BICARBONATE ANION AND TAED AS ACTIVATORS IN PEROXIDE BLEACHING OF A MECHANICAL PULP

RAYMOND C. FRANCIS,[*] ANTTI LUUKKONEN,[**] FRANCIS K. ATTIOGBE[***] and
DONATIEN P. KAMDEM[****]

[*]*Department of Paper and Bioprocess Engineering, State University of New York (SUNY), College of Environmental Science and Forestry (ESF), Syracuse, NY 13210, USA*
[**]*Andritz Inc., Springfield R&D Center, Springfield, OH 45504, USA*
[***]*Department of Energy and Petroleum Engineering, University of Energy and Natural Resources, Sunyani, Ghana*
[****]*School of Packaging, Michigan State University, East Lansing, MI 48824, USA*
✉ *Corresponding author: R. C. Francis, francis@esf.edu*

Earlier research demonstrated that the bicarbonate anion (HCO_3^-) activated hydrogen peroxide and made it into an effective bleaching agent for both chemical and mechanical pulps at pH ~ 8.5. The peroxide/bicarbonate treatment is designated as a P_B stage. It was also observed that in P_B bleaching of chemithermomechanical pulps (CTMPs), a higher initial pH resulted in more H_2O_2 being consumed and the achievement of a higher bleached brightness. This research focused on using Na_2CO_3 instead of $NaHCO_3$ to achieve a higher pH in P_B bleaching of softwood CTMP. Further activation of the H_2O_2 was obtained by the addition of N, N, N', N'-tetraacetylethylenediamine (TAED). There was a high peroxide residual when 3.0% H_2O_2 on pulp (oven-dried or OD basis) was used in a conventional alkaline peroxide (P) stage. Sodium carbonate was added to the P stage effluent (with or without TAED), which was recycled and used to pretreat unbleached pulp. A significant increase in brightness (~3 points) was obtained when the pretreated pulp was regularly bleached with 3.0% H_2O_2 on pulp in a P stage.

Keywords: peroxide bleaching, mechanical pulp, hydrogen peroxide, peroxymonocarbonate anion, TAED

INTRODUCTION

Hydrogen peroxide bleaching of chemical, chemimechanical and mechanical pulps has been in large scale commercial practice for over 40 years. However, new additives[1,2] and optimization strategies[3-5] are still being investigated in hopes of improving brightness or decreasing peroxide usage. In one earlier investigation, it was demonstrated that the bicarbonate anion (HCO_3^-) was an effective activator of hydrogen peroxide when used for the brightening of chemithermomechanical pulps (CTMPs) from both softwoods and hardwoods.[6] A distinguishing feature of the H_2O_2/HCO_3^- oxidizing system in the bleaching of CTMP was a sizeable brightness gain with a low consumption of H_2O_2 at pH ~ 8.5.[6] Lignin model compounds and chemical pulps were also oxidized by H_2O_2/HCO_3^-;[7] the results in their totality (lignin model compounds and pulps) were convincing that the peroxymono-

carbonate anion (HCO_4^-) was the key intermediate.[6,7] This anion is known to be generated by reactions between HCO_3^-/CO_2 and H_2O_2/HOO^- resulting in the net reaction shown in Equation (1).[8-11]

$$HCO_3^- + H_2O_2 \rightleftharpoons {}^-O\overset{\overset{\displaystyle O}{\|}}{C}OOH + H_2O \qquad (1)$$
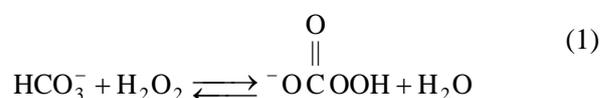
The present research is a continuation of the earlier effort and it started with two primary objectives. The first objective was to try to increase the degree of peroxide activation by a) increasing the alkalinity of the H_2O_2/HCO_3^- (P_B) stage to an initial pH > 9.5, and b) adding TAED to P_B to give a P_{BT} stage. N, N, N', N'-tetraacetylethylenediamine (TAED) is a peroxide activator that increased the whiteness of cotton fibers in the pH range of 7-10.[12] In the earlier

