

## THE PEROXYMONOCARBONATE ANIONS AS PULP BLEACHING AGENTS. PART 1. RESULTS WITH LIGNIN MODEL COMPOUNDS AND CHEMICAL PULPS

Francis K. Attiogbe,<sup>a</sup> Samar K. Bose,<sup>a</sup> Wei Wang,<sup>b</sup> Alastair McNeillie,<sup>c</sup> and Raymond C. Francis<sup>a,\*</sup>

The peroxymonocarbonate mono-anion ( $\text{HCO}_4^-$ ) is generated when the bicarbonate anion is added to a  $\text{H}_2\text{O}_2$  solution. The mono-anion is believed to have a  $\text{pK}_a$  value of ca. 10 and as such would start dissociating to the di-anion ( $\text{CO}_4^{2-}$ ) at pH ca. 8. The mono-anion should demonstrate electrophilic properties, while the di-anion should be a nucleophile. In an alkaline, non-sulfur pulping process such as soda/AQ,  $\text{Na}_2\text{CO}_3$  could be obtained from the chemical recovery system and carbonated with  $\text{CO}_2$  from a flue gas stream to produce  $\text{NaHCO}_3$ . In such a case only  $\text{H}_2\text{O}_2$  would need to be purchased to generate the peroxymonocarbonate (PMC) anions. Bicarbonate anions could also be produced from the carbonation of solutions containing  $\text{NaOH}$ ,  $\text{Mg}(\text{OH})_2$  or mined  $\text{Na}_2\text{CO}_3$ . One or both of the PMC anions was found to be effective in oxidizing two lignin model compounds as well as lowering the lignin content of kraft and soda/AQ hardwood pulps. The PMC anions were generated in-situ by  $\text{NaHCO}_3$  or  $\text{Na}_2\text{CO}_3 + \text{CO}_2$  addition to dilute  $\text{H}_2\text{O}_2$  solutions.

*Keywords:* Lignin oxidation; Nucleophilic reactions; Hydrogen peroxide; Chlorine dioxide; Carbonation

*Contact information:* a: Department of Paper & Bioprocess Engineering (PBE) and the Empire State Paper Research Institute (ESPRI), SUNY College of Environmental Science & Forestry, 1 Forestry Drive, Syracuse, NY 13210 USA; b: Solvay Chemicals, Inc., 3500 Industrial Way, Longview, WA 98632 USA; c: Solvay Chemicals, Inc., 3333 Richmond Ave., Houston TX 77098 USA.

### INTRODUCTION

The peroxymonocarbonate mono-anion ( $\text{HCO}_4^-$ ) has long been identified (by  $^{13}\text{C}$  NMR) in  $\text{H}_2\text{O}_2/\text{HCO}_3^-$  solutions of pH 7.0 to 9.5 (Flanagan et al. 1986; Richardson et al. 2000; Trindale et al. 2006). However, there is no prior report of this species being used to delignify and/or brighten, i.e. bleach wood pulps. The possibility of  $\text{HCO}_4^-$  acting as a pulp bleaching agent has been mentioned in the literature (Lee et al. 1994; Ali 1997), but no one has investigated its bleaching performance or the relative oxidative properties of the mono- or di-anion ( $\text{HCO}_4^-$ ,  $\text{CO}_4^{2-}$ ) as compared to the conventionally used oxidants. The equilibrium reaction and equilibrium constant associate with  $\text{HCO}_4^-$  generation are presented in equations [1] and [2] (Richardson et al. 2000).



$$K = 0.32\text{M}^{-1} = \frac{[\text{HCO}_4^-]}{[\text{H}_2\text{O}_2][\text{HCO}_3^-]} \quad (2)$$

When the rate of  $\text{HCO}_4^-$  oxidation of ethylphenylsulfide was compared to that of  $\text{H}_2\text{O}_2$  oxidation the former peroxide ( $\text{HCO}_4^-$  or PMC mono-anion), it was found to be about 300 times more reactive (Richardson et al. 2000). The proposed reaction mechanism is initiated with the nucleophilic sulfur atom reacting with the electrophilic oxygen atom in  $\text{HCO}_4^-$ . The electrophilic oxygen atom was identified as the one connected to the hydrogen atom (Richardson et al. 2000). Essentially, those authors concluded that the  $\text{COO}^-$  group attached to the other peroxidic oxygen was electron-withdrawing ( $^-\text{OOCO}^{\delta-}-\delta^+\text{OH}$ ). This should afford  $\text{HCO}_4^-$  some reactive properties that are observed with peracetic acid ( $\text{CH}_3\text{COOOH}$ ), where the acetyl or  $\text{CH}_3\text{CO}$  group is electron-withdrawing, and the peroxymonosulfate anion ( $\text{HOOSO}_3^-$ ), where the sulfonate or  $\text{SO}_3^-$  group is electron-withdrawing. The  $\text{HO}^{\delta+}$  end of peracids and anionic peracids is known to hydroxylate aromatic rings. For example, when peracetic acid and the peroxymonosulfate anion ( $\text{HSO}_5^-$ ) are used, hydroxylation is readily achieved (Gierer 1986; Kawamoto et al. 1995).

Both peracetic acid (Strumila and Rapson 1975) and hydrogen peroxide (Gellerstedt and Agnemo 1980) are known to participate in nucleophilic brightening reactions at pH values that are approximately two units lower than their respective  $\text{pK}_a$  values of 8.2 (Koubek et al. 1963) and 11.6 (Legrini et al. 1993). The  $\text{pK}_a$  of the PMC mono-anion is believed to be approximately 10 (Bennett et al. 2001; Vakhitova et al. 2006). Therefore, in a  $\text{H}_2\text{O}_2/\text{HCO}_3^-/\text{CO}_3^{2-}$  solution with pH ca. 9 there should be significant dissociation of  $\text{HCO}_4^-$  to the PMC di-anion ( $\text{CO}_4^{2-}$ ). If highly reactive, this di-anion should participate in nucleophilic addition to conjugated carbonyl groups such as those found in mechanical pulp bleaching and in the nucleophilic displacement of  $\text{Cl}^-$  from lignin, if the PMC treatment ( $\text{P}_B$  stage - peroxide/bicarbonate) were to follow a  $\text{ClO}_2$  or D stage in chemical pulp bleaching.

