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ALKALINE HYDROGEN PEROXIDE BLEACHING A STUDY OF THE EVOLVED GASES

A Thesis

By

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the Faculty of Graduate Studies and Research

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for the degree of Doctor of Philosophy

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ABSTRACT

The principle objectives of this thesis are to determine which gases are evolved during alkaline hydrogen peroxide bleaching, and to develop techniques to measure these gases. Also, the relationship of the composition of the evolved gases from alkaline hydrogen peroxide bleaching of mechanical pulp to the reaction kinetics was elucidated. We have shown that the only gas being evolved into the bleaching headspace is oxygen; whereas, carbon dioxide is produced and fixed in solution as carbonate.

A new non-invasive technique for measuring the amount of oxygen evolved throughout the bleaching reaction was developed. This technique is able to be used in laboratory bleaching experiments that simulated most industrial parameters except consistency, which is limited to hand mixing at medium (10-12%) consistencies. With this method, we have shown that pulp washing, caustic charge and addition of chelating agent play key roles in the rates of oxygen evolution due to the decomposition of hydrogen peroxide. Better washing and higher chelating agent additions result in significant lowering of the rates of oxygen evolution. The rate of decomposition has been related to the dissociation of hydrogen peroxide which is dependent on pH.

The effect of transition metal ions on the kinetics of hydrogen peroxide decomposition during alkaline hydrogen peroxide bleaching of mechanical pulps was investigated. Iron, whether added or native to the pulp, did not contribute to the decomposition of hydrogen peroxide in the presence of lignin. Manganese is the main catalyst for peroxide decomposition, whether added or native to the pulp. The initial rate of oxygen evolution, in the presence of manganese, varies linearly with manganese concentration. Although alkali itself does decompose hydrogen peroxide, increased

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caustic charge results in an increase in the manganese induced decomposition rate. Kinetic equations are presented, which account for manganese concentration and caustic charge. The effect of DTPA on reducing the rate of hydrogen peroxide decomposition has been attributed to the chelation of manganese.

The relationship between hydrogen peroxide decomposition and the oxidation state of iron and manganese was determined visually. The effect of other bleaching additives on the catalyzed decomposition of hydrogen peroxide were also evaluated. Manganese is unreactive in the +II state, yet very reactive in the +III and +IV forms. Iron is not reactive in the presence of lignin. The presence of cellulose acts to prevent the formation of large low surface area precipitates of manganese III and IV. Manganese IV is the most likely reactive species in alkaline hydrogen peroxide bleaching. DTPA will bind Mn(II) but not the other oxidation states. The DTPA-manganese complex once formed is stable even after the pH is increased.

A new technique for the determination of carbon dioxide produced during hydrogen peroxide bleaching is presented. Carbon dioxide is produced during alkaline hydrogen peroxide bleaching, from reactions of hydrogen peroxide and lignin. The rate of carbon dioxide evolution varies linearly with lignin concentration. Kinetic equations are presented and rate constants have been calculated. The source of carbon dioxide is most likely decarboxylation of carboxylic acid groups formed in lignin by alkaline hydrogen peroxide oxidation.

RÉSUMÉ

Les principaux objectifs de cette thèse sont la détermination des gaz émis lors du blanchiment par le péroxyde d'hydrogène en milieu alcalin, et le développement de techniques permettant de mesurer les émissions de ces gaz. De plus, la relation entre la composition des gaz émis lors du blanchiment de la pâte mécanique par le péroxyde d'hydrogène en milieu alcalin et la cinétique de la réaction a été élucide. Nous avons montré que le seul gaz émis dans l'espace de blanchiment est l'oxygène; le dioxyde de carbone, quant a lui, est produit et fixé en tant que carbonate en solution.

Une nouvelle technique non-intrusive a été développée pour mesurer la quantité d'oxygène émis au cours de la réaction de blanchiment. Cette technique peut être utilisée pour des expériences de blanchiment à l'échelle du laboratoire qui simulent la plupart des paramètres industriels, sauf la consistance, qui est limitée a une valeur intermédiaire (10-12%) en raison du mélange manuel.

Grâce à cette méthode, nous avons montré que le lavage de la pâte, la charge caustique et l'addition d'agents chélatants jouent des rôles clés dans les taux d'émission d'oxygène suite a la décomposition du péroxyde d'hydrogène. Les taux d'émission d'oxygène peuvent être abaissés de façon significative en procédant a un meilleur lavage et à des additions plus élevées d'agent chélatant. Le taux de décomposition est relie a la dissociation de péroxyde d'hydrogène qui dépend du pH.

Nous avons aussi examiné des métaux de transition sous forme ionique sur la cinétique de blanchiment de pâte mécanique par le péroxyde d'hydrogène en milieu alcalin. Le fer, qu'il soit ajouté ou présent initialement dans la pâte, n'est pas

réactive avec d'hydrogène en présence de lignine. Le manganèse est réactive avec péroxyde, qu'il soit ajoute ou présent initialement dans la pâte.

En présence de manganèse, le taux initial d'émission d'oxygène varie linéairement avec la concentration en manganèse. Bien que l'alcali décompose lui-même le péroxyde d'hydrogène, une augmentation en charge caustique entraîne un accroissement du taux de décomposition induit par la présence de manganèse. Par ailleurs, des équations de cinétique sont présentées. Elles rendent compte de la concentration en manganèse et en charge caustique. L'effet du DTPA sur la réduction du taux de décomposition de péroxyde d'hydrogène est attribué à la chélation du manganèse.

Nous avons déterminé visuellement la relation entre la décomposition du péroxyde d'hydrogène et l'état d'oxydation du fer et du manganèse. L'effet d'autres additifs blanchissants sur la décomposition catalysée du péroxyde d'hydrogène a aussi été évalué. Le manganèse est inerte lorsqu'il est à son deuxième état d'oxydation, mais il est très réactif à son troisième et quatrième état d'oxydation. Le fer n'est pas réactif lorsqu'il est en présence de lignine. La présence de cellulose agit en évitant la formation de gros précipités de manganèse III et IV à faible surface. Le manganèse IV est probablement l'espèce la plus réactive dans le blanchiment par le péroxyde d'hydrogène en milieu alcalin. Le DTPA se lie au manganèse II mais pas aux autres états d'oxydation du manganèse. Une fois formé, le complexe DTPA-manganèse est stable, même lorsque le pH augmente.

Une nouvelle technique est présentée : elle permet de déterminer le dioxyde de carbone produit lors du blanchiment par le péroxyde d'hydrogène. Au cours du blanchiment, le dioxyde de carbone est produit à partir des réactions entre le péroxyde d'hydrogène et la lignine. Le taux d'émission de dioxyde de carbone varie linéairement

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avec la concentration en lignine. Les équations de cinétique sont présentées et les constantes cinétiques ont été calculées. L'origine de dioxyde de carbone est probablement la décarboxylation de groupes d'acide carboxylique formés en lignine par oxydation du péroxyde d'hydrogène en milieu alcalin.

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LIST OF SYMBOLS

Symbol	Definition
AOX	Aromatic organic halides
DTPA	Diethylenetriaminepetnaaceticacid-pentasodium salt
EPR	Electron Paramagnetic Resonance
GC	Gas Chromatograph
K _{eq}	Reaction equilibrium constant
Μ	Lignin mass equivalent for each mole of CO ₂ produced
Me	Metal
MWL	Milled Wood Lignin
PAPRICAN	Pulp and Paper Research Institute of Canada
Q	Chelating Agent
TCD	Thermal Conductivity Detector
TIC	Total Inorganic Carbon
TMP	Thermomechanical Pulp
TOC	Total Organic Carbon
UV	Ultraviolet Light

CHAPTER 1

INTRODUCTION

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Alkaline hydrogen peroxide bleaching is a widely accepted way to produce high brightness gains in mechanical pulps. This process is able to selectively remove the chromophores in lignin while preserving desirable pulp properties and yield. The reason for hydrogen peroxide's popularity is effectiveness, environmental friendliness, and ease of use¹. Alkaline hydrogen peroxide bleaching is also beneficial to mechanical pulp properties. Both the smoothness of the paper product and its strength are improved following alkaline hydrogen peroxide bleaching^{2, 3}.

Today we are aware that chlorine compounds produce AOX (aromatic organic halides) which bio-accumulate in nature, producing toxic effects in fish and wildlife. The focus of the paper industry is now on oxygen containing brightening and bleaching agents. Hydrogen peroxide bleaching is not a new method to bleach wood pulps. In an early review of peroxide bleaching of pulp by Reichert and Pete⁴, they reference a German patent from 1905. They go further to say that in 1949 peroxide bleaching was in commercial operation. However, it was only in the last two decades that hydrogen peroxide has been widely used in the paper industry. Since the chemical pulp industry is also using oxygen and oxygen/peroxide bleaching stages for the removal of lignin, the results of work with peroxide bleaching of mechanical pulps may be applicable to the chemical pulping process using oxygen based delignifying agents^{5, 6, 7}. Using peroxide, most softwood mechanical pulps can be bleached to 80% ISO brightness or higher, while hardwood may reach as high as 89% ISO⁸. Hydrogen peroxide's greatest asset is its environmental friendliness; followed by its selectivity for removing chromophores while preserving pulp yield.

