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

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Received September 19, 2019

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 PB stage. It was also observed that in PB bleaching of chemithermomechanical pulps (CTMPs), a higher initial pH resulted in more H$_2$O$_2$ being consumed and the achievement of a higher bleached brightness. This research focused on using Na$_2$CO$_3$ instead of NaHCO$_3$ to achieve a higher pH in PB bleaching of softwood CTMP. Further activation of the H$_2$O$_2$ was obtained by the addition of N, N, N', N'-tetraacetylethylenediamine (TAED). There was a high peroxide residual when 3.0% H$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$/HCO$_3^-$ oxidizing system in the bleaching of CTMP was a sizeable brightness gain with a low consumption of H$_2$O$_2$ at pH ~ 8.5.$^6$ Lignin model compounds and chemical pulps were also oxidized by H$_2$O$_2$/HCO$_3^-$; the results in their totality (lignin model compounds and pulps) were convincing that the peroxymonocarbonate 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$_2$O$_2$/HOO$^-$ resulting in the net reaction shown in Equation (1).$^8-11$

$$
O

\begin{align}
\text{HCO}_3^- + \text{H}_2\text{O}_2 \rightleftharpoons \text{O}_\text{COOH} + \text{H}_2\text{O}
\end{align}

$$

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$_2$O$_2$/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 P₉ BLEaching of a hardwood CTMP at initial pH ~ 9.5, compared to ~8.6. The second objective was to add HCO₃⁻ 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 HCO₃⁻ and/or TAED into the pulp slurry from the P stage and allow for further oxidation. That would result in P→P₉ or P→PBT 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 HCO₃⁻ and/or TAED to it and use it to bleach fresh unbleached pulp. That would result in P₉→P or PBT→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 (H₂CO₃) affords HCO₃⁻ as the major species (≥60% of the total H₂CO₃ + HCO₃⁻ + CO₃²⁻ concentration) over a wide pH range; approximately pH 6.5-10.0. 13 If a P₉ stage were to be performed in the pH range of 9.5-10, peroxide activation by HCO₃⁻ 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 H₂O₂ to the perhydroxyl anion (HOÖ⁻). This nucleophile (HOÖ⁻) is reactive with lignin and is an effective brightener of wood pulps. The addition of TAED to the P₉ stage would be another approach for enhanced activation of the H₂O₂. The reaction scheme in which two moles of H₂O₂ 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 H₂O₂ in each buffer. 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 10.0-10.519,20

The P→P₉ or P→PBT 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 ≥4.0% H₂O₂ on pulp is used. Carbonation of residual NaOH in the second stage effluent to Na₂CO₃ (Eq. (2)) would be the only change required to convert the first P stage to a P₉ stage. Adding TAED to this recycled stream, before or after carbonation, would afford a PBT stage. Carbonation of NaOH to Na₂CO₃ is a simple reaction that would require only a short retention time (<1 minute) at a slightly elevated pressure. When investigating P₉→P or PBT→P BLEaching in the present research, Na₂CO₃ 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 Na₂CO₃.

\[
2 \text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \quad (2)
\]

**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 (Na₅DTPA) 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% Na₅DTPA in a Q stage performed at 70 °C and 10% consistency for 1.0 h. A buffering solution consisting of NaHSO₃ (0.25 M on a SO₂ 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% H₂O₂, 2.50-3.25% NaOH, 2.0% sodium silicate (41 Be) and 0.5% MgSO₄·7H₂O 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.