Three potential benefits that may be accrued from a  $\text{P}_B$  stage are: 1) a lower discharge of adsorbable organic halogens (AOX), 2) the flexibility of accepting soda/anthraquinone (AQ) pulps with higher unbleached kappa number than kraft pulps, and 3) mechanical pulp bleaching at a lower pH, which should decrease alkaline darkening. It may be possible to replace the  $\text{E}_o$  stage ( $\text{NaOH} + \text{O}_2$ ) in chemical pulp bleaching with a  $\text{P}_B$  stage at an initial pH ca. 9.5. Alkaline extraction would be less efficient, but PMC anions are likely to be superior oxidants when compared to oxygen used in an  $\text{E}_o$  stage. This could decrease the  $\text{ClO}_2$  requirement in the prior stage and lower AOX discharge.

The feasibility of the large scale production of Fischer Tropsch fuels at a pulp mill would be much improved if the kraft process were to be replaced by the non-sulfur soda/AQ process (Francis et al. 2008). However, the chemical balances at a soda/AQ mill may require bleaching of a pulp with a higher unbleached kappa number than for a kraft pulp. This may not be a major problem if an additional stage of bleaching is not too expensive. If sodium carbonate were to be obtained from the pulping chemical recovery system, then it could be added along with  $\text{H}_2\text{O}_2$  and  $\text{CO}_2$  into a mixer at the bottom of a



### Oxidation of LMCs

The LMCs at 5mM were oxidized by 30mM H<sub>2</sub>O<sub>2</sub> in a solution comprised of 0.005M Mg(OH)<sub>2</sub> (ultrapure grade, Fluka Biochemika). Sodium acetate (0.1M) was added for control runs, while 0.1M NaHCO<sub>3</sub> was used for PMC runs. A concentration of 0.0075M Mg(OH)<sub>2</sub> was also investigated for **II** to achieve the desired initial pH approximately 9.5. A temperature of 40°C was used for all runs, 0.2 g/l of sodium diethylenetriaminepentaacetate (Na<sub>5</sub>DTPA) was added for transition metal deactivation, and 2% ethanol (v/v) was added as a radical scavenger. An aliquot of the reaction mixture was withdrawn after specific time intervals. A fraction of the aliquot was used to determine residual H<sub>2</sub>O<sub>2</sub> by iodometric titration, while another fraction was neutralized with NaHSO<sub>3</sub>, acidified, then extracted with dichloromethane (DCM). The DCM extract was then analyzed for residual LMC by gas chromatography. A HP 5890A gas chromatograph equipped with a flame ionization detector (FID) and a DB-1 (dimethylpolysiloxane) capillary column (30m x 0.53mm; film thickness 1.0 μm) was used. Nitrogen was the carrier gas (1 mL/min), and the split ratio was 1:20. The injector temperature was 250°C, while the detector temperature was 270°C. The following temperature profile was used: initial temperature 120°C, holding time at initial temperature 5 min, a ramp from 120°C to 269°C at 5°C/min, and a hold at maximum temperature for 5 minutes.

### Chemical Pulp Bleaching Conditions

**Do Stage:** In plastic bags at 10% consistency, 70°C, 1 h with initial pH ca. 4.0 (before the addition of ClO<sub>2</sub>) and end pH 2.4 for the 15.5 kappa number kraft pulp. A kappa factor of 0.10 (% equiv. Cl<sub>2</sub>/incoming kappa number) was used. Sulfuric acid and ClO<sub>2</sub> were mixed into the fibers at room temperature, heated to ca. 70°C in a 1.1 kW microwave oven, then placed in a water bath. The chemicals were mixed into the fibers at room temperature and the slurry heated in the microwave to initiate all subsequent bleaching stages that were performed in plastic bags.

**Ep Stage:** In plastic bags at 12% consistency, 80°C, 2h with 2.0% NaOH, 1.0% H<sub>2</sub>O<sub>2</sub>, and 0.1% MgSO<sub>4</sub>·7H<sub>2</sub>O on pulp.

**P<sub>B</sub> Stage:** A wide range of conditions were used for P<sub>B</sub> and P<sub>B</sub>→P stages in both a Quantum Mark IV reactor or in plastic bags. The P<sub>B</sub> and P<sub>B</sub>→P reaction conditions will be described in the Result and Discussion section.

**P<sub>B</sub>→E<sub>P</sub> Stage:** In plastic bags at 12% consistency for 2h at 80°C with 1.0% H<sub>2</sub>O<sub>2</sub>, 2.0% NaHCO<sub>3</sub>, 0.2% Na<sub>5</sub>DTPA (P<sub>B</sub>); followed by the addition of 2% NaOH and 0.1% MgSO<sub>4</sub>·7H<sub>2</sub>O on pulp and 90 minutes of additional retention.

**P<sub>N</sub>→E<sub>P</sub> Stage:** Same as P<sub>B</sub>→E<sub>P</sub> but with the NaHCO<sub>3</sub> replaced by 0.3% NaOH on pulp; pH decreased from ca. 9.0 to ca. 7.0 during the P<sub>N</sub> treatment

**Q Stage** (chelation treatment): In plastic bags at 12% consistency for 2h at 80°C with 2.0% NaHCO<sub>3</sub> and 0.2% Na<sub>5</sub>DTPA on pulp along H<sub>2</sub>SO<sub>4</sub> acidification to pH ca. 7.

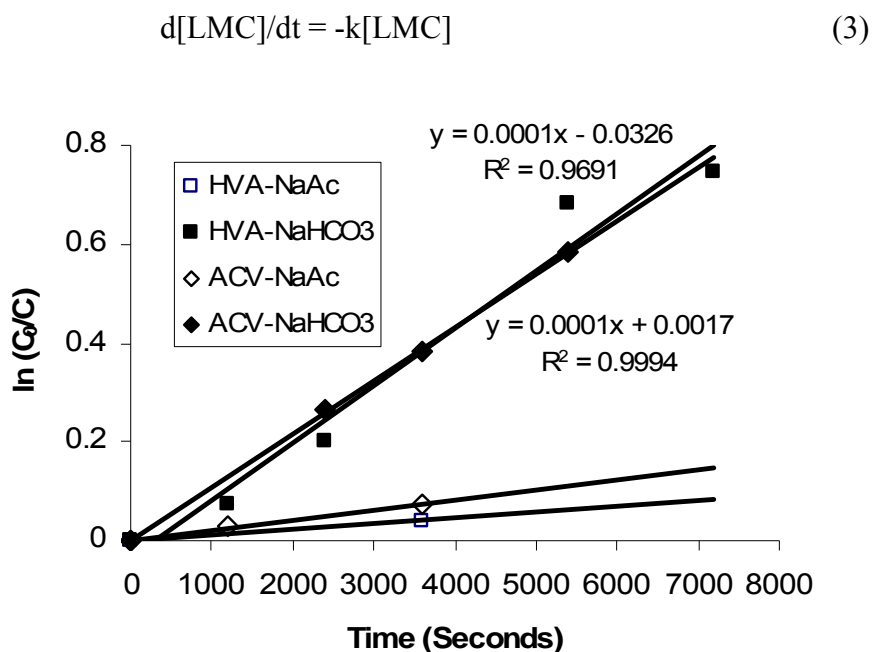
**P Stage:** In plastic bags at 12% consistency, 80°C, 2h with 3.0% NaOH, 1.7% or 2.0% H<sub>2</sub>O<sub>2</sub> and 0.5% MgSO<sub>4</sub>·7H<sub>2</sub>O on pulp.