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Hydrogen peroxide bleaching is optimum in the alkali pH range⁹⁻¹³. This has been attributed to the dissociation of hydrogen peroxide to form perhydroxyl anions (HOO⁻), as shown in equation 1. Perhydroxyl anion is 200 times a stronger nucleophile than hydroxyl ions (OH⁻)¹. Research has shown that the perhydroxyl anion participates directly in bleaching reactions¹⁴. The perhydroxyl anion is considered responsible for most of the bleaching reactions during alkaline hydrogen peroxide bleaching of lignin¹.

$$H_2O_2 + OH^- \to HOO^- + H_2O \tag{1.1}$$

Lignin is a three-dimensional polymer comprised of coniferyl alcohol (softwood) or a mixture of coniferyl and sinapyl alcohol (hardwood) units. In general, these phenylpropane units are linked by carbon-carbon and carbon-oxygen bonds forming a crosslinked and branched structure found in wood¹⁵. The perhydroxyl anion is a strong nucleophile which, during bleaching, converts electron rich chromophores like α , β unsaturated aldehydes and ketones, and phenolic ring-conjugated ethylenic or carbonyl groups to their non-chromophoric counterparts. The reaction of peroxide on lignin is not reversible and leads to the permanent removal of most of the chromophoric groups present in the lignin molecule¹. Through research with model compounds^{5, 16-18}, milled wood lignin¹⁹ and native lignin residuals²⁰⁻²², many products have been determined and numerous mechanisms have been proposed^{1, 20, 23}. The purposes of these reactions are to reduce the number of chromophore in the lignin; thus making the pulp whiter and brighter. Some examples of chromophores oxidizing reactions are presented below. Figure 1.1 demonstrates the reactions of perhydroxyl anions with β type enones (A); and with coniferaldehyde type structures (B). In both cases, the conjugated double bond number is reduced, and the chromophore is eliminated.



In Figure 1.2, the reaction pathway for the elimination of ortho- and para-quinones is presented²³. In reactions A and B, the para-quinone is subjected to attack by the perhydroxyl anion, which results in rupture of the aromatic ring, or degradation to carboxylic acid fragments. In reactions C and D, ortho-quinone is subjected to attack by the perhydroxyl anion. As with the reaction of para-quinone, the ring may simply be ruptured in one pathway (E), or degraded to carboxylic acid fragments in the second pathway (F). In Figure 1.3, the reaction of quinone-methide type (reaction mechanism G) lignin molecules with hydrogen peroxide under alkaline conditions is presented. In this case, there is an oxirane intermediate during the elimination of the chromophore. Reaction mechanism H represents the elimination of stilbene quinone-type chromophores using hydrogen peroxide. Alkaline hydrogen peroxide reactions with lignin result in the formation of carboxylic acid groups as the major product. In all, hydrogen peroxide is an excellent chromophore remover for use with mechanical pulp bleaching.





The principle drawback with using hydrogen peroxide is its tendency to decompose, resulting in serious losses in brightening capacity. The two main hydrogen peroxide decomposition reactions are: spontaneous and transition metal catalyzed.

The spontaneous decomposition of hydrogen peroxide is the result of its ability to act as a weak acid. Therefore this type of decomposition is dependent on the pH of the solution. Hydrogen peroxide's dissociation constant is 1×10^{-11} at 60°C. Therefore, the dissociation of peroxide to its perhydroxyl anion should only start above pH 9⁹. The main spontaneous decomposition reaction would be a reaction between the perhydroxyl anion and hydrogen peroxide itself, as seen in equation 1.2.

$$H_2O_2 + HOO^- \rightarrow H_2O + OH^- + O_2 \tag{1.2}$$

With this equation the maximum rate of decomposition would occur when hydrogen peroxide is 50% ionized. The pKa for hydrogen peroxide is 11.8, so the maximum spontaneous decomposition is expected at this pH. This is related to the alkali induced decomposition. Many researchers believe that hydrogen peroxide decomposes in the presence of alkali^{10, 24}, and they have proposed equations 1.3 and 1.4.

$$H_2O_2 + HO^- \to HOO^- + H_2O \tag{1.3}$$

$$H_2O_2 + HOO^- \rightarrow O_2 + H_2O + OH^- \tag{1.4}$$

However, work done in 1955 by Nicoll and Smith²⁵ has shown that hydrogen peroxide is stable in alkaline solutions, provided that the caustic is free from trace metals, and the solution is free of particulate matter.

The second method for hydrogen peroxide decomposition is transition metal catalyzed decomposition. Hydrogen peroxide decomposes to form water and oxygen according to the following equation:

$$2H_2O_2 \to 2H_2O + O_2 \tag{1.5}$$

The free enthalpy change for equation 1.5 is $-210.71 \text{ kJ/mol}^{10}$.

The three most common detrimental transition metals found in the pulp are manganese, iron and copper²⁶⁻³¹. Most of the iron (90%) and copper (80%) present in thermomechanical pulp is picked up during the refining process; manganese, on the other hand, originates totally from the wood²⁶.

The three widely accepted mechanisms for transition metal catalyzed hydrogen peroxide decomposition are:

 base-catalyzed ionic mechanism, equations 1.6 and 1.7, involving the combination of undissociated hydrogen peroxide and its conjugate base (perhydroxyl anion) to form a six-membered ring in the transition state²⁴;

$$H_2O_2 + HO^- \to HO_2^- + H_2O \tag{1.6}$$

$$H_2O_2 + HO_2^- \to O_2 + H_2O + HO^-$$
 (1.7)

2. base-catalyzed free radical chain reaction mechanism, equations 1.8 to 1.11, involving hydroxyl and superoxide radical anions³¹, and

$$H_2O_2 + HO^- \to HO_2^- + H_2O$$
 (1.8)

$$H_2O_2 + HO_2^- \rightarrow HO^\bullet + O_2^{\bullet-} + H_2O \tag{1.9}$$

$$HO^{\bullet} + O_2^{\bullet-} \to O_2 + HO^- \tag{1.10}$$

$$H_2O_2 + HO_2^- \to O_2 + HO^- + H_2O$$
 (1.11)

transition metal ion-catalyzed free radical chain reaction mechanism, equations
 1.12 to 1.15, involving hydroxyl and superoxide anion radicals, where M is the transition metal^{1, 12}.

$$M + H_2 O_2 \rightarrow M^+ + HO^{\bullet} + HO^{-} \tag{1.12}$$

$$M^{+} + HO_{2}^{-} + HO^{-} \rightarrow M + O_{2}^{\bullet-} + H_{2}O$$
 (1.13)

$$M^+ + O_2^{\bullet-} \to M + O_2 \tag{1.14}$$

$$O_2^{\bullet-} + HO^{\bullet} \to O_2 + HO^{-} \tag{1.15}$$

The debate over heterolytic or homolytic transition metal catalyzed decomposition of hydrogen peroxide has been going on since the beginning of peroxide's use in the paper industry and continues today^{32, 12, 24}. Heterolytic decomposition occurs if one of the reactants is in a different phase than the others. In this case the metal is in the solid phase (as a precipitate), and hydrogen peroxide is in the aqueous phase. Research has shown that manganese (II) ion is not reactive with peroxide³³⁻³⁶. However, manganese oxide (MnO_{2 (s)}) is a catalyst for peroxide decomposition. This leads to the discussion of the phase of the transition metals during alkaline hydrogen peroxide bleaching.

Since pulp is bleached by hydrogen peroxide in alkaline media, the phase of the transition metal is a question of their form at high pH. Manganese and iron both form precipitates in the range of alkaline peroxide bleaching of mechanical pulps³⁷⁻⁴⁰. Since the metals are not completely insoluble in alkaline solution, some of the metal will remain in

solution. The question regarding whether the solid precipitate or the small amounts of metal hydroxide in solution catalyzes the decomposion of hydrogen peroxide, has been addressed³⁸. When the precipitate was ultra-filtered from the solution, it was shown that the remaining dissolved metals were inactive as catalysts for hydrogen peroxide decomposition. Overall, the heterolytic decomposition of hydrogen peroxide during alkaline mechanical pulp bleaching is the most likely mechanism.

Since metals cannot be prevented from entering the pulp, the transition metals need to be removed, or controlled. Mechanical pulp washing is performed using chelating agents to bind the transition metals followed by filtration. The metals are removed from the pulp with the filtrate^{7, 28}. However, this method is not complete in removing the transition metals from the pulp. Metals such as iron are often tightly bound in the pulp, and DTPA is not effective enough to remove them⁴¹⁻⁴³. Another method to remove metals, which relates to the form of the metal, is to use acid washing. Iron, manganese and copper are all soluble in acidic aqueous solutions. Although acid washing is much more effective at removing metals^{28, 26}, it is unselective in which metals are removed⁴³. The removal of alkali earth metals, magnesium in particular, is not beneficial to peroxide bleaching.

The alkali earth metal magnesium is added with the bleaching chemicals as a stabilizer for hydrogen peroxide during alkaline peroxide bleaching of mechanical pulps. The role of magnesium, in alkaline peroxide bleaching, has been challenged for decades. There are three main theories of how magnesium helps stabilize hydrogen peroxide during mechanical pulp bleaching. The first is a theory that assumes that magnesium co-precipitates with manganese, iron and other catalytically active transition metals⁴⁴⁻⁵⁰. The second theory is that magnesium acts as a radical scavenger removing decomposition

intermediate radicals, such as the superoxide anion ^{45, 48}. The radical scavenging ability of magnesium was tested using electron paramagnetic resonance (EPR) measurements ⁵¹, and the results show a significant reduction in radicals formed in the presence of magnesium, even radicals formed by gamma radiation were reduced in the presence of magnesium. Since the more stable form of magnesium in alkaline conditions is Mg(OH)₂ (s), that Mg²⁺ is a weak complex former, and the activity of Mg²⁺ ions will be very low in alkaline media due to the hydrolysis of the ion. The co-precipitation theory is more likely. For oxygen delignification, the co-precipitation of magnesium can be beneficial if it is impregnated before the bleach to prevent radical formation (as shown in the decomposition mechanisms), and subsequent attack, of these radicals, on cellulose, leading to cellulose degradation^{44, 45, 49, 52}.