investigation by Attiogbe *et al.*,[6] a higher brightness was obtained for P_B bleaching of a hardwood CTMP at initial pH ~ 9.5, compared to ~8.6. The second objective was to add HCO_3^- and/or TAED to the peroxide-containing solution at the end of a P stage and use the new liquor to achieve incremental bleaching. Two approaches were considered: the first was to mix HCO_3^- and/or TAED into the pulp slurry from the P stage and allow for further oxidation. That would result in P→P_B or P→P_{BT} bleaching without inter-stage washing. The second approach was to press free liquor from the pulp slurry after the P stage to generate an effluent, add HCO_3^- and/or TAED to it and use it to bleach fresh unbleached pulp. That would result in P_B→P or P_{BT}→P bleaching with the peroxide in the first stage coming from the second stage effluent. A schematic for this process is shown in the Results and Discussion section.

As for the first objective, the pH dependent speciation of carbonic acids (H_2CO_3) affords HCO_3^- as the major species ($\geq$60% of the total $H_2CO_3 + HCO_3^- + CO_3^{2-}$ concentration) over a wide pH range; approximately pH 6.5-10.0.[13] If a P_B stage were to be performed in the pH range of 9.5-10, peroxide activation by HCO_3^- would decrease because the bicarbonate percentage of total carbonate would decrease from >95% (pH ~8.6) to ~70% at pH 9.5-10.[13] However, at pH >9.5, there would be some dissociation of H_2O_2 to the perhydroxyl anion (HOO^-). This nucleophile (HOO^-) is reactive with lignin and is an effective brightener of wood pulps. The addition of TAED to the P_B stage would be another approach for enhanced activation of the H_2O_2. The reaction scheme in which two moles of H_2O_2 react with one mole of TAED to form two moles of peracetic acid is widely described in the literature.[12,14] At pH >9.5, the peracetic acid (PAA) would be significantly dissociated to the peracetate anion since the pKa of PAA is 8.2.[15] The peracetate anion is a nucleophile that is effective at brightening wood pulps.[16] Xu *et al.*[12] prepared 0.1M buffer solutions at pH 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0 and 11.0. They bleached cotton fibers with H_2O_2 in each buffer.[12] The bleaching trials were performed with and without TAED addition. Peroxide bleaching was activated by TAED in the pH range of 5-11.[12] TAED activation appeared to be highest at pH~8. However, with TAED addition, the differences in whiteness were not large in the pH range of 7-10.[12] Research by other groups appear to support

the finding of Xu *et al.*[12] An investigation involving lignin model compounds found TAED activation to be most pronounced at pH ~8.2.[17] Significant activation was also observed in pulp bleaching systems in the pH range of 5-6,[18] and 10.0-10.5.[19,20]

The P→P_B or P→P_{BT} approach in the second objective would be applicable to mills with only one bleaching tower. A mixer and a second bleaching tower would be required between the existing tower and the washing system. On the other hand, peroxide bleaching of mechanical pulps to high brightness using two towers with the effluent from the second tower (second stage) being partially recycled to the first tower (first stage) is practiced commercially by some mills. The residual peroxide in the second stage effluent can be quite high if a dose of $\geq$4.0% H_2O_2 on pulp is used. Carbonation of residual NaOH in the second stage effluent to Na_2CO_3 (Eq. (2)) would be the only change required to convert the first P stage to a P_B stage. Adding TAED to this recycled stream, before or after carbonation, would afford a P_{BT} stage. Carbonation of NaOH to Na_2CO_3 is a simple reaction that would require only a short retention time (<1 minute) at a slightly elevated pressure. When investigating P_B→P or P_{BT}→P bleaching in the present research, Na_2CO_3 powder was simply dissolved in the effluent being recycled from the P stage. In commercial practice, a small amount of NaOH would be added to the recycle stream before all of the residual NaOH contained in it is carbonated to Na_2CO_3.

$$2\ NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \qquad (2)$$

EXPERIMENTAL
Pulps and chemicals

The CTMP was a commercial pulp made from softwoods only. It was treated with sodium sulfite and diethylene-triamine-pentaacetic acid pentasodium salt (Na_5DTPA) in the mill and had a brightness of 51.9% Elrepho when it arrived in the laboratory. All chemicals used in this investigation were reagent grade or higher.