## RESULTS AND DISCUSSION

### Reactions of Lignin Model Compounds (LMCs)

Initial research was conducted with the two LMCs to see if there were indeed higher reaction rates for PMC as compared to  $\text{H}_2\text{O}_2$ . The LMCs (**I** and **II** in Fig. 1) were oxidized by  $\text{H}_2\text{O}_2$  in dilute  $\text{Mg}(\text{OH})_2$  (ultrapure grade, Fluka Biochemika) with agitation from a magnetic spin bar. Sodium acetate (0.1M) was added for control runs, while 0.1M  $\text{NaHCO}_3$  was used for PMC runs (Materials and Methods)

Compound **I** (HVA) was unreactive towards  $\text{H}_2\text{O}_2$  in  $\text{Mg}(\text{OH})_2$  + sodium acetate (NaAc) at pH 9.2 to 9.5. First order plots for the disappearance of LMC (in accordance with equations (3) are shown in Fig. 2. Not much  $\text{H}_2\text{O}_2$  was consumed by **I**, and  $\text{H}_2\text{O}_2$  decomposition was insignificant in the case of that LMC (Fig. 3). Phenolic monomers such as **I** with an unreactive sidechain should not be significantly degraded by a stabilized  $\text{H}_2\text{O}_2$  solution at pH < 11 and <50°C (Agnemo and Gellerstedt 1979; Omori and Dence 1981). However, when the 0.1M NaAc was replaced by 0.1M  $\text{NaHCO}_3$  there was significant degradation of **I**, indicating that PMC is a much stronger oxidant than  $\text{H}_2\text{O}_2$  (Fig. 2). The aromatic ring activated by the phenolic group should be more reactive towards  $\text{HCO}_4^-$  than the two carbons in the ethylol sidechain, and ring-opening reactions are the likely cause of the significant consumption of  $\text{H}_2\text{O}_2$  (Fig. 3).



**Figure 2.** First order plots of LMC disappearance when oxidized by  $\text{H}_2\text{O}_2$  at an initial mole ratio of 6:1.

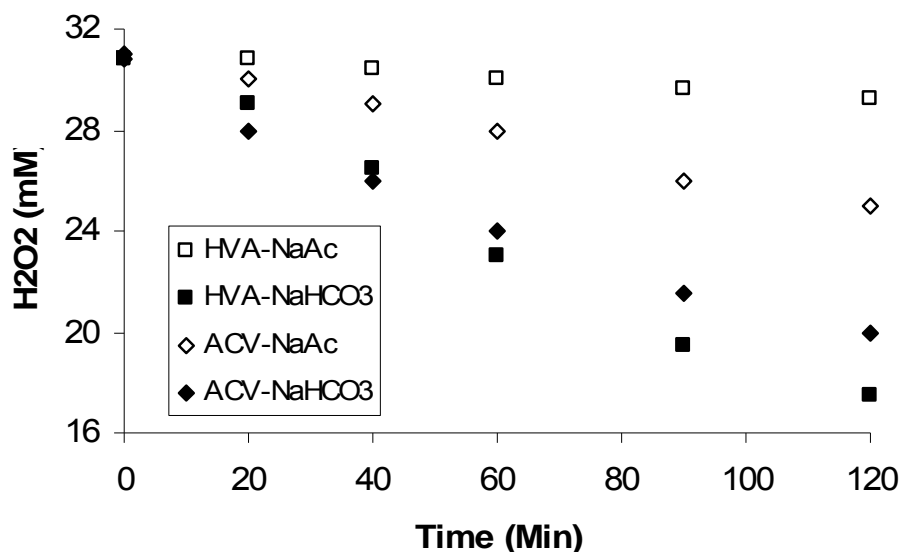
When **II** was treated in 0.005M  $\text{Mg}(\text{OH})_2$  and 0.1M NaAc, the initial pH was ca. 9.0, and degradation of the LMC was minimal after 2h. The initial pH increased to ca. 9.5 when 0.0075M  $\text{Mg}(\text{OH})_2$  was used, and there was ca. 7% degradation of **II** after 60