Diethylenetriaminepentaacitic acid (DTPA) is widely used in the paper industry as a chelating agent for iron, copper and manganese, and as was mentioned previously for washing transition metals from the pulp prior to bleaching. Equations 16 and 17 have been proposed to account for the behaviour of DTPA under alkaline peroxide bleaching conditions³⁵. The data in table 1 were calculated with the assumption that DTPA was in the form where all ionisable protons have been removed. Partial ionization of DTPA will affect the number of sites available for complexing with the transition metal.

$$M^{+n} + Q^{-r} \leftrightarrow MQ^{n-r} \tag{1.16}$$

$$K_{eq} = \frac{\left[MQ^{n-r}\right]}{\left[M^{+n}\right]Q^{-r}}$$
(1.17)

Table 1.1The complexing strength of each metal ion		
with DTPA		
Metal Ion	Log K _{eq} for DTPA	
Ca ⁺²	10.5	
Fe ⁺²	16.5	
Fe ⁺³	29	
Mg ⁺²	9.0	
Mn ⁺²	18.5	

From Table 1.1 we can see that, as was proposed by other authors^{37, 49} magnesium and calcium will both compete for DTPA's binding sites. Although 90% of magnesium exists as Mg(OH)_{2 (s)}, the remainder is available to consume DTPA³⁷. Another interesting observation is that the DTPA complex with iron decomposes hydrogen peroxide⁵³⁻⁵⁶. This further confirms that iron is bound within the pulp and is not available to decompose peroxide^{26, 57}; otherwise, DTPA would not be effective in the prevention of hydrogen peroxide decomposition. The optimum pH for chelating pulps is 5⁵⁸. At this pH, manganese is still in the +II state and is readily chelated and made inert as a catalyst for hydrogen peroxide decomposition, even after the solution is made alkaline for bleaching³⁷.

Similarly, there is some debate on the mechanism of the peroxide stabilizing effect of sodium silicate. Some researchers believe that silicate deactivates or binds transition metals by forming binuclear complexes of the type (Mn-O-Si) thus making them inactive⁵⁹. The other more widely accepted theory is that this additive works by deactivating finely dispersed colloidal particles of metal hydroxides and hydrated oxides which decompose hydrogen peroxide, by incorporating them into a gel like precipitate^{12,39}.

Although the pulp is washed and stabilized, some decomposition still occurs. This decomposition can be monitored, by following the amount of oxygen formed⁵⁷. Martin^{61, 27}, using very low consistency pulp suspensions and room temperature, measured the amount of oxygen evolved during alkaline hydrogen peroxide bleaching. He proposed that the total initial peroxide addition is equal to the residual hydrogen peroxide, the peroxide lost in producing oxygen and the peroxide consumed in brightening reaction. This work was updated using a modern bleaching recipe and more conventional temperatures by Yang and Ni⁶². Work was also done to determine the effects of transition metals and stabilizers during alkaline hydrogen peroxide bleaching of groundwood⁶³.

Although there are several papers on the kinetics of pulp brightening with hydrogen peroxide⁶⁴⁻⁷⁰, none have determined the link between the headspace gases and the kinetics of peroxide decomposition. Further, although some researchers have hypothesized the formation of carbon dioxide none has measured its formation during alkaline hydrogen peroxide bleaching²⁰⁻²¹.

This project proposes to develop a method of accurately measure the amount of gas evolved throughout alkaline hydrogen peroxide bleaching of mechanical pulp. The types of gases evolved and their rate of evolution were to be determined. Relationships between the chemicals used in conjunction with an alkaline hydrogen peroxide bleach of mechanical pulp and gas evolution were to be examined. Finally, kinetic equations would be presented for the evolution of gases.

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CHAPTER 2

KINETICS OF OXYGEN EVOLUTION DURING H₂O₂

BLEACHING OF MECHANICAL PULP

ABSTRACT

A non-invasive method has been developed to monitor the oxygen evolved during alkaline peroxide bleaching of mechanical pulp, while maintaining industrial parameters. However, this method is limited to hand mixing consistencies. Using this method, we have shown that pulp washing, caustic charge and chelating agent addition play key roles in the rates of peroxide decomposition reactions. Better washing and higher chelating agent addition result in significant lowering of the initial rates of hydrogen peroxide decomposition. Alkaline pH is necessary for decomposition reactions to occur. The rate of decomposition has been related to the dissociation of hydrogen peroxide to perhydroxyl anions, and is not attributable to alkaline decomposition
INTRODUCTION

Alkaline hydrogen peroxide bleaching has become the most widely used highbrightening agent for mechanical pulps. During alkaline hydrogen peroxide bleaching of mechanical pulp, peroxide is consumed in two ways: oxidation reactions with the pulp, and decomposition reactions¹. The decomposition of hydrogen peroxide with transition metals is catalytic, and these reactions are responsible for considerable losses of peroxide concentration. As much as one third of the hydrogen peroxide added may be lost to decomposition².

The decomposition reaction with hydrogen peroxide produces water and oxygen³. For every mole of oxygen that is produced, two moles of peroxide have been decomposed⁴. Early work, by Simon and Drelich⁵, measured oxygen evolution by performing the reaction in a jar, while bleaching cotton. They believe that this oxygen oxidized chromophores in cotton. Later, Martin⁶ measured oxygen evolution from hydrogen peroxide bleaching as an indication of how much hydrogen peroxide was lost to wasteful reactions. Martin also determined that the oxygen produced by hydrogen peroxide decomposition does not oxidize chromophores in lignin. Recently, Yang and Ni⁷ have measured oxygen formation by water displacement while performing the reaction in large 8 L polyethylene bags

To minimize the effects of transition metals, most alkaline bleaching operations include a chelation step prior to bleaching. However, this transition metals-washing stage is not able to completely remove the transition metals^{8, 9}, further addition of chelating agent with the bleaching chemicals is often necessary. The quality of transition metals

removal is a balance between money spent on chelating agents and money spent on hydrogen peroxide.

Alkali induced hydrogen peroxide decomposition has been accepted by researchers^{10, 11}, and they have proposed these reactions:

$$H_2O_2 + HO^- \to HOO^- + H_2O \tag{2.1}$$

$$H_2O_2 + HOO^- \rightarrow O_2 + H_2O + OH^-$$
(2.2)

However, work done in 1955 by Nicoll and Smith¹² has demonstrated that hydrogen peroxide is stable in alkaline solutions, provided that the caustic is free from trace metals, and the solution is free of particulate matter.

It was the purpose of this paper to develop a technique that would permit the measurement of the oxygen produced above an alkaline hydrogen peroxide bleach without interrupting the reaction while monitoring the evolution of oxygen over time. With this method, we proposed to examine how the bleaching parameters were related to the rate of oxygen evolution. Both washing and DTPA charge during bleaching were examined. Finally, the effect of caustic charge was also investigated to better understand the effect of alkalinity on the decomposition of hydrogen peroxide.

EXPERIMENTAL

A mill in eastern Canada provided black spruce TMP. Two types of samples were supplied. The first, which will be designated throughout the paper as refiner pulp, was sampled directly from the output of the secondary refiner prior to the latency chest. The second pulp sample, which will be designated throughout this paper as mill washed, was sampled after the latency chest following the high consistency press. The important difference between the two pulps is that the second (mill wash) was chelated by the mill within the latency chest as a means to complex some of the transition metals. The parameters of this washing stage are 80°C, 45 min, 2-3% consistency, and a charge of 0.45% DTPA by weight of dry pulp. The third pulp used throughout these experiments was designated lab washed, is mill washed pulp that was subsequently chelated with DTPA, in our lab. The parameters for our washing stage are 60°C, 60 minutes, and 1% consistency and a charge of 0.2% DTPA on pulp. These three pulps represent different concentrations of native transition metals found in industry.

Deionised water was used in all bleaching experiments and handsheet preparations. Hydrogen peroxide was purchased from Fisher Scientific. The 30% by weight solution was analyzed weekly to monitor decomposition.

The bulk of pulp samples were kept frozen to prevent degradation. Prior to bleaching, 5 gram pulp samples were weighed into polyester-polyethylene bags. The bleaching chemicals, except peroxide, were measured into 50 mL beakers. The order of addition was water, magnesium sulphate, diethylenetriaminepentaacetic acid pentasodium salt (DTPA), sodium silicate, and sodium hydroxide. The addition of DTPA was limited to specific experiments. The addition of DTPA reduces the amount of catalytic decomposition of hydrogen peroxide and was anticipated to reduce the sensitivity and accuracy of the experiments. Table 1 presents the concentrations of each added chemical based on its charge on pulp by mass. The chemicals were poured from the beakers into the polyester-polyethylene bags containing the pulp. A heat sealer was used to form an airtight weld across the opening of the bag. Manual mixing was performed for 30 seconds to distribute the chemicals throughout the pulp. A known amount of neon gas was injected into the bag as an internal calibration standard. The headspace in the bag was then sampled and analyzed on a gas chromatograph. Gas chromatography is discussed in more detail later in the experimental section. Finally, peroxide was injected into the bag using a syringe, and the puncture was sealed with duct tape. The headspace above the bleach must be sampled prior to the addition of peroxide, so that all the oxygen formed as a result of peroxide bleaching can be accounted for. The sample was kneaded by hand for one minute before being immersed in a constant temperature bath set at 60±0.1°C using a Neslab RTE 110 controller. After the desired bleaching time, the samples were removed from the bath. The pulp was diluted to 1% consistency and neutralized to pH 6.0 using sodium metabisulfite. The brightness of the dried handsheets was determined using a Technibright[™] Micro TB-1C according to TAPPI test method T452 om-92.

