IMPROVEMENT IN HYDROGEN PEROXIDE BLEACHING BY DECREASING MANGANESE-INDUCED PEROXIDE DECOMPOSITION

by

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ABSTRACT

This work is designed to find effective ways to minimize manganese-induced peroxide decomposition. Under alkaline conditions, manganese, at its high oxidation state, $Mn(+III)$, is much more reactive to catalyze hydrogen peroxide decomposition than $Mn(+II)$ when the same stabilizers, such as DTPA, magnesium sulfate, sodium silicate were added under the same conditions. DTPA was found to be able to reduce $Mn(+III)$ to $Mn(+II)$ under slightly acidic conditions. Subsequent addition of more DTPA to the reduced manganese containing system results in a decreased peroxide decomposition.

Hydrogen peroxide, under acidic conditions, can reduce manganese in its high oxidation state, $Mn(+III)$, to its low oxidation state, $Mn(+II)$. Such a reaction takes place stoichiometrically, not catalytically. Subsequently, the addition of conventional stabilizers, such as magnesium sulfate and sodium silicate, will decrease the peroxide decomposition. Results obtained from applying this concept to bleaching of a TMP have shown that the bleaching performance is improved. in terms of both the brightness gain and hydrogen peroxide consumption, when compared with conventional peroxide bleaching.

Two other methods, namely, nitrogen purge and the addition of neutralized sodium silicate and magnesium sulfate, were also investigated to decrease the oxidation of low valence manganese. It was found that both of the methods can decrease the manganese-induced peroxide decomposition.

ACKNOWLEDGEMENTS

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NOMENCLATURE

TCF	Totally Chlorine Free
DTPA	Diethylenetriaminepentaacetic Acid
EDTA	Ethylenediaminetetraacetate Acid
Q	Chelation Stage
P	Alkaline Hydrogen Peroxide Stage
TMP	Thermomechanical Pulp
o.d.	Oven Dried
SGW	Stone Groundwood Pulp
% ISO	International Standards Organization Brightness
CTMP	Chemithermomechanical Pulp
CPPA	Canadian Pulp and Paper Association
TAPPI	Technical Association of Pulp and Paper Industry

CHAPTER 1

INTRODUCTION

1.1 General Introduction

In recent years environment friendly bleaching techniques have been developed rapidly and many mills have adopted these techniques. Historically, pulp has been bleached with chlorine gas, but the emission of chlorinated organics made this method obsolete. Totally chlorine free (TCF) bleaching has received much attention. Hydrogen peroxide is one of leading chemicals in TCF bleaching.

Some transition metal ions like Mn, Cu, Fe catalyze H_2O_2 decomposition; Other ions (e.g. Mg^{2+}) inhibit the peroxide decomposition. Although both types of metal ions are present in wood and consequently in pulp, the overall effect is a drastic increase in H_2O_2 decomposition [1]. Moreover, the metal ions in process water may further cause enhanced peroxide decomposition. Therefore, optimal H_2O_2 bleaching requires a careful management of the metal ions present in the system. Stabilizing agents such as sodium silicate, magnesium salts, and complexing agents such as DTPA (diethylenetriaminepentaacetic acid) and EDTA (ethylenediaminetetraacetate acid) are commonly used to reduce metal ions induced peroxide decomposition.

1.2 Objectives

The most detrimental metal among the transition metal ions is manganese, followed by iron and copper [2, 3]. It has been demonstrated that the catalytic effect of manganese is dependent on its oxidation state: high valence manganese acts as a decomposition catalyst, while its low valence form has a much less harmful effect [4]. The purpose of this thesis is to determine how the different oxidation states of manganese

catalyze the hydrogen peroxide decomposition and how to use available techniques to decrease hydrogen peroxide decomposition, thereby maximizing the peroxide bleaching efficiency.

1.3 Outline of the Thesis

This thesis studied the relation between the oxidation states of manganese and alkaline hydrogen peroxide decomposition, based on the fact that higher valence of manganese is much more effective than its lower valence counterpart in decomposing hydrogen peroxide under peroxide bleaching conditions. Several strategies have been investigated to decrease the catalytic activities of higher valence form of manganese, thus decreasing or completely inhibiting the manganese-induced peroxide decomposition during alkaline peroxide bleaching.

The relevant literature review on hydrogen peroxide bleaching, hydrogen peroxide decomposition, manganese at its different oxidation states and their relevance to hydrogen peroxide decomposition, and the use of DTPA as a chelant to minimize the peroxide decomposition is presented in chapter 2.

In chapter 3, the use of DTPA as the sole stabilizer to decrease hydrogen peroxide decomposition is studied. The results obtained from systems with or without pulp fibres are compared and the role of DTPA under acidic condition is further identified. Explanations to account for the increased DTPA charge at a higher pH are given.

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Chapter 4 describes how to use hydrogen peroxide as a reducing agent to convert higher oxidation state, Mn(+III), to lower oxidation state, Mn(+II), thus stabilizing alkaline peroxide bleaching liquor. This technique is also discussed in relation to industrial applications.

In chapter 5, two other methods, namely, nitrogen purge and the addition of neutralized sodium silicate and magnesium sulfate were successfully developed to decrease the manganese-induced peroxide decomposition.

Chapter 6 summarizes conclusions and provides recommendations for future work.

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CHAPTER 2

LITERATURE REVIEW

2.1 Hydrogen Peroxide Bleaching

Hydrogen peroxide has found its application in the pulp and paper industry as an oxidative bleaching reagent, particularly for the bleaching of mechanical pulps.

Hydrogen peroxide is a clear, colorless liquid that is available commercially as an aqueous solution in concentrations ranging from 30% to 70%. Its popularity in the pulp and paper industry resides in its non-toxic decomposition products, high brightness gain, easy handling and use. Hydrogen peroxide is rather stable under acidic conditions; however, alkaline peroxide solution decomposes readily if not stabilized. Hydrogen peroxide residual is defined as the amount of peroxide not consumed at the end of the bleaching stage as determined by analysis of a filtrate sample at the discharge of the bleach tower. In the bleaching of (chemi)mechanical pulps, it is of great importance to maintain a residual peroxide level of approximately 10% of the original application for peroxide applications of less than 2.5% in bleach plants, while for high consistency bleach plants and a higher peroxide applications (3-6% in a single stage), residual peroxide levels are commonly in the range of 30% or more of the applied amount [1]. A low or no residual at the bottom of the bleaching tower is a signal of problems, namely, that hydrogen peroxide decomposition is too extensive during bleaching.

The perhydroxyl anion, HOO⁻, is generally accepted as the active bleaching species in alkaline hydrogen peroxide systems. Although the anion is normally present in equilibrium with undissociated hydrogen peroxide, the formation of the anion can be regulated by increasing or decreasing the pH and temperature [1]. As illustrated in the

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following equation, the addition of an alkaline source to a peroxide solution forces the equilibrium to the right.

$$H_2O_2 + OH^- \rightarrow OOH^- + H_2O \tag{1}$$

The peroxide bleaching chemistry for chemical and mechanical pulps is different in that for chemical pulp the goal is to maximize the removal of lignin while for mechanical pulp the objective is to brighten the pulp with almost no dissolution of wood constituents, thus preserving pulp yield [2]. The brightening of (chemi)mechanical pulps is achieved by selectively eliminating chromophores. During bleaching, perhydroxyl anion (OOH⁻), which is a strong nucleophile, converts electron-rich chromophores typified by α, β-unsaturated aldehydes and ketones, and phenolic ring-conjugated ethylenic or carbonyl groups to their non-chromophoric counterparts. Although these chromophore elimination reactions are accompanied by chromophore formation reactions, the resulting brightness gain or loss is an expression of the extent to which one type of reaction outweighs the other [3].

Until recently, hydrogen peroxide had not been widely used in the bleaching of kraft pulps because bleaching economics favored using chlorine or chlorine dioxide. Current and proposed environmental regulations on the discharge of chlorinated organics in chlorine-based bleaching have accelerated commercial use of hydrogen peroxide to partially or completely eliminate chlorine containing compounds in kraft pulp bleaching. Bleaching chemical pulps to high brightness with alkaline hydrogen peroxide has been considered to require: 1) the elimination of conjugated carbonyl groups in the lignin

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structures by the perhydroxyl anion (OOH⁻), 2) a substantial removal of lignin, through

degradation/dissolution, by reaction with hydroxyl (HO·) and superoxide anion (O_2^-)

radicals [4]. However, the reactivity of HO· and O_2^- towards aromatic lignin (phenonic

structure) is only slightly higher than towards cellulose (primary and secondary alcohols).

Therefore, if H_2O_2 decomposes too fast and the concentrations of HO· and O_2^- become

too high, selectivity towards lignin is lost and cellulose degradation occurs as well as

lignin degradation. Thus, it is necessary to control hydrogen peroxide decomposition

during kraft pulp bleaching.

2.2   Hydrogen Peroxide Decomposition

In order to understand the effects of metal ions on peroxide decomposition, a clear

perspective of the H_2O_2 decomposition mechanism is helpful. The mechanism proposed

to account for hydrogen peroxide decomposition has been a subject of much discussion in

the literature. Colodette *et al.* [5] have summed up the following five mechanisms: (1) a

base-catalyzed ionic mechanism involving the combination of undissociated hydrogen

peroxide and its conjugated base (perhydroxyl anion) to form a six-membered ring in the

transition state; (2) a base-catalyzed free radical chain reaction mechanism involving

hydroxyl and superoxide anions radicals; (3) a transition metal ion-catalyzed free radical

chain reaction mechanism involving hydroxyl and superoxide anions radicals; (4) a

transition metal reaction with perhydroxyl ions to form unstable peroxides or complexes;

and (5) a heterogeneous surface-catalyzed reaction caused by colloidal transition metal

oxides/hydroxides.

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Under acidic conditions free from impurities, hydrogen peroxide with a dissociation constant of approximately 10^{-11} at 60°C is remarkably stable and can be stored for many months with negligible loss of available oxygen [6]. In alkaline conditions hydrogen peroxide undergoes a rapid decomposition; this is particularly so if transition metal ions are present. One of the proposed mechanism is as follows [4]:

$$H_2O_2 + M \rightarrow HO^- + HO^- + M^- \qquad (2)$$

$$M^- + HO_2^- + HO^- \rightarrow M + O_2^- + H_2O \qquad (3)$$

$$M^- + O_2^- \rightarrow M + O_2 \qquad (4)$$

$$O_2^- + HO^- \rightarrow O_2 + HO^- \qquad (5)$$
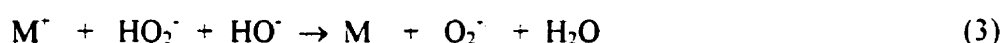
where M represents transition metal ions.

These reactions show that the presence of metal ions which can readily change oxidation states will trigger a catalytic cycle resulting in the rapid decomposition of hydrogen peroxide. Metals differ in their ability to catalyze H_2O_2 decomposition. Since metal ions are alternately oxidized and reduced, those with higher electron transfer rate result in higher metal catalyzed H_2O_2 decomposition rates [6]. Among various transition metal ions it was reported [1,7,8] that manganese represents the most harmful effect during alkaline peroxide bleaching.

2.3 Manganese Chemistry and its Relevance to Hydrogen Peroxide Decomposition

Manganese may originate from the wood and is loosely, but, homogeneously complexed with wood components. Due to partial closure system, manganese can accumulate in the process water. Simulations have predicted that if all the Mn redoposits

onto the pulp fibre, then a large increase in the Mn concentration fed to the bleach plant will result [9,10].

Manganese has seven valance electrons $(3d^5 4s^2)$ and exists in its ions and compounds in positive oxidation states of 2,3,4,6 and 7. The divalent state Mn(+II) is the most stable oxidation state for the element. In neutral or acid aqueous solution it exists as the very pale pink hexaaqua ion $[Mn(H_2O)_6]^{2+}$, which is quite resistant to oxidation. In basic media, however, it is quite readily oxidized [11]. The oxidation reaction paths in the laboratory synthesis of manganese oxides at 25°C and one atmosphere pressure are shown in Fig. 2.1 [12]. In every case, with the possible exception of the mixture of Mn_3O_4 and β-MnOOH (hydrohausmannite), $Mn(OH)_2$ is precipitated first. It seems that as drops of strong base enter the Mn^{2+} solution, local supersaturation could cause precipitation of $Mn(OH)_2$. It was found that the most highly oxidized compound that could be synthesized using air/oxygen was γ-MnOOH.

