

THE PEROXYMONOCARBONATE ANIONS AS PULP BLEACHING AGENTS. Part 2. MECHANICAL PULP BRIGHTENING AND EFFECTS OF METAL IONS

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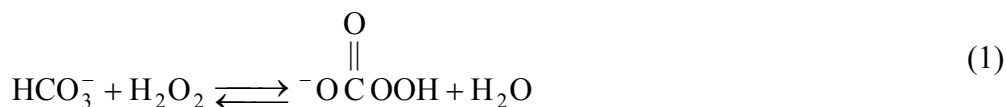
The peroxymonocarbonate mono-anion (HCO_4^-) is generated in solutions containing bicarbonate anions (HCO_3^-) and hydrogen peroxide (H_2O_2). The mono-anion is believed to have a pK_a value of ca. 10 and as such would start dissociating to the di-anion (CO_4^{2-}) at pH ca. 8. The mono-anion should demonstrate electrophilic properties, while the di-anion should be a nucleophile. Results that appear to be due to electrophilic reactions of HCO_4^- were presented in Part 1 of this series for lignin model compounds (LMCs) and chemical pulps. Some evidence was also observed for nucleophilic reactions with LMCs in the pH range of 8.8 to 9.5. Results are now being presented for mechanical pulp brightening, where nucleophilic reactions were observed. Hydrogen peroxide decomposition in the HCO_3^- solutions was significant on some occasions, and Fe catalyzed decomposition was the most significant contributor in both pulp slurries and pulp-free solutions.

Keywords: Lignin oxidation; Mechanical pulps; Nucleophilic reactions; Hydrogen peroxide; Peroxyacid dissociation

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INTRODUCTION

The peroxymonocarbonate anion (HCO_4^-) has long been identified (by ^{13}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 has been no prior report of peroxymonocarbonate (PMC) anions being used to delignify and/or brighten, i.e. bleach wood pulps. The possibility of HCO_4^- acting as a pulp bleaching agent has been mentioned in the literature (Lee et al. 1994; Ali 1997), but no one has correlated a variation in bleaching outcome(s) with a likely variation in concentration of HCO_4^- , CO_4^{2-} or $\text{HCO}_4^- + \text{CO}_4^{2-}$. The equilibrium reaction and constant associate with HCO_4^- generation are presented in equations (1) and (2) (Richardson et al. 2000).



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

As discussed in Part 1 (Attigbe et al. 2010), this research was initiated with the belief that HCO_4^- with a pK_a of ca. 10 (Bennett et al. 2001; Vakhitova et al. 2006) should act as a weak peracid. Also, in a $\text{HCO}_3^-/\text{CO}_3^{2-}$ solution with pH ca. 9 there should be significant dissociation of PMC mono-anion to the dianion (CO_4^{2-}). If highly reactive, this dianion should participate in nucleophilic addition and chromophore destruction in mechanical pulp bleaching. The nucleophile HOO^- , which is generated by the dissociation of H_2O_2 ($\text{pK}_a = 11.6$), is believed to be the principal brightening agent in peroxide bleaching of mechanical pulps (Presley and Hill 1996). Data was also provided in Part 1 to show that low concentrations of HOO^- were quite reactive towards conjugated carbonyls. If $\text{H}_2\text{O}_2/\text{HCO}_3^-$ is effective at destroying mechanical pulp chromophores at pH ca. 9, then that should alleviate brightness reversion during bleaching due to a significantly lower extent of alkaline darkening (Ni 2005).

We are now reporting on PMC bleaching (P_B stage - peroxide/bicarbonate) of three chemi-thermomechanical pulps (CTMPs) from both softwood and hardwood. During the investigation it became obvious that metal-catalyzed peroxide decomposition could adversely affect P_B bleaching. Therefore, the topic was investigated, and some preliminary results on transition metal catalysis are also included.