Residual peroxide was determined using iodiometric titration in accordance with CPPA standard method J.16P.

A Tracor 540 gas chromatograph, equipped with a thermal conductivity detector (TCD), was used to separate and analyze the headspace gas samples. Bags were removed from the bath, sampled, and returned to the bath immediately, accounting for roughly 30

seconds. Gas was removed from the bleaching headspace, using a gas tight micro-syringe. The 10μ L samples were injected into the gas chromatograph. The volume of oxygen calculated from the initial headspace analysis was subtracted from the volumes of oxygen measured following the addition of peroxide. Metal analyses were performed at Paprican in Pointe Claire, QC.

Table 2.1List of the chemicals, their charge on pulp by mass, and their				
molarities in solution				
Chemical	Charge on pulp (%)	Molarities in liquor (M)		
H ₂ O ₂	4.00	0.168		
NaOH	5.00	0.179		
NaOH + NaOH from silicates	5.50	0.196		
Na ₂ SiO ₃	3.00	0.153		
MgSO ₄	0.25	2.97•10 ⁻³		
DTPA-Na ₅	0.20	5.68•10 ⁻⁴		

RESULTS AND DISCUSSION

Previous work on gas evolution during alkaline peroxide bleaching has shown that there are no gases, other than oxygen, being evolved into the headspace. This might have been due to the small sample sizes used by other researchers or that many experiments were performed in the absence of pulp. To test whether oxygen was the only detectable gas being evolved into the headspace, we equipped a gas chromatograph with a special dual column (Figure 2.1) that would permit the separation of several gases in one pass (CO, CH₄, CO₂, O₂, and N₂). Figure 2.2 demonstrates the calibration output of the dual column while separating the possible gases. Figure 2.3 demonstrates that there are no other detectable gases being evolved into the headspace, from peroxide bleaching of mechanical pulp when using our detection system. Since the only gas found in the headspace, other than those trapped inside during sample preparation, was oxygen; we changed our gas chromatographic set up for a more precise single column that would separate oxygen and nitrogen.

With the single bore column, Figure 2.4 demonstrates the linear relationship between the volumes of oxygen injected and the responses of the gas chromatograph. In order to determine the amount of oxygen evolved, we required a measure of the initial total volume of the headspace. This challenge was met using an internal standard. We chose neon. Figure 2.5 shows the linear response of the gas chromatograph to various volumes of injected neon.

A known amount of neon was injected into the sealed bag containing the bleaching reaction before any peroxide has been added, the headspace was analyzed. This



Figure 2.1 Cut-away view of the CTR1 column. The sample is divided and recombined after the column. This allows the column to separate gas using two separate techniques at the same time.



Figure 2.2 The calibration output of the dual CTR1 column separating all possible gases.



Figure 2.3 Actual data produced using the CTRl column. When compared with Figure 2.2, it is apparent that no carbon dioxide or other separable gas is present in the headspace.



Figure 2.4 Oxygen Calibration, in the absence of pulp. This figure shows a linear relationship between oxygen volume injected into the gas chromatograph and the response on the integrator.



Figure 2.5. Neon Calibration, in the absence of pulp. This figure shows a linear relationship between the volume injected into the gas chromatograph and the response on the integrator.

data gave us the baseline for the system, and this value was subtracted from the overall response. Peroxide was then injected to start the reaction. Alkaline darkening was a concern because peroxide was not initially present in the pulp to protect the pulp from the alkalinity.

The effect on the brightness of the pulp, of exposing pulp fibres to alkaline conditions in the absence of peroxide was determined. Three sets of pulp samples were used to determine the effect of alkaline darkening in our system. The three sets included: lab washed, which was metal chelated here in the lab; mill washed, which was metal chelated at the mill; and refiner, which was not chelated or washed. Table 2.2 presents the metal analysis results for each of the three pulps used throughout this paper.

Table 2.2The results of metal analysis of the refiner, mill washed, and lab				
washed pulps.				
Element (ppm)	Refiner	Mill Washed	Lab Washed	
Cu	1.17	~0.4	~0.3	
Fe	6.71	5.76	5.52	
Mn	113	37.3	3.68	
Mg	147	121	126	
Al	9.84	18.71	6.67	

Brightness measurements on hand-sheets prepared with deionised water gave the initial brightness data in Table 2.3. Column three of Table 2.3 contains the brightness data for hand-sheets prepared in the same manner as before, but this time all chemicals except

peroxide were added and permitted to react for two minutes. During the two minute reaction time darkening was immediately visible. Two minutes was the length of time needed to add the neon, and analyze a sample of the headspace, on the gas chromatograph. Although the pulp samples had become visibly darker, the brightness was recovered when the charge was neutralized, to pH 6.0, with sodium metabisulfite,. Column three of Table 3 confirms that the effect of alkaline darkening is not a problem, and that the washing of pulp samples with DTPA does not appear to improve the initial brightness. The brightness gain for refiner pulp may be due to the dilution of the pulp sample before neutralization to 1%, and subsequently filtering the sample. This procedure may have washed out some of the dirt and debris, as this pulp was sampled directly from the refiner. The other, more probable explanation is that the pulps were not originally set to the same pH. The higher the initial pH of the pulp; the darker the pulp becomes. The influence of pH on pulp brightness has been attributed to the ionization of phenolic groups to phenolate ions as the pH increases. Phenolate ions are resonance conjugated and therefore produce colour in the pulp. The effect of alkali darkening was mitigated by lowering the pH for our research; because the pulp has not been heated¹³. Work by Kutney and Evans has shown that alkali darkening does not take place, and the darkening of pulp is due to other factors¹⁴. This corroborates well with our findings. Another possibility for the increase in brightness for mill washed and refiner pulps after exposure to caustic followed by neutralisation may be attributed to precipitation of Fe^{3+} that is complexed to the lignin. If the iron was complexed to catechols or phenolic groups, then the alkaline environment may have decomposed these compounds and caused the precipitation of Fe^{3+} as hydroxides or oxides.

Table 2.3.The effect of exposing the pulp samples to alkaline conditions before			
bleaching.			
1) Pulp Type	2) Initial Brightness	3) Brightness after exposure to Caustic	
Lab Washed	60.24	60.26	
Mill Washed	58.88	61.23	
Refiner	54.52	60.22	

Our bleaching experiments were carried out in plastic bags. Before deciding on which of the three possible bags to choose from, we tested them. Two bags were polyethylene (2 mm and 4 mm thickness) and the third was polyethylene-polyester laminate. Neon was injected into each bag, and the concentration of neon was monitored over time using the gas chromatograph. Figure 2.6 shows the changes in neon concentration within the bags, over time, at room temperature. The polyethylene-polyester laminate had the best performance. Curiously, the 2 mm polyethylene bag performed slightly better than the 4 mm bag of the same material. The results were attributed to the seams of each bag. The 4 mm bags have three heat seals, making up the sides and bottom of the bag. On the other hand, the 2 mm bag had only the bottom side heat sealed. The sides are continuous. Apparently the material itself is impermeable, but the thin heat seals in the 4mm bag are permeable. Since our experiments will be performed at 60°C, the experiment was repeated at this elevated temperature. Figure 7 shows the permeability of the three bags at 60°C over time. All three bags showed



Figure 2.6 Bag Permeability test at room temperature. Demonstrating that gases are lost through the material and seams. Even though the 4mm bag is thicker the seams are narrow and more permeable than the 2mm bag. The polyester-polyethylene bag is more resistant to gas transmission than either polyethylene bag.





permeability, although the polyethylene-polyester laminate showed less than 2% loss of neon, in the first two hours. All of the experiments reported in this chapter were conducted for two hours. Interestingly, the 2mm bag had lower permeability at 60°C. This has been attributed to the bags being submersed in the hot water bath. Our experiments were run with the polyethylene-polyester bags whenever gas analysis was performed.

Early work by Simon and Drelich hypothesized that oxygen was the active oxidizing agent during alkaline hydrogen peroxide bleaching⁵. Although today oxygen is no longer considered the main active agent working to oxidize chromophores during alkaline hydrogen peroxide bleaching, there still remains some debate over whether it is active or not^{1, 15}. The question "does oxygen in our system enhance the brightness gain during alkaline bleaching of mechanical pulp?" was tested. Two experiments were performed: the first experiment had a pure oxygen headspace before the reaction started, and the second had a pure nitrogen headspace before the reaction started. Even though the first experiment had a concentrated oxygen headspace there was no measurable difference in the brightness gain for either reaction. We believe that the answer is simply the low solubility of oxygen at 60 °C in aqueous solutions. Industrial oxygen bleaching reactions require high pressure to forcibly increase the solubility of oxygen, so that it is available to react. Also, oxygen bleaching delignifies and darkens the pulp, whereas alkaline peroxide is a lignin-retaining bleaching process

One of the advantages of our method of headspace analysis is that the sampling does not affect the bleaching reaction, and can be done throughout the bleaching process to gain a profile of oxygen evolved over time. However, other measurements such as pH, brightness, and residual hydrogen peroxide all require that the bleaching reaction be interrupted or stopped.