Chelation treatment

The pulp was treated with 0.2% Na_5DTPA in a Q stage performed at 70 °C and 10% consistency for 1.0 h. A buffering solution consisting of $NaHSO_3$ (0.25 M on a SO_2 basis) and 0.02 M NaOH was added to the Q stage. The buffer typically had a pH in the range of 5.8-5.9 and was added at a dosage of 1.0 mL/g of pulp. The chemicals were added to the wet pulp in a plastic bag at room temperature. After sealing the bag, the slurry was mixed by hand and placed in a 1.1 kW

microwave oven to attain a temperature close to the treatment temperature (70 °C). The plastic bag was mixed again, then placed in the water bath for the specified time. There was occasional mixing during the retention period in the water bath. The end pH of the Q stage effluent consistently fell in the range of 5.1-5.2.

Bleaching stages
P stages: The range of conditions were 2.0-4.0% H_2O_2, 2.50-3.25% NaOH, 2.0% sodium silicate (41 Be) and 0.5% $MgSO_4.7H_2O$ on pulp for 3.0-4.0 h at 15% or 18% consistency. The temperature for all P stages was 70 °C. The chemicals were mixed into the pulp at room temperature and heated in a microwave oven, as described above.

P_B and P_{BT} stages: These stages were performed in plastic bags at 15% consistency, 70 °C or 80 °C for 1.0 h or 2.0 h. The chemical doses and exact reaction conditions will be provided in the appropriate tables in the Results and Discussion Section. When used, TAED was added to the pulp slurry as small, non-sticky granules, obtained from Sigma Aldrich. It was not dissolved in water or the recycled liquor beforehand.

Neutralization stages: Before thick pads (~600 g/m^2) were made for brightness measurement, the washed pulp from a Q or bleaching stage was converted to a dilute and well-mixed slurry with deionized water, and enough 0.25 M NaHSO$_3$ was added to achieve a slurry pH of 6.0-6.2. The slurry was mixed again and allowed to sit for ~5 minutes at room temperature. Residual chemicals were then washed out of the fibers and brightness pads made with deionized water only. The pads were pressed at ~0.45 MPa and air-dried at room temperature.

Analyses: All brightness measurements were obtained on a Zeiss Elrepho brightness meter with diffuse reflectance. The concentrations of transition and other metals in the untreated and Q-treated pulps were determined by ICP-AES in the Andritz Inc. Laboratory, Glens Falls, NY.

RESULTS AND DISCUSSION
P_B and P_{BT} bleaching of CTMP
The metal contents of the untreated and Q-treated pulps are summarized in Table 1. The untreated pulp did not contain a high concentration of any of the transition metals whose complexes are known to be quite efficient at decomposing H_2O_2 under alkaline conditions. The four key transition metals are Mn, Fe, Cu and Co.[21] The concentration of each of those four metals in the Q-treated pulp was much lower than the value typically found in softwood or hardwood mechanical pulps.

The first bleaching trial was a comparison of NaHCO$_3$ and Na$_2$CO$_3$ as the alkali source in a P_B stage. It was estimated that 3.0% Na$_2$CO$_3$ on pulp should be high enough to give an initial pH >9.5.[6] Two P_B stages were performed for 2.0 h, one with 3.0% Na$_2$CO$_3$ on pulp and the other with 4.75% NaHCO$_3$ on pulp (equal to 3.0% Na$_2$CO$_3$ on a Na$_2$O basis). The bleaching temperature was 70 °C and 1.0% H_2O_2 on pulp was used. The results are summarized in Table 2. A significant brightness increase was observed, but in both cases H_2O_2 consumption (in oxidation and decomposition reactions) was <0.5% on pulp. That was after 2.0 h at 70 °C.

The bleaching was repeated, but on this occasion 1.0% TAED on pulp was added with the expectation that both peroxide consumption and pulp brightness would increase. A small amount of NaOH (0.25% on pulp) was added along with the 3.0% Na$_2$CO$_3$ on pulp in order to ensure that an initial pH >9.5 was attained. The initial pH was measured on this occasion and a value of 10.1 was obtained.

