraction delignification is a function of *both* lignin degradation [26] and lignin fragment diffusion from within the fiber [12,37-39]. Peroxide can either degrade D_0 oxidized lignin [12,26] or undergo wasteful alkali-induced [40] and/or transitional metal-induced decomposition. Most of these chemical and physico-chemical processes are affected by the extraction temperature to differing degrees. Higher extraction temperatures may shift the lignin removal process to be more dominated by lignin diffusion than lignin degradation by H_2O_2. At the lower extraction temperatures, the processes of chemical lignin degradation and diffusion may be more complementary than competitive. Likewise, elevated temperatures may favor alkali-induced H_2O_2 decomposition so it overshadows the H_2O_2 degradation of D_0 oxidized lignin. Transition metal ions, such as Fe and Mn, act as catalysts to decompose H_2O_2. Chelants, bleach stabilizers, or more commonly, Mg-salts, may be employed to inhibit these catalytic reactions [19-21,23,28].

CONCLUSIONS

This investigation re-analyzed the data of Basta et al. [30] to show how elevated extraction temperatures, H_2O_2 reinforcement, and combinations thereof can effect ClO_2 consumption in three- and five-stage ECF sequences for a conventional Southern pine kraft pulp. Approximately 60% to 65% of the total ClO_2 needed for bleaching should be applied in the D_0-stage with the remainder applied in the latter brightening stages. The amount of ClO_2 that can be replaced by H_2O_2 inclusion in extraction widely varies from 0.6 to 2.5 (wt. ClO_2/wt. H_2O_2). Increasing the (EO) temperature by Δ 10°C is equivalent to a 70°C (EOP) utilizing 0.25% to 0.30% H_2O_2. The individual positive effects of H_2O_2 reinforcement and higher extraction temperatures (>70°C) are not additive when used together to extend extraction delignification. This likely reflects competing physico-chemical and chemical mechanisms involved in extraction delignification and H_2O_2 decomposition, as well as which modes are dominant at 70°C versus 90°C.

This detailed analysis illustrated the importance of balancing of ClO_2 charges across three- and five-stage bleach sequences when manipulating extraction variables, instead of optimizing to fixed post-extraction kappa numbers; this observation becomes less relevant as extraction temperature approached 90°C. The stoichiometric data from this rigorous analysis can be employed to guide decision-making of how best to minimize costs associated with bleaching [41]. **TJ**

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ABOUT THE AUTHORS

Operators and managers seek to optimize their operations to lower production costs. Too often, many efforts focus on optimizing a single unit operation but fail to conceptualize that such changes affect other processes of pulp production. This "silo thinking" can lead to overall cost increases that offset the savings from that single operation. Our goal was to show how caustic extraction variables affect the various chlorine dioxide stages in the bleach plant from a holistic perspective. Very few scientists have investigated how extraction affects bleaching optimization.

A challenge with this study was acquiring the data. We live in an age where we are constrained by human and monetary resources. These constraints place limits on conducting extensive laboratory studies. We thoroughly scrutinized the published literature to identify laboratory data for re-analysis. We found an exceptional study published by Jiri Basta and coworkers at the 1992 TAPPI Pulping Conference. Their research examined a wide range of process variables with ECF bleach sequences to minimize the AOX in the effluents to very low levels (<0.5 kg/t pulp). Although Basta et al. did not specifically discuss overall chemical optimization, their study contained a wealth of information for us to re-analyze for our purposes.

We demonstrate how peroxide reinforcement and/or higher extraction temperatures affect total chlorine dioxide consumption, as well as the allocation of chlorine dioxide in the D-stages. Operators, engineers, and managers can use this information as a guide for how to alter process conditions/targets when the cost of bleaching chemicals and energy fluctuate. We will illustrate this in our ensuing publication.

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Many of our findings complement the conclusions from other ECF optimization studies. However, we uncovered two surprises: 1) the variable replacement ratio of peroxide for chlorine dioxide makes comparing the performance of different sequences by a total kappa factor misleading; and 2) optimizing to a target post-extraction kappa number does not always result in the lowest total chlorine dioxide usage. The second finding clarifies some of my previous experiences, where we altered extraction stage variables at the mill and observed the amount of chlorine dioxide in *both* delignification and brightening readjust to minimize the total chlorine dioxide used in the sequence.

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