We have profiled several parameters in the bleaching process. The first parameter shown in Figure 2.8 is the change in pH throughout the bleaching process. The three pulps with different levels of washing were analyzed. The change in pH is most dramatic in the first 30 min, and all three pulps follow the same pattern. Further, the initial pH varied for each of the samples even though the preparation of each sample was identical. This relates to the initial brightness measurements which were discussed earlier. The lower the pH the brighter the pulps became, and each pulp has a different starting pH before and after the chemicals were added.

Figure 2.9 shows the profiles of all three pulp's brightness over time. Although each pulp has a different initial brightness their final brightness measurements were similar. The amount of caustic added was set at 5% on pulp mass. Normally, the caustic charge is optimized to give the highest brightness gain, for each new pulp to be bleached. Therefore, the brightness of the three pulps would be higher had they been optimized for caustic. We however, wanted to change only one parameter for comparison reasons, and in this case, it was pulp washing. What should be noted was the rapid initial gain in brightness during the first 30 minutes (85% of the brightness gain occurs in the first thirty minutes). This corresponds with the rapid initial change in pH. After 30 min, the brightness gain is much slower, yet continues. The final brightness has been related to the residual peroxide charge ¹⁶.

The residual peroxide is a measure of the peroxide remaining in the bleaching liquor that was not consumed in either bleaching or decomposition reactions, and can be

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Figure 2.8 The change in pH over time during alkaline hydrogen peroxide bleaching. This figure demonstrates the drop in pH during the peroxide bleach. Initially the pH falls quickly and then levels off. Except on the initial pH, the extent of washing does not appear to have a detectable effect



Figure 2.9 Brightness change over time. There is an initial sharp gain in brightness followed by a more gradual increase in brightness.

converted to the amount of peroxide consumed by taking the difference between what remains and how much was added. In all three pulps, there was a rapid consumption of peroxide in the first 30 minutes, shown in Figure 2.10, which paralleled both the pH and brightness data. However, there was a greater margin of difference between the three pulps in the amount of peroxide consumed, which demonstrates that washing played a major role in decreasing the amount of peroxide needed to reach a given brightness. The better the chelation wash; the more residual peroxide can be expected under the same bleaching conditions.

Peroxide decomposition reactions result in the formation of oxygen and water. Using our gas chromatograph, we analyzed the headspace above each bleaching reaction to determine the amount of oxygen evolved. Figure 2.11 shows the amount of oxygen evolved over time for each of the three pulps. The well chelated lab washed pulp showed no detectable oxygen evolution, while the other two pulps both showed a rapid evolution of oxygen during the first 30 min. After 30 min, the evolution of oxygen reached a plateau. Comparing the oxygen evolution (Figure 2.10) and peroxide consumed (Figure 2.11), it can be seen how closely the two refiner profiles match. This would imply that the plateau for refiner was due to a lack of peroxide as there was little or no residual oxidant remaining. The second important consideration, when comparing the two figures, is the two profiles for lab washed pulp. Since there was no oxygen evolved, the amount of hydrogen peroxide consumed in bleaching reactions can be calculated from the difference in the amount of hydrogen peroxide added and the residual. This value was considered to represent the amount of peroxide used to bleach the pulp¹. Further, we can consider the consumption of peroxide



Figure 2.10 The amount of peroxide consumed over time. This figure shows how peroxide consumption does not follow the brightness gain as seen in Figure 2.9.



Figure 2.11 Oxygen evolved from peroxide bleaching reactions involving: lab washed pulp, mill washed pulp, and unwashed refiner pulp.

in bleaching lab washed pulp to be the amount of peroxide necessary to reach 76 ISO brightness, in Figure 2.9, as there were no decomposition reactions producing oxygen.

DTPA is added in industry, and the lab to chelate transition metal ions. A typical laboratory DTPA addition would be 0.2% by weight on o.d. pulp. In Figure 2.12, the effect of DTPA charge on pulp is shown. The pulp used for this experiment was mill washed. What is important to note is that if enough DTPA was added to the system the decomposition reactions were effectively slowed. The effect of the DTPA addition can be seen in the initial slopes of the bleaching reactions. As more DTPA is added to the system, fewer transition metal ions are available for reaction with hydrogen peroxide, as they are complexed with the DTPA. This procedure has the same effect as washing, except this time the transition metals are present but inactive as catalysts for hydrogen peroxide decomposition. Finally, in Figure 2.13, the initial rates of oxygen evolution are plotted against the amount of DTPA added to the system. From this plot, an increase in DTPA will result in a decrease in the rate of oxygen evolution, for DTPA additions of 0 to 0.6% on pulp. For mill washed pulp, an addition of 0.6% DTPA eliminated the oxygen producing decomposition reactions.

The effect of caustic charge was investigated. In this experiment, we varied the caustic charge to see whether the rate and amount of oxygen evolved would be affected. Figure 2.14 shows the effect of caustic charge on oxygen evolution over time. Interestingly, for charges less than 3% on pulp, the oxygen evolution becomes almost negligible. For 2% charge there was no detectable oxygen evolved from the reaction. Finally, the initial rates of oxygen evolution were plotted against caustic charge, in Figure 2.15. The initial rate of oxygen evolution increased as the amount of caustic increased, above a 3% charge.

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Figure 2.12 The effect of DTPA on the amount of oxygen evolved from mill washed pulp.



Figure 2.13 The initial rates of oxygen evolution with varying DTPA additions to mill washed pulp. Above a 0.6% addition the rate of oxygen evolution becomes negligible.



Figure 2.14 The effect of changing the caustic charge on the amount of oxygen evolved, while bleaching mill washed pulp.





The effect of alkalinity on the decomposition of peroxide was investigated. We have calculated the effect of pH on the concentration of the perhydroxyl anion in solution. Then we reviewed the thermodynamics of peroxide dissociation, and Equation 2.3 represents peroxides equilibrium with perhydroxyl anions. The free energy of formation (ΔG_f) for aqueous hydrogen peroxide, ionic hydrogen and perhydroxyl anion are -134.10, 0 and, -67.4 kJ/mol respectively. The reaction free energy is the difference between the free energy of the products and the reactants, which is 16.05 kJ/mol¹⁷.

$$H_2 O_2 \Leftrightarrow H^+ + HOO^- \tag{2.3}$$

Figure 16 depicts how peroxide's equilibrium with the perhydroxyl anion is affected by pH. We measured the initial pH of the bleaching liquor at various caustic charges. Table 2.4 details the measured pH on pulp and after the liquor was separated from the pulp. Note how close the transition pH is to the initial pH at which decomposition commences as seen in Table 2.4. An important issue to note: all the values of ΔG were valid for temperatures at 25°C¹⁷. Our experiments were performed at 60°C. However, this gives an indication of the trend that would be followed.

Table 2.4Initial pH both on pulp and off pulp for caustic				
charge				
Caustic Charge (%)	pH on pulp	pH of liquor		
2	10.94	10.88		
3	11.12	11.12		
4	11.45	11.32		
5	11.55	11.60		
6	11.65	11.79		
7	12.12	12.20		

-



Figure 2.16 The effect of pH on the percentage of HOO⁻ anions with respect to peroxide. Below pH 10, the concentration of HOO⁻ anions available for reactions is very low.

CONCLUSIONS

- 1. Only oxygen gas is evolved into the headspace above the peroxide bleaching reactions with mechanical pulp.
- 2. The use of neon as an internal standard permitted the quantitative analysis of oxygen evolved from the bleaching reaction with a gas chromatograph.
- 3. The polyethylene material used to produce the 2 and 4 mm bags appears to be gas impermeable, however the heat sealed factory seams are not. The 4mm bag is more permeable than the 2mm bag; because the 4mm bag has three factory seams where the 2mm bag has only 1.
- Exposing the pulp to the alkaline bleaching conditions in the absence of peroxide before the bleaching reaction does not affect the final brightness, and is easily reversed by pH adjustment.
- 5. Brightness gain following metal chelation may be due to lowering the pulp pH rather than the removal of chromophoric metals.
- 6. The change in pH decreased rapidly during the first 30 minutes, and changed slowly for the remainder of the reaction.
- 7. Brightness increased rapidly in the first 30 minutes. Of the total brightness gain over two hours, 85% is achieved in the first 30min.
- 8. Residual peroxide data showed a trend similar to brightness and pH where the initial 30 minutes were characterized by a rapid consumption of peroxide, however the residual content continued to decrease when the other parameters became stable with time.

- Oxygen evolution into the bleaching headspace decreased with increasing chelation during the washing stage.
- 10. Lab washed pulp, which had the most efficient chelation of the pulps in these experiments, showed no detectable oxygen evolution. Therefore, all of the peroxide that was consumed must have gone towards bleaching reactions.
- 11. Increased charges of DTPA in mill washed pulp decreased the rate of oxygen evolution, up to an addition of 0.6% charge based on pulp mass.
- 12. Alkaline decomposition of hydrogen peroxide can be linked to the concentration of perhydroxyl anions in solution. If the pH was too low to permit a significant formation of perhydroxyl anions then there was no detectable oxygen evolution during the bleaching reaction.

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CHAPTER 3

EFFECTS OF TRANSITION METALS ON O₂ EVOLUTION

DURING H₂O₂ BLEACHING
ABSTRACT

The effect of transition metal ions on the kinetics of hydrogen peroxide decomposition during alkaline hydrogen peroxide bleaching of mechanical pulps was investigated. Iron, whether spiked or native, was not reactive to peroxide in the presence of pulp. Whether native or spiked, manganese is the main catalyst for peroxide decomposition. The initial rate of oxygen production from the decomposition of peroxide, in the presence of manganese, increases linearly with increasing manganese concentration. Although alkali itself does not decompose hydrogen peroxide, the initial rate of manganese induced decomposition increases with increasing caustic charge. This research presents a two electron transfer mechanism for manganese catalyzed decomposition of hydrogen peroxide in the presence of caustic. Further, kinetic equations are presented that account for manganese concentration and caustic charge. Finally, the effect of increasing the charge of DTPA results in a decrease in the initial rate of oxygen evolution, due to the complexation of manganese.

