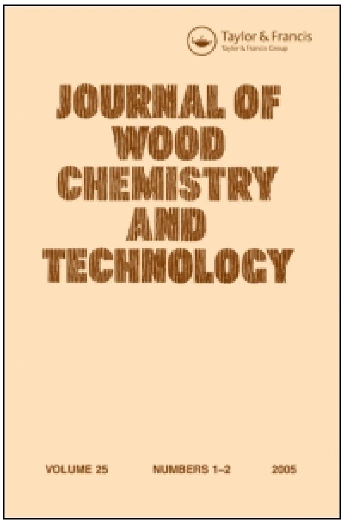

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Formation of Hydroxyl Radicals from Hydrogen Peroxide and their Effect on Bleaching of Mechanical Pulps

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ABSTRACT

The formation of hydroxyl radicals from hydrogen peroxide in alkaline solutions and under the conditions of hydrogen peroxide bleaching of pulps was investigated. The results lend support to the generally accepted view that the decomposition of alkaline hydrogen peroxide is catalyzed by redox processes involving transition metal ion species. The formation of hydroxyl radicals by one-electron reduction of hydrogen peroxide in this process is believed to be catalyzed primarily by mononuclear transition metal ion complexes, polynuclear species being far less efficient in this respect. It was found that a certain formation of hydroxyl radicals during alkaline hydrogen peroxide bleaching of pulp may have a beneficial effect on the final brightness. This finding is ascribed to the cleavage of cross-links in the rigid lignin matrix which facilitates penetration of the bleaching reagent(s). Silicate does not appreciably suppress the formation of hydroxyl radicals in alkaline hydrogen peroxide solution. The stabilizing effect of this additive is probably due to deactivation of finely dispersed colloidal particles of metal hydroxides and hydrated oxides which decompose hydrogen peroxide to give mainly molecular oxygen and water.

INTRODUCTION

Alkaline hydrogen peroxide is used in large quantities as a non-delignifying agent for bleaching various types of mechanical pulps. This bleaching chemical is also used to an increasing extent in the production of fully bleached chemical pulps to achieve both bleaching and delignification, e.g. in reinforcing the alkaline extraction step and in driving the Lignox process recently patented by EKA NOBEL[1].

For many years, the bleaching action of alkaline hydrogen peroxide has been interpreted in terms of the action of its dissociated form, the hydroperoxide anion HO_2^-, which is a strong nucleophile and reacts with chromophores of the enone type, e.g quinonoid structures, present in lignin. This is considered to be the main mode of chromophore elimination in lignin-retaining bleaching using hydrogen peroxide[2].

However, some effects observed with alkaline hydrogen peroxide cannot be simply attributed to the nucleophilic character of its anion. Among these are the findings that the stoichiometry and the rate of bleaching at a constant peroxide charge are improved by increasing the pulp consistency[3, 4] and that the addition of a radical scavenger (2,6-dimethoxyphenol) to the bleaching liquor reduces the rate of bleaching[5]. Moreover, it was found that the brightness gain is less when metal ions are carefully removed from the pulp before bleaching with hydrogen peroxide[6]. These observations indicate that metal ions induce the decomposition of hydrogen peroxide to give radicals which facilitate chromophore elimination.

Different opinions about the course of hydrogen peroxide decomposition under alkaline conditions have been advanced[7]. Usually, it is assumed that this decomposition involves redox processes catalyzed by transition metal ions. However, under actual hydrogen peroxide bleaching conditions, transition metals, predominantly Fe, Cu and Mn, can hardly exist as free ions. Rather, they are present as finely dispersed colloidal particles of hydrated oxides/hydroxides in the bleaching liquor, or bound to the pulp.

The decomposition of hydrogen peroxide may generate exceedingly reactive hydroxyl radicals. A reaction sequence leading to formation of hydroxyl radicals may be outlined as follows[8]:

$$M^{n+} + H_2O_2 \text{ ------> } M^{n+1} + \cdot OH + {}^{-}OH \qquad [1]$$

In order to achieve a catalytic cycle, M^{n+1} must be reconverted to M^{n+}. This step may involve hydroperoxide and/or superoxide anions:

$$M^{n+1} + HO_2^{-} \text{ ------> } M^{n+} + O_2^{\cdot -} + H^{+} \qquad [2]$$

$$M^{n+1} + O_2^{\cdot -} \text{ ------> } M^{n+} + O_2 \qquad [3]$$

According to this simplified mechanism, the decomposition of hydrogen peroxide involves an interplay between the dissociated and undissociated forms of hydrogen peroxide. The minimum stability of hydrogen peroxide and, consequently, the maximum yield of hydroxyl radicals may therefore be expected to occur in the vicinity of the pKa-value of hydrogen peroxide, i.e. at pH ≈ 11.6.