Table 1
Concentration of transition and other metals in untreated and Q-treated CTMP

Metal	Conc. in untreated sample, mg/kg or ppm	Conc. in Q-treated sample, mg/kg or ppm
Aluminum, Al	5.5	4.0
Barium, Ba	11.5	11.6
Calcium, Ca	760	519
Magnesium, Mg	179	104
Manganese, Mn	25.7	1.2
Iron, Fe	--	5.7
Copper, Cu	1.3	0.7
Cobalt, Co	<0.1	<0.1

Table 2
P_B bleaching of softwood CTMP in bicarbonate and carbonate solutions

Alkali source [1]	H_2O_2 dose, % on pulp	Residual H_2O_2, % on pulp	End pH	Brightness, % Elrepho
–	–	–	–	53.7 [2]
4.75% NaHCO$_3$	1.0	0.70	8.5	60.8
3.0% Na$_2$CO$_3$	1.0	0.57	8.8	62.0

[1] 0.1% Na$_5$DTPA on pulp, 15% consistency, 2 h at 70 °C; [2] Brightness after Q stage

Table 3
P_{BT} bleaching of softwood CTMP; effect of TAED addition

Alkali source [1]	H_2O_2 dose, % on pulp	Residual H_2O_2, % on pulp	End pH	Brightness, % Elrepho
–	–	–	–	53.7 [2]
4.75% NaHCO$_3$	1.0	0.56	8.4	62.4
3.0% Na$_2$CO$_3$	1.0	0.41	8.5 (10.1)[3]	63.8

[1] 1.0% TAED and 0.1% Na$_5$DTPA on pulp, 15% consistency, 2 h at 70 °C; [2] Brightness after Q stage;
[3] Initial pH in parentheses, 0.25% NaOH on pulp added with Na$_2$CO$_3$

The P_{BT} bleaching results are summarized in Table 3. Somewhat surprisingly, TAED addition resulted in peroxide consumption increasing by <0.20% on pulp. However, that small increase in H_2O_2 consumption caused brightness to increase from 62.0% to 63.8% Elrepho when Na$_2$CO$_3$ was the alkali source (Table 3). A brightness increase of 10.1 points (53.7% to 63.8% Elrepho) was obtained for a H_2O_2 consumption of only 0.59% on pulp when Na$_2$CO$_3$ was the alkali source. The preliminary assessment was that the results for both P_B and P_{BT} were impressive and most likely could be improved if the bleaching temperature were to be increased to 80 °C or higher.

It was deemed necessary to obtain the brightness response of the pulp toward a conventional P stage before endeavoring to improve upon the P_B and P_{BT} results so far obtained. It was possible that this CTMP had above-average P stage bleachability, particularly in light of its low contents of transition metals. The P stage results (2.0-4.0% H_2O_2) are summarized in Table 4. TAED is generally more expensive than H_2O_2. Therefore, the initial P stage was conducted with 2.0% H_2O_2 on pulp; a treatment whose overall chemical cost would be nearly equal to that of 1.0% H_2O_2 and 1.0% TAED on pulp. When 2.0% H_2O_2 on pulp was applied, 1.44% on pulp was consumed and brightness increased 15.2 points from 53.7% to 68.9% Elrepho. This is a higher than usual brightness gain for a softwood CTMP. When 3.0% H_2O_2 on pulp was applied, a bleached brightness of 73.5% was obtained for 2.5% NaOH on pulp and 73.8% for 2.75% NaOH (Table 4). At the 4.0% H_2O_2 on pulp application level, bleached brightness of 75.9% and 76.2% was obtained for 15% and 18% consistency, respectively. A brightness gain of 22.5 points (76.2-53.7%) in a single P stage was achieved for this pulp.

Table 4
Results obtained from single P stage bleaching of CTMP with 2.0-4.0% H_2O_2 on pulp

% H_2O_2 [1]	% NaOH [1]	Pulp consistency	Residual H_2O_2 [1]	End pH	Brightness, % Elrepho
2.0	2.5	15	0.56	10.4	68.9
3.0	2.5	15	1.03	9.7	73.5 [2]
3.0	2.75	15	0.98	9.9	73.8
4.0	3.25	15	1.41	9.7	75.9 [3]
4.0	3.25	18	1.46	9.8	76.2 [3]

[1] % on pulp; [2] Ten runs under this condition; average brightness of 73.4% with a standard deviation of 0.14 point of brightness; corresponding values for residual H_2O_2 were 1.03% and 0.02% on pulp; [3] Retention time of 4 h was used with 4.0% H_2O_2 on pulp; 3 h was used for 2% or 3% H_2O_2 on pulp

Various combinations of P_B or P_{BT} with a P stage were attempted. On all occasions, the P stage condition was 3.0% H_2O_2 and 2.5% NaOH on pulp (Table 4). Ten runs were performed under that particular condition and an average brightness of 73.4% was obtained with a standard deviation of only 0.14 brightness point. Similarly, the residual peroxide was 1.03% on pulp with a standard deviation of only 0.02% on pulp.