INTRODUCTION

Peroxide bleaching is the main process used to increase the brightness of mechanical and high-yield pulps. During alkaline hydrogen peroxide bleaching of mechanical pulp, hydrogen peroxide is consumed in two ways: oxidation reactions with lignin, and decomposition reactions with transition metals. Two of the most common transition metals believed to be detrimental are manganese and iron¹⁻⁵. The mechanism for the decomposition of hydrogen peroxide by transition metals is not well understood. The three most common mechanisms for transition metal catalyzed hydrogen peroxide decomposition are:

 base-catalyzed ionic mechanism, Equations 3.1 and 3.2, involving the combination of undissociated hydrogen peroxide and its conjugate base (perhydroxyl anion) to form a six-membered ring in the transition state⁷;

$$H_2O_2 + HO^- \to HO_2^- + H_2O \tag{3.1}$$

$$H_2O_2 + HO_2^- \to O_2 + H_2O + HO^-$$
 (3.2)

 base-catalyzed free radical chain reaction mechanism, Equations 3.3 to 3.6, involving hydroxyl and superoxide anions radicals⁸, and

$$H_2O_2 + HO^- \to HO_2^- + H_2O \tag{3.3}$$

$$H_2O_2 + HO_2^- \to HO^{\bullet} + O_2^{\bullet-} + H_2O$$
 (3.4)

$$HO^{\bullet} + O_2^{\bullet-} \to O_2 + HO^- \tag{3.5}$$

$$H_2O_2 + HO_2^- \to O_2 + HO^- + H_2O$$
 (3.6)

transition metal ion-catalyzed free radical chain reaction mechanism, Equations
 3.7 to 3.10, involving hydroxyl and superoxide anion radicals, where M represents a transition metal^{6,9}.

$$M + H_2 O_2 \to M^+ + HO^{\bullet} + HO^{-} \tag{3.7}$$

$$M^{+} + HO_{2}^{-} + HO^{-} \rightarrow M + O_{2}^{\bullet-} + H_{2}O$$
 (3.8)

$$M^+ + O_2^{\bullet-} \to M + O_2 \tag{3.9}$$

$$O_2^{\bullet-} + HO^{\bullet} \to O_2 + HO^{-} \tag{3.10}$$

Transition metals enter the pulp through natural metabolic processes within the tree and by processing in the mill. Over 90% of the iron present in thermomechanical pulp (TMP) is picked up during the refining process; manganese, on the other hand, originates totally from the biosynthetic processes within the wood¹. Since it is not feasible to prevent transition metals from being part of the composition of pulp, control of metal during bleaching is necessary through chelation, and the addition of stabilizers^{10, 3}.

One of the most effective methods of metals control is chelation prior to bleaching. However, this metals-washing stage is not able to remove the transition metals completely¹¹⁻¹³; further addition of chelating agent with the bleaching chemicals is often necessary. The second method of metals control is the addition of stabilizers, such as sodium silicate, to the bleaching reaction¹⁴⁻¹⁸.

The decomposition of hydrogen peroxide can be monitored by measuring the amount of oxygen evolved during the reaction¹⁹. Hydrogen peroxide, in the presence of transition metals, decomposes to produce water and oxygen. For every mole of oxygen produced, two moles of hydrogen peroxide have been decomposed^{2, 18, 20, 21}.

The purpose of this research was to investigate the effects of transition metal ions, iron and manganese, on the decomposition of hydrogen peroxide during alkaline bleaching, by monitoring the evolution of oxygen gas in the headspace above the reaction. The effect of adding metals to the pulp *versus* native metals already found in the pulp was evaluated. The relationship between hydrogen peroxide decomposition and caustic charge was determined. Further, the effect of DTPA charge was examined.

EXPERIMENTAL

A mill in eastern Canada provided black spruce TMP. Two types of samples were supplied. The first, which is as refiner pulp designated throughout this paper, was sampled directly from the output of the secondary refiner prior to the latency chest. The second pulp sample, which is designated as mill washed throughout this paper, was sampled after the latency chest following the high consistency press. The important difference between the two pulps is that the mill washed pulp was chelated in the mill within the latency chest, as a means of complexing some of the transition metals. The parameters of this washing stage were 80°C, 45 minutes, 2-3% consistency, and a charge of 0.45% DTPA by weight of dry pulp. The third pulp that was used throughout these experiments was designated lab washed, and represented a mill washed pulp that was subsequently chelated with DTPA, in our lab. The parameters for our washing stage were 60°C, 60 minutes, and 1% pulp consistency and a charge of 0.2% diethylenetriaminepentaacetic acid pentasodium salt (DTPA) on pulp. These three pulps represent different concentrations of transition metals found in industry.

Transition metal ions were added to pulps using the chloride salts of iron (II), iron (III), and manganese (II). Diluted solutions of the metals were added to the pulp samples in a Hobart mixer and blended for several minutes. Metal analysis was later performed to ensure the metal concentration matched the predicted values. The metal analysis of the pulps was performed by inductively coupled plasma spectroscopy at Paprican in Pointe Claire, Quebec.

Deionised water was used in all bleaching experiments and handsheet preparations. The hydrogen peroxide used was purchased from Fisher Scientific. The 30% by weight solution was analyzed weekly to monitor decomposition.

The bulk of the pulp samples were kept frozen to prevent degradation. Samples were thawed days in advance and the consistency was determined. Prior to bleaching, 5 gram pulp samples were weighed into polyester-polyethylene bags. The bleaching chemicals, except peroxide, were measured into a 50 mL beaker. The order of addition was water, magnesium sulphate, DTPA, sodium silicate, and sodium hydroxide. DTPA was limited to specific reactions. The addition of DTPA reduces the catalytic decomposition of hydrogen peroxide and would reduce the sensitivity and accuracy of the experiments. DTPA was not added to the bleaching system unless specified. The chemicals were poured from the beaker into the polyester-polyethylene bag containing the pulp. A heat sealer was used to form an airtight weld across the opening of the bag. Manual mixing was performed for 30 seconds to distribute the chemicals throughout the pulp. A known amount of neon gas was injected into the bag as an internal calibration standard. The headspace was then sampled and analyzed on a gas chromatograph. Finally, peroxide was injected into the bag via a syringe, and the puncture was sealed with duct tape. The headspace above the bleach was sampled prior to the addition of peroxide, so that all the oxygen formed as a result of peroxide bleaching could be accounted for. Mixing of peroxide with the pulp sample was critical for uniform bleaching. The sample was kneaded by hand for one minute before being immersed in a constant temperature bath set at 60±0.1°C using a Neslab RTE 110 controller. After the desired bleaching time was reached the samples were removed from the bath. The pulp was diluted to 1%

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consistency and neutralized to pH 6.0 using sodium metabisulfite. Using a Teflon screen in a 10 cm Büchner funnel, the neutralized pulp was filtered twice to ensure that all the fines (short thin fibres) were collected with the pulp. Handsheets were made by disintegrating 4 grams of the pulp for one and a half minutes in a British Disintegrator followed by dilution to 0.8% in the handsheet maker, and subsequent filtration on a standard handsheet screen. The samples were pressed only once and then dried. The brightness of the dried handsheets was determined using a Technibright[™] Micro TB-1C according to TAPPI test method T452 om-92.

Residual peroxide was determined using iodiometric titration in accordance with CPPA standard method J.16P. Total hydrogen peroxide concentration ($[H_2O_2] + [HO_2^-]$) was determined immediately after the sampling by adding 4mL of concentrated sulphuric acid, 10mL of 10% KI, 50 mL of deionised water, and 3 drops of 3% ammonium molybdate to 1mL of sample. This solution was titrated iodometrically with 3 mol/L sodium thiosulphate solution with use of starch as an indicator.

A Tracor 540 gas chromatograph, equipped with a thermal conductivity detector (TCD), was used to separate and analyze the headspace gas samples. Bags were removed from the bath, sampled, and returned to the bath immediately. The sampling procedure took approximately 30 seconds. Gas was removed from the bleach headspace using a gas tight microsyringe. The 10 μ L samples were injected into the gas chromatograph. The volume of oxygen calculated from the initial headspace analysis was subtracted from the volume of oxygen measured following the addition of peroxide.

RESULTS AND DISCUSSION

Three pulp samples were used in the experiments, as introduced in the experimental section, lab washed, milled washed and refiner. Table 1 provides the concentrations of transition metals in each of the pulps. Copper, which is easily removed by washing, and is therefore not of serious concern to the industry, was not studied. Magnesium and aluminium concentrations increase during the washing stage. This can be attributed to the mill using recycled white water containing alum (aluminum sulphate) and other additives to wash the pulp.