The hydroxyl radical is an electrophile and one of the strongest one-electron oxidants available in aqueous media[9]. It rapidly oxidizes a variety of inorganic and organic compounds. Organic substrates are oxidized in two different ways:

I. by electrophilic addition to double bonds or aromatic nuclei.

II. by H-atom abstraction, usually from an aliphatic group.

The addition reaction **I** is diffusion-controlled and about one order of magnitude faster than the abstraction reaction **II**[10,11]. Hydroxyl radicals arising during the bleaching of pulp attack both lignin and carbohydrate components. The reactions with lignin belong predominantly to reaction type **I**. They initiate a variety of consecutive processes, such as undesired oxidative coupling, and desired oxidation or cleavage of bonds in side chains and demethoxylation or hydroxylation of aromatic nuclei[12]. The reactions with cellulose are of type **II**, resulting in the formation of carbonyl structures which opens the way for alkaline degradation through β-elimination (peeling)[13]. This leads to a lower yield and lower strength properties of the bleached pulp. The selectivity of hydroxyl radicals in bleaching processes may thus be defined as a competition between the reactions of types **I** and **II**[14].

Hydroxyl radicals also react with hydrogen peroxide [4] and its anion [5]. Notably, reaction [5] is much faster than reaction [4][10]:

$$\cdot OH + H_2O_2 \text{ ------> } H_2O + HO_2\cdot \qquad k = 2.7 \cdot 10^7 M^{-1}s^{-1} \qquad [4]$$

$$\cdot OH + HO_2^- \text{ ------> } H_2O + O_2^{\cdot -} \qquad k = 7.5 \cdot 10^9 M^{-1}s^{-1} \qquad [5]$$

Thus, at $pH \geq 11.6$ hydrogen peroxide acts as an efficient scavenger of hydroxyl radicals. This may suggest that bleaching at high pH is a convenient way to reduce the effect of hydroxyl radicals. However, in strongly alkaline solution the hydroxyl radical dissociates to give the oxyl anion radical ($O^{-}\cdot$) (pKa = 11.9)[10]. This is a considerably weaker oxidant than the hydroxyl radical and shows no tendency to add preferentially to aromatic nuclei according to reaction type **I**, and reacts with hydrogen peroxide anions at a rate not exceeding $4 \cdot 10^8 M^{-1}s^{-1}$ [10]. Hence, bleaching above pH 12 is probably of no further advantage since the selectivity is reduced and the scavenging of reactive radical species by hydrogen peroxide becomes less efficient.

In the first part of the present work, the formation of hydroxyl radicals through the decomposition of hydrogen peroxide under different conditions has been studied. In the second part, an attempt has been made to evaluate the effect of hydroxyl radicals on the bleaching of mechanical pulps with hydrogen peroxide.

A very sensitive and selective chemiluminescence method for the detection of hydroxyl radicals[15] has been used in this study. The method is based on the hydroxylation of non-chemiluminescent phthalic hydrazide by hydroxyl radicals to give strongly chemiluminescent 3-hydroxyphthalic hydrazide. Oxidative conversion of 3-hydroxyphthalic hydrazide to 3-hydroxyphthalic acid is accompanied by light emission which is monitored in a luminometer. The method is selective since other strong oxidants do not hydroxylate the aromatic ring in phthalic hydrazide but only induce decomposition of the hydrazide moiety to give (unsubstituted) phthalic acid.

EXPERIMENTAL

Materials

The chemicals used were of reagent grade unless otherwise stated. Hydrogen peroxide (35%) was purchased from Kebo and phthalic hydrazide from Aldrich-Chemie. Sodium hydroxide, *puriss* (Cu $\leq$ 0.1ppm, Mn $\leq$ 0.1 ppm, Fe $\leq$ 10 ppm), was supplied by EKA NOBEL and sodium hydroxide purified from metal ions, Suprapur® (Cu $\leq$ 0.01ppm, Mn $\leq$ 0.01 ppm, Fe $\leq$ 0.05 ppm), by Merck. The water used in all experiments was deionized and bi-distilled in a quartz apparatus. In experiments studying the effect of transition metals, $FeCl_3 \cdot 6\,H_2O$, $CuSO_4$ and $MnSO_4 \cdot H_2O$ were used. Stock solutions (5 mM of each metal ion) were prepared by dissolving the salts in 0.1 M HCl. Na-silicate of technical grade was supplied by EKA NOBEL. DTPA was purchased from Aldrich-Chemie.