$MnSO_4$ is quite stable and can be used as the source of Mn(+II) and/or its analysis. Dissolved manganese in the manganous state is not a catalyst itself for hydrogen peroxide decomposition [13,14].

Trivalent manganese ion is a strong oxidizing agent. It is most stable in acid solutions. The cinnamon brown triacetate $Mn(OAC)_3 \cdot 2H_2O$ is the simplest isolable carboxylate complex of Mn(+III). MnOOH occurs in native manganite. Ni et $al.$ [14] have proposed that MnOOH could be the cause of accelerated alkaline hydrogen

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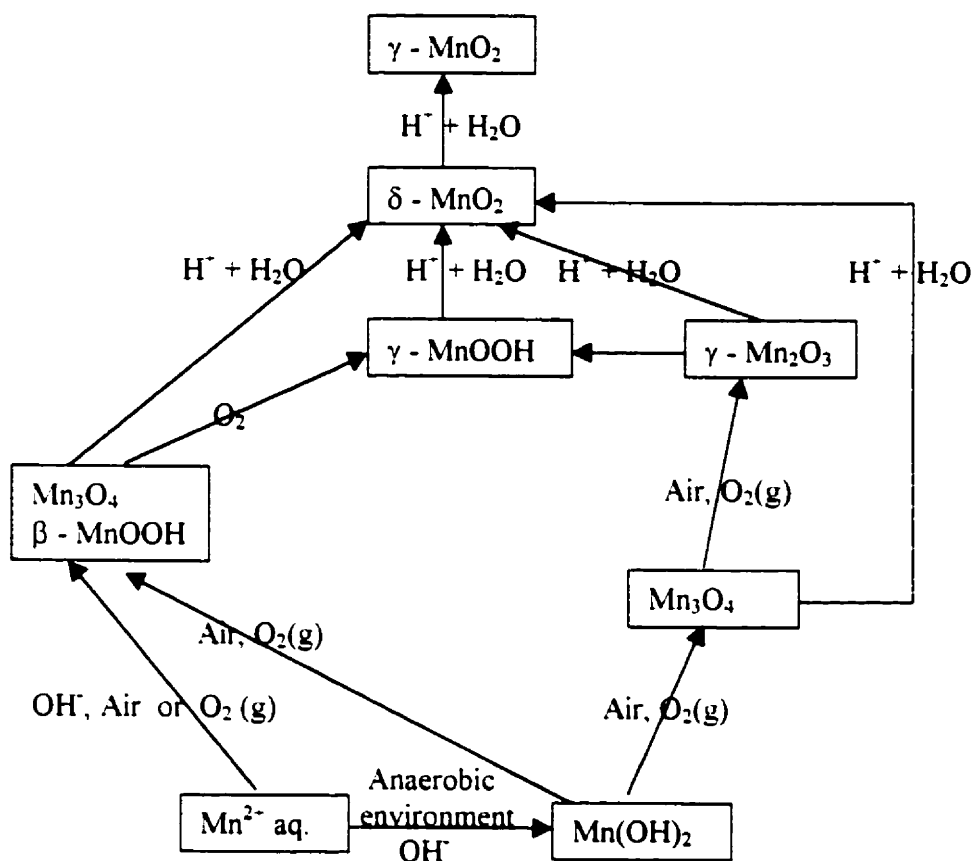
Fig. 2.1 Reaction pathways in the system $Mn-O_2-H_2O$ at $25^{\circ}C$ and one atmosphere total pressure [12]

peroxide decomposition.

Mn(+IV) has been ascribed to an increased rate of hydrogen peroxide decomposition by many authors. Agnemo and Gellerstedt [15] pointed out that Mn(+IV) greatly accelerate the reaction between hydrogen peroxide and α-methylsyringyl alcohol due to an increased rate of hydrogen peroxide decomposition. It was shown that the addition of Mn(+IV) or Fe(+III) ions to a solution containing hydrogen peroxide, alkali, sodium silicate and DTPA is able to decompose hydrogen peroxide, thus leading to an increased rate of oxidation of acetoguiacone. On the other hand, addition of Mn(+II) or Fe(+II) does not affect the oxidation rate to any noticeable extent. A study by Broughton and Wentworth [13] revealed that when manganous ion is added to very dilute hydrogen peroxide solutions of various alkalinities, no catalysis occurred until the solubility product for $Mn(OH)_2$, approximately 10^{-14}, is reached. They noticed exchange occurs between manganous ion and colloidal manganese dioxide as the decomposition takes place, thereby postulating a mechanism:

$$MnO_2 + H_2O_2 + 2H^- \rightarrow Mn^{2-} + 2H_2O + O_2 \qquad (6)$$

$$Mn^{2-} + 2H_2O \rightarrow Mn(OH)_2 + 2H^- \qquad (7)$$

$$Mn(OH)_2 + H_2O_2 \rightarrow MnO_2 + 2H_2O \qquad (8)$$
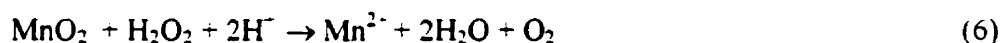
However, it is known that the composition of manganese dioxide seldom corresponds exactly to the formula MnO_2 and that the oxide having this exact composition is a weak catalyst. Mooi and Selwood [16] found that the activity is at a maximum when the oxidation state of manganese is between +3 and +4, and an oxidation-reduction cycle involving manganese dioxide and Mn_2O_3 was therefore suggested. Kutney and Evans [8] identified the black colored Mn(+IV) precipitates as an active peroxide decomposition

catalyst. Lidén and Öhman [17] observed a stronger brightness reversion caused by a mixture of several oxidation states in the manganese precipitate.

It has also been demonstrated [14] that the catalytic effect of manganese in decomposing alkaline peroxide solutions is dependent on its oxidation state: high valence manganese is much more reactive than its low valence form under peroxide bleaching conditions. The addition of chemicals, such as magnesium sulfate and sodium silicate, is proved to be effective in reducing the manganese-induced peroxide decomposition. Ni *et al.* [14] also found that when manganese in pulp fibres is present in Mn(+III), a reduction to Mn(+II) by an acid treatment followed by the addition of $MgSO_4$, Na_2SiO_3 and/or chelants can significantly improve the stability of manganese containing alkaline peroxide solution against decomposition.

2.4   The Use of DTPA

DTPA is traditionally the chemical of choice to remove transition metal ions from mechanical pulp in a pretreatment stage due to its higher oxidative stability with hydrogen peroxide and its ability to form highly stable metal ion complexes in comparison to other commercial chelants [18]. The chelant is usually thoroughly mixed with the stock before the hydrogen peroxide bleach solution is added. A convenient procedure for this is to add the chelant to the low consistency stock in the cleaning system, or when the stock is delivered to the decker. The chelated metals are then removed during the dewatering phase, and the total metal ion concentration in the pulp is significantly reduced. However, as new process technologies and the need for increased

brightness have emerged, addition of chelating agents for effective metal ion management has shifted to an alternate location(s), (i.e. chip impregnation, bleach liquor) in the process [18].

The metals in the pulp are reduced and converted to their sulfides and hydroxides during alkaline kraft pulping and those metal ions become insoluble and remain strongly attached to the pulp fibres. So the function of a strong chelating agent, such as DTPA and EDTA, is to displace the metals, making them soluble in the form of metallic DTPA or EDTA complexes and then removed by washing [4]. The washing step is critical since chelation alone does not necessarily remove the H_2O_2 catalytic properties of a metal. The rate of electron transfer can be either increased or decreased by complexation with the metal ion [6]. For example, the catalytic activity of the Fe-DTPA chelate is higher than Fe, while the activity of the Mn-DTPA chelate is lower than Mn^{2+} [15].

Bryant and Edwards [9] reported an optimum pH range for DTPA chelation of Mn is 4.5-5.5 for kraft pulp. It was also noted that consistency has a small but measurable impact on Mn removal efficiencies in acidic DTPA chelation. At the same time, increasing the DTPA applied from 0.1% to 0.4% increases the Mn removal efficiency from 92% to 96% while a further increase to 2.0% DTPA increases removal efficiency to 97%. DTPA can effectively form complexes with manganese even in alkaline solution (pH 10-11) [19], and when used in a slight stoichiometric excess, DTPA can bind 60% of manganese.

It was shown [11] that manganese(+II) and iron(+II) can be protected against oxidation in highly alkaline and oxidative environments by being incorporated in magnesium precipitates in the presence of wood pulp or an anionic polymer, thus their catalytic action through a cyclic alteration of oxidation state in a Fenton-type reaction is disrupted. Bambrick [20] proposed that Na_5DTPA, as a negatively charged compound, can form a ringed structure with positively charged ions, such as Mn^{2+}. This new complex, $Na_5MnDTPA$, is stabilized by an overall negative charge and the metal ion is thus inhibited from entering into undesirable reactions.

The use of DTPA as a sequestering agent for TMP has been investigated by Prasakis et al. [21]. Their study showed that for a chelation temperature varying from $23^{\circ}C$ to $60^{\circ}C$ manganese removal is constant for both DTPA and EDTA. Chelant concentration plays an important role in sequestering manganese and should be set at a maximum of 0.5% (40% active) on o.d. pulp for all chelants studied. pH is an important factor in sequestering metal ions.

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CHAPTER 3

USING DTPA TO DECREASE MANGANESE-INDUCED PEROXIDE

DECOMPOSITION

3.1 Abstract

The catalytic activity of Mn(+II) and Mn(+III) in decomposing hydrogen peroxide was studied by using DTPA as the only stabilizer. It was found that the addition of DTPA to Mn(+II) containing system is more effective than if it is added to Mn(+III) containing system. To decrease the catalytic effect of Mn(+III), sodium borohydride and DTPA under acidic conditions were considered to reduce Mn(+III) to Mn(+II). The effect of pH on using DTPA to decrease the Mn-induced peroxide decomposition was studied and discussed.

3.2 Introduction

The control of hydrogen peroxide decomposition is critical to peroxide bleaching. The decomposition of peroxide is greatly enhanced in the presence of transition metal ions, resulting in less active chemical available for bleaching. Among various transition metal ions, it was reported [1,2] that manganese is the most harmful species during alkaline peroxide bleaching. Therefore, it is a common practice for pulp mills to perform a chelation stage with chemicals, such as DTPA and EDTA, as pretreatment to remove transition metal ions from pulp fibres.

It has been realized that $Mn(+II)$ is much less effective than $Mn(+III)$ and/or $Mn(+IV)$ in decomposing hydrogen peroxide under the bleaching conditions [3,4,5]. Based on recent studies [4,5,6], it is most likely that $Mn(+III)$ is involved in the process of catalytic hydrogen peroxide decomposition, and its mechanism is that manganese changes its oxidation states in a cyclic manner. The utilization of magnesium sulfate, sodium silicate to stabilize manganese containing peroxide solutions has been well documented [4,5,7,8]. The use of chelate Na_5DTPA (pentasodium salt of diethylenetriaminepentaacetic acid), in conjunction with magnesium salt and sodium silicate, was also studied to reduce peroxide decomposition [5,8]. In this paper, we studied to use DTPA as the only stabilizer, to decrease the Mn-induced peroxide decomposition. The objectives are

-   to examine the effect of the oxidation states of manganese, e.g. $Mn(+II)$, $Mn(+III)$, on the stability of alkaline peroxide solutions when using DTPA as the only stabilizer

- to study potential techniques to decrease the Mn-induced peroxide decomposition.

3.3 Experimental

All hydrogen peroxide decomposition runs were carried out in a 100 mL polyethylene bottle. DTPA was prepared by dissolving H₅DTPA (diethylenetriaminepentaacetic acid), which was obtained from Aldrich Chemical Co., in an alkaline solution, and the solution was then neutralized. Manganese sulfate monohydrate, Mn(+III) acetate bihydrate, sodium hydroxide, sulfuric acid, sodium borohydride, hydrogen peroxide from Fisher Scientific were used without any further purification. Deionized and distilled water was used throughout all the experiments. In all the decomposition runs involving pulp fibres, a bleached sulfite pulp, which was chelated with 0.2% DTPA at 70°C for 30 min and followed by a thorough washing, was used. with pulp fibres, the pulp was added prior to the addition of sodium hydroxide and hydrogen peroxide in all these cases.