min (Fig. 2,  $k = 2.0 \times 10^{-5} \text{ s}^{-1}$ ). Gellerstedt and Agnemo (1980) observed approximately 33% loss of **II** after 60 min at pH 10.5 and 35°C ( $k = 1.1 \times 10^{-4} \text{ s}^{-1}$ ) with  $\text{H}_2\text{O}_2$  and NaOH. The reaction mechanism proposed by those authors involved nucleophilic addition of  $\text{OH}^-$  and  $\text{HOO}^-$  to the carbonyl group in the sidechain of **II**. The concentration of both of those anions would be lower by a factor of at least ten in the present case (pH 9.2 to 9.5), and 7% degradation appears reasonable. When NaAc was replaced by  $\text{NaHCO}_3$ , there was a much more significant loss of **II** (Fig. 2). A possible explanation is  $\text{HCO}_4^-$  formation and dissociation to the nucleophilic species  $\text{CO}_4^{2-}$ , which should participate in a mechanism similar to that proposed by Gellerstedt and Agnemo (1980). Those authors supported their proposed mechanism by identifying reaction products, a feature not included in the present investigation. Hydrogen peroxide is only approximately 1% dissociated at pH 9.5 ( $\text{pK}_a$  11.6), while  $\text{HCO}_4^-$  would be ca. 10% dissociated if the  $\text{pK}_a$  value of 10.6 (Bennett et al. 2001) is accepted. However, at a  $[\text{HCO}_3^-]$  of 0.1 M the ratio of  $[\text{HCO}_4^-]:[\text{H}_2\text{O}_2]$  equals 0.032 ( $0.32 \times 0.1$  in equation (2)).  $\text{HCO}_4^-$  would be dissociated to a degree that is ca. 10 times as high as  $\text{H}_2\text{O}_2$ , but the ratio of  $\text{CO}_4^{2-}$  to  $\text{HOO}^-$  would only be about 0.32 ( $0.032 \times 10$ ). Therefore, the involvement of  $\text{CO}_4^{2-}$  would only be a credible explanation if it is a much more reactive nucleophile than  $\text{HOO}^-$ . It should be noted that two separate research projects have recently found evidence of a highly nucleophilic species in  $\text{HCO}_3^-/\text{H}_2\text{O}_2$  solution at pH 8.0 to 8.5. One of the publications suggests that  $\text{HCO}_4^-$  is a nucleophile (Savelova et al. 2005), while the other publication correlated the rate constants for their nucleophilic reaction with pH and tentatively concluded that  $\text{CO}_4^{2-}$  was the nucleophile but that the  $\text{pK}_a$  of  $\text{HCO}_4^-$  is ca. 9.4 (Vakhitova et al. 2006). If that were to be the case, then  $\text{HCO}_4^-$  would be >50% dissociated at pH 9.5. If  $\text{HCO}_4^-$  is indeed a nucleophile, then it would be a challenge to explain its high reactivity towards **I**, where neither the aromatic ring nor the ethylol sidechain should be reactive. A  $\text{pK}_a$  of  $\leq 10.0$  for  $\text{HCO}_4^-$  would be quite favorable for  $\text{P}_B$  bleaching systems because both the electrophile,  $\text{HCO}_4^-$ , and the nucleophile,  $\text{CO}_4^{2-}$ , would be present at low but significant concentrations in the pH range of 8.0 to 10.0. It should be noted that the  $\text{pK}_a$  for  $\text{HCO}_4^-$  in aqueous solution without co-solvent or surfactant addition has not yet been determined, and the above discussion assumes that it is close to the value determined by Bennett et al. (2001), who used a solvent system consisting of 20% ethanol or Vakhitova et al. 2006, who added cetyl trimethyl ammonium bromide (CTAB) to their reaction system.

Since the reaction media in the present investigation contained 2% ethanol (v/v), the  $\text{pK}_a$  of 10.6 appears more relevant, and the  $[\text{CO}_4^{2-}]$  was likely to be lower than the  $[\text{HOO}^-]$  at pH 9.2 to 9.5 (as discussed above). The higher rate of oxidation of **II** with  $\text{NaHCO}_3$  as compared to NaAc may be due to ring oxidation by  $\text{HCO}_4^-$ , despite the electron-withdrawing acetyl sidechain on **II**.

If a  $\text{pK}_a$  of 10.6 is assumed for  $\text{HCO}_4^-$ , then the concentration of  $\text{HCO}_4^-$  will dominate over that of  $\text{CO}_4^{2-}$  in bleaching systems at pH ca. 9. Conjugated carbonyl compounds are generated when both phenolic and non-phenolic  $\text{C}_9$  units are treated with electrophilic bleaching agents (Gierer 1986; Dence 1996). Therefore,  $\text{HCO}_4^-$  is likely to be generating conjugated carbonyls during bleaching at pH ca. 9. However, it is possible that the very low concentration of  $\text{CO}_4^{2-}$  could degrade those carbonyls and improve pulp brightness. This is based on the apparently high reactivity of  $\text{ROO}^-$  towards such

carbonyls. Also, the rates of such reactions do not appear to strongly be dependent on the  $[\text{ROO}^-]$ . Gellerstedt and Agnemo (1980) oxidized 3,4-dimethoxy-cinnamyl aldehyde (methylated coniferyl aldehyde) with 0.4 M  $\text{H}_2\text{O}_2$  at  $0^\circ\text{C}$  and pH 9.0, 10.5, or 11.0. A high  $\text{H}_2\text{O}_2$  to LMC mole ratio was used. The authors confirmed that  $\text{HOO}^-$  was the reactive species and estimated its concentration at 0.28 mM, 8.8 mM, and 26.0 mM at pH 9.0, 10.5, and 11.0, respectively. The observed rate constants for LMC oxidation in accordance with Equation (3) were  $0.0476 \text{ min}^{-1}$ ,  $0.0673 \text{ min}^{-1}$ , and  $0.189 \text{ min}^{-1}$  for the three respective pHs. Therefore, increasing the  $[\text{HOO}^-]$  by a factor of 93 (0.28 mM to 26 mM) only increased the oxidation rate by a factor of 4 ( $0.0476 \text{ min}^{-1}$  to  $0.189 \text{ min}^{-1}$ ). This apparently high reactivity of  $\text{HOO}^-$  may explain why mechanical pulps can be brightened with  $\text{H}_2\text{O}_2$  and  $\text{Mg}(\text{OH})_2$  at  $\text{pH} < 9.0$  (Ni 2005). The protonated species corresponding to  $\text{HOO}^-$  is  $\text{H}_2\text{O}_2$ , and unlike the peracids and anionic peracids, it does not react directly with lignin to generate conjugated carbonyls.



**Figure 3.** Hydrogen peroxide disappearance due to oxidation of **I** and **II** plus decomposition

### Chemical Pulp Bleaching

The bleaching sequence used to whiten chemical pulps is most typically  $\text{OD}_0\text{E}_{\text{OP}}\text{D}_1\text{E}_2\text{D}_2$  or  $\text{D}_0\text{E}_{\text{OP}}\text{D}_1\text{E}_2\text{D}_2$  (where O is a pressurized alkaline  $\text{O}_2$  stage;  $\text{D}_0$  is chlorine dioxide delignification with an end pH of 2 to 3;  $\text{E}_{\text{OP}}$  is alkaline extraction with sodium hydroxide and  $\text{O}_2$  plus  $\text{H}_2\text{O}_2$  for incremental delignification and brightening;  $\text{E}_2$  is extraction with NaOH only; and  $\text{D}_1$  and  $\text{D}_2$  are chlorine dioxide brightening stages with an end pH of 3.7 to 5.5). Modifications to these sequences sometimes involve the use of ozone at pH 2 to 4 (Z stage), peracetic acid at pH 4 to 6 (Paa stage), and  $\text{H}_2\text{O}_2$  at pH  $> 10.0$  (P stage).