Two different commercial mechanical pulps (stone groundwood from spruce) were investigated:

Pulp **A** was pre-bleached in the conventional way in the mill at the defibration stage with recycled hydrogen peroxide and pretreated with DTPA (initial brightness: 68.3% ISO)

Pulp **B** was a reference pulp neither pre-bleached nor pretreated (initial brightness: 60.3% ISO).

Determination of the stability of hydrogen peroxide.

Phthalic hydrazide was dissolved in water (0.6 mM) in a polyethylene bottle. Hydrogen peroxide was added to this solution to reach a concentration of 0.1 M and the pH was adjusted to the desired value with a 1 M NaOH solution (*puriss* or Suprapur®). Metal ions were pipetted from the stock solutions. The experiments were started by immersing the bottle in a thermostated water bath. Samples (1 mL) were withdrawn from the reaction mixture at chosen time intervals and chemiluminescence and the amount of residual hydrogen peroxide were immediately measured. The peroxide concentration was determined by iodometric titration.

Hydrogen peroxide bleaching of mechanical pulps.

The bleaching chemicals used were hydrogen peroxide (4%) and NaOH (4%) calculated on oven dry (o.d.) pulp. Phthalic hydrazide (0.7% on o.d. pulp) was dissolved in the sodium hydroxide solution. The additives to the bleaching liquor were: sodium silicate (4% on o.d. pulp) and DTPA (0.9% on o.d. pulp, added as a neutralized aqueous solution). In some experiments, $FeCl_3 \cdot 6\,H_2O$ (0.2% on o.d. pulp) was dissolved in water and added to the pulp before the bleaching was started. The bleaching liquor was mixed with the pulp (3 g o.d.) and the consistency was adjusted to 10% by adding water. The initial pH at the ambient temperature (24 °C) was about 11.7. The bleaching experiments were carried out in polyethylene bags. The bleachings were started by immersing the bags in a water bath (60 °C) and terminated after different periods of time (5, 15, 25, 35, 75 and 120 min.) by rapid cooling of the bags with tap water. The bleaching liquor was separated from the pulp by filtration. Chemiluminescence, pH and residual hydrogen peroxide in the spent bleaching liquor were immediately measured. The peroxide concentration was determined by iodometric titration. The pH of the bleached pulp was adjusted with dilute sulphuric acid to 4.0-5.5 and the final brightness was measured according to SCAN-C11.

Chemiluminescence measurements

Details of the chemiluminescence method are given elsewhere[15,16]. A trace amount of phthalic hydrazide was added to the reaction system. At chosen time intervals, a sample (0.1 mL) was withdrawn and made alkaline by addition of a solution (1 mL) containing 1 M sodium carbonate and 25 mM EDTA. The resulting alkaline solution was oxidized in a LKB 1250 luminometer by addition of a solution (0.1 mL) containing 50 mM of sodium persulphate and hydrogen peroxide. If the sample contained 3-hydroxyphthalic hydrazide, a long lasting chemiluminescence signal was recorded and the height of the signal was measured. Usually, the chemiluminescence (arbitrary units, a.u.) was plotted against reaction time and the initial slope, $(\Delta CL/\Delta t)_0$, was taken as a measure of the rate of formation of hydroxyl radicals corresponding to the starting conditions in the reaction system.

RESULTS AND DISCUSSION

1. Conditions affecting the generation of hydroxyl radicals by decomposition of hydrogen peroxide.

The chemiluminescence observed as a result of decomposition of hydrogen peroxide solutions was strongly dependent on the temperature, the pH and the metal ion content of the solution. In a control experiment it was shown that the decomposition of hydrogen peroxide was not affected by the presence of phthalic hydrazide

1.1. Temperature dependence

The chemiluminescence is plotted against time at different temperatures in Fig. 1.

After temperature equilibrium was established (2 min), the chemiluminescence increased linearly over a period of at least 20

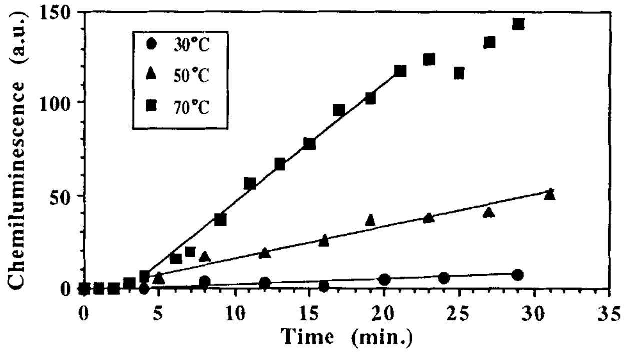

FIGURE 1. Chemiluminescence plotted against reaction time for different temperatures.
0.6 mM phthalic hydrazide and 60 mM H_2O_2, pHo = 11.0.

min. Applying the Arrhenius equation to the slopes of the linear part, an activation energy of 69 kJ·mol^{-1} was obtained for the formation of hydroxyl radicals under the prevailing conditions. This activation energy is close to a value previously reported for the decomposition of dilute hydrogen peroxide solutions determined by iodometric titration[17].