**PB and PBT 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/m²) 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 NaHSO₃ 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**

**PB and PBT 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 H₂O₂ under alkaline conditions. The four key transition metals are Mn, Fe, Cu and Co. 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 NaHCO₃ and Na₂CO₃ as the alkali source in a PB stage. It was estimated that 3.0% Na₂CO₃ on pulp should be high enough to give an initial pH >9.5. Two PB stages were performed for 2.0 h, one with 3.0% Na₂CO₃ on pulp and the other with 4.75% NaHCO₃ on pulp (equal to 3.0% Na₂CO₃ on a Na₂O basis). The bleaching temperature was 70 °C and 1.0% H₂O₂ on pulp was used. The results are summarized in Table 2. A significant brightness increase was observed, but in both cases H₂O₂ 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% Na₂CO₃ 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

| 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                                   |

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The PBT 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 H₂O₂ consumption caused brightness to increase from 62.0% to 63.8% Elrepho when Na₂CO₃ was the alkali source (Table 3). A brightness increase of 10.1 points (53.7% to 63.8% Elrepho) was obtained for a H₂O₂ consumption of only 0.59% on pulp when Na₂CO₃ was the alkali source. The preliminary assessment was that the results for both PB and PBT 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 PB and PBT 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% H₂O₂) are summarized in Table 4. TAED is generally more expensive than H₂O₂. Therefore, the initial P stage was conducted with 2.0% H₂O₂ on pulp; a treatment whose overall chemical cost would be nearly equal to that of 1.0% H₂O₂ and 1.0% TAED on pulp. When 2.0% H₂O₂ 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% H₂O₂ 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% H₂O₂ 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 2

| Alkali source ¹ | H₂O₂ dose, % on pulp | Residual H₂O₂, % on pulp | End pH | Brightness, % Elrepho |
|-----------------|----------------------|--------------------------|--------|------------------------|
|                 |                      |                          |        |                        |
| –               | –                    | –                        | –      | 53.7 ²                  |
| 4.75% NaHCO₃    | 1.0                  | 0.70                     | 8.5    | 60.8                   |
| 3.0% Na₂CO₃     | 1.0                  | 0.57                     | 8.8    | 62.0                   |

¹ 0.1% Na₅DTPA on pulp, 15% consistency, 2 h at 70 °C; ² Brightness after Q stage

Table 3

| Alkali source ¹ | H₂O₂ dose, % on pulp | Residual H₂O₂, % on pulp | End pH | Brightness, % Elrepho |
|-----------------|----------------------|--------------------------|--------|------------------------|
|                 |                      |                          |        |                        |
| –               | –                    | –                        | –      | 53.7 ²                  |
| 4.75% NaHCO₃    | 1.0                  | 0.56                     | 8.4    | 62.4                   |
| 3.0% Na₂CO₃     | 1.0                  | 0.41                     | 8.5(10.1)³ | 63.8                   |

¹ 1.0% TAED and 0.1% Na₅DTPA 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 Na₂CO₃

Table 4

| % H₂O₂ ¹ | % NaOH ¹ | Pulp consistency | Residual H₂O₂ ³ | 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 H₂O₂ were 1.03% and 0.02% on pulp; ³ Retention time of 4 h was used with 4.0% H₂O₂ on pulp; 3 h was used for 2% or 3% H₂O₂ on pulp
Various combinations of PB or PBT with a P stage were attempted. On all occasions, the P stage condition was 3.0% H₂O₂ 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→PBT bleaching of CTMP**

Two P stages were performed using 3.0% H₂O₂ 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% Na₂CO₃ 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 (PBT 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 H₂O₂ on pulp. After P→PBT the pulp had a brightness of 75.4% and its effluent had an end pH of 9.7 and contained 0.54% residual H₂O₂ on pulp. Therefore, 0.51% H₂O₂ on pulp was consumed in the PBT 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% H₂O₂ 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% H₂O₂ and 2.75% NaOH on pulp were used, 2.02% H₂O₂ on pulp was consumed and a brightness of 73.8% was obtained. The application of 4.0% H₂O₂ 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 PBT stage in a P→PBT sequence to consume some of the residual peroxide from the P stage. A mixer would be required to mix the TAED and Na₂CO₃ into the pulp slurry at medium to high consistency and a tower would be needed to retain the pulp for 1-2 h during PBT treatment. The more realistic option for the use of PBT or PB 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 (PBT or PB stage). That possibility was investigated and is reported on below.