MATERIALS AND METHODS

Chemicals

The sodium bicarbonate used in this research was from EMD Chemicals and contained <10 ppm Fe; sulfuric acid was Baker Reagent grade containing 3 ppb of Fe; while the sodium hydroxide (1 M solution) was from Fisher Scientific and contained <1 ppm Fe.

The peroxymonosulfate anion was derived from Curox ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) donated by Solvay Chemicals, Inc., while peracetic acid (Paa) was from Sigma-Aldrich Chemicals and contained 32.9 wt% Pa and 4.4 wt% H_2O_2 by iodometric and ceric sulfate titrations.

Chemi-Thermo Mechanical Pulps

Two commercial CTMPs (softwoods) were obtained and mixed in a 2:1 ratio to give a sample (CTMP1) with an unbleached brightness of 63.4% Elrepho (after treatment with Na_5DTPA and NaHSO_3 ; Na_5DTPA = sodium diethylenetriaminepentaacetate). An in-house sample was also prepared from Norway spruce (*Picea abies*) using a KRK refiner. Sodium sulfite (2.0% on chips) was injected into the eye of the refiner, and the resulting pulp (an in-refiner CTMP) had an unbleached brightness of 65.3% Elrepho. The pulp was treated with a chelation or Q-stage using Na_5DTPA and NaHSO_3 then bleached with 2.0% H_2O_2 , 3% NaOH , 4% sodium silicate (41° Baume), 0.5% $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 12% consistency, for 2 h at 70°C. This sample (CTMP2) had a brightness

of 73.4% Elrepho. A commercial pulp from 100% aspen (*Populus tremuloides*) with an unbleached brightness of 71.2% Elrepho (after Q stage with Na₅DTPA and NaHSO₃) was CTMP3.

Chelation Treatments

Q₁ stage: This stage was performed in plastic bags in a water bath at 10% consistency for 1h at 80°C with 0.2% Na₅DTPA and NaHSO₃ (2.5% SO₂) on pulp. The end pH of Q₁ stage effluent fell within pH 5 to 6 on all occasions and was typically around 5.5.

Q₁Q₂ treatment: The Q₁ pulp from above was treated with 0.2% Na₅DTPMPA (phosphonic acid counterpart to Na₅DTPA) and 4.0% NaHCO₃ at 10% consistency for 1h at 80°C (end pH 8.6).

Bleaching Stages

Conditions used for HSO₅⁻, Paa, P_B, and P stage bleaching are described in the Results and Discussion section. A consistency of 12% was the only parameter common to all of the stages.

Peroxide Decomposition Catalyzed by Ferric Sulfate or Ferric-Citrate Complex

Hydrogen peroxide solutions (0.05M) were allowed to decompose at 40°C for up to 2h. The solutions consisted of 0.1 M NaHCO₃ and 0.025ppm to 0.10ppm Fe from ferric sulfate or a ferric dicarboxylate catalyst. The ferric dicarboxylate was prepared by dissolving Fe₂(SO₄)₃·H₂O in citric acid. The [Fe³⁺] was 0.018M (1,000 ppm), and citric acid was added at a 5:1 mole ratio to Fe³⁺. The final solution contained no particles and was non-turbid when its pH was raised from 1.9 to 7.0 with NaHCO₃. Similar protocols were used when Mn(SO₄) and Cu(SO₄) catalysis were investigated.

Analyses of Residual Peroxides

Iodometric titration was used for H₂O₂ and HSO₅⁻, while ceric sulfate titration was used for H₂O₂ contained in Paa solutions. The total peroxide concentration in a Paa solution was obtained by iodometric titration, and the Paa concentration was the difference between the iodometric and ceric sulfate titrations.

Quantification of p-Hydroxybenzoic acid Generated from Hydroxylation of Benzoic Acid

Benzoic acid was added to some of the peroxide decomposition runs (above) as a radical scavenger. After 90 min of decomposition, the residual solution was neutralized with NaHSO₃, acidified, divided into two equal aliquots, and extracted with ether. The ether extract was dried over anhydrous MgSO₄, decanted, and then evaporated to dryness at reduced pressure. The dry residue along with the internal standard, benzhydrol, were dissolved in 1.0 ml of dichloromethane (DCM). A fraction of the DCM solution (100 μl) was added to another vial along with 100 μl of BSTFA [N,O-bis(trimethylfluoromethylsilyl)acetamide]] and a drop of pyridine. The mixture was allowed to sit at room

temperature overnight or for ca. 30 minutes at 40°C before GC analysis using the conditions described in Part 1 (Attigboe et al. 2010).