In the runs where Mn(+III) acetate was reduced either by NaBH₄ or by the combination of NaBH₄ and DTPA, the Mn(+III) containing solution was first adjusted to pH 9.0. After addition of the reducing agent(s), the solution was adjusted to pH 3.5 and then placed into a temperature bath at 70°C for 10 min to achieve a complete reduction. After the solution was cooled down, 0.3 g o.d. pulp was added to the solution to make a 0.3% pulp suspension if pulp is required. Finally sodium hydroxide and hydrogen peroxide were charged in that order to carry out the hydrogen peroxide decomposition run. In some cases, a small amount of NaOH was added to reach the target pH.

For the bleaching runs, a TMP pulp from an Eastern Canadian mill was used. 10 g o.d. TMP pulp (initial brightness of 61% ISO, Mn content of about 80ppm) was dispersed into the required amount of water in a plastic bag to make the final bleaching consistency of 12%. A pre-determined amount of DTPA was charged to the pulp slurry, which was then adjusted to pH 3.5. After the treatment in a 70°C water bath for 10 min, sodium hydroxide and hydrogen peroxide were added in that order. Finally a small amount of sodium hydroxide was added to reach the initial pH. The plastic bag along with its contents was then placed to a water bath at 60°C for 120 min. The residual H_2O_2 was measured following CPPA Standard Testing Methods J16P. The brightness of bleached pulp hand sheets was measured with a TECHIBRITE™ TB-1C.

3.4   Results and Discussion

Peroxide Decomposition in the Absence of Pulp

As expected, without the addition of any stabilizers, the alkaline peroxide solution containing Mn(+II) is not stable at all, and the residual peroxide was zero after 60 min at 70°C as shown in Run #1, Table 3.1. These results are in agreement with those by Kutney and Evans [3], Ni et al. [5] and Galbács et al. [10], with or without pulp fibres.

In Run #2, 1 equivalent molar DTPA was added to a polyethylene bottle containing 3ppm Mn(+II), followed by the addition of sodium hydroxide, and then hydrogen peroxide to reach the target pH. The residual hydrogen peroxide concentration after 60 min at 70°C was 1.0 g/L, indicating that under the conditions studied, the addition of DTPA completely stabilizes the alkaline peroxide solution against

decomposition. When the DTPA to Mn molar ratio was further increased to 2, as in Run #3, the alkaline peroxide solution containing 3ppm Mn(+II) was stable again.

We then applied the same experimental approach to systems containing Mn(+III) (added as Mn(+III) acetate bihydrate), it was found that the Mn(+III)-induced peroxide decomposition is inevitable, as shown in Run #4. The addition of DTPA to Mn(+III) containing system will decrease the catalytic peroxide decomposition to some extent, as shown in Runs #5, #6 and #7; however, the stabilizing effect of DTPA by increasing DTPA charge is not as drastic as in the case of Mn(+II), where complete stabilization of alkaline peroxide solution is obtained with 1 equivalent molar of DTPA at pH 10.5. Similarly, 2 equivalent molar of DTPA can stabilize the Mn(+II) containing solution, but not the Mn(+III) containing system, at an initial pH of 11.0 as in Runs #8 and #9.

Since Mn(+II) is much more readily stabilized than Mn(+III) by increasing DTPA charge, as shown above, next, we studied the effect of reducing Mn(+III) on the stability of alkaline peroxide systems containing Mn(+III). In Run #10, Table 3.2, sodium borohydride was chosen as the reducing agent. The pH was 10.5 and the DTPA/Mn molar ratio was 2. Evidently, the stability of the peroxide solution was improved significantly as the residual H_2O_2 concentration was 0.99 g/L. This is compared to a residual H_2O_2 concentration of 0.61 g/L of Run #6, Table 3.1, which was obtained without the reduction of Mn(+III) by sodium borohydride, under otherwise the same conditions. Run #11 in Table 3.2 shows the result by reducing Mn(+III) with sodium

borohydride, then carrying out the decomposition run at pH 11.0 and DTPA/Mn molar ratio of 2. Again, a much-improved peroxide stability is evident.

In Run #12, DTPA (DTPA/Mn molar ratio was 2) was added to Mn(+III) solution and the solution pH was decreased from 9 to 3.5. The original brown solution, characteristic of Mn(+III) solution, disappeared. This may indicate that Mn(+III) is reduced to Mn(+II) by DTPA. Subsequently, sodium hydroxide and peroxide solution were added in that order. A small amount of sodium hydroxide was finally added into the solution to bring the pH to 11. The residual peroxide concentration was 0.79 g/L, which is substantially higher than 0.38 g/L as shown in Run #9, where no acidification was carried out after DTPA was added to Mn(+III) solution. These results suggest that the reduction of Mn(+III) by DTPA to Mn(+II) needs an acidic condition. At the same time, the increase in DTPA charge results in further improvement in the stability of peroxide solutions as shown in Runs #13 and #14, which were conducted by following the same procedure as that in Run #12 except that the DTPA/Mn ratio was 3 and 4 respectively. This is due to the fact that more DTPA is available to complex with Mn(+II), leading to less manganese hydroxide to be formed, as will be discussed in subsequent sections.

With respect to the mechanism of the reduction of Mn(+III) to Mn(+II) by amino acid based chelants, Schroeder and Hamm [11] reported that EDTA can reduce Mn(+III) to Mn(+II) and that carbon dioxide and formaldehyde are the products from EDTA. Fig. 3.1 illustrates the proposed reactions. They found that the reaction can proceed in the pH range of 2 to 5. Since DTPA and EDTA have similar structure, it may be reasonable to

assume that DTPA can reduce Mn(+III) to Mn(+II) under a slightly acidic condition, as evidenced by above results. Lidén and Öhman [4] also pointed out that DTPA can reduce manganese(+III) compound at slightly acidic solution due to the high oxidation potential of manganese(+III), based on the transition of the pink-colored Mn(+III)(EDTA)⁻ complex to the colorless $Mn(+II)(EDTA)^{2-}$ complex at pH 5.

Effect of Pulp Fibres

We continued the study by determining the effect of pulp fibres on the Mn-induced peroxide decomposition. The results obtained at pH 10.5 are presented in Table 3.3. In Run #15, 2 equivalent molar of DTPA were added to a Mn(+II) containing polyethylene bottle. This was then followed by the addition of pulp fibres. Subsequently, sodium hydroxide and hydrogen peroxide were added in that order to the polyethylene bottle. Finally a small amount of sodium hydroxide was added to reach the target pH. The residual hydrogen peroxide concentration after 60 min at 70°C was 0.99 g/L, indicating that the peroxide decomposition under the conditions tested is very small, if any. Also, in comparison with Run #3, Table 3.1, one may conclude that the presence of pulp fibres has a negligible effect on the peroxide decomposition.

In Run #16, 2 equivalent molar of DTPA were added into a Mn(+III) containing solution at pH 10, which is the natural pH of a 3ppm Mn(+III) acetate containing solution. Note that no acid was added here. The subsequent procedure was the same as Run #15. The residual hydrogen peroxide was 0.67 g/L after 60 min at 70°C. This is compared with 0.93 g/L residual hydrogen peroxide concentration in Run #17, Table 3.3,

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where sulfuric acid was added to reach a pH of 3.5, after the addition of DTPA to the Mn(+III) containing polyethylene bottle. The difference in the peroxide decomposition between Runs #16 and #17 is due to the fact that reduction of Mn(+III) to Mn(+II) by DTPA occurs only at an acidic condition, not an alkaline condition.

In Run #18, both NaBH$_4$ and DTPA were used to reduce Mn(+III) to Mn(+II). The synergetic effect of reduction and stabilization renders almost no decomposition of alkaline peroxide solution. As long as Mn(+III) is reduced to Mn(+II) by NaBH$_4$ at various NaBH$_4$/Mn ratios, the addition of DTPA always stabilizes the subsequent alkaline peroxide solution.

Lidén and Öhman [4] noticed the difference in redox stability of manganese in the presence and absence of pulp. It was concluded that pulp fibres impart a colloidal nature to the magnesium precipitates formed, thus giving more efficient protection against catalytic peroxide decomposition during pulp bleaching. They proposed that the carboxylate groups on the pulp may be involved in the redox stabilization and help to stabilize manganese in the +II oxidation state by changing the physical characteristics of the coprecipitate when magnesium ions are present. However, the results in our system using only DTPA as stabilizer show that the presence of pulp has no effect on the stability of alkaline peroxide solutions containing manganese, when comparing Runs #15 and #16 of Table 3.3 with Runs #3 and #6 of Table 3.1, respectively. Our explanation is as follows: when DTPA is used as the only stabilizer, since it is a stronger chelant for transition metal ions than the carboxylate groups in pulp fibres, manganese present in the

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system is preferably complexed with DTPA, rather than carboxylates. Therefore, when DTPA is added, the carboxylate effect, and thus the pulp effect is negligible.

We also studied the reduction of Mn(+III) by NaBH₄ or DTPA on the stability of alkaline peroxide solutions containing Mn(+III) in the presence of pulp fibres at pH 11.0 and the results are shown in Table 3.4. In comparison with those results in Table 3.3, one can conclude that at pH 11.0, 2 equivalent molar DTPA is not adequate to stabilize the reduced Mn(+II) and that a good stabilization is achieved only at a higher DTPA/Mn molar ratio. These are in agreement with the results in Table 3.2 in the absence of pulp fibres, and may be explained by the hypothesis that an increase in pH will lead to a decrease in the chelating ability of DTPA. In a system consisting of manganous ions, DTPA and hydroxide ions, there is a competition between chelating agent and hydroxide ions for Mn^{2+}, since at a higher pH, manganous ions will tend to form $Mn(OH)_2$ and $(MnDTPA)^{3-}$ complex [12] as illustrated in the following reactions:

$$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2 \tag{1}$$

$$Mn^{2+} + DTPA^{5-} \rightarrow (MnDTPA)^{3-} \tag{2}$$
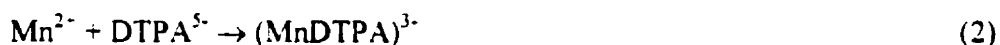
At a higher pH, more OH⁻ ions are present in the system, therefore, more Mn^{2+} are in the form of manganous hydroxide, $Mn(OH)_2$, while relatively speaking, less are chelated with DTPA via Reaction 2. However, this can be compensated by a higher DTPA concentration by adding more DTPA to the system. This, then, is responsible for the experimental evidence that at a higher pH, more DTPA is needed to stabilize alkaline peroxide solution against Mn-induced peroxide decomposition.

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A more quantitative explanation for the results in Table 3.4 is from the conditional stability constant, $K_{M'L'(ML)'}$, defined as

$$K_{M'L'(ML)'} = \frac{([ML])}{(M')(L')}$$

where (M') is the total concentration of metal in a solution that is not chelated

(L') is the total free chelating agent

$([ML]')$ is the total metal chelate concentration

It is known that the conditional stability constant is a more practical expression of chelate strength than a simple stability constant, K_{ML}. The conditional stability constant has been corrected for metal which is complexed with OH^- and the chelating agent for interaction with H^+; and the chelate corrected for chelates which include OH^- or H^- [11]. The conditional stability constant of $(DTPA-Mn)^{3-}$ reaches a maximum at pH 10.5, which is very close to pK_5 of DTPA, 10.42 [13]. A further increase in pH beyond 10.5 leads to a decrease in the conditional stability constant, resulting in more peroxide decomposition under otherwise the same conditions. Moreover, the influence of side reactions can be evaluated by the calculation of side-reaction coefficients, which is defined by the ratio of metal ion concentration that has not reacted to yield the products of the main complexation reaction to the total metal ion concentration. The side-reaction coefficient for complexation equilibrium between Mn^{2-} and DTPA increases from 14.27 at pH 10.5 to 14.47 at pH 11 [14]. These may be also used to explain the observation, most recently made by Lidén and Öhman [7], that the effect on adding DTPA or EDTA to improve

peroxide bleaching of chemical pulps is rather poor since the pH under these conditions is much higher than 10.5.