1.2. pH dependence

The decomposition of alkaline hydrogen peroxide at 50 °C was determined as a function of pH. As can be seen in Fig. 2, the decomposition rate of hydrogen peroxide reaches a broad maximum at about pH ≈ 11.5.

The initial rate of development of chemiluminescence, $(\Delta CL/\Delta t)_0$, determined at different pH values in alkaline hydrogen peroxide solutions is shown in Fig. 3.

A comparison of Figs. 2 and 3 may give the impression that the decomposition of hydrogen peroxide and the formation of hydroxyl

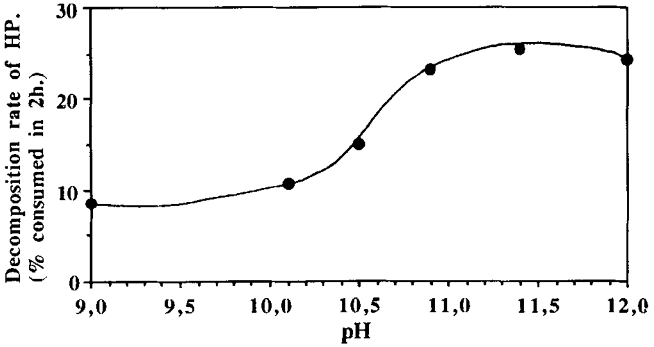

FIGURE 2 Decomposition rate of hydrogen peroxide (HP) plotted against pH. 0.6 mM phthalic hydrazide, 0.1 M hydrogen peroxide, 50 °C.

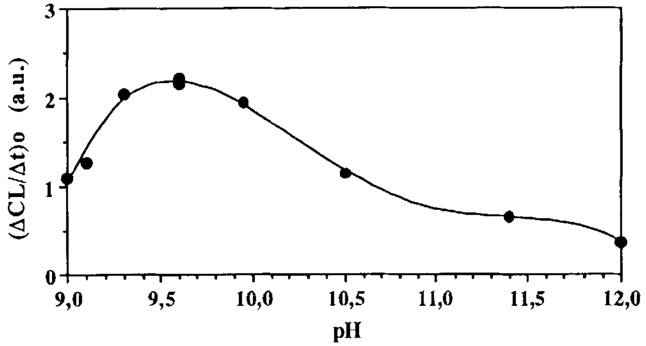

FIGURE 3 (ΔCL/Δt)o plotted against pH. 0.6 mM phthalic hydrazide, 0.1 M hydrogen peroxide, 50 °C.

radicals are two independent processes. The decrease of $(\Delta CL/\Delta t)_0$ observed in alkaline solution can however be explained by the increasing formation of hydroperoxide anions. These react with hydroxyl radicals (reaction [5]) at almost the same rate ($7{,}5 \cdot 10^9\ M^{-1}s^{-1}$) as phthalic hydrazide ($5 \cdot 10^9\ M^{-1}s^{-1}$). A calculation based on these reaction rates and the concentrations of hydrogen peroxide and phthalic hydrazide used, shows that above pH 9.2 the reaction of hydroxyl radicals with hydroperoxide anions exceeds that with

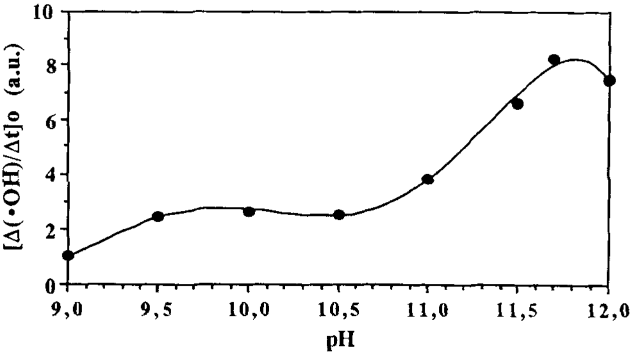

FIGURE 4 Rate of formation of hydroxyl radicals plotted against pH. 0.6 mM phthalic hydrazide, 0.1 M hydrogen peroxide, 50 °C.

phthalic hydrazide. Hence, the hydroperoxide anion will act as a scavenger for hydroxyl radicals, resulting in the observed reduction in the chemiluminescence intensity.