$P \rightarrow P_{BT}$ bleaching of CTMP

Two P stages were performed using 3.0% H_2O_2 and 2.5% NaOH on pulp (2 of the 10 in the footnotes of Table 4). The pulp and effluent from one of the two P stages were analyzed, while the plastic bag containing the second pulp was open and 1.0% TAED and 1.32% Na_2CO_3 on pulp added as solids. The two chemicals were mixed into the pulp and the slurry re-heated (microwave oven). The slurry was returned to the water bath for an additional one hour of retention (P_{BT} stage). The sample analyzed after the P stage had a brightness of 73.4% and its effluent had an end pH of 9.8 and contained 1.05% residual H_2O_2 on pulp. After $P \rightarrow P_{BT}$ the pulp had a brightness of 75.4% and its effluent had an end pH of 9.7 and contained 0.54% residual H_2O_2 on pulp. Therefore, 0.51% H_2O_2 on pulp was consumed in the P_{BT} treatment stage and that increased bleached brightness from 73.4% to 75.4%.

The additional peroxide consumption for this 2.0-point brightness gain (0.51% H_2O_2 on pulp) was nearly equal to the incremental peroxide consumed for a nearly similar brightness gain observed in Table 4, *i.e.* when the peroxide dose was increased from 3.0% to 4.0% on pulp at 15% consistency. When 3.0% H_2O_2 and 2.75% NaOH on pulp were used, 2.02% H_2O_2 on pulp was consumed and a brightness of 73.8% was obtained. The application of 4.0% H_2O_2 and 3.25% NaOH on pulp resulted in a peroxide consumption of 2.59% on pulp and a brightness of 75.9%. Therefore, an increase in peroxide consumption of 0.57% on pulp afforded a brightness increase of 2.1 points.

A two-point incremental brightness gain does not appear high enough to justify adding a P_{BT} stage in a $P \rightarrow P_{BT}$ sequence to consume some of the residual peroxide from the P stage. A mixer would be required to mix the TAED and Na_2CO_3 into the pulp slurry at medium to high consistency and a tower would be needed to retain the pulp for 1-2 h during P_{BT} treatment. The more realistic option for the use of P_{BT} or P_B to consume unused peroxide from a P stage appeared to be using the activator(s) in an existing bleach plant with two bleaching towers and with effluent from the second tower (P stage) being recycled to the first tower (P_{BT} or P_B stage). That possibility was investigated and is reported on below.

$P \rightarrow P$, $P_B \rightarrow P$ and $P_{BT} \rightarrow P$ bleaching of CTMP

The typical flowsheet for a two-tower bleaching system is shown in Figure 1. In this flowsheet, most or all of the peroxide would be added in the mixer ahead of the second tower. Peroxide containing effluent would be pressed from the pulp leaving the second tower and would be recycled to the first tower (a fraction of the effluent would be retained by the fibers after they had been pressed to ~30% consistency). Activators could then be added to the recycle flow stream identified as "Residual H_2O_2" or to the mixer ahead of the first tower.

In the present research, $P_{BT} \rightarrow P$ was actually simulated by three stages of bleaching. The sequence was P-sim $\rightarrow P_{BT} \rightarrow$ P-act with P-sim or P-simulated used to generate a second stage effluent (P stage in Fig. 1) for recycle to the P_{BT} stage. The P-sim treatment was a regular P stage using 3.0% H_2O_2 and 2.5% NaOH on Q treated pulp (described in Table 4). Enough effluent was collected from duplicate P-sim treatments to dilute fresh Q treated pulp from exactly 30% consistency to exactly 15% consistency, thus initiating the P_{BT} stage. After the P_{BT} stage, the pulp was once again pressed to ~30% consistency. Hydrogen peroxide, NaOH, stabilizers and dilution water were then added to initiate the P-act or P-actual treatment. At this early stage of development, it was assumed that the recycled liquor from P-sim would be nearly equal to that from P-act in the $P_{BT} \rightarrow P$ sequence. The consistency achieved after pressing was consistently in the range of 27% for both the P-sim and P_{BT} stages. All three bleaching stages (P-sim, P_{BT} and P-act) were performed at exactly 15% consistency.