Based on the results presented in the previous sections one can draw the conclusion that when DTPA is used as the stabilizer for Mn(+II), either from $MnSO_4$ itself or from the reduction of Mn(+III), the Mn-induced peroxide decomposition is negligible at pH 10.5 and 11.0, provided that the DTPA charge is sufficient. Its underlying mechanism could be that the Mn^{2-}-DTPA complexes with a pKa value of 15.1 are so chemically stable that the redox cycle of manganese, which is responsible for decomposing hydrogen peroxide, is stopped.

Bleaching of TMP Pulp at Various DTPA Charges

We then studied to bleach a TMP pulp by a peroxide stage with DTPA as the only stabilizer. The DTPA charge was varied. DTPA was mixed to pulp fibres and the pH of the mixture was adjusted to 3.5, see Experimental for details. Results are illustrated in Table 3.5. In Run #26, no DTPA or other stabilizers was added, and thus the peroxide decomposition occurs extensively, resulting in poor brightness gain and no residual H_2O_2 at the end of bleaching. In Runs #27, #28, and #29, when more and more DTPA was used, the bleaching performance, as expected, becomes better and better; although, further benefit arising from DTPA charge of more than 1% is difficult to be justified.

Based on the results presented in previous sections, one may understand that the function of DTPA is two-fold: 1) to reduce the high oxidation state manganese which may be present in the pulp fibres, 2) to chelate the reduced form manganese, either from previous reduction step or from original pulp fibres.

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3.5 Conclusions

DTPA, as the only stabilizer, was studied to decrease the manganese-induced peroxide decomposition. The results showed that the addition of DTPA to Mn(+II) containing system is more effective than if it is added to Mn(+III) containing system. Furthermore, the higher reactivity of Mn(+III) in catalyzing peroxide decomposition can be retarded by reducing Mn(+III) to Mn(+II) and by stabilizing the reduced manganese with DTPA. Sodium borohydride and DTPA under an acidic condition can serve well to reduce Mn(+III) to Mn(+II). The results obtained from systems with or without pulp fibres are very similar. At a higher pH, more DTPA is needed to minimize the peroxide decomposition, and this is explained by the fact that hydroxide ions are competing with DTPA for the transition metal ions.

3.6 References

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Table 3.1   Addition of DTPA to Mn(+II) or Mn(+III) containing systems to decrease the Mn-induced peroxide decomposition in the absence of pulp

(3ppm Mn(+II) or Mn(+III), initial H_2O_2 1.0 g/L, 70°C, 60 min)

Run #	Initial pH	Mn Oxidation State	DTPA/Mn Molar Ratio	Residual H_2O_2 (g/L)
1		Mn(+II)	0	0
2		Mn(+II)	1	1.0
3		Mn(+II)	2	1.0
4	10.5	Mn(+III)	0	0
5		Mn(+III)	1	0.52
6		Mn(+III)	2	0.61
7		Mn(+III)	5	0.69
8	11.0	Mn(+II)	2	0.98
9		Mn(+III)	2	0.38

Table 3.2   Reduction of Mn(+III) by NaBH₄ or DTPA on the stability of an alkaline peroxide solution containing Mn(+III) in the absence of pulp fibres

(3ppm Mn(+III), initial H_2O_2 1.0 g/L, 70°C, 60 min)

Run #	Initial pH	Reducing Agent	DTPA/Mn Molar Ratio	Residual H_2O_2 (g/L)
10	10.5	NaBH₄	2	0.99
11	11.0	NaBH₄	2	0.93
12	11.0	DTPA	2	0.79
13	11.0	DTPA	3	0.95
14	11.0	DTPA	4	0.95

Table 3.3   **Reduction of Mn(+III) by NaBH₄ or DTPA on the stability of an alkaline peroxide solution containing Mn(+III) in the presence of pulp fibres at pH 10.5**

(3ppm Mn(+II) or Mn(+III), initial pH 10.5, pulp consistency 0.3%,
initial H_2O_2 1.0 g/L, 70°C, 60 min)

Run #	Experimental Sequence	DTPA/Mn Molar Ratio	Residual H_2O_2 (g/L)
15	1. Mn(+II) 2. DTPA at pH 6 3. pulp	2	0.99
16	1. Mn(+III) acetate 2. DTPA at pH 10 3. pulp	2	0.67
17	1. Mn(+III) acetate 2. DTPA, pH 3.5, 70°C, 10 min 3. pulp	2	0.93
18	1. Mn(+III) acetate 2. NaBH₄ & DTPA, pH from 8.0 to 3.5, 70°C, 10 min 3. pulp	2	0.98 ~ 0.94

Table 3.4   Reduction of Mn(+III) by NaBH₄ or DTPA on the stability of an alkaline peroxide solution containing Mn(+III) in the presence of pulp fibres at pH 11.0

(3ppm Mn(+III), initial pH 11.0, initial H_2O_2 1.0 g/L, 70°C, 60 min)

Run #	Experimental Sequence	DTPA/Mn Molar Ratio	Residual H_2O_2 (g/L)
19	1. Mn(+III) acetate 2. DTPA, pH 3.5, 70°C, 10 min 3. pulp	2	0.57
20		2.5	0.83
21		3	0.95
22		4	0.96
23	1. Mn(+III) acetate 2. NaBH₄, DTPA, pH3.5, 70°C, 10 min 3. pulp	2	0.50
24		3	0.97
25		4	0.97

Table 3.5   Effect of DTPA charge on bleaching of TMP

(12% consistency, initial pH 11.0, H_2O_2 charge 5%, 60°C, 120 min)

Run #	DTPA Charge (%)	Residual H_2O_2 (% on pulp)	Brightness (% ISO)	Initial pH	End pH
26	0	0	61.89	11.0	9.55
27	0.2	0.47	71.87	11.0	9.32
28	1	1.62	73.07	11.0	9.00
29	5	1.64	74.72	11.0	9.78
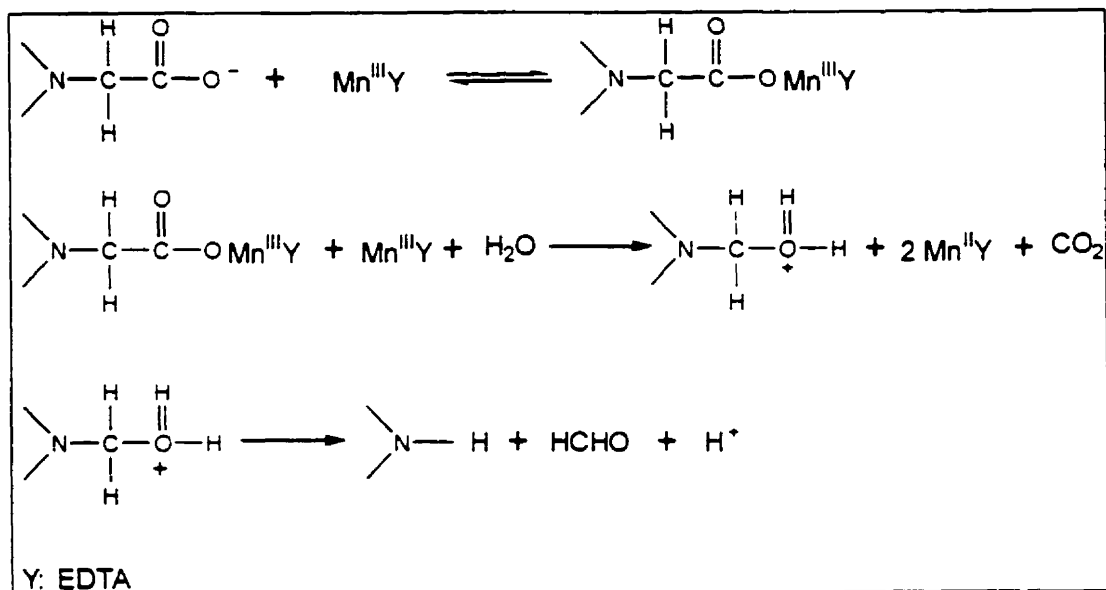
Fig. 3.1 Mechanism of Mn(+III)-EDTA reaction proposed by Schroeder and Hamm [11]

CHAPTER 4

ACIDIC HYDROGEN PEROXIDE PRETREATMENT TO IMPROVE

PEROXIDE BLEACHING OF MECHANICAL PULPS

4.1 Abstract

Pretreatment of pulp fibres with a small amount of hydrogen peroxide under acidic conditions prior to a peroxide stage can improve its bleaching performance. This is explained by the experimental evidence that hydrogen peroxide can reduce high valence manganese, Mn(+III), to its low valence form, Mn(+II), and that addition of stabilizers, such as sodium silicate and magnesium sulfate, to a Mn(+II) system is more effective in decreasing hydrogen peroxide decomposition than if they are added to a Mn(+III) system. Detailed results from a laboratory study are presented.

4.2 Introduction

Hydrogen peroxide is the most commonly used chemical to improve the brightness of mechanical pulps. Unfortunately, under the typical peroxide bleaching conditions, hydrogen peroxide decomposition is unavoidable, particularly in the presence of transition metal ions. The peroxide decomposition results in not only less hydrogen peroxide available for bleaching, but also the formation of new chromophores by the reactive species. which are the reaction intermediates during the peroxide decomposition process. Among various transition metal species available in pulp bleaching. it was reported [1,2] that manganese is the most detrimental one in catalyzing hydrogen peroxide decomposition.

Many options are available in improving peroxide bleaching. For example. Lachenal *et al.* [3] found that an acidic peroxide pretreatment prior to a typical alkaline peroxide stage leads to a considerable decrease of the H_2O_2 consumption and they proposed that the high residual H_2O_2 was attributed to the improvement of the bleaching selectivity. In bleaching mechanical pulps, Hobbs and Abbot [4,5,6] also observed that a bleaching sequence, consisting of an acidic peroxide stage and an alkaline peroxide stage. results in higher brightness than the conventional peroxide process. They explained the improved results by proposing that free radical species are generated via the decomposition of hydrogen peroxide under acidic conditions and that these free radical species may render the chromophores present in the pulp more susceptible to subsequent alkaline peroxide bleaching.

Manganese in various oxidation states has different reactivities in catalyzing peroxide decomposition [7-10]. The lower valence manganese, Mn(+II), is much less active than the higher valence species, such as Mn(+III), in decomposing hydrogen peroxide under the bleaching conditions. Implicit here is that if high oxidation state of manganese is reduced to its low valence form, the manganese-induced peroxide decomposition may be decreased, and consequently, peroxide bleaching can be improved. Although hydrogen peroxide is usually an oxidizing agent, under acidic conditions, it could be a reducing agent. One example is the hydrogen peroxide based chlorine dioxide generation process, whereby hydrogen peroxide reduces chlorate to generate chlorine dioxide, and itself is oxidized to oxygen. Therefore, the improved bleaching performance by the acidic-alkaline peroxide bleaching process may partly arise from the fact that the high valence manganese is reduced to its low oxidation state by hydrogen peroxide under acidic conditions, as a result, there would be a decreased hydrogen peroxide decomposition in the subsequent alkaline peroxide stage. This work presents experimental evidence to support such a hypothesis.

4.3 Experimental

Hydrogen peroxide, manganous sulfate monohydrate, Mn(+III) acetate bihydrate, DTPA (diethylenetriaminepentaacetic acid), sulfuric acid, and sodium hydroxide were supplied by Fisher Scientific and used without any further purification. Water was purified by a deionization-distillation-deionization process.

Reduction of Mn(+III) acetate by H_2O_2 under acidic conditions were performed in

a 250 mL Erlenmeyer flask. 1 mmol Mn(+III) were added into 150 mL H_2O at specified

acidic pH and then 1 mmol H_2O_2 was added. The solution was allowed to stand for 10

min at room temperature and the residual H_2O_2 concentration was titrated, following

CPPA Technical Section Standard Testing Methods J16P.