RESULTS AND DISCUSSION

Preliminary Bleaching Trials

PMC bleaching of CTMP 1 & 2 (Q_1 chelation only) was investigated within the pH range of 8.4 to 8.6. The P_B stage increased the brightness of CTMP 1 from 63.4% to 69.7% (a 6.3 points increase) with the consumption of only 0.32% H_2O_2 on pulp, while the brightness of CTMP 2 increased 3.4 points from 73.4% to 76.8% with a consumption of only 0.25% H_2O_2 (Table 1).

Table 1. P_B Bleaching of Two Softwood CTMPs¹

Pulp	Treatment	Initial pH	Final pH	H_2O_2 Consumed ¹	Brightness, % (Elrepho)
CTMP1	Q_1	-	5.5	-	63.4
CTMP1	Q_1P_B	ca. 8.5	8.4	0.32	69.7
CTMP2	Q_1P				73.4
CTMP2	Q_1PP_B	ca. 8.5	8.6	0.25	76.8

¹ 2.0% H_2O_2 , 4.0% $NaHCO_3$, 0.1% $MgSO_4 \cdot 7H_2O$, 0.1% Na_5DTPA and 0.1% $Na_5DTPMPA$ on pulp (phosphonic acid counterpart to Na_5DTPA), 12% consistency, 2h at 80°C

² % on pulp

Both results were quite impressive because a H_2O_2 consumption of ca. 1.0% on pulp would be required to increase the brightness of a spruce CTMP (such as CTMP2) from 73.4% to 76.8%. It appears that a two-stage bleaching process (P_BP or PP_B) should be quite effective for mechanical pulps. Of the two possibilities P_BP would appear more attractive at first glance. There is typically a residual of 0.5 - 1.0% H_2O_2 on pulp after the second stage of a two-tower PP bleaching system. It would appear that this small amount of H_2O_2 would be more effective in a P_B stage as compared to a P stage when recycled to the first tower. Also carbonation (discussed in Part 1) could be used to convert the residual NaOH being recycled to a first tower to $NaHCO_3$. Some Na_2CO_3 would have to be added to the liquor being recycled, and it would also be partially or totally carbonated to $NaHCO_3$. A mill may be required to purchase some Na_2CO_3 , but it would likely achieve a higher final brightness without increasing its H_2O_2 application.

Effect of pH on HSO_5^- , Pa, and P_B Bleaching

As discussed in Part 1, the pK_a for HCO_4^- in purely aqueous solution has not yet been determined. Bennett et al. (2001) used a solvent system consisting of 20% ethanol and estimated a pK_a of 10.6, while Vakhitova et al. (2006) added cetyl trimethyl ammonium bromide (CTAB) to their reaction system, which indicated a pK_a of 9.4. The difference between the two values may not be that significant if CO_4^{2-} , at low concentrations, is highly reactive toward conjugated carbonyls (as discussed in Part 1).

Some preliminary research was performed with HSO_5^- ($pK_a = 9.4$), peracetic acid ($pK_a = 8.2$), and PMC to try and obtain a rough estimate for the pK_a of HCO_4^- under pulp

