Revised Steady-State Model for Chlorine Dioxide Brightening that Considers Extraction Washer Carryover Effects

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Past TAPPI PEERS talks proposed simple, generalized models to simulate Elemental Chlorine-Free (ECF) bleach stages, e.g. $D_1$ Brightening Stage:

$$y_1 = f(x_1, \ldots)$$

**Inputs**

- $x_1$, ...

**Extracted**

- Kappa & Brightness

**% ClO$_2$ on Pulp**

**D$_1$ Stage**

**Output**

- $y_1$

- $D_1$ Brightness
Generalized $D_1$ Brightening Model

- Model constant parameters: $\beta_{11}$ and $\beta_{12}$
- Entering brightness is Extracted Pulp Brightness ($B_E$)
- Post $D_1$ brightness is $y_1$ (% ISO)
- Chlorine dioxide charge in $D_1$ is $x_1$ (% ClO$_2$ on o.d. pulp)

Enterering brightness = $B_E = 92 - \frac{\beta_{11}}{\beta_{12} + x_1}$

Ultimate brightness limit = 92% ISO

$y_1 = 92 - \frac{\beta_{11}}{\beta_{12} + x_1}$

$\beta_{11}/\beta_{12}$ = Max $D_1$ stage gain

Brogdon, TAPPI J. (2014)
\( \beta_{11} \) Parameter vs. Extracted Kappa

- \( \beta_{11} \) parameter is \( f(x) \) of extracted kappa of \( D_0(EO) \), etc.
- Also found to represent \((CD)(EO)D_1\), \((DC)(EO)D_1\), etc.

Calculated from laboratory data from various literature sources
Testing $D_1$ Model with Bleach Plant Data

- $D_0$(EOP)$D_1$ sequence with Southern US pine pulp (~ 23-kappa)
- (EOP) pulp: ~ 3.15-kappa and ~ 55% ISO
- Mill utilizes wash press between (EOP) & $D_1$
- $D_1$ model over predicts brightness by 2.4 - 4.4 pts.
- (EOP) washer carryover affecting $D_1$ stage
- Historical (EOP) carryover: 13 – 17 kg TDS/t pulp
Extraction Washer Carryover

- Composition of dissolved solids not well characterized
- Typically measured as chemical oxygen demand (COD)
- 2004 PAPTAC mill survey: 3 – 17 kg COD/t extracted pulp; $\bar{x} \approx 12$ kg COD/t [drum washers]
- Others measured extraction carryover as a “kappa number”
- Carryover as kappa units: $\sim 0$ (low) to 8.5 (very high)
Quantifying Carryover as Kappa No.

- Kappa test (T 236) conducted on a pulp sample that is well-washed in the lab

- Unwashed (“wet”) kappa test conducted on washer mat sample that includes carryover (as-is discharged from washer)

- Difference between these values is the kappa contribution from extraction washer carryover
Modifying $D_1$ Model: Hypothesis

- Replace kappa in $\beta_{11}$ for well-washed pulp ($Kappa_E$) with:
  \[
  \text{Apparent Kappa} = Kappa_E + Kappa_{\text{Carryover}}
  \]

- Extracted pulp with carryover brightens in $D_1$ like a pulp with higher kappa (i.e., Apparent Kappa)
Testing Hypothesis: Pattyson et al. Lab Data

N. Ontario Softwood
Well-washed $E_1$ Kappa = 5.1

- (CD)$E_1 D_1$ bleaching with various $E_1$ carryover levels in $D_1$
- $D_1$ Multiple based on well-washed $E_1$ kappa no.