Experiments of stabilizers, magnesium sulfate and sodium silicate, on the

Mn(+II)- and Mn(+III)-induced hydrogen peroxide decomposition were carried out in

polyethylene bottles. The total solution volume was 100 mL containing 3ppm Mn(+II) or

Mn(+III), 300ppm magnesium sulfate and 2500ppm sodium silicate and 600ppm sodium

hydroxide. Mn(+II) was from manganous sulfate monohydrate; Mn(+III) sources were

either from Mn(+III) acetate or from oxidation of an equivalent molar of $MnSO_4$ at pH 11

by air for 10 minutes. Magnesium sulfate, sodium silicate and sodium hydroxide were

always mixed first in a vial, and then transferred into the Mn(+II)/Mn(+III) containing

solution. The solution pH increased to 11.8. After addition of the required amount of

hydrogen peroxide, it decreased to 11.6. The bottle was then placed in a 70°C bath and

the residual H_2O_2 was determined after 60 minutes.

A lab chelated pulp, prepared by treating the bleached sulfite pulp with 0.2%

DTPA at 3% consistency for 30 minutes, filtering and then thoroughly washing the pulp

with the deionized water, was used in runs regarding the effect of pulp fibres on peroxide

decomposition. The manganese content in the resulting pulp is 1.4ppm. The pulp

suspension was stirred for 2 minutes for good dispersion before the addition of

Mn(+II)/Mn(+III), stabilizers, caustic soda and hydrogen peroxide.

The peroxide bleaching experiments were performed on a mill chelated TMP from an Eastern Canadian paper mill with a manganese content around 60ppm. The pulp was stored at 18% consistency and 4°C until used. For those runs involving reduction, sulfuric acid was first applied to pulp suspension in a polyethylene bag to reach the desired pH. H_2O_2 was then charged and the plastic bag was put into 60°C water bath for 10 min. In the case of a low consistency pretreatment (3%), at the completion of 10 min the pulp slurry was filtered and pressed to reach to about 13% pulp consistency prior to the alkaline bleaching experiment. Subsequently, $MgSO_4$, Na_2SiO_3, NaOH and the required amount of H_2O_2 were added in that order to a beaker, then charged to the above obtained pulp which was pretreated with acidic hydrogen peroxide. A thorough mixing was provided at this point. At the end of each experiment a liquid sample was taken for the determination of residual H_2O_2. The pulp suspension was soured to pH 5.5 before washing thoroughly with deionized water for handsheets making. The brightness of bleached pulp handsheets was measured with a TECHIBRITE™ TB-1C. The conventional bleaching process was carried out by mixing all required chemicals first in a beaker and then transferring the mixture to a polyethylene bag containing pulp. The subsequent procedures were the same as above.

4.4   Results and Discussion

The reaction of reducing Mn(+III) to Mn(+II) by hydrogen peroxide was conducted at various pHs with Mn(+III) acetate, which is commercially available from Fisher Scientific (see Experimental for detailed procedures). In all the three cases listed in Table 4.1, the brown particles of Mn(+III) were gradually disappeared, with the evolution

of a gas product and a final solution being colorless. Based on the hydrogen peroxide consumption during the course of reaction, and the initial amount of Mn(+III) present, a stoichiometry between Mn(+III) and hydrogen peroxide of 2 to 1 can be established. All of these observations are consistent with the following reaction:

$$2Mn^{3+} + H_2O_2 \rightarrow 2Mn^{2+} + O_2\uparrow + 2H^+ \qquad (1)$$

Evidently Mn(+III), under the conditions studied, is not a catalyst for consuming hydrogen peroxide. Instead, it reacts with hydrogen peroxide in a stoichiometric manner, following Reaction (1). Therefore, under acidic conditions, high valence manganese, Mn(+III), can be reduced to Mn(+II) by hydrogen peroxide. In the next section we will examine the effect of reducing Mn(+III) by hydrogen peroxide on the hydrogen peroxide decomposition under typical peroxide bleaching conditions.

In Run #1 of Table 4.2, 300ppm magnesium sulfate, 2500ppm sodium silicate and 600ppm sodium hydroxide were first mixed in a vial, and then added to a flask containing 3ppm Mn(+II) (as manganese sulfate). The solution pH increased to around 11.8. Hydrogen peroxide was added to make an initial concentration of 1 g/L. The initial pH was 11.6. The content of the flask was then subjected to 70°C for 60 min. The residual hydrogen peroxide was 0.51 g/L.

In Run #2, the experiment was carried out following exactly the same procedures and conditions except that 3ppm Mn(+III) from Mn(+III) acetate, instead of 3ppm

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Mn(+II), was present in the system. The residual hydrogen peroxide concentration was 0.15 g/L. In Run #3, Mn(+III) was made in-situ from Mn(+II) by oxidization with air at pH 11, under otherwise the same conditions, the residual H_2O_2 concentration was 0.31 g/L. In comparison with the residual H_2O_2 concentration in Run #1, one can conclude that addition of stabilizers to a Mn(+III) containing system is not as effective in stabilizing alkaline peroxide solutions as if they are added to a Mn(+II) containing system. This result is consistent with the earlier one [9].

In Run #4, equivalent to 1 g/L hydrogen peroxide was added to flask containing 3ppm Mn(+III) acetate with its pH controlled at 3. The goal here was to reduce Mn(+III) to Mn(+II) by following Reaction 1. The brown precipitates disappeared immediately and the solution became colorless, indicating the reaction did take place. A mixture consisting of magnesium sulfate, sodium silicate and sodium hydroxide was charged to the flask. The decomposition trial was operated at 70°C for 60 min. The residual hydrogen peroxide concentration was 0.42 g/L. In comparison with Run #2, we can conclude that the reduction of Mn(+III) by hydrogen peroxide leads to a significant decrease in the hydrogen peroxide decomposition under otherwise the same conditions.

Run #5 was conducted in the same manner as that in Run #4 except that Mn(+III) made in situ from Mn(+II), not Mn(+III) acetate, was used. Again, the strategy was to reduce the high valence manganese to its low valence form, and thus, decreasing its catalytic ability to decompose hydrogen peroxide. Such an approach was proved to be successful, since the residual hydrogen peroxide concentration in Run #5 is identical to

that of Run #1 and it is much higher than that in Run #3.

Subsequently, we added pulp fibres to the system. The pulp used was bleached sulfite pulp which was further chelated with DTPA. Table 4.3 shows that the presence of pulp fibres does not change the chemistry: Mn(+III) is still much more reactive than Mn(+II) in decomposing hydrogen peroxide when sodium silicate and magnesium sulfate were added (the residual hydrogen peroxide in Run #7 and 8 was substantially lower than that in Run #6). Moreover, the reduction of Mn(+III) to Mn(+II) by hydrogen peroxide under acidic conditions (Run #9 and 10) can diminish the increased effect of Mn(+III) in catalyzing the peroxide decomposition. These results indicate that even if manganese is initially present in pulp fibres as Mn(+III), hydrogen peroxide can reduce it to Mn(+II) under acidic conditions; subsequently when magnesium sulfate and sodium silicate are added, the peroxide decomposition can be decreased.

In summary, the reduction of Mn(+III) to Mn(+II) by hydrogen peroxide under acidic conditions, followed by the addition of stabilizers, such as sodium silicate and magnesium sulfate, can significantly decrease the manganese-induced peroxide decomposition. Therefore, it is expected that the efficiency of peroxide bleaching would be improved.

The above concept was then applied to a mill chelated TMP pulp. For the first set of experiments, the acidic hydrogen peroxide treatment was performed as a separate stage under the conditions of 60°C, 10 min, 3% pulp consistency, 0.2% H_2O_2 and pH 3. At the

completion of 10 min, the pulp slurry was filtered and pressed to about 13% pulp consistency and then the peroxide bleaching was continued by adding the bleach liquor consisting of 4.8% H_2O_2, 0.05% $MgSO_4$, 3.0% Na_2SiO_3 to the above pulp suspension which was pretreated with hydrogen peroxide under acidic conditions. The peroxide bleaching conditions were: 70°C, 12% pulp consistency, 60 minutes. The resulting pulp has a brightness of 76.3 (% ISO), and the residual hydrogen peroxide was 2.7% on pulp, as shown in Table 4.4.

The same mill chelated pulp was subjected to peroxide bleaching under the same conditions without the acidic H_2O_2 pretreatment (the control run, Table 4.4). The brightness of resultant pulp was 75.3% ISO and the residual H_2O_2 was 1.2% on pulp. It should be pointed out that the above comparison was made at the same total hydrogen peroxide charge. A pretreatment with hydrogen peroxide under acidic condition indeed improves the peroxide bleaching in terms of both the brightness and the H_2O_2 consumption. These results are consistent with those from Lechenal et al. [3] and Abbot and Hobbs [4,5,6] who reported that better bleaching is achieved with an acidic hydrogen peroxide treatment either as a pretreatment or as a separate stage prior to alkaline peroxide bleaching of mechanical pulps. The improved bleaching can be at least partly explained by decreased H_2O_2 consumption because high oxidation states of manganese are reduced to its low valence form by hydrogen peroxide under acidic conditions.

Table 4.4 also includes the other two runs whereby 0.5% H_2O_2, or 1% H_2O_2, was added to the pretreatment stage, and 4.5%, or 4% H_2O_2, was added, respectively, in the

bleaching stage. Again the pulp consistency in the pretreatment stage was 3%. The results showed that an increase in the H_2O_2 charge during the pretreatment stage leads to slight decreases of both brightness and residual peroxide. This is due to the fact that at a higher peroxide charge during the pretreatment, the filtrate of the pretreatment liquor contains more peroxide, which is not available for the peroxide bleaching stage. This leads to less hydrogen peroxide for bleaching since the comparison is made on the same total peroxide charge of 5%, which is the sum of peroxide in the pretreatment and bleaching stages. It should be noted that the standard deviation for brightness is about 0.15-0.25, therefore, a brightness change of a small scale can be discernable. A schematic diagram to follow the above concept consisting of a pretreatment stage with a small amount of peroxide under acidic conditions and a subsequent peroxide bleaching stage is illustrated in Fig. 4.1, where a press is required between the pretreatment stage and the alkaline peroxide stage.

We also studied to carry out the acidic pretreatment with hydrogen peroxide at a medium consistency condition. The results are included in Table 4.4. Again, in comparison with those of the control run, acidic pretreatment with peroxide leads to higher brightness gain and higher residual H_2O_2. The difference between the low consistency and medium consistency pretreatment is that for the latter option, there is no need for a press between the acidic pretreatment and subsequent alkaline bleaching stage. Fig. 4.2 illustrates this concept. After the pretreatment, the pulp is mixed with the bleach liquor from the cascade system to complete the alkaline peroxide bleach process.

The third option is that the chemicals, namely, hydrogen peroxide, stabilizers, and

sodium hydroxide are added sequentially, as shown in Fig. 4.3. In this case, hydrogen peroxide is mixed first with pulp slurry (pH3-4), for the purpose of reducing the manganese at its high oxidation state to its low oxidation state. Magnesium sulfate and sodium silicate are then added to stabilize the low valence manganese, so that the manganese-induced peroxide decomposition is decreased. Finally caustic soda is charged to start the bleaching reactions.

It should be pointed out that hydrogen peroxide at pH 3-4, is very stable even in the presence of pulp fibres containing transition metal ions. Separate experiments showed that more than 95% hydrogen peroxide remained after a pulp suspension containing 5% H_2O_2 (on pulp) at pH 3.5, was subjected to a treatment under the condition of 3% pulp consistency, 60°C, 30 min. This is expected as hydrogen peroxide is very stable under acidic conditions and the small amount of hydrogen peroxide consumed is mainly attributed to the reduction reaction, as outlined in Reaction (1).

We then compared the bleaching results obtained from the process outlined in Fig. 4.3, with those from conventional peroxide bleaching. Table 4.5 shows that the new process as described in Fig. 4.3 produces a bleached TMP pulp with higher brightness, yet at a lower hydrogen peroxide consumption. These results further support the concept that reduction followed by stabilization of reduced transition metal ions is a viable way to improve bleaching of mechanical pulps with hydrogen peroxide.

All of the above three options can improve hydrogen peroxide bleaching. A

higher brightness gain and a less residual peroxide consumption have been achieved in each case. The first option, described in Fig. 4.1 has the highest residual peroxide, although an additional press is needed. However, the option that will be chosen will depend to a great degree on the target brightness, residual H_2O_2 recycle requirement, the economics, and the limitations of the particular application with respect to equipment and capital.