The total slurry weight for 50 g of pulp (OD basis) at 15% consistency is 333.3 g, *i.e.* 50 g of pulp and 283.3 g of liquor. When pressed to 30% consistency, the slurry weight decreases to 166.7 g. Therefore, 166.6 g of effluent needs to be pressed out in going from 15% to 30% consistency. The flowsheet in Figure 1 calls for

both the entrance and exit consistency to be 30% and for both bleaching stages to be conducted at 15% consistency. Of the 283.3 g of liquor leaving the second stage, 166.6 g needs to be pressed out and recycled to the first stage (166.6/283.3 = 59%).
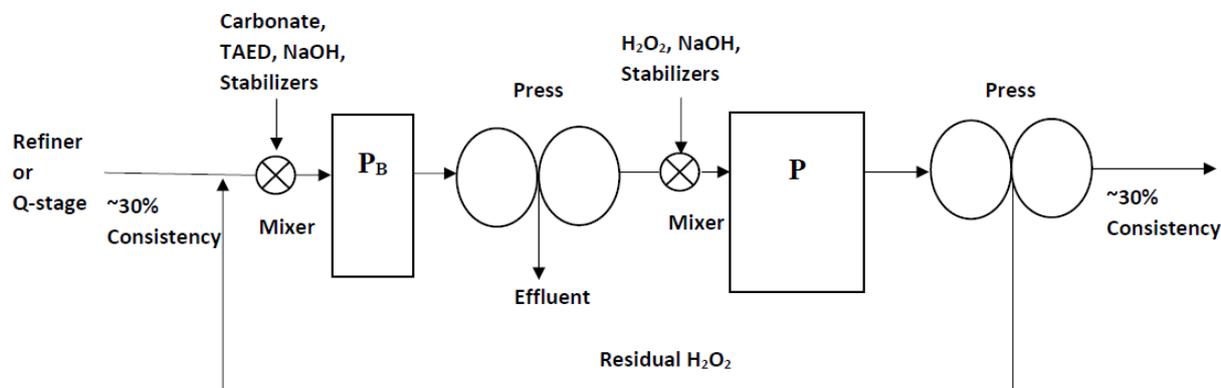
Figure 1: Proposed scheme for two-stage bleaching of mechanical pulps with liquor recycle. P is a conventional peroxide stage with H_2O_2 and NaOH; P_B is a stage with H_2O_2 and HCO_3^-; P_B becomes P_{BT} when TAED is added along with HCO_3^-

In the first run attempted, two 50 g samples of Q-treated CTMP were bleached with 3.0% H_2O_2 and 2.5% NaOH on pulp (P-sim) and ~53% of the total liquor pressed from them (0.53 x 283.3 = 150 g). The two effluents were combined and the mixture analyzed. The liquor pH was 9.8 and its residual peroxide concentration corresponded to 1.02% H_2O_2 on pulp. A P-stage liquor recycle rate of 59% meant that 0.60% H_2O_2 on pulp would be recycled from P-sim to the first bleaching stage, a P_{BT} stage in this case. The chemical addition to the P_{BT} stage was 0.66% Na_2CO_3 on pulp added to 166.6 g of the recycled liquor and 0.60% TAED on pulp added to the slurry of fresh Q-treated pulp and the recycled liquor. The P_{BT} stage was conducted at 70 °C for one hour, then the pulp was once again pressed to ~27% consistency. To that P_{BT} pre-bleached pulp, 3.0% H_2O_2 and 2.5% NaOH were added along with sodium silicate and magnesium sulfate to initiate the P-act stage. Some water was also added to achieve exactly 15% consistency. The pulp was placed in the water bath for 3 h, thus completing the simulated $P_{BT}\rightarrow P$ sequence. A final brightness of 76.3% Elrepho was obtained (Table 5).