bleaching conditions. The question is whether the true value lie somewhere between 9.4 and 10.6. The first experiment was performed with HSO_5^- at a dosage of 2.0% equiv. H_2O_2 on pulp. The effect of HCO_4^- in chemical pulp bleaching appeared to be equivalent to the effect that would have been anticipated for HSO_5^- (Part 1). We wanted to see if any equivalency would be observed when HSO_5^- bleaching of CTMP was compared to that of HCO_4^- . The pulp sample used was CTMP 3 after Q_1 pretreatment. The metals profiles of CTMP 3 after Q_1 and Q_1Q_2 pretreatments are presented in Table 2. The HSO_5^- treatment was performed in a plastic bag at 80°C with the addition of 0.1% Na_5DTPA , 0.1% Na_5DTPMPA , and 0.1% $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ for the deactivation of transition metals along with 5.0% NaOH on pulp. The initial pH of the pulp slurry was approximately 9.0, and the pulp appeared to brighten significantly (visual observation) within the first 20 minutes. However, the pulp got darker and darker, and when the bleaching was terminated after 60 minutes the effluent pH was 3.1, and the pulp appeared darker than the unbleached sample. Research with HSO_5^- was terminated without determination of residual peroxide or bleached pulp brightness. The speculation was that once the pH fell to ca. 6.4 (3 units lower than the pK_a of HSO_5^-), nucleophilic bleaching by SO_5^{2-} ceased and electrophilic bleaching by HSO_5^- continued generating conjugated carbonyls (as discussed in Part 1).

Peracetic acid (Paa) was investigated instead because there was a better chance of observing the transition from joint electrophilic/nucleophilic bleaching to electrophilic only bleaching with this oxidant. That transition should occur at pH ca. 5.2, corresponding to 3 pH units lower than the pK_a of 8.2. The equilibrium Paa solution that was used (Materials and Methods) contained unconverted H_2O_2 and acetic acid. The pK_a of acetic acid is ca. 4.7. Therefore, almost all of the acetic acid in the Paa solution would convert to the acetate anion if an initial pH of ca. 8.5 were used for Paa bleaching. Also, when Paa loses its active oxygen, acetic acid/acetate is generated. The acetic acid/acetate buffering system would start becoming significant at pH ca. 5.7, and the bleaching pH should fall more slowly beyond that point.

Table 2. Transition and Alkaline Earth Metals in CTMP 3 Before and After Q Stages

Metal	Untreated Pulp	Q_1 -treated	Q_1Q_2 -treated
Mg	355	55	62
Cu	8.3	4.9	5.2
Mn	11.3	3.2	0.5
Fe	29.0	8.7	8.6
Co	0.07	0.06	0.07

The same stabilizers were used as with HSO_5^- , and Q_1 pretreated CTMP3 was also used. The dose of Paa was 2.0% equiv. H_2O_2 , and it was used along with 8.0% NaOH on pulp (70°C). The variation of brightness with bleaching time and liquid phase pH is documented in Table 3 (a separate plastic bag was used for each reaction time). Pulp brightness increased from 71.2% to 78.4% in the first 20 min. (pH decreased from 8.7 to 7.3). This rapid initial brightening was anticipated, because the optimum pH for

Paa/peracetate brightening reactions is 8.0 ± 0.3 (Hu et al. 2006; Gursoy and Dayioglu 2000). The brightness increased further to 81.8% after 40 min (pH down to 6.1). However, the brightness decreased to 80.3% when the reaction time was increased from 40 and 60 minutes (end pH 5.4). There were still residual amounts of Paa and H_2O_2 after 60 minutes (Table 3). It appears that at pH <6.1, electrophilic reactions between lignin and CH_3COOOH occurred without nucleophilic reactions between CH_3COOO^- and the conjugated carbonyls that were being generated. A very tentative conclusion can be drawn that when a substituted peroxide (containing an electron withdrawing group) is being used, nucleophilic brightening can be clearly seen only when the reaction pH is higher than a value that is ca. 2.5 units less than the pK_a of the peroxide ($8.2 - 2.5 = 5.7$ for Paa).