4.5 Conclusions

Hydrogen peroxide, under acidic conditions, can reduce manganese in its high oxidation state, $Mn(+III)$, to its low oxidation state, $Mn(+II)$. Such a reaction takes place stoichiometrically, not catalytically. Subsequently, the addition of conventional stabilizers, such as magnesium sulfate and sodium silicate, will decrease the peroxide decomposition. Results obtained from applying the concept to bleaching of a TMP have shown that the bleaching performance is improved, in terms of both the brightness gain and hydrogen peroxide consumption, when compared with conventional peroxide bleaching.

4.6 References

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Table 4.1   Reduction of Mn(+III) to Mn(+II) by hydrogen peroxide under acidic conditions

Sample	Description	H_2O_2 Consumption (Mmol)
Mn(+III) as Mn(+III) Acetate	1mmol Mn(+III) acetate + 1 mmol H_2O_2, 10 min, pH 2.0	0.51
	1mmol Mn(+III) acetate + 1 mmol H_2O_2, 10 min, pH 3.0	0.51
	1mmol Mn(+III) acetate + 1 mmol H_2O_2, 10 min, pH 4.1	0.48

Table 4.2 Effect of reduction of Mn(+III) and subsequent addition of sodium silicate and magnesium sulfate on the stability of hydrogen peroxide in the absence of pulp fibres

(3ppm manganese, 300ppm magnesium sulfate, 2500ppm sodium silicate, 600ppm NaOH

1 g/L initial H_2O_2)

Run #	Description	Residual H_2O_2 (g/L)
1	$Mn(+II) + (Mg^{2+} + SiO_3^{2-} + NaOH) \rightarrow H_2O_2$, 70°C, 60 min	0.51
2	$Mn(+III)$ acetate + $(Mg^{2+} + SiO_3^{2-} + NaOH) \rightarrow H_2O_2$, 70°C, 60 min	0.15
3	$Mn(+III)$ from $Mn(+II) + (Mg^{2+} + SiO_3^{2-} + NaOH) \rightarrow H_2O_2$, 70°C, 60 min	0.31
4	$Mn(+III)$ acetate $\rightarrow$ pH 3 + H_2O_2, , $\rightarrow (Mg^{2+} + SiO_3^{2-} + NaOH)$, 70°C, 60 min	0.42
5	$Mn(+III)$ from $Mn(+II) \rightarrow$ pH 3 + H_2O_2, $\rightarrow (Mg^{2+} + SiO_3^{2-} + NaOH)$, 70°C, 60 min	0.51

Table 4.3 **Effect of reduction of Mn(+III) and subsequent addition of sodium silicate and magnesium sulfate on the stability of hydrogen peroxide in the presence of pulp fibres**

(0.8% pulp consistency. 3ppm manganese. 300ppm magnesium sulfate, 2500ppm sodium silicate, 600ppm NaOH, 1 g/L initial H_2O_2)

Run #	Description	Residual H_2O_2 (g/L)
6	Mn(+II) +fibres + (Mg^{2+} + SiO$_3^{2-}$ + NaOH)→ H_2O_2, 70°C, 60 min	0.41
7	Mn(+III) acetate + fibres + (Mg^{2+} + SiO$_3^{2-}$ + NaOH)→ H_2O_2, 70°C, 60 min	0.05
8	Mn(+III) from Mn(+II) + fibres + (Mg^{2+} + SiO$_3^{2-}$ + NaOH)→ H_2O_2, 70°C, 60 min	0.17
9	Mn(+III) acetate + fibres → pH 3 + H_2O_2→ (Mg^{2+} + SiO$_3^{2-}$ + NaOH), 70°C, 60 min	0.43
10	Mn(+III) from Mn(+II) + fibres → pH 3 + H_2O_2 → (Mg^{2+} + SiO$_3^{2-}$ + NaOH), 70°C, 60 min	0.43

Table 4.4   Improving peroxide bleaching by an acidic pretreatment with peroxide as a separate stage

(Pretreatment condition: 60°C, 10 minutes, pH 3

bleaching condition: 5% total H_2O_2, 0.05% $MgSO_4$, 3.0% Na_2SiO_3, 12% pulp consistency)

Process Description		Brightness (% ISO)	Residual H_2O_2 (% on Pulp)
Control run		75.3	1.2
3% pretreatment consistency	0.2% H_2O_2 in pretreatment stage	76.3	2.7
	0.5% H_2O_2 in pretreatment stage	76.1	2.5
	1 0% H_2O_2 in pretreatment stage	75.8	2.2
15% pretreatment consistency	0.2% H_2O_2 in pretreatment stage	75.9	1.7
	0.5% H_2O_2 in pretreatment	76.1	1.8
	1.0% H_2O_2 in pretreatment stage	76.2	1.7

Table 4.5   Improving peroxide bleaching by reduction, followed by sequential addition of stabilizers and caustic soda

(TMP pulp. 0.05% $MgSO_4$. 2.0% Na_2SiO_3.

1.5% NaOH. 3% total H_2O_2. bleaching consistency 12%, 60°C. 120 min)

Process Description	Brightness (% ISO)	Residual H_2O_2 (% on Pulp)
H_2O_2 + pulp slurry. pH 3, 10 min, → (Mg^{2+} + SiO_3^{2-}, NaOH)	70.4	0.64
Control run	68.7	0.29
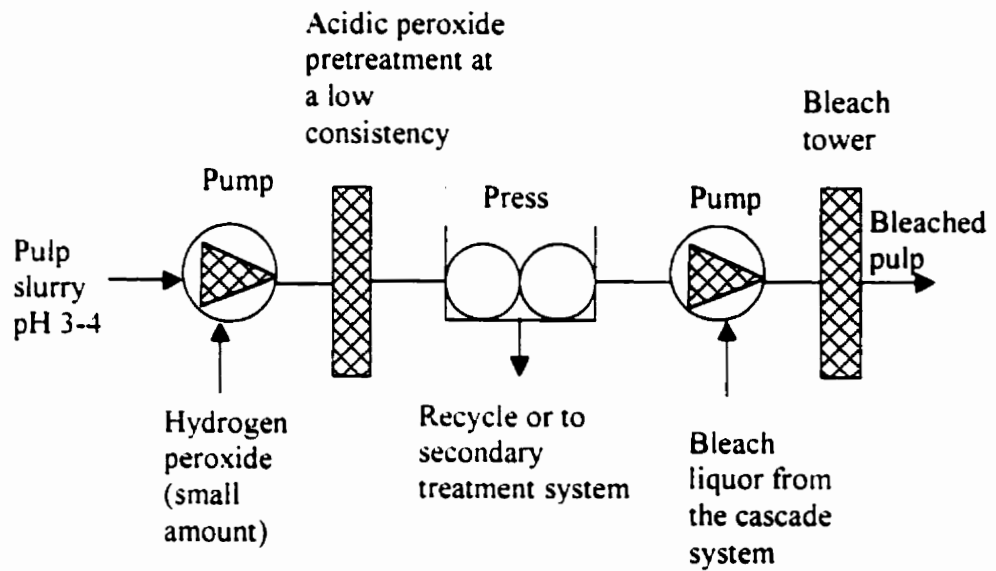
Fig. 4.1 **Acidic peroxide pretreatment as a separate stage at a low consistency**

Acidic
peroxide
pretreatment
at a medium
consistency

Bleach
tower

Pump

Pump

Pulp
slurry
pH 3-4

Bleached
pulp

Hydrogen
peroxide
(small
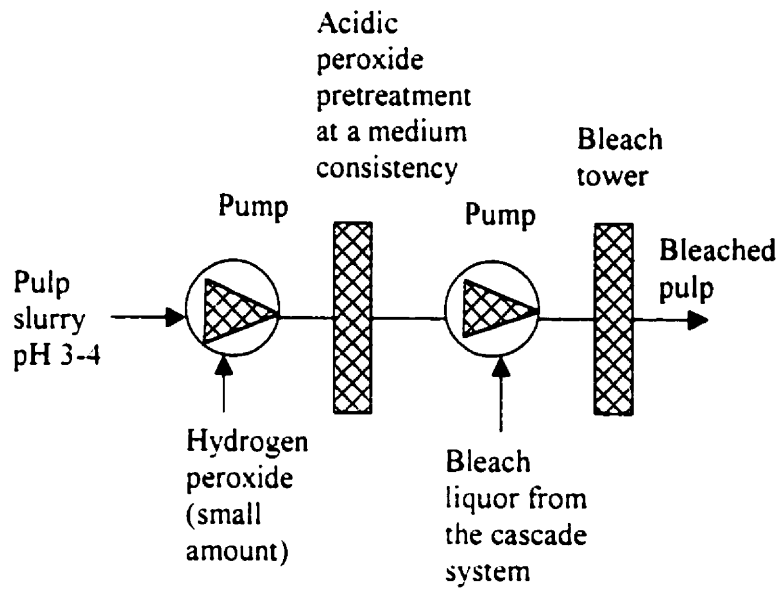amount)

Bleach
liquor from
the cascade
system

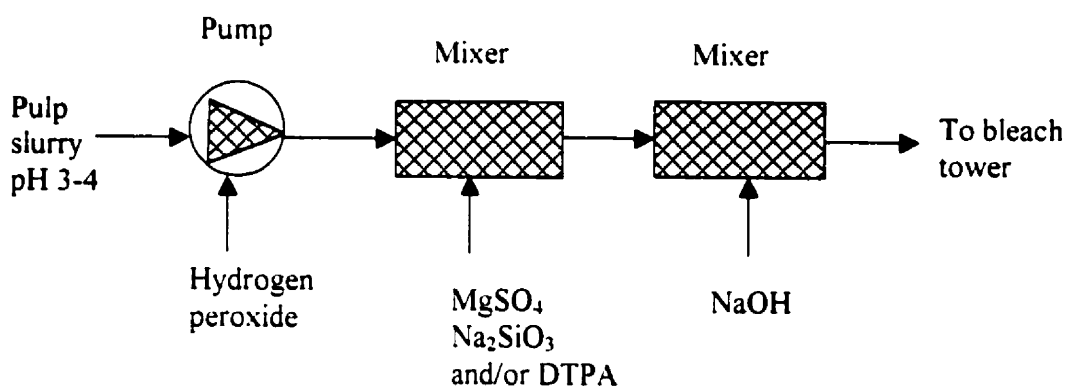**Fig. 4.2**　　Acidic peroxide pretreatment as a separate stage at a medium consistency

Fig. 4.3 Sequential addition of hydrogen peroxide, stabilizers, and sodium hydroxide to improve peroxide bleaching

CHAPTER 5

METHODS TO DECREASE THE MANGANESE-INDUCED

PEROXIDE DECOMPOSITION

5.1 Abstract

Based on the earlier results that a transition metal ion in its high oxidation states, such as $Mn(+III)$, is much more catalytically active in decomposing alkaline peroxide solutions than the same transition metal ion but in its low oxidation states (e.g. $Mn(+II)$), we studied the potential techniques to decrease the manganese–induced peroxide decomposition by minimizing the oxidation of $Mn(+II)$ by air/oxygen to $Mn(+III)$ under an alkaline condition. Two methods were discussed, namely (1) to add a neutralized Na_2SiO_3-$MgSO_4$ mixture, followed by the addition of sodium hydroxide and then hydrogen peroxide to reach the desired conditions for alkaline peroxide bleaching, (2) to remove air/oxygen in the system by purge with nitrogen. The results showed that both techniques were successful.

Keywords: manganese, oxidation states, peroxide decomposition, sodium silicate, magnesium sulfate

5.2 Introduction

It was reported [1,2,3,4] that the catalytic activity in decomposing hydrogen peroxide under an alkaline condition is different for the same transition metal but at different oxidation states. For example, $Mn(+II)$ is not catalytically reactive in the manganese-induced H_2O_2 decomposition, however, $Mn(+III)$ and $Mn(+IV)$ are. Furthermore, it was found [2,4] that the addition of stabilizers, such as magnesium sulfate and sodium silicate, to a $Mn(+II)$ containing system is more effective in decreasing the peroxide decomposition than when they are added to $Mn(+III)$ containing solution.