In chemical pulp bleaching it is unusual to use more than 1.0%  $\text{H}_2\text{O}_2$  on pulp in one of the bleaching stages (4 to 6 stages in total), and the treatment is normally performed at 12% consistency, i.e. 12g fiber (on oven-dried basis) plus 88g or ca. 88ml of solution. At 12% consistency, 100g of pulp would be in about 0.733 L of solution. If

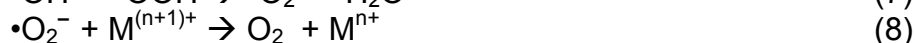
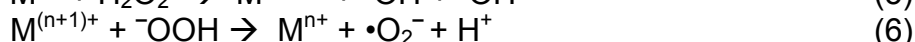
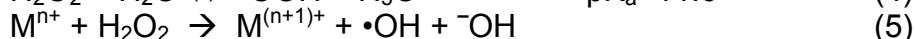
1% H<sub>2</sub>O<sub>2</sub> and 3% NaHCO<sub>3</sub> on pulp were added on a weight basis, then the initial H<sub>2</sub>O<sub>2</sub> and NaHCO<sub>3</sub> concentrations would be 0.040M and 0.049M, respectively. If these values are inserted into equation (2) the initial [HCO<sub>4</sub><sup>-</sup>] would be 6.3 x 10<sup>-4</sup>M, i.e. 0.32 x 0.040 x 0.049. This low initial [HCO<sub>4</sub><sup>-</sup>] may be the reason why in-situ H<sub>2</sub>O<sub>2</sub>/HCO<sub>3</sub><sup>-</sup> bleaching of wood pulp (delignification and/or brightening) has gone undetected/un-investigated for so long.

The chlorine dioxide dose in the D<sub>0</sub> stage is normally calculated by the formula: wt% chlorine dioxide on pulp = 0.076 x kappa number of O<sub>2</sub> or unbleached pulp. The minimization of ClO<sub>2</sub> use is critical to chemical pulp mills without an O stage because the discharge of adsorbable organic halogens (AOX) increases with ClO<sub>2</sub> use, particularly in the D<sub>0</sub> stage. In our first experiment we decreased the dose factor in the D<sub>0</sub> stage from 0.076 to 0.038 for the 15.5 kappa number of unbleached hardwood kraft pulp. This ClO<sub>2</sub> application corresponded to a kappa factor of 0.10 (% equiv. Cl<sub>2</sub> on pulp = 0.10 x 15.5). Sulfuric acid was added to the D<sub>0</sub> stage to achieve an end pH of 2.4. Seven hundred and fifty grams of pulp was bleached in five plastic bags, and all the pulp was mixed together, washed, pressed, fluffed, and stored in a plastic bag. Smaller samples of the D<sub>0</sub> pulp were then bleached with 1.0% H<sub>2</sub>O<sub>2</sub>, 2.0% NaHCO<sub>3</sub>, 0.2% Na<sub>5</sub>DTPA at 12% consistency for 2h at 80°C (P<sub>B</sub> stage). The objective of this trial was to see if a P<sub>B</sub> stage could hydroxylate the lignin ahead of an E<sub>P</sub> stage (NaOH + H<sub>2</sub>O<sub>2</sub>). If the P<sub>B</sub> stage were to hydroxylate some C<sub>9</sub> units, then more lignin should be removed in the subsequent E<sub>P</sub> stage, because H<sub>2</sub>O<sub>2</sub> is much more reactive to C<sub>9</sub> units containing a phenolic hydroxyl group as compared to non-phenolic units (Francis and Reeve 1987).

The results are summarized in Table 2. The brightness increase at pH>7 was surprisingly high, with an increase of >20 points being achieved at a very low H<sub>2</sub>O<sub>2</sub> consumption of only 0.12% on pulp. A partial explanation is that the acidic condition of the D<sub>0</sub> stage extracted transition metals from the pulp, thus decreasing the rate of wasteful hydrogen peroxide decomposition in the subsequent P<sub>B</sub> stage. The P<sub>B</sub> treatment with HCO<sub>3</sub><sup>-</sup> but no H<sub>2</sub>SO<sub>4</sub> was repeated in duplicate at a later date (same D<sub>0</sub> pulp). After 2h, bleaching of one sample was terminated, while 2% NaOH and 0.1% MgSO<sub>4</sub>·7H<sub>2</sub>O on pulp were added to the other and the reaction continued for 90 minutes to give a P<sub>B</sub>→E<sub>P</sub> stage (Materials and Methods). The sample analyzed after the P<sub>B</sub> stage consumed 0.14% H<sub>2</sub>O<sub>2</sub> on pulp and had an effluent end pH of 8.6. The P<sub>B</sub> brightness was 67.9% ISO. Overall, the D<sub>0</sub>P<sub>B</sub> results reproduced those in Table 2 very well. There was full consumption of H<sub>2</sub>O<sub>2</sub> after the P<sub>B</sub>→E<sub>P</sub> stage and a pulp with kappa number 4.3 and 83.4% brightness was obtained. When the pulp was bleached by P<sub>N</sub>→E<sub>P</sub> (Materials and Methods), a kappa number of 4.8 and a brightness of 81.1% were obtained (full consumption of H<sub>2</sub>O<sub>2</sub>). Peroxide consumption after P<sub>N</sub> treatment was only 0.10% on pulp. The D<sub>0</sub>P<sub>B</sub> pretreatment activated the E<sub>P</sub> stage to a greater degree than D<sub>0</sub> P<sub>N</sub>.

It was of interest to see whether a P<sub>B</sub> stage would activate an E<sub>P</sub>, O or P stage if a D<sub>0</sub> treatment was not involved. There are many similarities in the reaction mechanisms associated with lignin oxidation by alkaline O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>. The reduction of O<sub>2</sub> to water by one-electron transfer reactions is well-established (Dence 1996; McDonough 1996). Under alkaline O<sub>2</sub> bleaching conditions ·O<sub>2</sub><sup>-</sup> and ·OH, H<sub>2</sub>O<sub>2</sub> and other organic peroxides are generated. In a slurry of de-mineralized pulp being treated in a P stage, oxygen, ·O<sub>2</sub><sup>-</sup> and ·OH will be generated by equations (4) through (8).