Research was then performed with P_B at $80^\circ C$, and those results are presented in Table 4. The pulp sample that was used was CTMP3 with Q_1 pretreatment. When bleaching was performed with 4.0% $NaHCO_3$ on pulp, an end pH of 8.6 (initial pH values in Table 4) and brightness of 77.3% were obtained after 1 h. The addition of 1.0% $NaOH$ on pulp to the bleaching formulation raised the initial pH to 9.5 and afforded a brightness of 78.3% after 1 h and 79.5% after 2 h. The addition of 8.0 mmoles $H_2SO_4/100g$ of pulp along with the 4.0% $NaHCO_3$ on pulp afforded an end pH of 8.1 and 75.9% brightness after 1 h. Finally, when 12.5 mmoles $H_2SO_4/100g$ of pulp was added along with 4.0% $NaHCO_3$ on pulp, the end pH was lowered to 7.6, and a brightness of 74.6% was obtained after 1 h. The initial brightness of CTMP3 was 71.2%, and the 74.6% brightness that was obtained with end pH 7.6 was interpreted as a sign of nucleophilic brightening. These results would suggest that the pK_a for HCO_4^- is in the range of 10.1 ($7.6 + 2.5$). Obviously, this is only a rough estimate; a more sophisticated method would be required to determine a pK_a value accurate to ± 0.1 .

Table 3. Paa Bleaching of CTMP3 (commercial aspen pulp)¹

Bleaching Time, Minutes	Paa as Equiv. H_2O_2	H_2O_2	pH	Brightness, %Elrepho
0	2.0 ²	0.6 ²	8.7	71.2
20	0.7	0.5	7.3	78.4
40	0.4	0.5	6.1	81.8
60	0.2	0.5	5.4	80.3

¹ 2.0% equiv. H_2O_2 from Paa, 8.0% $NaOH$, 0.1% $MgSO_4 \cdot 7H_2O$, 0.1% Na_5DTPA and 0.1% $Na_5DTPMPA$ on pulp, 12% consistency, $70^\circ C$

²% on pulp

Peroxide Decomposition

Peroxide decomposition was investigated because a high rate was observed when a reagent grade $Mg(OH)_2$ (Fisher Scientific, USP/FCC grade) was used for pH elevation. The $Mg(OH)_2$ contained 161 ppm of Fe. Peroxide decomposition was more significant in pulp slurries of mechanical pulps as compared to chemical pulps (results not included). Peroxidation of reactive phenylpropane units in the lignin in a CTMP (>17 wt% lignin) is likely to generate much more dicarboxylic acids (Bailey and Dence 1969; Kadla et al. 1997) as compared to that generated from the generally un-reactive residual lignin in chemical pulps (<4 wt% lignin).

Table 4. P_B bleaching of CTMP3 with Unbleached Brightness of 71.2% Elrepho¹

P _B Treatment Condition	Initial pH	Final pH	Bleaching Time, h	H ₂ O ₂ Consumed ²	Brightness, %Elrepho
Standard + NaOH ³	9.5	8.7	1.0	0.69	78.3
Standard + NaOH ³	9.5	8.5	2.0	0.90	79.5
Standard ¹	8.5	8.6	1.0	0.42	77.3
Standard + H ₂ SO ₄ ⁴	8.2	8.1	1.0	0.38	75.9
Standard + H ₂ SO ₄ ⁵	7.8	7.6	1.0	0.35	74.6

¹ 2.0% H₂O₂, 4.0% NaHCO₃, 0.1% MgSO₄·7H₂O, 0.1% Na₅DTPA and 0.1% Na₅DTPMPA on pulp, 12% consistency at 80°C

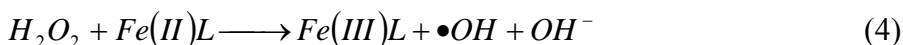
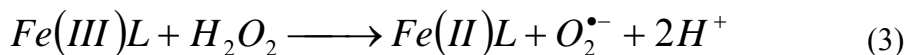
² % on pulp

³ 1.0% NaOH on pulp in addition to footnote #1

⁴ 8.0 mmoles of H₂SO₄/100g of pulp in addition to note #1

⁵ 12.5 mmoles of H₂SO₄/100g of pulp in addition to note #1

We speculated that Fe when complexed with dicarboxylic acids would be soluble under mildly alkaline conditions and might have catalyzed peroxide decomposition by a chain mechanism that included the Haber-Weiss cycle described in equations (3) and (4) (Koppenol and Butler 1985). Citrate complexes of Fe (II) and Fe (III) are reported to be quite effective in one electron transfer reactions involving H₂O₂, and ferric- citrate was chosen as a model catalyst (Zepp et al. 1992). The ferric citrate preparation was very soluble at a [Fe³⁺] of 1.0 g/l in the neutral pH range (Materials and Methods).