Table 5
Pulp and effluent characterization for $P\rightarrow P$, $P_B\rightarrow P$ and $P_{BT}\rightarrow P$ bleaching sequences

Sequence	1st Stage H_2O_2 doses[1]	1st Stage end pH	2nd Stage H_2O_2 doses[2]	2nd Stage end pH	Final brightness, %
$P_{BT}\rightarrow P$[3]	0.60/0.32	8.4	3.15/1.04	9.9	76.3
$P\rightarrow P$[4]	0.60/0.13	8.7	3.06/1.03	10.3	75.0
P_B (70 °C)$\rightarrow P$[5]	0.61/0.31	8.6	3.15/1.05	10.2	75.9
P_B (80 °C)$\rightarrow P$[5]	0.61/0.19	8.5	3.09/1.05	10.1	76.6

[1] Initial and final H_2O_2 doses (% on pulp); initial H_2O_2 dose from P-sim (see text for description of P-sim); [2] Approx. 47% of 1st stage H_2O_2 residual is carried over to the 2nd stage; therefore, initial dose >3.0% H_2O_2 on pulp; [3] 0.6% TAED and 0.66% Na_2CO_3 on pulp added to 1st stage; [4] 1.0% NaOH on pulp added to 1st stage; [5] 1.32% Na_2CO_3 on pulp added to first stage

The P-act bleaching effluent had a pH of 9.9 and residual peroxide concentration corresponding to 1.04% H_2O_2 on pulp. These values are nearly identical to those from P-sim (pH 9.8 and 1.02% H_2O_2 on pulp). At this preliminary stage, we did not recycle 53-59% of the P-act effluent and use it to bleach fresh Q-treated pulp. However, the $P_{BT}\rightarrow P$ sequence

appears to be much more efficient than the P→P$_{BT}$ sequence. In the latter case (P→P$_{BT}$), 1.0% TAED and 1.32% Na$_2$CO$_3$ on pulp were mixed into the P-bleached pulp and a final brightness of only 75.4% was achieved. In the former case (P$_{BT}$→P), only 0.6% TAED and 0.66% Na$_2$CO$_3$ on pulp were added and a final brightness of 76.3% was obtained. The chemical doses and peroxide residuals in the various streams in P$_{BT}$→P bleaching are summarized in Table 5. The results are also presented for the P→P sequence and the P$_B$→P sequence with the P$_B$ stage (no TAED) conducted at both 70 °C and 80 °C for one hour.

Mills with existing two-tower bleach plants generally practice the P→P sequence in Table 5. When the P-sim effluent and 1.0% NaOH on pulp were added to the fibers in the first P stage, a final brightness of 75.0% was obtained for P→P (Table 5). This value was significantly lower than the 76.3% value obtained for P$_{BT}$→P. However, the extra chemical cost for the TAED may hinder the economic attractiveness of P$_{BT}$→P bleaching. The P$_B$→P sequence was then investigated. When the P-sim liquor and 1.32% Na$_2$CO$_3$ on pulp were added to a P$_B$ stage at 70 °C for 1 h, a brightness of 75.9% was achieved. The temperature in the P$_B$ stage was increased to 80 °C, since there was a peroxide residual of 0.31% H$_2$O$_2$ on pulp when the P$_B$ stage was conducted at 70 °C. The P$_B$ stage at 80 °C afforded a peroxide residual of 0.19% H$_2$O$_2$ on pulp and a final P$_B$→P brightness of 76.6% Elrepho. Therefore, for a mill operating a P→P sequence with liquor recycle from the second to the first stage, a simple addition of 1.0% NaOH on pulp to that liquor followed by its carbonation could significantly increase final brightness.

CONCLUSION

A distinguishing feature of the H$_2$O$_2$/HCO$_3^-$ bleaching system previously reported was a sizeable brightness gain with a low consumption of H$_2$O$_2$ at pH ~ 8.5 (Attiogbe *et al.*).[6] In this research, increased activation of H$_2$O$_2$/HCO$_3^-$ bleaching (P$_B$ stage) of a CTMP was investigated by replacing NaHCO$_3$ with Na$_2$CO$_3$ to increase the pH range of bleaching and also by adding TAED, a peroxide activator that is efficient in the pH range of 7-10. It was observed that if Na$_2$CO$_3$ was added to the peroxide containing effluent from a conventional P stage (with or without TAED) and the effluent was recycled to pretreat unbleached pulp, then bleachability could be

significantly improved. When the pretreated pulp was regularly bleached with a P stage, there was an increase in brightness of ~3 points. A flowsheet is presented for this approach and it is designated as a P$_B$→P sequence.