Table 3.1 Metal Analysis				
Element (ppm)	Refiner	Mill Washed	Lab Washed	
Cu	1.17	~0.4	~0.3	
Fe	6.71	5.76	5.52	
Mn	113	37.3	3.68	
Mg	147	121	126	
Al	9.84	18.71	6.67	

Figure 3.1 shows the effect of washing on the evolution of oxygen during an alkaline peroxide bleach of mechanical pulp. The well chelated Lab washed pulp shows no detectable oxygen evolution, while the refiner pulp shows a rapid evolution of oxygen



Figure 3.1 Oxygen evolution for the three pulps plotted against time.

and then plateaus. The results for Mill washed pulp lie between the lab and refiner pulps data. Figure 3.2 shows the residual peroxide concentrations over time. Oxygen evolution from refiner pulp reached a plateau at the same reaction time as the residual peroxide was completely consumed. However, the lab washed pulp, which did not evolve oxygen also consumed peroxide. This loss of residual peroxide, in lab washed pulp, was attributed to pulp brightening reactions. The difference in the oxygen evolution and the residual peroxide during the peroxide bleaching of the three pulps was associated with the concentration of the transition metals. Therefore, transition metals play a key role in the oxygen producing reactions with peroxide.

Iron, which is known for its ability to catalytically decompose hydrogen peroxide, was added into lab washed $pulp^{22}$. The concentration of iron was 20 ppm on pulp for both Fe(II) and Fe(III). Figure 3.3 presents an average the oxygen evolution with time for the trials with Fe(II) or Fe(III). In all of the trials, no detectable oxygen was evolved. This is not surprising considering the data in Table 3.1. Lab washed pulp contains almost as much iron as refiner pulp and there is no oxygen evolution for lab washed pulp.

Manganese ions are efficient catalysts for peroxide decomposition, and various amounts were added to lab washed pulp. These pulps had a range of manganese concentrations between 4 and 104 ppm on dry pulp. Figure 3.4 shows the amount of oxygen evolved from each of the pulps with added manganese ions and pulps containing native manganese ions during hydrogen peroxide bleaching. Obviously, the manganese ion plays a major role in the oxygen producing reactions. The data also shows that there is a minimum manganese concentration of about 14 ppm needed to produce detectable amounts of oxygen in the headspace. Finally, Figure 3.5 shows the initial rates of oxygen evolution *versus* manganese



Figure 3.2 The percentage of hydrogen peroxide consumed over time for the three pulps.



Figure 3.3 The effect of iron on the amount of evolved oxygen from a peroxide bleach. Without Manganese present, no oxygen can be detected from lab washed pulp with iron(II) or iron(III).



Figure 3.4 The amount of oxygen evolved over time is plotted for various manganese concentrations.





ion concentration. First, the rate of oxygen evolution increases linearly with increasing manganese concentrations. Second, the pulps with native manganese ions fall into line with the pulps with added manganese ions, which indicates that the manganese in mechanical pulps is readily accessible and reactive to peroxide. From Table 3.1, the concentration of other transition metal ions (e.g. Cu and Fe) are not reactive to any significant degree in the native pulps, as the refiner, mill and lab washed pulps all fall into line with the spiked pulps. If iron or copper were reactive the refiner (unwashed) pulp would be significantly higher than the spiked pulp of the same manganese concentration. Although manganese ion content contributes to peroxide decomposition, it is not the only influence on the decomposition of peroxide.

The amount of chelating agent added is also a determining factor in the amount of oxygen which is evolved from peroxide bleach of mechanical pulp. Figure 3.6 presents the effect of DTPA additions on the evolution of oxygen over time with mill washed pulp. The mill washed pulp contains 37 ppm manganese ion. A standard addition of DTPA in the lab is 0.2% on dry pulp. In this experiment, we have added more and less than the standard addition to determine the effect. After taking the initial slopes of the data in Figure 3. 6, Figure 3. 7 shows the initial rates of oxygen evolution with respect to manganese ion concentrations. Up to 0.6% the evolution of oxygen decreases with increasing DTPA charge. More than 0.6% DTPA addition and the rate of oxygen evolution is negligible. Since the mill washed pulp contains 37 ppm manganese is roughly 0.8% on dry pulp. The mole ratio of DTPA to manganese is 24:1 for 0.8% charge. The presence of calcium and magnesium are responsible for some of the excess DTPA needed to bind the transition metals. Both their solubility and their atomic radius are similar to manganese



Figure 3.6 The effect of various DTPA charges on the amount of evolved oxygen is plotted against time.



Figure 3.7 The effect of DTPA charge on the initial rate of oxygen evolution.

and iron, and they will form complexes with $DTPA^{23, 24}$. Finally, we consider that DTPA manganese complex is in equilibrium with free manganese, and that an excess DTPA is needed to push the equilibrium further to the right, as in Equation 3.11.

$$Mn(OH)_2 + DTPA \to Mn(DTPA) + 2OH^-$$
(3.11)

The initial rate of oxygen evolution was plotted against the initial pH of the bleaching liquor, in Figure 3.8, using data presented in Chapter 2, Table 3.4. Below a charge of 3% the evolution of oxygen from a peroxide bleach of mill washed pulp becomes undetectable. The manganese ions added to the pulp were in the Mn(II) form. Manganese's oxidation state changes when exposed to an alkaline environment. However, the pH at which manganese ions oxidise is less than pH 9²⁵. Our system has an initial pH of 10.9 to 12.1 as seen in Table 2, so the effect of caustic is not directly related to the oxidation state of manganese. The other possibility is that the peroxide becomes more susceptible to decomposition at higher pH. Figure 3.9 shows the ratio of perhydroxyl anion (HOO⁻) to hydrogen peroxide (H₂O₂) as a function of pH. The shift in equilibrium of peroxide to the perhydroxyl anion reaches approximately 18% at pH 11, and quickly rises from there. This coincides with Figure 3.8 and Table 3.2. Therefore, the effect of caustic is attributed to the shift in the equilibrium of peroxide to the perhydroxyl anion, which in turn is more reactive to manganese ions under bleaching conditions.



Figure 3.8. The initial rates of oxygen evolution are plotted against the initial pH of the bleaching liquor.



Figure 3.9. The effect of pH on the proportion of HOO⁻ vs. H₂O₂ is demonstrated. Below pH 10 the concentration of HOO⁻ is very small.

Table 3.2.Initial pH of pulp and liquor as afunction of caustic charge.				
Caustic Charge (%)	pH on pulp	pH of liquor		
2	10.94	10.88		
3	11.12	11.12		
4	11.45	11.32		
5	11.55	11.60		
6	11.65	11.79		
7	12.12	12.20		

KINETICS

The kinetics of manganese induced hydrogen peroxide decomposition are related to the pH. Further, the rate of oxygen evolution is proportional to manganese ion concentration, as seen in Figure 3.8. We propose Equations 3.12 and 3.13 to account for the decomposition of hydrogen peroxide by manganese.

$$Mn(OH)_2 + HO_2^- \leftrightarrow MnO_2 + H_2O + OH^-$$
(3.12)

$$MnO_2 + H_2O_2 \to Mn(OH)_2 + O_2 \uparrow$$
(3.13)

$$H_2O_2 + OH^- \leftrightarrow HO_2^- + H_2O \tag{3.14}$$

The mechanism for Equations 3.12 and 3.13 explain the results obtained, with respect to the effect of pH (Figure 3.8), and the effect of manganese ion concentration (Figure 3.5). MnO_2 catalyses hydrogen peroxide decomposition to increase O_2 evolution. The other key factor is the concentration of manganese ions. In this case (Figure 3.5), the relationship is linear. When the concentration of manganese ions increases the rate of oxygen production also increases. From Equation 3.13 the rate equation for oxygen evolution is presented in Equation 3.14.

$$\frac{d[O_2]}{dt} = k[MnO_2][H_2O_2]$$
(3.15)

Expressing $[MnO_2]$ in terms of $[Mn(OH)_2]$, using the equilibrium constant of Equation 3.12 and expressing $[H_2O_2]$ in terms of $[HOO^-]$ using the equilibrium constant for Equation 3.14.

$$\frac{d[O_2]}{dt} = k^* \left[Mn(OH)_2 \right] \left(\frac{\left[HOO^- \right]}{\left[OH^- \right]} \right)^2$$
(3.16)

Equation 3.16 can explain the results of Figures 3.8, 3.10, and 3.11:

- 1. the oxygen evolution is proportional to the manganese concentration;
- 2. the oxygen evolution decreases with DTPA, since DTPA decreases the concentration of active Mn(OH)₂; and
- the initial rate of oxygen evolution increases with increasing pH since the ratio of [HOO⁻]/[OH⁻] increases with pH.

CONCLUSIONS

The quality of the pulp washing is directly related to the evolution of oxygen gas from decomposition reactions during alkaline hydrogen peroxide bleaching of mechanical pulps. Even though iron is difficult to remove using a DTPA washing stage, in the presence of pulp, this transition metal is no longer reactive towards hydrogen peroxide. Manganese ions are responsible for the oxygen forming decomposition reactions with hydrogen peroxide. ions The rate of oxygen evolution is proportional to the concentration of manganese, during alkaline hydrogen peroxide bleaching of mechanical pulp. Further, whether the manganese was naturally present in the pulp or added in the laboratory, had no effect on its reactivity with hydrogen peroxide. An addition of 24 moles of DTPA to 1 mole of manganese ions was sufficient to deactivate the 37 ppm manganese found in mill washed pulp. When caustic and iron are present there is no detectable evolution of oxygen. Therefore neither parameter is directly responsible for producing oxygen. The rate of decomposition increases with increasing caustic charge, above a charge of 2% on pulp for bleaching mill washed pulp containing 37 ppm Mn. This effect is attributed to the dissociation of hydrogen peroxide to perhydroxyl anions which oxidize Mn(OH)₂ to MnO₂. Finally, the kinetics of oxygen formation from the decomposition of hydrogen peroxide during alkaline bleaching of mechanical pulp can be explained by the catalytic decomposition of hydrogen peroxide by MnO₂.