This research was critically important because a peroxide decomposition mechanism dominated by a reaction like that in equation (4) is very harmful to both chemical and mechanical pulp bleaching. Hydroxyl radical generation at a moderate rate does not result in a noticeable increase in peroxide utilization but significantly lowers the brightness in mechanical pulp bleaching (Gierer et al. 1993) and lowers the degree of polymerization (DP) of cellulose in chemical pulps to unacceptable levels (Francis et al. 1994).

Table 5. Effect of Transition Metals on H₂O₂ Decomposition and Brightness Development During P_B Bleaching of CTMP 3

Added Metal ¹	Residual ² H ₂ O ₂	Final pH	Brightness, % Elrepho
None ³	1.61	8.6	77.6
Cu ⁴	1.50	8.6	77.4
Mn	1.38	8.5	77.2
Fe	0.96	8.4	76.1

¹ 2.0% H₂O₂, 4.0% NaHCO₃ on pulp, 12% consistency, and 60 min at 80°C

² % on pulp

³ Na₅DTPA, Na₅DTPMPA and MgSO₄·7H₂O added

⁴ 1.0 ppm of Cu, Mn or Fe on pulp; no stabilizers

Our investigation started with P_B bleaching of Q_1Q_2 pretreated CTMP 3 with the addition of 1.0 ppm of Fe (III), Mn (II), or Cu (II) on pulp. The sulfate salts of the three cations were used. Cu was the least effective at catalyzing H_2O_2 decomposition, while Fe was the most aggressive (Table 5). Hydrogen peroxide decomposition was then investigated in pulp-free 0.1 M $NaHCO_3$ solution at 40°C. On this occasion both the metal sulfate and metal complexed with citrate were investigated. Those results are summarized in Fig. 2, and the key observation was that Fe (III) catalysis was significantly accelerated by citrate complexation.

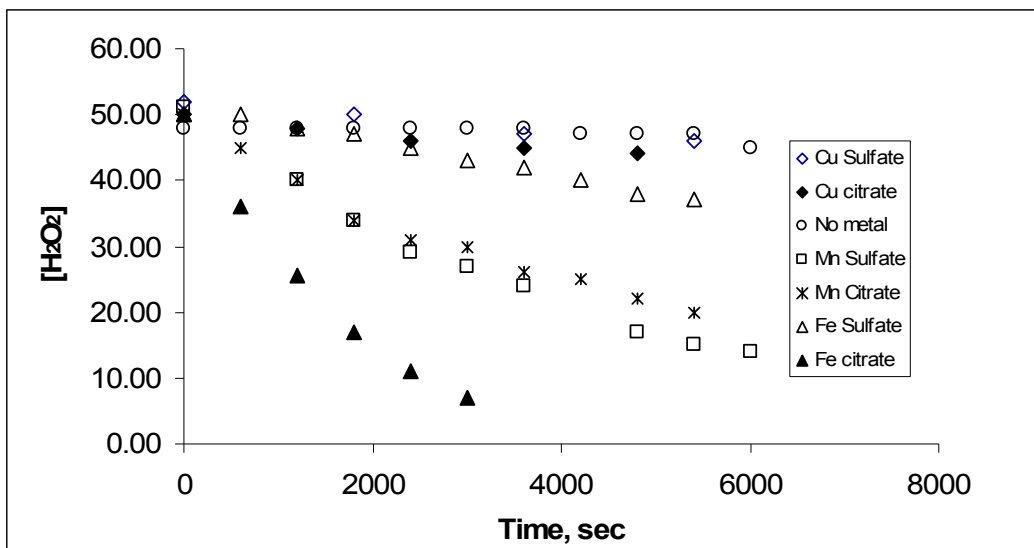


Figure 2. Decomposition of H_2O_2 catalyzed by Fe, Mn and Cu either as sulfate salts or citrate complexes (0.1 M $NaHCO_3$, 40°C, 0.1 ppm Fe (III), Mn (II), or Cu (II) in solution)