REFERENCES
[1] Z. Li, H. Dou, Y. Fu and M. Qin, *Carbohyd. Polym.*, **132**, 430 (2015), https://doi.org/10.1016/j.carpol.2015.06.062
[2] N. Das, S. K. Bose and R. C. Francis, *Tappi J.*, **18**, 409 (2019), https://doi.org/10.32964/TJ18.7.409
[3] J.-H. Seo and H.-J. Kim, *Ultrason. Sonochem.*, **23**, 347 (2015), https://doi.org/10.1016/j.ultsonch.2014.10.013
[4] J. Fiskari, T. Vihelä, K. Ruuttunen, V. Ali-Rekola, S. Hautala *et al.*, *Cellulose Chem. Technol.*, **51**, 857 (2017), http://www.cellulosechemtechnol.ro/pdf/CCT9-10(2017)/p.857-861.pdf
[5] X. Sun and Q. Hou, *J. Bioresour. Bioprod.*, **3**, 35 (2018), https://doi.org/10.21967/jbb.v3i1.110
[6] F. K. Attiogbe, W. Wang, A. McNeillie and R. C. Francis, *Bioresources*, **5**, 2221 (2010), https://doi.org/10.15376/biores.5.2.2221-2231
[7] F. K. Attiogbe, W. Wang, A. McNeillie and R. C. Francis, *Bioresources*, **5**, 2208 (2010), https://doi.org/10.15376/biores.5.2.2208-2220
[8] D. E. Richardson, H. Yao, K. M. Frank and D. A. Bennett, *J. Am. Chem. Soc.*, **122**, 1729 (2000), https://doi.org/10.1021/ja9927467
[9] M. Liu, X. Cheng, L. Zhao and J.-M. Lin, *Luminescence*, **21**, 179 (2006), https://doi.org/10.1002/bio.903
[10] E. V. Bakhmutova-Albert, H. Yao, D. E. Denevan and D. E. Richardson, *Inorg. Chem.*, **49**, 11287 (2010), https://doi.org/10.1021/ic1007389
[11] S. Zhao, H. Xi, Y. Zuo, Q. Wang, Z. Wang *et al.*, *J. Hazard. Mater.*, **344**, 136 (2018), https://doi.org/10.1016/j.jhazmat.2017.09.055
[12] C. Xu, X. Long, J. Du and S. Fu, *Carbohyd. Polym.*, **92**, 249 (2013), https://doi.org/10.1016/j.carbpol.2012.08.088
[13] O. Pedersen, T. D. Colmer and K. Sand-Jensen, *Front. Plant Sci.*, **4**, Article 140 (2013), https://doi.org/10.3389/fpls.2013.00140
[14] D. M. Davies and M. E. Deary, *J. Chem. Soc., Perkin Trans.*, **2**, 1549 (1991), https://doi.org/10.1039/p29910001549
[15] E. Koubek, M. L. Haggett, G. J. Battaglia, K. M. Ibne-Rasa, H. Y. Pyun *et al.*, *J. Am. Chem. Soc.*, **85**,

2263 (1963), https://doi.org/10.1021/ja00898a016

[16] G. Strumila and H. Rapson, *Pulp Paper Can.*, **76** (9), 74 (1975)

[17] Q. Y. Hu, C. Daneault and S. Robert, *J. Wood Chem. Technol.*, **26**, 165 (2006), https://doi.org/10.1080/02773810600704335

[18] F. Zeinaly, J. Shakhes and N. Zeinali, *Carbohyd. Polym.*, **92**, 976 (2013), https://doi.org/10.1016/j.carbpol.2012.10.043

[19] J. S. Hsieh, C. Agrawal, R. Maurer and J. Mathews, *Tappi J.*, **5**, 27 (2006), https://www.researchgate.net/publication/297304248_The_effectiveness_of_TAED_on_the_peroxide_bleaching_of_mechanical_chemical_and_recycled_pulp

[20] P. Khristova, J. Tomkinson and G. Lloyd Jones, *Ind. Crop. Prod.*, **18**, 101 (2003), https://doi.org/10.1016/S0926-6690(03)00030-X

[21] D. G. Brown, Doctoral Dissertation, University of Tasmania, Australia, 1993, https://eprints.utas.edu.au/18872/