It is possible to correct the $(\Delta CL/\Delta t)_0$ value in basic solution for the presence of HO_2^- by taking into account the rates of reaction of hydroxyl radicals with phthalic hydrazide, HO_2^- and H_2O_2. The corrected $(\Delta CL/\Delta t)_0$ value, Fig. 4, is taken as a measure of the true rate of formation of hydroxyl radicals in the unperturbed system.

Figs. 2 and 4 show similar pH dependencies indicating that the decomposition of hydrogen peroxide and the formation of hydroxyl radicals are interdependent processes. In both figures, the shape of the curves indicates that both the decomposition of hydrogen peroxide and the formation of hydroxyl radicals involve an interplay between the undissociated and dissociated forms of hydrogen peroxide. The latter form is required to complete the redox cycle (eqs. [1-3]).

1.3. Effect of metal ion contamination.

As shown in Fig. 5, the rate of decomposition of alkaline hydrogen peroxide is markedly reduced when extremely pure sodium

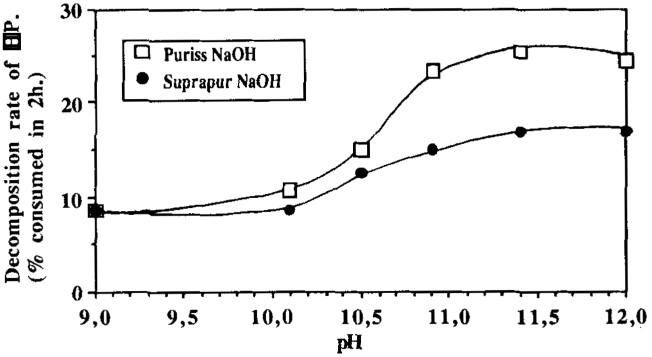

FIGURE 5 Rate of decomposition of hydrogen peroxide (HP) in puriss and Suprapur® NaOH, plotted against pH.
0.6 mM phthalic hydrazide, 0.1 M hydrogen peroxide, 50 °C.

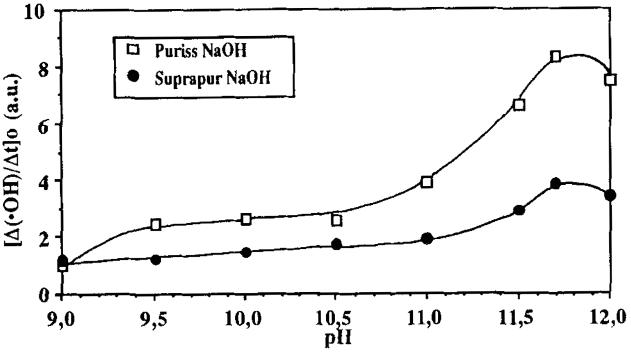

FIGURE 6 Corrected initial rate of formation of hydroxyl radicals in puriss (see Fig.4) and Suprapur® NaOH, plotted against pH.
0.6 mM phthalic hydrazide, 0.1 M hydrogen peroxide, 50 °C.

hydroxide (Merck Suprapur®) is used instead of *puriss* sodium hydroxide.

The same is true of the rate of formation of hydroxyl radicals, as shown in Fig. 6.

The reduction in the rates of decomposition of hydrogen peroxide and formation of hydroxyl radicals when NaOH, highly purified from transition metal ions, is used strongly indicates that reactions catalyzed by such ions are involved.

The pH dependence of $(\Delta CL/\Delta t)_0$ determined in solutions containing unpurified sodium hydroxide showed a maximum at a pH value of about 9.6 (Fig. 3). This maximum was absent when Suprapur® sodium hydroxide was used, but reappeared at different heights when 1 ppm of Cu^{2+} or Fe^{3+} was added to this solution (Fig. 7). The addition of Mn^{2+} ions did not, however, show such an effect.

Addition of Cu^{2+} ions enhanced the chemiluminescence very strongly (Fig. 7, lower part), suggesting that Cu^{2+} ions are extremely efficient in producing hydroxyl radicals from alkaline hydrogen peroxide. This result is in agreement with previous reports[7, 18]. Addition of Fe^{3+} or Mn^{2+} ions had a much smaller effect on the chemiluminescence intensity (Fig. 7, upper part). At $pH < 9.2$, Mn^{2+} ions tend to promote and Fe^{3+} ions to suppress the formation of hydroxyl radicals. At $pH > 9.2$ the effect of these ions is the opposite. The formation of hydroxyl radicals in alkaline hydrogen peroxide solutions thus seems to be determined primarily by adventitious Cu^{2+} ions present mainly as an impurity in the sodium hydroxide.