Ferric citrate catalysis of H_2O_2 decomposition in 0.1M $NaHCO_3$ was investigated in greater depth. The first order plots for H_2O_2 decomposition with varying concentration of Fe(III) are presented in Fig. 3. When the rate constants (k) from Fig. 3 were plotted against $[Fe(III)]$ ($-\ln k$ vs $-\ln [Fe(III)]$) the relationship had a slope of 1.0 ($R^2 = 0.994$), indicating that the rate expression was first order in $[Fe(III)]$.

A tentative conclusion was drawn that the H_2O_2 was being decomposed by a mechanism involving the Haber-Weiss cycle. The rate of decomposition was equal for 0.05 and 0.1 M $NaHCO_3$ and decreased slightly when 0.15 M $NaHCO_3$ was used. A rate expression that is first order in both Fe(III) and H_2O_2 is normally observed in cases where the Haber-Weiss cycle is involved (Walling and Goosen 1973; Walling 1975; Walling et al. 1975). This tentative conclusion was supported by the stabilizing effect of benzoic acid, as shown in Fig. 4 (Walling and Goosen 1973; Walling 1975; Walling et al. 1975). The hydroxyl radical adds to aromatic rings to form a cyclohexadienyl radical intermediate that subsequently loses a hydrogen atom ($H^+ + e^-$) to generate a phenolic group (Oturán and Pinson 1995). When benzoic acid was added at a concentration of 10 mM, it decreased the rate of peroxide decomposition from $4.9 \times 10^{-4} s^{-1}$ to $1.7 \times 10^{-4} s^{-1}$, presumably by trapping $\bullet OH$ and disrupting the free radical chain mechanism. The peroxide concentration decreased from 50.0 mM to 20.0 mM after 90 minutes when

benzoic acid (BA) was added, and 8.5 mM of p-hydroxybenzoic acid (p-HBA) was generated. Decomposition experiments were repeated with new solutions of NaHCO_3 and ferric citrate prepared from the various crystals/powder. On this occasion the decomposition rate was $4.4 \times 10^{-4} \text{ s}^{-1}$ without BA and $1.4 \times 10^{-4} \text{ s}^{-1}$ with BA. The peroxide concentration decreased from 50.5 mM to 24.0 mM after 90 minutes in the presence of BA and 10.0 mM of p-HBA was generated.