**P→P, PB→P and PBT→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 H₂O₂” or to the mixer ahead of the first tower.

In the present research, PBT→P was actually simulated by three stages of bleaching. The sequence was P-sim→PBT→P-act with P-sim or P-simulated used to generate a second stage effluent (P stage in Fig. 1) for recycle to the PBT stage. The P-sim treatment was a regular P stage using 3.0% H₂O₂ and 2.75% 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 PBT stage. After the PBT 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 PBT→P sequence. The consistency achieved after pressing was consistently in the range of 27% for both the P-sim and PBT stages. All three bleaching stages (P-sim, PBT 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%).

In the first run attempted, two 50 g samples of Q-treated CTMP were bleached with 3.0% H₂O₂ 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% H₂O₂ on pulp. A P-stage liquor recycle rate of 59% meant that 0.60% H₂O₂ on pulp would be recycled from P-sim to the first bleaching stage, a PBT stage in this case. The chemical addition to the PBT stage was 0.66% Na₂CO₃ 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 PBT stage was conducted at 70 °C for one hour, then the pulp was once again pressed to ~27% consistency. To that PBT pre-bleached pulp, 3.0% H₂O₂ 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 PBT→P sequence. A final brightness of 76.3% Elrepho was obtained (Table 5).

The P-act bleaching effluent had a pH of 9.9 and residual peroxide concentration corresponding to 1.04% H₂O₂ on pulp. These values are nearly identical to those from P-sim (pH 9.8 and 1.02% H₂O₂ 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 PBT→P sequence

![Figure 1: Proposed scheme for two-stage bleaching of mechanical pulps with liquor recycle. P is a conventional peroxide stage with H₂O₂ and NaOH; P_B is a stage with H₂O₂ and HCO₃⁻; P_B becomes P_BT when TAED is added along with HCO₃⁻.](image-url)

**Table 5**
Pulp and effluent characterization for P→P, P_B→P and P_BT→P bleaching sequences

| Sequence      | 1st Stage H₂O₂ doses | 1st Stage end pH | 2nd Stage H₂O₂ doses | 2nd Stage end pH | Final brightness, % |
|---------------|----------------------|------------------|----------------------|------------------|---------------------|
| P_BT→P        |                      | 8.4              | 3.15/1.04            | 9.9              | 76.3                |
| P→P           | 0.60/0.32            | 8.4              | 3.06/1.03            | 10.3             | 75.0                |
| P_B (70 °C)→P | 0.61/0.31            | 8.6              | 3.15/1.05            | 10.2             | 75.9                |
| P_B (80 °C)→P | 0.61/0.19            | 8.5              | 3.09/1.05            | 10.1             | 76.6                |

1 Initial and final H₂O₂ doses (% on pulp); initial H₂O₂ dose from P-sim (see text for description of P-sim); 2 Approx. 47% of 1st stage H₂O₂ residual is carried over to the 2nd stage; therefore, initial dose >3.0% H₂O₂ on pulp; 3 0.6% TAED and 0.66% Na₂CO₃ on pulp added to 1st stage; 4 1.0% NaOH on pulp added to 1st stage; 5 1.32% Na₂CO₃ on pulp added to first stage.
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% Na₂CO₃ 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% Na₂CO₃ 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% Na₂CO₃ 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% H₂O₂ 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% H₂O₂ 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 H₂O₂/NaHCO₃ bleaching system previously reported was a sizeable brightness gain with a low consumption of H₂O₂ at pH ~ 8.5 (Attiogbe et al.). In this research, increased activation of H₂O₂/NaHCO₃ bleaching (P_{B} stage) of a CTMP was investigated by replacing NaHCO₃ with Na₂CO₃ 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 Na₂CO₃ 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.

**ACKNOWLEDGMENTS:** The authors are most grateful for the financial support from NSF Award CHE 1105726 and Andritz, Inc. The determination of metal contents of the CTMP by the Andritz’s Glens Falls Laboratory is also much appreciated.

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