A conventional peroxide stage to bleach mechanical pulps is conducted in the following manner: the bleach liquor is prepared in a cascade system by mixing sodium silicate, Epsom salt, sodium hydroxide and hydrogen peroxide. Subsequently, this alkaline peroxide bleach liquor is added to pulp fibres. Because the bleach liquor is an alkaline solution, when mixing with pulp fibres, manganese in its low oxidation form can be oxidized to its high oxidation forms [5]. Consequently, more transition metal ion induced hydrogen peroxide may take place.

The oxidation of $Mn(+II)$ to $Mn(+III)$ requires the following conditions:

- the presence of oxygen

- a high enough alkalinity

One may propose (1) to eliminate the presence of oxygen by purge with nitrogen, and (2) to add sodium silicate and magnesium sulfate at a neutral pH, may decrease the oxidation

of Mn(+II) to Mn(+III), thus decreasing the manganese-induced peroxide decomposition. This paper provides experimental evidence to verify the above hypotheses.

5.3 Experimental

Manganese-Induced Peroxide Decomposition

All runs were carried out in a 100 mL polyethylene bottle. 30% hydrogen peroxide solution, manganese sulfate, magnesium sulfate, sodium silicate and sodium hydroxide from Fisher Scientific were used in the experiments without any further purification. The deionized and distilled water was used throughout the experiments.

Magnesium sulfate and sodium silicate were mixed together in a vial. If a neutralized $MgSO_4$-Na_2SiO_3 mixture was needed, sulfuric acid was added to decrease its pH. If an alkaline mixture was needed, NaOH was introduced to reach the required pH. Mn(+II) from manganese sulfate was dissolved into water in a polyethylene bottle. The $MgSO_4$-Na_2SiO_3 mixture was then transferred from the vial to the bottle. Hydrogen peroxide was added at the last. A total volume of 100 mL was finally reached to achieve the required initial concentration for each component in the bottle. The bottle was immersed in a 70°C water bath for 60 minutes. The residual peroxide concentration was determined following CPPA Standard Test Methods, J16P

When nitrogen purge was applied, a gas sparger was used to distribute nitrogen in the solution. If nitrogen was purged only at the time to add chemicals, it was executed 30 seconds before and after the chemical addition. In the case of "nitrogen purge all the

time", nitrogen was used to purge the solution from the very beginning when handling the manganese containing solution till the end of the experimental run.

Determination of the Oxidation States of Manganese

The method is based on the theory that at a specified pH (e.g. pH 4) no reaction occurs between Mn(+II) and hydrogen peroxide while 2 mol of Mn(+III) consume 1 mol of hydrogen peroxide, as expressed by the following reactions:

$$Mn^{2+} + H_2O_2 \rightarrow no\ reaction \tag{1}$$

$$2\ Mn^{3+} + H_2O_2 \rightarrow 2Mn^{2+} + O_2 \uparrow + 2H^+ \tag{2}$$

The pH of the sample containing Mn(+III) and Mn(+II) in a beaker was pre-adjusted to 4. Subsequently, a known amount of hydrogen peroxide was added. The reaction was allowed for 10 min at room temperature. At the completion of 10 min, the reaction was stopped by adding potassium iodide solution from a graduated cylinder and the pH was adjusted to about 2 by adding sulfuric acid. Ammonium molybdate was then added, followed by the same procedure as that for the determination of hydrogen peroxide concentration, CPPA test methods, J16P. The residual peroxide was compared with the initial peroxide charged to calculate the peroxide consumption during the reaction. Considering the 2:1 stoichiometry in Reaction (2), one can determine the Mn(+III) content in the original sample. This method was checked against reagent grades of Mn(+III) acetate bihydrate and Mn(+II) sulfate. The results are shown in Table 5.1. Evidently, one can conclude that the method is accurate and reliable.

5.4   Results and Discussion

Sodium silicate is an alkali, for example, a 2.22% sodium silicate solution has a natural pH of 11.8. As a sequence, when a mixture of magnesium sulfate and sodium silicate, a commonly used stabilizing system, was added to a flask containing 3ppm $Mn(+II)$ (as manganese sulfate), the initially colorless solution rapidly turned brown. The obvious color change in the solution reflects the oxidation of $Mn(+II)$ to $Mn(+III)$, since $Mn(+III)$ has a characteristic brown color. In contrast, when a mixture of magnesium and sodium silicate was neutralized first to pH 7 and then added to a $Mn(+II)$-containing solution, the solution turned to very weak brown color, suggesting that the oxidation of $Mn(+II)$ to $Mn(+III)$ is much less.

Based on the above observation, we compared the stability of alkaline peroxide solutions between the following two cases:

1. An alkaline solution consisting of magnesium sulfate, sodium silicate, and sodium hydroxide was added to a $Mn(+II)$ containing solution, followed by the addition of hydrogen peroxide.

2. The mixture of magnesium sulfate and sodium silicate was first neutralized to pH 7, then added to the $Mn(+II)$ solution, followed by the addition of sodium hydroxide and hydrogen peroxide.

The other conditions were same at: 3ppm $Mn(+II)$, 0.11g/L $MgSO_4$, 2.22 g/L Na_2SiO_3, initial pH 11.6, 1 g/L initial H_2O_2 concentration, 70°C, 60 minutes. The results are shown in Fig. 5.1. Evidently, Case 1 has much more peroxide decomposition than Case 2. We explain these results as follows:

– When a neutralized Na_2SiO_3-$MgSO_4$ solution is added to a Mn(+II) containing system, the condition as such does not favor the formation of Mn(+III) from oxidation of Mn(+II) by oxygen/air. As a result, much less Mn(+III) is formed. Consequently, the Mn(+II) present is stabilized by the Na_2SiO_3-$MgSO_4$ system, resulting in a decreased manganese-induced peroxide decomposition.

– When an alkaline mixture of Na_2SiO_3 and $MgSO_4$ is added to a Mn(+II) containing system, due to the high pH of the solution, more manganese originally present as Mn(+II) is oxidized by air/oxygen to Mn(+III). It is known that addition of stabilizers, such as sodium silicate and magnesium sulfate, to a solution containing Mn(+III) is less effective in decreasing the hydrogen peroxide decomposition than if they are added to a Mn(+II) solution [4].

To further support the above hypothesis we determined the oxidation state of manganese under the conditions of Cases 1 and 2 by following the iodometric titration method (see Experimental Section for details). The results are summarized in Table 5.2. In Trial 1, we added a neutralized Na_2SiO_3-$MgSO_4$ solution (pH 7) to a flask containing 0.1 mmol Mn(+II) (as manganese sulfate) and kept stirring for 10 min. Subsequently, we added sodium hydroxide to the flask to increase its pH to 11.8. The initially colorless solution turned to brown, indicating that some Mn(+III) is formed. The iodometric titration showed that about 60% of the original 0.1 mmol of Mn(+II) was oxidized to Mn(+III). In Trial 2, we performed the experiment following the same procedure as that in Trial 1 except that a natural Na_2SiO_3-$MgSO_4$ mixture (pH11.6) was added to the 0.1 mmol Mn(+II) solution. The color of the solution in the flask was darker than that in Trial 1. The iodometric titration indicated that about 87% of the original Mn(+II) was oxidized

to Mn(+III). In Trial 3, the alkaline mixture of magnesium sulfate, sodium silicate and sodium hydroxide with a pH of 11.8 was added to the same Mn(+II) containing solution. The solution thus prepared had a color significantly darker than that of Trial 1. We found that all of the Mn(+II) charged was oxidized to Mn(+III), see Table 5.2.

The above results support the conclusions that in comparison with an alkaline Na_2SiO_3-$MgSO_4$ solution, adding a neutralized Na_2SiO_3-$MgSO_4$ solution to a Mn(+II) system leads to the formation of less Mn(+III) by the oxidation reaction. This, then, is responsible for the observation in Fig. 5.1 that adding an alkaline silicate solution to a Mn(+II) system has more peroxide decomposition than when a neutralized silicate solution was added to the system.

In the subsequent section we studied the effects of purge nitrogen on the peroxide decomposition under an alkaline condition. The results are shown in Fig. 5.2. In the first case nitrogen was continuously purged through the solution in a polyethylene bottle, and a mixture of magnesium sulfate, sodium silicate and sodium hydroxide was added to the solution. Hydrogen peroxide was added last. The conditions were: initial pH of 11.6, 0.11 g/L $MgSO_4$, 2.22 g/L Na_2SiO_3, 1.0 g/L H_2O_2, 100 ml total solution, 70°C. The nitrogen purge was carried out throughout the entire decomposition experiment. In the second case, a nitrogen purge was done only while adding the alkaline silicate solution and hydrogen peroxide and it was not during the decomposition experiment. In the third case, there was no nitrogen purge at all. Evidently, the hydrogen peroxide decomposition follows an increasing order of

- continuous nitrogen purge

- nitrogen purge only when bleach liquor is charging

- no nitrogen purge.

We offered following explanations for the above results:

- By eliminating the presence of oxygen in solution with nitrogen purge, the oxidation of $Mn(+II)$ to $Mn(+III)$ is largely avoided although the bleach liquor is alkaline. In contrast, without the nitrogen purge, the oxidation of $Mn(+II)$ to $Mn(+III)$ occurs when adding an alkaline bleach liquor, as was shown in the previous section. Since the addition of the stabilizers to a $Mn(+II)$ system is more effective in decreasing the hydrogen peroxide decomposition than if they are added to a $Mn(+III)$ system, one would expect that the nitrogen purge can decrease the manganese-induced peroxide decomposition.

- The oxygen formed from the decomposition of H_2O_2 can oxidize $Mn(+II)$ to $Mn(+III)$. Such a reaction is essentially prevented by a continuous N_2 purge. This is then responsible for the observation in Fig. 5.2.

We also determined the oxidation state of manganese in a $Mn(+II)$ solution when a Na_2SiO_3-$MgSO_4$ solution was introduced with or without a nitrogen purge. The results are shown in Table 5.3. In Trial 4 nitrogen purge was on when an alkaline solution consisting of silicate, magnesium sulfate and sodium hydroxide was added to the $Mn(+II)$ solution. After stopping nitrogen purge, the solution was stirred in the air for 10 min and then the manganese oxidation state was determined. The originally colorless solution turned to brownish and the iodometric titration showed that about 71% of the originally

presented Mn(+II) was oxidized to Mn(+III). Less Mn(+II) was oxidized to Mn(+III) when compared with Trial 3 in Table 5.2. Trial 5 was performed following the same procedure as that in Trial 4 except that nitrogen was continuously bubbled through the system during the entire experiment. The final solution remained colorless and there was no Mn(+III) formed based on the iodometric titration method. In Trial 6, the experiment was conducted in the same manner as that in Trial 4 except that a neutralized, instead of an alkaline Na_2SiO_3-$MgSO_4$ solution, was added to the Mn(+II) solution. Again the results showed that with a nitrogen purge only when adding chemicals, less Mn(+III) was formed in comparison with Trial 1 in Table 5.2. It is not unexpected that when nitrogen purge was on all the time and the neutralized Na_2SiO_3-$MgSO_4$ solution was used, there was no Mn(+III) detected, as shown in Trial 7.

Therefore one can conclude that a nitrogen purge can retard the oxidation of Mn(+II) to Mn(+III), and consequently increase the stability of alkaline peroxide solutions containing Mn(+II). This may be partly responsible for the enhanced bleaching performance by the so-called P_{N2} process [6], whereby an alkaline peroxide bleaching was performed in the presence of nitrogen gas. The P_{N2} process can produce bleached CTMP Maple pulps with higher brightness and less peroxide consumption than the conventional peroxide process under otherwise the same conditions.

5.5 Conclusions

Two potential methods to decrease the manganese–induced peroxide decomposition were studied. Manganese in its low oxidation state can be readily oxidized by air to its high oxidation state when mixed with the alkaline bleach liquor (NaOH, Na_2SiO_3 and $MgSO_4$). The formation of high valence manganese substantially increases the peroxide decomposition. It was found that the oxidation reaction could be stopped if the addition of an alkaline silicate solution to Mn(+II) solutions is performed in a nitrogen atmosphere so that oxygen/air is absent. This is then responsible for the decreased manganese-induced peroxide decomposition when purge with nitrogen. Also, by adding a neutralized Na_2SiO_3-$MgSO_4$ mixture to a Mn(+II) containing system, followed by the addition of sodium hydroxide, and then hydrogen peroxide to reach the peroxide bleaching condition, the oxidation of Mn(+II) to Mn(+III) occurs to much less extent; consequently, the manganese-induced peroxide decomposition is decreased in comparison with the control run.