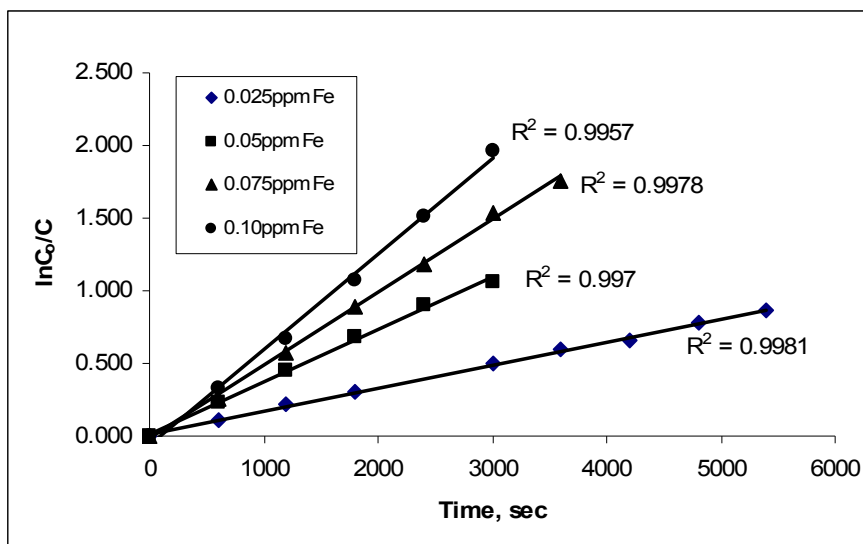


Figure 3. First order rate constant for peroxygen decomposition in the presence of increasing concentrations of Fe(III) citrate complex at 40°C , pH 8.6-8.8, $[\text{HCO}_3^-] = 0.10\text{M}$, $[\text{H}_2\text{O}_2] = 0.05\text{M}$. Slopes = $1.6 \times 10^{-4} \text{ s}^{-1}$, $3.5 \times 10^{-4} \text{ s}^{-1}$, $4.9 \times 10^{-4} \text{ s}^{-1}$, $6.3 \times 10^{-4} \text{ s}^{-1}$

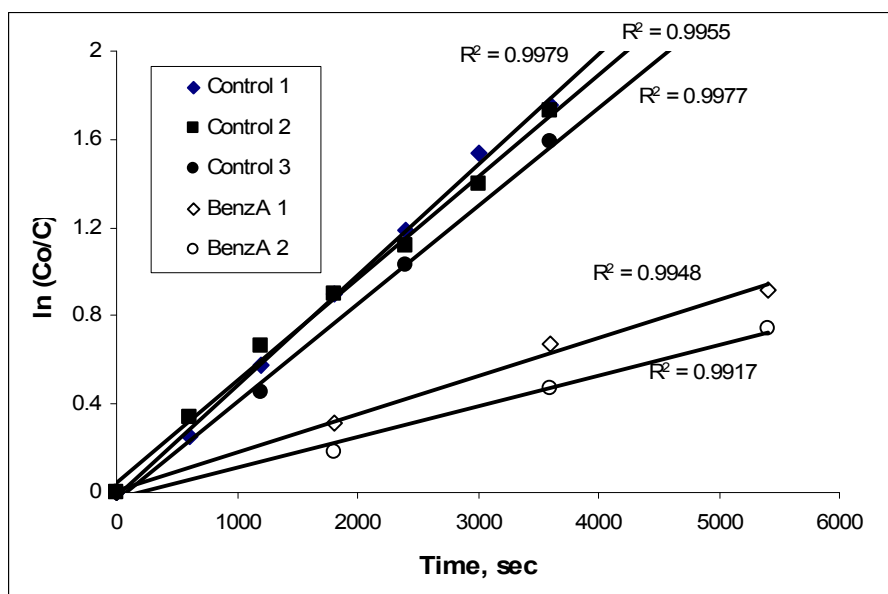


Figure 4. Effect of radical scavenger on peroxygen decomposition catalyzed by 0.075 ppm Fe(III) citrate complex at 40°C , pH 8.6-8.8, $[\text{HCO}_3^-] = 0.10\text{M}$, $[\text{H}_2\text{O}_2] = 0.05\text{M}$. Rate for Control 1&2 = $4.9 \times 10^{-4} \text{ s}^{-1}$; Control 3 = $4.4 \times 10^{-4} \text{ s}^{-1}$; BenzA 1 = $1.7 \times 10^{-4} \text{ s}^{-1}$; BenzA 2 = $1.4 \times 10^{-4} \text{ s}^{-1}$ (Control 3 and BenzA 2 run at a later date).

CONCLUSIONS

The conclusions from this preliminary investigation are:

1. Peroxymonocarbonate anions are effective at bleaching mechanical pulps; a low peroxide consumption affords a high brightness increase at pH ca. 8.5.
2. Peroxide decomposition catalyzed by Fe, and to a lesser degree Mn and Cu, has to be controlled during a P_B bleaching stage. It appears likely that Fe catalysis of peroxide decomposition in slurries containing mechanical pulps may involve formation of the hydroxyl radical.

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