Also, it was recently observed that the amount of lignin removed by an O stage was highly correlated with that removed by a P stage for eleven kraft, kraft/AQ, and soda/AQ pulps from hardwoods (Francis et al. 2008). When kappa numbers after the O stage were plotted against kappa numbers after QP for seven kraft pulps plus the kraft/AQ sample, a linear correlation was obtained with  $R^2 = 0.98$ .

**Table 2.** Bleaching of D<sub>0</sub> Pulp with H<sub>2</sub>O<sub>2</sub> and NaHCO<sub>3</sub> (P<sub>B</sub> stage) at 80°C in Plastic Bags<sup>1</sup>

Stages	H <sub>2</sub> SO <sub>4</sub> mmoles/100g pulp	Initial pH	Final pH	H <sub>2</sub> O <sub>2</sub> consumed <sup>2</sup>	Brightness, %ISO
D <sub>0</sub>	-	-	-	-	46.8
D <sub>0</sub> P <sub>B</sub>	0	ca. 8.5	8.6	0.12	67.2
D <sub>0</sub> P <sub>B</sub>	3	ca. 7.5	7.3	0.12	67.0
D <sub>0</sub> P <sub>B</sub>	7.5	ca. 6.5	6.3	0.10	63.7
D <sub>0</sub> P <sub>B</sub>	10	ca. 6.0	5.4	0.10	62.1

<sup>1</sup>1.0% H<sub>2</sub>O<sub>2</sub>, 0.2% Na<sub>5</sub>DTPA and 2.0% NaHCO<sub>3</sub> on pulp, HCO<sub>3</sub><sup>-</sup> doses = 23.8 mmoles/100g pulp

<sup>2</sup>% H<sub>2</sub>O<sub>2</sub> on pulp

A likely approach for producing HCO<sub>4</sub><sup>-</sup> in a pulp mill would be to add NaOH, Mg(OH)<sub>2</sub> or Na<sub>2</sub>CO<sub>3</sub> and inject CO<sub>2</sub> in a mixer at the bottom of an upflow pre-retention tube. These pre-retention tubes are commonly attached to D and Eo stage towers, and the hydrostatic pressure at the bottom is normally in the range of 4.0 x 10<sup>5</sup> Pa. After some preliminary experiments on carbonation of pulp slurries to neutralize Na<sub>2</sub>CO<sub>3</sub> to NaHCO<sub>3</sub>, we treated the 24.3 kappa number hardwood soda/AQ pulp with 0.5% H<sub>2</sub>O<sub>2</sub>, 3.0% Na<sub>2</sub>CO<sub>3</sub>, and 0.2% Na<sub>5</sub>DTPA at 90°C and 12% consistency. Even though we were working with dilute H<sub>2</sub>O<sub>2</sub> (ca. 60 g/L), we elected not to use CO<sub>2</sub> gas pressure to force the peroxide into the Quantum reactor through an injector. There would be a risk of heat generation from the reaction of H<sub>2</sub>O<sub>2</sub> and 30 psig CO<sub>2</sub> gas (2.1 x 10<sup>5</sup> Pa) to form percarbonic acid (H<sub>2</sub>CO<sub>4</sub>) in the thick-walled plastic chamber ahead of the injector. Depending on the magnitude of the enthalpy of reaction, the peroxide mixture could be heated to a high temperature and spontaneously decomposed. We added the carbonate and peroxide to the pulp and mixed them at a pH of ca. 10. The system was then pressurized with CO<sub>2</sub> (30 psig initial pressure) for 3 minutes. After that time the residual CO<sub>2</sub> pressure was used to discharge a small amount of the bleaching solution from the pulp slurry. It had a pH of ca. 7.5, and the residual H<sub>2</sub>O<sub>2</sub> was calculated as 0.37% on pulp. Most of the 0.13% H<sub>2</sub>O<sub>2</sub> consumption occurred at pH ca. 10 before CO<sub>2</sub> addition.

The reaction was allowed to continue for 57 additional minutes with further H<sub>2</sub>O<sub>2</sub> consumption of 0.16% on pulp (end pH 7.0).

The NaHCO<sub>3</sub> was washed out of the P<sub>B</sub> treated pulp, and it was delignified further with 1.7% H<sub>2</sub>O<sub>2</sub>, 3.0% NaOH, and 0.5% MgSO<sub>4</sub>·7H<sub>2</sub>O (P<sub>B</sub>P). The results are compared (in Table 3) to QP treatment of the unbleached pulp with 2.0% H<sub>2</sub>O<sub>2</sub> on pulp. It can be seen that with a total H<sub>2</sub>O<sub>2</sub> consumption of 2.0% on pulp the P<sub>B</sub>P sample was lower in kappa number by 2.7 units as compared to the QP sample. It also had a brightness advantage of 7.3 ISO units.

The lower kappa number for P<sub>B</sub>P treatment as compared to QP (Table 3) would suggest that HCO<sub>4</sub><sup>-</sup> is a fairly effective electrophile that probably hydroxylated some of the aromatic rings in the lignin of the unbleached pulp. The improvement in kappa number after the P stage was approximately equal to the improvement seen when HSO<sub>5</sub><sup>-</sup> was used ahead of an O stage (Springer and McSweeney 1993). The results in Table 3 appear to confirm our belief that the pK<sub>a</sub> of HCO<sub>4</sub><sup>-</sup> should be in the same range (approximately) as that of HSO<sub>5</sub><sup>-</sup>. The pK<sub>a</sub> for the dissociation of HSO<sub>5</sub><sup>-</sup> to SO<sub>5</sub><sup>2-</sup> is reported to be 9.4 (Ball and Edwards 1956). If that were to be the case, then the dissociation of HCO<sub>4</sub><sup>-</sup> to CO<sub>4</sub><sup>2-</sup> should be significant at pH 9, and a P<sub>B</sub> stage in that pH range should be able to brighten mechanical pulps. This topic was investigated and will be discussed in a Part 2 of this series of papers.