A characteristic feature of many metal ions is aggregation or condensation by the formation of hydroxo-bridged polynuclear complexes when the hydrogen ion concentration is lowered. Polynuclear species may be regarded as soluble precursors of precipitates of hydrated oxides/hydroxides[19]. Thus, a low concentration of Fe^{3+} ions in alkaline solution may form a colloidal suspension containing polynuclear $[FeO(OH)]_n$ species[20]. Above $pH \approx 9$, manganese and hydroxide ions form polynuclear aggregates, which can be oxidized by molecular oxygen to $[MnO(OH)]_n$ and eventually to MnO_2[20]. Colloidal MnO_2 is known to decompose hydrogen peroxide rapidly to give oxygen and

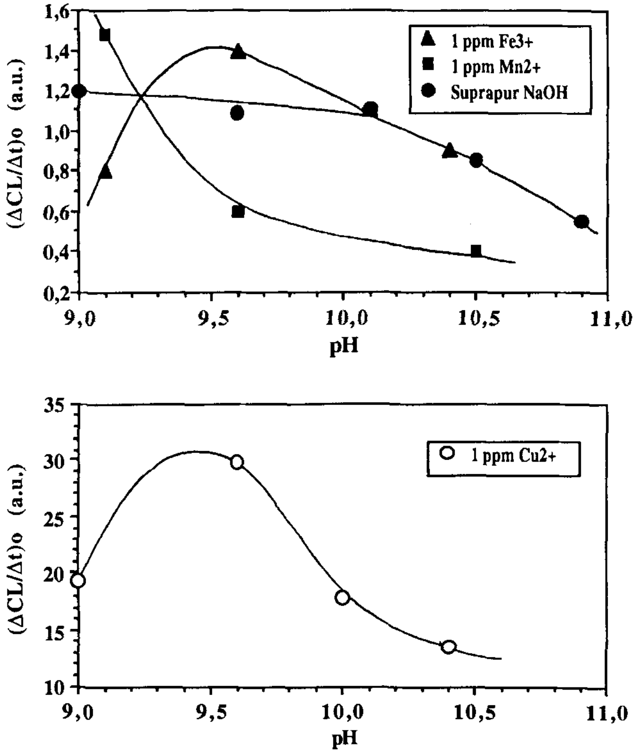

FIGURE 7 (ΔCL/Δt)o measured on addition of 1 ppm of Cu^{2+}, Fe^{3+} or Mn^{2+} to aquous solutions of Suprapur® NaOH.
0.6 mM phthalic hydrazide and 0.1 M hydrogen peroxide, 50 °C.
In the upper and lower figure, the same arbitary units (a.u.) apply but they are plotted on different scales.

water without producing any significant yield of hydroxyl radicals[21]. In contrast, traces of Cu^{2+} ions in alkaline solution may form rather stable mononuclear ion complexes, predominantly $[Cu(OH)_3(H_2O)]^-$[22].

The foregoing leads to the suggestion that the formation of hydroxyl radicals by one-electron reduction of hydrogen peroxide in alkaline solution is catalyzed primarily by mononuclear transition metal ion complexes, and that polynuclear species are far less efficient in this respect. The heterogeneous surface-catalyzed decomposition of hydrogen peroxide caused by colloidal transition metal oxides/hydroxides seems to occur mainly by consecutive electron transfer processes to give oxygen and water.

The addition of complexing agents may convert polynuclear species into mononuclear ones which should facilitate the formation of hydroxyl radicals. In fact, complexation of Fe^{2+} to EDTA or DTPA has been found to strongly accelerate reaction [1]. This reflects the ability of these ligands to stabilize Fe^{3+} ions more strongly than Fe^{2+} ions, which lowers the redox potential for the Fe^{3+}/Fe^{2+} couple[23]. However, for the same reason, the regeneration of Fe^{2+} from Fe^{3+} by reactions [2] and [3] should be retarded, resulting in a reduction of the rate of formation of hydroxyl radicals. The observed reduction of the rate of hydroxyl radical formation by the above complexing agents (see below) shows that the latter effect seems to prevail.

The results and conclusions drawn from this study regarding the formation of hydroxyl radicals by the decomposition of alkaline hydrogen peroxide under various conditions are in general agreement with those previously obtained in a number of thorough investigations[7, 24, 25].

Under actual bleaching conditions, transition metal ions may be adsorbed or complexed to the pulp. This could affect their redox properties but, nevertheless, the results here reported should in the main apply also to systems containing pulp.