D₁ Multiple from calculated E₁ wet kappa no. at ~79% ISO

E₁ pulps w/ carryover exhibit common bleaching response with well-washed pulp w/ wet kappa no. value
Testing Hypothesis: Pattyson *et al.* Lab Data

- Data curve-fitted to the $D_1$ brightening model ($r^2 > 0.99$)
- Regression of $E_1$ pulps w/ carryover were within ±0.8 pts. of actual lab data
\[ \beta_{11} = 4.535 \cdot (\text{app. kappa}) - 7.434 \]

- \( \beta_{11} \) values determined from previous regression were plotted vs. wet kappa no. (i.e., Apparent Kappa no.)
- \( \beta_{11} \) values of E₁ pulps w/ carryover follows well-washed E₁ kappa vs. \( \beta_{11} \) value
Re-examining Mill Data with Revised Model

- Examine revised $D_1$ model with mill data using *Apparent Kappa* in place of well-wash pulp kappa ($Kappa_E$)

- $D_0$(EOP)$D_1$ sequence with US southern pines pulp (~ 23-kappa)

- Graph is with $Kappa_{Carryover}$ contribution set to zero

- Equations can be solved to calculate *Apparent Kappa* & $Kappa_{Carryover}$ using mill’s $D_1$ brightness as an input variable
Revised Model: Washer Carryover Estimates

- Apparent Kappa > Kappa_E by 1 to 1.9 units
- Carryover contributing ~45% additional kappa load to D_1
Mill’s D₀(EOP) pulp ($Kappa_E = 3.15$) with carryover bleaches in D₁ stage like well-washed D₀(EOP) pulp with a kappa of 4.55
Analysis with revised model suggests ~48% of mill’s $D_1$ bleach charge is consumed by extraction carryover.

Follows extra kappa load that (EOP) carryover contributes.
Estimating (EOP) Washing Effectiveness

- Effectiveness of mill’s (EOP) press washer estimated
- Effectiveness is % of total solubilized material generated in (EOP) that is removed
- Based on $Kappa_{Carryover}$ & kappa number drop across (EOP) stage
- Approximately 78% of the theoretical (EOP) kappa drop removed in the press washer
ClO$_2$ Uptake by Extraction Carryover

- Various N.A. mills & lit. data analyses suggest bleach consumption caused by carryover is $f(x)$ $D_1$ brightness

- 1 kappa unit of carryover consumes 2.5 – 4.6 kg ClO$_2$/t (78 to 84% ISO)
ClO$_2$ Uptake by Extraction Carryover

Bleach consumption similar to Reeve et al. (1977) study:
2.6 – 3.4 kg ClO$_2$/kappa of carryover
Summary: $D_1$ Brightening Response

Generalized $D_1$ brightness equation can model bleach plant data:

$$ y_1 = 92 - \frac{\beta_{11}}{\beta_{11}} \left( 92 - B_E \right) + x_1 $$

- **Inputs** $x_1, B_E, \beta_{11}$
- **D$_1$ Stage**
- **Output** $y_1$

Extracted pulp properties

% ClO$_2$ on Pulp

$D_1$ Brightness
Summary: Extracted Pulp Properties

- $\beta_{11}$ parameter influenced by the pulp’s extracted kappa number & its carryover (expressed as kappa units):

$$\beta_{11} = 4.535 \times \text{Apparent Kappa} \approx 7.434$$

![Graph showing brightness limit and extracted brightness](image)

$$\text{Apparent Kappa} = \text{Kappa}_{E} + \text{Kappa}_{\text{Carryover}}$$
Summary: Use of Model with Mill Data

- Modified model can be used to calculate impact of extraction washer carryover on $D_1$ Bleaching

$$y_1 = f(x_1, B_E, \beta_{11}, \text{Kappa})$$

- $\text{Kappa}_{\text{Carryover}}$
- $\text{Kappa}_E \& B_E$
- $x_1, \% \text{ClO}_2$ on Pulp
- $y_1, D_1$ Brightness
Equations can be solved to estimate extraction washer carryover, washing effectiveness, bleach consumption caused from carryover, & opportunities for optimization.

\[
y_1 = f(x_1, B_E, \beta_{11}, \text{Kappa})
\]
Summary: Carryover ClO\(_2\) Consumption

- Bleach Consumption by extraction washer carryover varies as function of D\(_1\) brightness

- Extraction washer carryover consumes 2.4 to 4.6 kg ClO\(_2\)/t pulp per kappa unit of carryover
Questions?
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