**Table 3.** Comparison of P<sub>B</sub>P and QP Bleaching of a Hardwood Soda/AQ Pulp

Stages	Final pH	H <sub>2</sub> O <sub>2</sub> Consumed <sup>1</sup>	Kappa no.	Brightness, %ISO
Unb			24.3	35.2
P <sub>B</sub>	7.0	0.29	-	-
P <sub>B</sub> P	12.0 <sup>2</sup>	1.70 <sup>2</sup>	12.3	56.8
QP	12.1 <sup>2</sup>	2.00 <sup>2</sup>	15.0	49.5

<sup>1</sup> % on pulp

<sup>2</sup> for the P stage at 80°C, 12% consistency for 2h with 3.0% NaOH and 0.5% MgSO<sub>4</sub>·7H<sub>2</sub>O on pulp

Another interesting aspect of the results in Table 2 was the apparent increase in D<sub>0</sub>P<sub>B</sub> brightness with an increase in the end pH of the P<sub>B</sub> stage. However, it is difficult to ascertain if this increase is due to nucleophilic brightening, because pulps are very prone to neutral or alkaline extraction of lignin after being afforded a D<sub>0</sub> treatment. It is possible that the higher brightness for P<sub>B</sub> treatment with end pH 8.6 vs. 6.3 (67.2% ISO vs. 63.7% ISO in Table 2) was due to greater extraction of lignin from the D<sub>0</sub> stage pulp. P<sub>B</sub> bleaching of the O<sub>2</sub> delignified soda/AQ pulp was investigated at pH ca. 7.6 and ca. 8.6. The pulp was also treated by a P<sub>N</sub>-stage (NaHCO<sub>3</sub> replaced by 0.3% NaOH) with initial and end pH of 9.9 and 9.2, respectively. The O<sub>2</sub> pulp had just left the oxygen stage at 90°C and end pH 11.7 followed by a Q stage at 80°C and pH ca. 7. Therefore the variation in amount of extracted lignin should be very minimal for pH 7.6 and 8.6.

The results are presented in Table 4, and it can be seen that a higher brightness was observed for P<sub>B</sub> at pH 8.6 as compared to 7.6. Also, the brightening achieved by a 0.14% dose of H<sub>2</sub>O<sub>2</sub> on pulp utilization (oxidation + decomposition) in P<sub>B</sub> at pH 8.6 compared quite favorably to that obtained by 0.41% H<sub>2</sub>O<sub>2</sub> on pulp utilization in P<sub>N</sub>. Also, the reduction in kappa number was equal in both cases.

The results in Table 4 also support the contention that it is the PMC anions (possibly aided by  $\text{HOO}^-$ ) that are principally responsible for the delignification and brightening that was observed in the  $\text{P}_B$  stages. It may be argued that the role of the  $\text{HCO}_3^-$  was to initiate a slow decomposition of  $\text{H}_2\text{O}_2$  to  $\cdot\text{OH}$ ,  $\text{CO}_3^{\cdot-}$  (carbonate radical anion), and  $\cdot\text{O}_2^-$ . The first two radicals are efficient at abstracting electrons, and both are known to cause ring-opening reactions with lignin (Gierer, 1986; Dence 1996; Mih and Thompson 1983). On the other hand the third radical, the superoxide anion, has nucleophilic properties and is quite reactive with conjugated carbonyls (Bielski et al. 1985). However, it would be difficult to explain the  $\text{P}_B$  stage brightness increase in going from pH 7.6 to pH 8.6 in terms of higher reactivity of any of the three radicals. There is no evidence for any significant change in reactivity for any of the three radical in that pH range. Also, there would be no significant change in the ionization state for any of the radicals. The  $\text{pK}_a$  of  $\cdot\text{OH}$  to  $\cdot\text{O}^-$  is 11.9 (Barnes and Sugden 1986); for  $\text{HCO}_3^{\cdot-}$  it is  $<0$  (Augusto et al. 2002), and it is 4.8 for  $\text{HOO}\cdot$  (Bielski et al. 1985).

**Table 4.** Bleaching of  $\text{O}_2$  Delignified Kraft Pulp with  $\text{H}_2\text{O}_2$  and  $\text{NaHCO}_3$  ( $\text{P}_B$  stage) or  $\text{NaOH}$  ( $\text{P}_N$  stage) at  $80^\circ\text{C}$  in Plastic Bags<sup>1</sup>

Stages	Initial pH	Final pH	$\text{H}_2\text{O}_2$ consumed <sup>2</sup>	Kappa Number	Brightness, %Elrepho
O	-	-	-	10.6	51.0
$\text{OQP}_B$	ca. 8.6	8.6	0.14	9.1	62.4
$\text{OQP}_B$	ca. 7.6 <sup>3</sup>	7.6	0.13	9.3	59.8
$\text{OQP}_N$	ca. 9.9	9.2	0.41	9.1	64.3

<sup>1</sup>1.0%  $\text{H}_2\text{O}_2$ , 0.2%  $\text{Na}_5\text{DTPA}$  and 2.0%  $\text{NaHCO}_3$  on pulp ( $\text{P}_B$ ) or 0.3%  $\text{NaOH}$  ( $\text{P}_N$ )

<sup>2</sup>%  $\text{H}_2\text{O}_2$  on pulp

<sup>3</sup>  $\text{H}_2\text{SO}_4$  added

## CONCLUSIONS

The conclusions from this preliminary investigation are:

1. The inclusion of  $\text{HCO}_3^-$  significantly increases the rate of LMC oxidation by  $\text{H}_2\text{O}_2$  within the pH range of 8.8 to 9.5.
2. An  $\text{H}_2\text{O}_2/\text{HCO}_3^-$  pretreatment ( $\text{P}_B$  stage) activates subsequent delignification and brightening of both hardwood kraft and soda/AQ pulps prepared with a conventional alkaline peroxide stage.
3. A  $\text{P}_B$  stage at pH ca. 8.6 increased the brightness of an oxygen delignified hardwood soda/AQ pulp from 51.0% to 62.4% even though only 0.14%  $\text{H}_2\text{O}_2$  on pulp was consumed.

## ACKNOWLEDGMENTS

The financial support from Solvay Chemicals, Inc. and the Empire State Paper Research Associates (ESPRA) is deeply appreciated.