5.6   References

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Table 5.1   Verification of the titration method for the determination of

Mn(+II) and Mn(+III)

(1 mmol Mn(+II) MnSO$_4$ or Mn(+III) acetate bihydrate, 1 mmol initial H$_2$O$_2$,
room temperature, 10 min)

Description	H$_2$O$_2$ Consumed (mmol)	Mn(+III) Recovered (mmol)
Mn(+II) sulfate	0	None
Mn(+III) acetate bihydrate	0.502	1.05

Table 5.2   Mn oxidation states   when adding alkaline silicate solution or

neutralised silicate solution to Mn(+II) solutions

(0.1mmol Mn(+II) as manganese sulfate, 0.11 g/L MgSO₄ 2.22 g/L Na₂SiO₃,
100 mL total volume, 10 min)

Trial No.	1	2	3
Procedure description	1. Mn^{2-} 2. Neutralized $MgSO_4$-Na_2SiO_3 solution (pH7.0) 3. NaOH to increase pH 11.8, stirring for 10 min and determine the Mn oxidation Mn^{2-} state	1. Mn^{2-} 2. Natural $MgSO_4$-Na_2SiO_3 solution (pH 11.64) 3. Add NaOH (pH 11.8), stir for 10 min and determine the Mn oxidation state	1. Mn^{2-} 2. Alkaline $MgSO_4$-Na_2SiO_3-NaOH solution (pH11.8) 3. Stir for 10 min and determine the Mn state
Color of the solution	brown	brown	brown
Mn(+III) formed (mmol)	0.06	0.087	0.1
Conversion to Mn(+III)	60%	87%	100%

Table 5.3   Effect of nitrogen purge on the Mn oxidation when adding silicate

solution to Mn(+II) solutions

(0.1mmol Mn(+II) as manganese sulfate, 0.11 g/L MgSO₄, 2.22 g/L Na₂SiO₃,

initial pH 11.8, 100 mL total volume, 10 min)

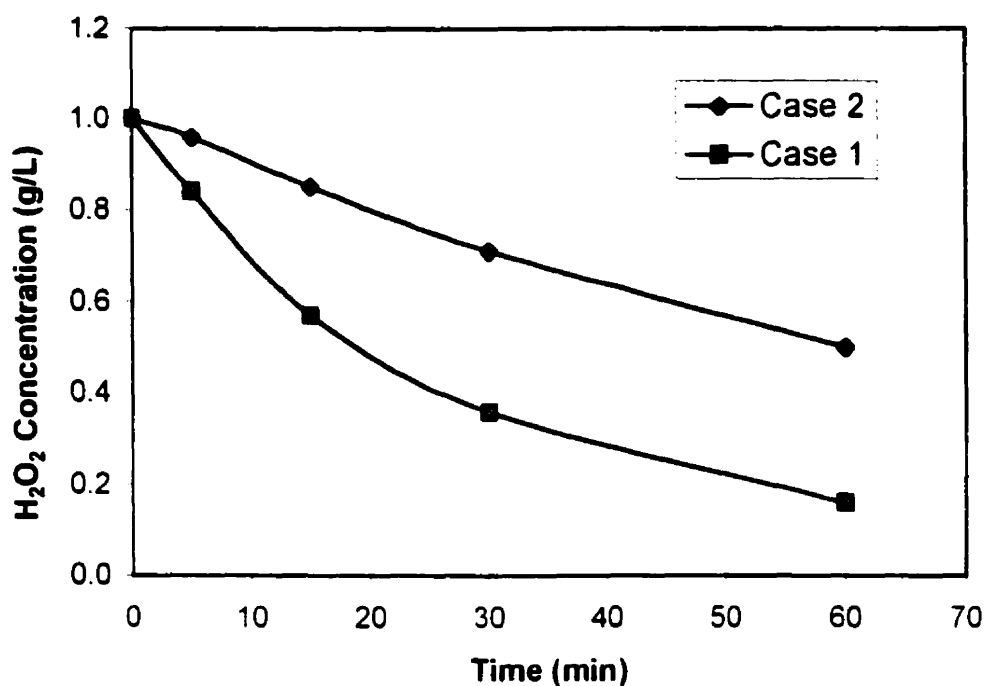| Trial No.	4 N₂ purge only when adding alkaline silicate solution	5 N₂ purge all the way; adding alkaline silicate solution	6 N2 purge only when adding neutralized silicate solution	7 N₂ purge all the way; adding neutralized silicate solution
Procedure Description	1) Add Mn²⁻ 2) Purge with N₂ 3) Add alkaline silicate solution 4) Stop N₂ purge, adjust to pH11.8 5) Stir in the air for 10 min, and then determine the Mn oxidation state	1) Purge with N₂ 2) Add Mn²⁻ 3) Add alkaline silicate solution 4) Adjust to pH 11.8 5) Stir for 10 min, and then determine the Mn oxidation state	1) Add Mn²⁻ 2) Purge with N₂ 3) Add neutralized silicate solution 4) Stop N₂ purge, adjust pH to 11.8 5) Stir in the air for 10 min, and then determine the Mn oxidation state	1) purge with N₂ 2) Add Mn²⁻ 3) Add neutralized silicate solution 4) Adjust pH to 11.8 5) Stir for 10 min, and then determine the Mn oxidation state
Color of the solution	brown	colorless	brown	colorless
Mn(+III) formed (mmol)	0.071	0	0.043	0
Conversion to Mn(+III)	71%	0	43%	0

80

Fig. 5.1 Effect of adding alkaline silicate solution or neutralized silicate solution on the stability of peroxide solution containing 3ppm Mn(+II)

(Conditions: Case 1, alkaline silicate solution; Case 2, neutralized silicate solution. 3ppm Mn(+II), 0.11g/L MgSO$_4$, 2.22g/L Na$_2$SiO$_3$, initial pH 11.6, 1g/L H$_2$O$_2$, 70°C)
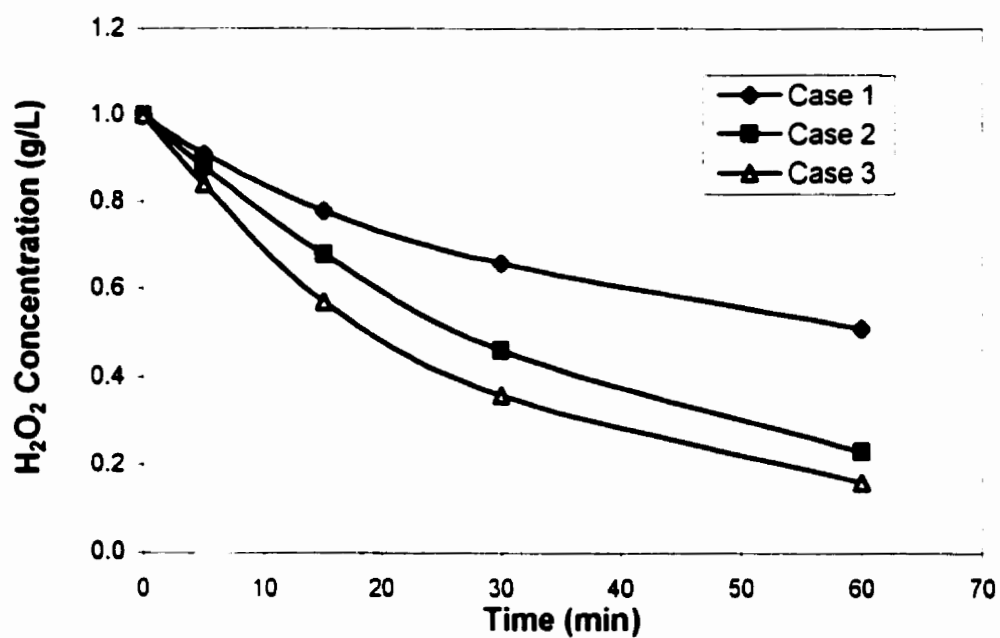
Fig. 5.2   **Effect of N_2 purge on the manganese-induced H_2O_2 decomposition**

(3ppm Mn(+II), 0.11g/L MgSO$_4$, 2.22 g/L Na$_2$SiO3, initial pH 11.6, 1 g/L initial H$_2$O$_2$, 70°C)

        Case 1, N$_2$ purge all the time;
        Case 2, N$_2$ purge only when adding bleaching liquor;
        Case 3, no N$_2$ purge at all

CHAPTER 6

CONCLUSIONS

6.1 General Summary

This thesis deals with improvement in hydrogen peroxide bleaching by controlling the manganese oxidation states during bleaching process so that the manganese-induced hydrogen peroxide decomposition is decreased.

It was recognized that different oxidation states of manganese present different catalytic reactivities towards hydrogen peroxide decomposition. Mn(+II) is much less reactive than Mn(+III) under bleaching conditions. DTPA was used as the sole stabilizer to reduce manganese-induced peroxide decomposition. The results showed that the addition of DTPA to Mn(+II) containing system is more effective than if it is added to Mn(+III) containing system. Furthermore, the higher reactivity of Mn(+III) in catalyzing peroxide decomposition can be retarded by reducing it to Mn(+II) and then stabilizing Mn(+II) with DTPA. Sodium borohydride and DTPA under acidic conditions are capable of working as reducing agents in this respect. The results obtained from systems with or without pulp fibres are very similar. At a higher alkalinity, more DTPA is required to obtain the expected results. This is explained by the fact that hydroxide ions are competing with DTPA for the transition metal ions.

Using DTPA as the only stabilizer to bleach TMP results in expected bleaching performance with 10 points brightness gain at 0.2% DTPA charge. The roles of DTPA are two-fold: to reduce high oxidation state manganese to its low oxidation state, and then to subsequently stabilize the reduced manganese at its low oxidation state.

Hydrogen peroxide, under acidic conditions, was able to reduce manganese from its high oxidation state, Mn(+III), to its low oxidation state, Mn(+II). Such a reaction takes place stoichiometrically, not catalytically. Subsequently, the addition of conventional stabilizers, such as magnesium sulfate and sodium silicate, will decrease the peroxide decomposition. Applying such a concept to bleaching of a TMP leads to improved bleaching performance when compared with conventional peroxide bleaching, as represented by a higher brightness gain and a higher peroxide residue. The higher residual peroxide achieved by acidic H_2O_2 pretreatment makes it possible to recycle the bleach filtrate in the bleaching process, thereby saving the chemical cost. Three schematics using this concept are provided for industrial practice.

Mn(+II) is quite stable in acidic and neutral conditions. The oxidation of Mn(+II) occurs only when contacting with air/oxygen under an alkaline condition. Therefore, conditions which are unfavorable to the oxidation of manganese will decrease the manganese-induced peroxide decomposition. This can be achieved by 1) eliminating the presence of oxygen by purge with nitrogen, and 2) adding sodium silicate and magnesium sulfate at a neutral pH. It was found that the oxidation of Mn(+II) to Mn(+III) can be stopped if the addition of an alkaline silicate to Mn(+II) solutions is performed in a nitrogen atmosphere so that oxygen/air is absent. Consequently, the manganese-induced peroxide decomposition is much decreased. Also, by adding a neutralized Na_2SiO_3-$MgSO_4$ mixture to a Mn(+II) containing system, followed by the addition of sodium hydroxide, and then hydrogen peroxide to reach the peroxide bleaching condition, the experimental results showed that the oxidation of Mn(+II) to Mn(+III) occurs less

favorably, and that the manganese-induced peroxide decomposition is much decreased in comparison with the control run.

6.2 Recommendations and Suggestions for Future Work

1. to determine the oxidation states of manganese in the different pulps,

2. to study the mechanism of peroxide decomposition catalyzed by manganese at higher oxidation states,

3. to investigate the stability of the manganese-DTPA complex in the downstream process,

4. to carry out mill trials on techniques developed in this study at mechanical pulp mills.