2. Involvement of hydroxyl radicals in hydrogen peroxide bleaching of mechanical pulps.

The formation of hydroxyl radicals was investigated during alkaline hydrogen peroxide bleaching of two different mechanical pulps, one prebleached with hydrogen peroxide and washed with DTPA, the other untreated. As before, the initial rate of formation of hydroxyl radicals was estimated from determination of $(\Delta CL/\Delta t)_0$. The activation energy of formation of hydroxyl radicals was almost the same as that obtained in the absence of pulp, indicating that hydroxyl radicals are formed by processes similar to those previously outlined.

The effect of different additives on the initial rate of formation of hydroxyl radicals is shown in Fig. 8.

Under otherwise identical conditions, the initial formation of hydroxyl radicals was more extensive in bleaching experiments using the untreated pulp (B) than in those with the pretreated pulp (A). Addition of agents to stabilize hydrogen peroxide lowered the initial yield of hydroxyl radicals. The addition of the metal ion-complexing agent DTPA showed the greatest inhibiting effect, whereas the addition of sodium silicate was much less efficient.

This shows that silicate does not primarily function as a complexing agent for metal ions or as a hydroxyl radical scavenger in bleaching processes. The latter conclusion is in agreement with the results of a recently reported pulse radiolysis study[26]. The well-known stabilizing effect of sodium silicate in alkaline hydrogen peroxide could rather be due to a deactivation of finely dispersed colloidal particles of polynuclear metal hydroxides and hydrated oxides which decompose hydrogen peroxide catalytically to give oxygen and water.

In Fig. 9, the final brightness of the bleached pulps is plotted against the initial rate of formation of hydroxyl radicals.

The brightness first rapidly increases to a maximum value and then decreases with increasing rate of hydroxyl radical production, indicating an elimination followed by a generation of chromophores.

In the present case, the efficiency of bleaching may be defined as the ratio of the change in brightness to the consumption of hydrogen

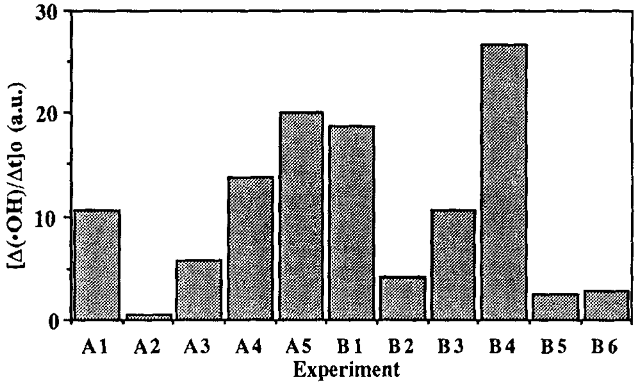

FIGURE 8 Initial rate of formation of hydroxyl radicals during hydrogen peroxide bleaching of two different pulps (A and B) with various additives:

Pulp A		**Pulp B**	
Exp.	Additive	Exp.	Additive
A1	No additive	**B1**	No additive
A2	0.9% DTPA	**B2**	0.9% DTPA
A3	4% Silicate	**B3**	4% Silicate
A4	0.9% DTPA and 0.2% Fe^{3+}	**B4**	0.9% DTPA and 0.2% Fe^{3+}
A5	0.2% Fe^{3+}	**B5**	Washed with DTPA No additive
		B6	Washed with DTPA 4% Silicate added

All chemicals are calculated on o.d. pulp.

Pulp A was prebleached with hydrogen peroxide and pretreated with DTPA, whereas pulp B was untreated.

Temperature 60 °C; Hydrogen peroxide and NaOH 4% each; Initial pH≈11.7; Phthalic hydrazide 0.7%.

peroxide. In Fig. 10, this quantity is plotted against the initial rate of formation of hydroxyl radicals. In this graph, the behaviour of both pulps is described by the same curve at low initial rates of formation of hydroxyl radicals. The maximum bleaching efficiency seems to lie close to point A3, corresponding to the pretreated pulp to which sodium silicate had been added. Apparently, silicate has an unique

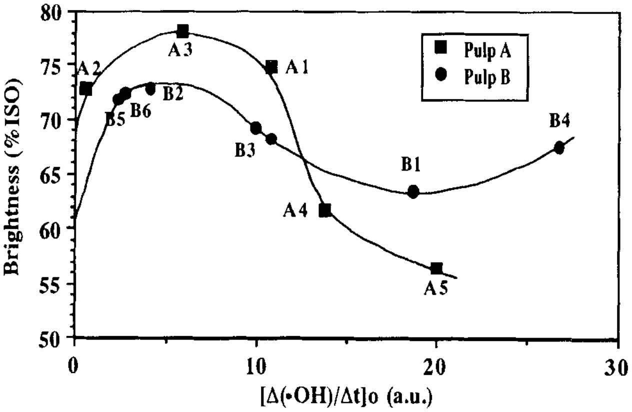

FIGURE 9 Final brightness of the bleached pulps plotted against the initial rate of formation of hydroxyl radicals.
Legends as in Fig. 8.
Initial brightness: Pulp A: 68.3 %ISO, Pulp B: 60.3 %ISO.