## REFERENCES CITED

- Agnemo, R. and Gellerstedt, G. (1979). "The reactions of lignin with alkaline hydrogen peroxide. Part II. Factors influencing the decomposition of phenolic structures," *Acta Chem. Scand.* B33, 337-342.
- Ali, O. F. (1997). "Ambient temperature pulp bleaching with peroxyacid salts," *US Patent* 5,656,130, granted August 12, 1997.
- Augusto, O., Bonini, M. G., Amanso, A. M., Linares, E., Santos, C. C. X., and De Menezes, S. L. (2002). "Nitrogen dioxide and carbonate radical anion: Two emerging radicals in biology," *Free Radical Biology & Medicine* 32(9), 841-859.
- Ball, D. L., and Edwards, J. O. (1956). "The kinetics and mechanism of the decomposition of Caro's acid," *J. Am. Chem. Soc.* 78, 1125-1129.
- Barnes, A. R. and Sugden, J. K. (1986). "The hydroxyl radical in aqueous media," *Pharm. Acta Helv.* 61, 218-227.
- Bielski, B. H. J., Cabelli, D. E., Arudi, R. L., and Ross, A. B. (1985). "Reactivity of HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> radicals in aqueous solution," *J. Phys. Chem. Ref. Data* 14, 1041-1100.
- Bennett, D. A., Yao, H., and Richardson, D. E. (2001). "Mechanism of sulfide oxidation by peroxymonocarbonate," *Inorg. Chem.* 40, 2996-3001.
- Dence, C. W. (1996). "Chemistry of chemical pulp bleaching," In: *Pulp Bleaching – Principles and Practice*, Dence and Reeve (eds.), TAPPI PRESS, Atlanta, p. 125-160.
- Flanagan, J., Jones, D. P., Griffith, W. P., Skapski, A. C., and West, A. P. (1986). "On the existence of peroxy-carbonates in aqueous solution," *J. Chem. Soc. Commun.* 1, 20-21.
- Francis, R. C., Bolton, T. S., Abdoulmoumine, N., Lavrykova, N., and Bose, S. K. (2008). "Positive and negative aspects of soda/anthraquinone pulping of hardwoods," *Bioresource Technology* 99, 8453-8457.
- Francis, R. C., and Reeve, D. W. (1987). "Hydrogen peroxide delignification – The effects of methylation and demethylation," *J. Pulp Pap. Sci.* 13, 171-174.
- Gierer, J. (1986). "Chemistry of delignification. Part 2: Reactions of lignins during bleaching," *Wood Sci. Technol.* 20, 1-33.
- Gellerstedt, G., and Agnemo, R. (1980). "The reactions of lignin with alkaline hydrogen peroxide. Part III. The oxidation of conjugated carbonyl structures," *Acta. Chem. Scand.* B34 275-280.
- Kawamoto, H., Chang, H.-M., and Jameel, H. (1995). "Reaction of peroxy acids with lignin and lignin model compounds," *Proceed. 8<sup>th</sup> International Symposium of Wood & Pulping Chemistry*, Helsinki, June 6<sup>th</sup> – 9<sup>th</sup>.
- Koubek, E., Haggett, M. L., Battaglia, G. J., Ibne-Rasa, K. M., Pyun, H. Y., and Edwards, J. O. (1963). "Kinetic and mechanism of the spontaneous decomposition of some peroxyacids, hydrogen peroxide and t-butyl peroxide," *J. Am. Chem. Soc.* 85, 2263-2268.
- Lee, C.-L., Murray, R. W., Hunt, K., Wearing, J. T., et al. (1994). "Bleaching of lignocellulosic material with in-situ generated dioxirane," *US Patent* 5,366,593, granted November 22, 1994.
- Legrini, O., Oliveros, E., and Bruan, A. M. (1993). "Photochemical processes for water treatment," *Chem. Rev.* 93, 671-698.

- McDonough, T. J. (1996). "Oxygen delignification," In: *Pulp Bleaching – Principles and Practice*, Dence and Reeve (eds.), TAPPI PRESS, Atlanta, p. 213-239.
- Mih, J.-F., and Thompson, N. S. (1983). "The effect of liquor composition on the rate of reaction of lignin model compound acetoguaiacone in oxygen and alkali," *J. Wood Chem. Technol.* 3, 145-159.
- Ni, Y. (2005). "A review of recent technological advances in the brightening of high-yield pulps," *Can. J. Chem. Eng.* 83, 610-617.
- Omori, S., and Dence, C. W. (1981). "The reaction of alkaline hydrogen peroxide with lignin model dimers," *Wood Sci. Technol.* 15, 113-123.
- Presley, J. R., and Hill, R. T. (1996). "Peroxide bleaching of (chemi)mechanical pulps," In: *Pulp Bleaching – Principles and Practice*, Dence and Reeve (eds.), TAPPI PRESS, Atlanta, p. 459-489.
- Richardson, D. E., Yao, H., Frank, K. M., and Bennett, D. A. (2000). "Equilibria, kinetics, and mechanism in the bicarbonate activation of hydrogen peroxide: Oxidation of sulfides by peroxymonocarbonate," *J. Am. Chem. Soc.* 122, 1729-1739.
- Savelova, V. A., Popov, A. F., Vakhitova, L. N., Solomoichenko, T. N., et al. (2005). "Nucleophilic reactivity of hydroxide and hydroperoxide ions in aqueous-alcoholic media and of  $\text{HCO}_4^-$  ion in water," *Russian J. Org. Chem.* 41, 1773-1781 (translated from *Z. Org. Khimii* 41, 1810-1818, 2005).
- Springer, E. L., and McSweeney, J. D. (1993). "Treatment of softwood kraft pulps with peroxymonosulfate before oxygen delignification," *Tappi J.* 76 (8), 194-199.
- Strumila, G., and Rapson, H. (1975). "Reaction products of neutral paracetic acid oxidation of model lignin phenols," *Pulp Paper Can.* 76(9), 74-78.
- Trindale, D. F., Gerchiaro, G., and Augusto, O. (2006). "A role for peroxymonocarbonate in the stimulation of biothiols peroxidation by the bicarbonate/carbon dioxide pair," *Chem. Res. Toxicol.* 19, 1475-1482.
- Vakhitova, L. N., Zhil'tsova, S. V., Skrypka, A. V., Razumova, N. G., et al. (2006). "Micellar catalytic effects in the oxidation of methylphenyl sulfide with hydrogen peroxide and the hydrogen peroxocarbonate anion," *Theor. Experimental Chem.* 42 (5), 287-294.

Article submitted: April 6, 2010; Peer review completed: May 31, 2010; Revised version received and accepted: August 17, 2010; Published: August 18, 2010.