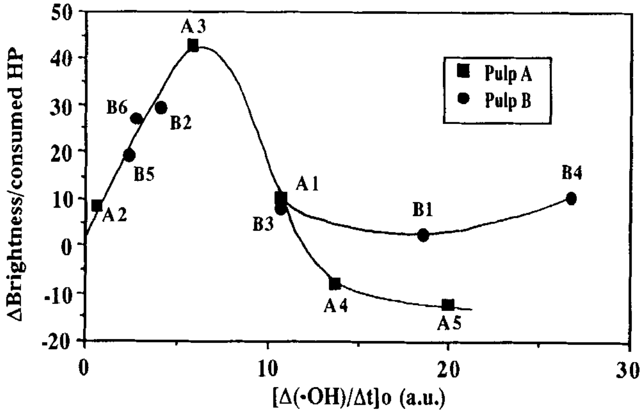

FIGURE 10 The change in brightness divided by the consumption of hydrogen peroxide (HP) plotted against the initial rate of formation of hydroxyl radicals. Legends as in Fig. 8

ability to stabilize hydrogen peroxide without appreciably suppressing the formation of hydroxyl radicals.

Mechanical pulps still contain most of the lignin originally present in the wood. This implies that hydroxyl radicals formed during bleaching react preferentially with the lignin component due to their facile addition to aromatic structures[10, 13]. This preference is likely to be accentuated by the site-specific generation of hydroxyl radicals at lignin centres to which transition metal ions are linked, in particular, to phenolic moieties. The positive effect of hydroxyl radicals on the result of hydrogen peroxide bleaching may thus be ascribed to:

1) Oxidation and destruction of chromophoric and potential chromophoric groups in the lignin.

2) Cleavage of cross-links in the rigid lignin matrix facilitating the penetration of bleaching reagents.

The first alternative appears less probable, since it is unlikely that extremely reactive hydroxyl radicals specifically destroy chromophoric and potential chromophoric groups in the lignin. It should be noted, however, that superoxide radical anions arise concurrently with hydroxyl radicals (eqs. [2] and [5]). Due to the low pKa-value of the corresponding conjugate acid ($HO_2^{\bullet}$, $pK_a = 4.8$), superoxide anions may be thought to penetrate from the alkaline solution more deeply into the fiber than hydrogen peroxide anions (H_2O_2, $pK_a = 11.6$) and attack certain chromophores nucleophilically.

The second alternative is supported by a two-stage hydrogen peroxide bleaching study recently reported[6]. The first stage involved treatment of the pulp in a slightly acidic solution (pH 5-6) in the presence of chromium ions which are known to degrade hydrogen peroxide under the conditions employed. No increase in brightness was observed after this step. However, after a subsequent step comprising a conventional treatment with alkaline hydrogen peroxide, a significant increase in brightness was obtained compared with that after a usual one-stage alkaline peroxide bleaching. This shows that the degradation products from hydrogen peroxide do not *per se* exert a bleaching effect on the pulp, but they probably make chromophores and potential chromophores in an otherwise inaccessible core of the lignin available to reactions with hydroperoxide anions.

CONCLUSIONS

The results of this work lend support to the view that the decomposition of alkaline hydrogen peroxide proceeds via two types of redox processes catalyzed by transition metal ion species. The first type involves a one-electron reduction of hydrogen peroxide with the formation of hydroxyl radicals and is ascribed to the action of mononuclear transition metal ion complexes. The second type is a heterogeneous surface-catalyzed process caused by colloidal polynuclear transition metal oxides/hydroxides and proceeds mainly by two consecutive one-electron transfer steps. This decomposition mode gives molecular oxygen and water but no free hydroxyl radicals.

The addition of sodium silicate does not appreciably suppress the formation of hydroxyl radicals in alkaline hydrogen peroxide solutions. The stabilizing effect of sodium silicate is probably due to a deactivation of finely dispersed colloidal particles of metal hydroxides and hydrated oxides which protects hydrogen peroxide against the second type of decomposition.

During hydrogen peroxide bleaching of pulp, a limited formation of hydroxyl radicals has a beneficial effect on the final brightness. This is ascribed to the cleavage of cross-links in the rigid lignin matrix which facilitates the penetration of the bleaching reagent(s).

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