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CHAPTER 4

TRANSITION METAL OXIDATION STATE AND

PEROXIDE DECOMPOSITION

ABSTRACT

The effect of caustic on the form of manganese and iron and their subsequent reactivity with hydrogen peroxide was investigated visually using a digital camera. Manganese in the (II) state is not reactive with hydrogen peroxide and forms a strong complex with DTPA. The (III) and (IV) manganese oxidation states are not easily complexed with DTPA and react vigorously with hydrogen peroxide. Iron is unreactive to hydrogen peroxide in the presence of lignin whether in the form of milled wood lignin or native lignin. Manganese is not influence by lignin. Cellulose does not itself react with hydrogen peroxide, but increases the reactivity of manganese and iron by providing a surface which prevents the formation of large precipitates. Colour photos are provided for visual inspection.

INTRODUCTION

Hydrogen peroxide is susceptible to decomposition induced by transition metals, during alkaline hydrogen peroxide bleaching of mechanical pulps. This loss of hydrogen peroxide can amount to as much as 30% of the bleaching potential¹.

The three most common detrimental transition metals found in the pulp are manganese, iron and copper¹⁻⁵. Most of the iron (90%) and copper (80%) present in thermomechanical pulp is picked up during the refining process; manganese, on the other hand, originates totally from the wood ².

The three most common mechanisms for transition metal catalyzed hydrogen peroxide decomposition are:

 base-catalyzed ionic mechanism, Equations 4.1 and 4.2, involving the combination of undissociated hydrogen peroxide and its conjugate base (perhydroxyl anion) to form a six-membered ring in the transition state⁶;

$$H_2O_2 + HO^- \to HO_2^- + H_2O \tag{4.1}$$

$$H_2O_2 + HO_2^- \to O_2 + H_2O + HO^-$$
 (4.2)

 base-catalyzed free radical chain reaction mechanism, Equations 4.3 to 4.6, involving hydroxyl and superoxide anions radicals⁷, and

$$H_2O_2 + HO^- \to HO_2^- + H_2O \tag{4.3}$$

$$H_2O_2 + HO_2^- \to HO^\bullet + O_2^{\bullet-} + H_2O \tag{4.4}$$

$$HO^{\bullet} + O_2^{\bullet-} \to O_2 + HO^- \tag{4.5}$$

$$H_2O_2 + HO_2^- \to O_2 + HO^- + H_2O$$
 (4.6)

transition metal ion-catalyzed free radical chain reaction mechanism, Equations
 4.7 to 4.10, involving hydroxyl and superoxide anion radicals, where as M represents transition metals^{8,9}.

$$M + H_2 O_2 \to M^+ + HO^{\bullet} + HO^{-} \tag{4.7}$$

$$M^{+} + HO_{2}^{-} + HO^{-} \rightarrow M + O_{2}^{\bullet-} + H_{2}O$$
 (4.8)

$$M^+ + O_2^{\bullet-} \to M + O_2 \tag{4.9}$$

$$O_2^{\bullet-} + HO^{\bullet} \to O_2 + HO^{-} \tag{4.10}$$

The debate over heterogeneous or homogeneous transition metal catalyzed decomposition of hydrogen peroxide has been going on since the beginning and continues today^{9, 6}. Heterolytic decomposition occurs when one of the reactants is in a different phase than the others. In this case the metal is in the solid phase (as a precipitate) where hydrogen peroxide is in the aqueous phase. Research has shown that manganese (II) ion is not reactive with peroxide ¹⁰⁻¹³; whereas, manganese oxide (MnO_{2 (s)}) is a catalyst for

peroxide decomposition. This leads to the discussion of which phase contains the active transition metals in during alkaline hydrogen peroxide bleaching.

Manganese and iron both form precipitates in the pH range of alkaline peroxide bleaching of mechanical pulps.¹⁴⁻¹⁷. Since the metals are not completely insoluble in alkaline solution, some of the metal will remain in solution. After ultra-filtration of the precipitate from the solution, the remaining dissolved metals were shown to be inactive as catalysts for hydrogen peroxide decomposition.¹⁵. Overall the heterolytic decomposition of hydrogen peroxide during alkaline mechanical pulp bleaching is the most likely mechanism.

Since metals cannot be prevented from being part of the pulp composition, the transition metals need to be removed, or controlled. Mechanical pulp washing is performed using chelating agents to bind the transition metals followed by filtration. The metals are carried out of the pulp with the filtrate^{3, 18}. However, this method is not complete in removing the transition metals from the pulp. Metals are often tightly bound in the pulp, especially iron, and they are resistant to DTPA chelation¹⁹⁻²¹. Another method to remove metals, which relates to the form of the metal, is to use acid washing. Iron, manganese and copper are all soluble in acidic aqueous solutions. Although acid washing is much more effective at removing metals ^{2, 3}, it is unselective for which metals are removed²¹. The removal of alkaline earth metals, magnesium in particular, is not beneficial to peroxide bleaching

The alkaline earth metal magnesium is added with the bleaching chemicals as a stabilizer for hydrogen peroxide during alkaline peroxide bleaching of mechanical pulps. The role of magnesium has been challenged for decades. There are two main theories of how magnesium helps to stabilize hydrogen peroxide during bleaching of mechanical

pulp bleaching. The first theory assumes that magnesium co-precipitates with manganese, iron and other catalytically active transition metals²²⁻²⁸. The second theory is that magnesium acts as a radical scavenger removing decomposition intermediate radicals, such as the superoxide anion^{23, 26}. The radical scavenging ability of magnesium was tested using electron paramagnetic resonance (EPR) measurements²⁹, and the results show an appreciable reduction in radicals formed in the presence of magnesium, even radicals formed by gamma radiation were reduced by the presence of magnesium. Since the more stable form of magnesium in alkaline conditions is Mg(OH)₂ (s), the activity of Mg²⁺ ions will be very low in alkaline media due to the hydrolysis of the ion. The co-precipitation theory is more likely.

Diethylenetriaminepentaacetic acid (DTPA) is used widely in the paper industry as a chelating agent for ions of iron, copper and manganese, and as was mentioned before for washing transition metals from the pulp prior to bleaching. Magnesium and calcium ions will both compete for DTPA's binding sites^{14, 27}. Although 90% of magnesium exists as Mg(OH)_{2 (s)}, the remaining Mg²⁺ has significant ability to consume DTPA¹⁴. Another interesting observation is that the DTPA complex with iron decomposes hydrogen peroxide^{31, 32, 33}. This further confirms that iron is bound within the pulp and is not available to decompose peroxide^{2, 34}; otherwise, DTPA would not be effective in the prevention of hydrogen peroxide decomposition. The optimum pH for chelating pulps is 5^{35} . At this pH, manganese is still in the +II state and is readily chelated and made inert as a catalyst for hydrogen peroxide decomposition, even after the solution has been made alkaline for bleaching¹⁴.

Similarly, there is some debate on the mechanism of the peroxide stabilising effect of sodium silicate. Some researchers believe that silicate deactivates or binds transition metals by forming binuclear complexes of the type (Mn-O-Si) thus making them inactive³⁶. The other more widely accepted theory is that this additive works by deactivating finely dispersed colloidal particles of metal hydroxides and hydrated oxides which decompose hydrogen peroxide^{9, 16}.

Although the pulp is washed and stabilized, some decomposition still occurs. This decomposition can be observed by monitoring the amount of oxygen formed³⁷. Using very low consistency and room temperature researchers measured the amount of oxygen during an alkaline hydrogen peroxide bleach^{1, 38}. He proposed that the total initial peroxide addition is equal to the residual hydrogen peroxide, the peroxide lost in producing oxygen and the peroxide consumed in brightening reaction. This was confirmed by Yang and Ni³⁹ who used modern industrial parameters, except consistency, which was low.

The purpose of this chapter is to provide simple visual evidence for the clarification of common misconceptions found in the paper industry regarding transition metal catalyzed hydrogen peroxide decomposition while bleaching mechanical pulp. We propose to determine if iron is reactive towards hydrogen peroxide during bleaching, and if not, why. We investigated the effect of pH on the forms of metals to better understand the heterolytic nature to the decomposition reactions with hydrogen peroxide, and to determine which form of the metal is most effective decomposition catalyst. The effect of pulp components on decomposition was determined. Finally, how DTPA, MgSO₄ and silicates help to reduce the rate of peroxide decomposition were studied.

EXPERIMENTAL

The experiments were performed in 20 mL vials at room temperature. Ferric chloride (FeCl₃•6H₂O) and Ferrous chloride (FeCl₂•4H₂O) solutions were prepared from the reagent grade hydrated salts supplied by Anachemia. Manganese ion was supplied by Acros in the form of manganese chloride (MnCl₂•4H₂O) of reagent quality. The solution of metals were prepared with deionized water, and further diluted for the experiments. Milled wood lignin (MWL) was prepared in our lab and was stored and added in dry powder form. Dissolving pulp was supplied by a mill in eastern Canada, and was used as our pure cellulose. The lignin content of the dissolved pulp was approximately 0.25% by mass. For the reactions, enough metal solution was added to the vial to produce a solution of 50 ppm. The silicates were supplied by Fisher Scientific in the form of a 40-42° Bé solution. Diethylenetriaminepentaacetic acid (DTPA) was supplied by Acros as a solution of its pentasodium salt. Both the silicate and DTPA solutions were of technical grade. Magnesium sulfate (MgSO₄) was supplied as an anhydrous reagent grade powder by Fisher Scientific. Sodium Hydroxide pellets were purchased from Fisher Scientific, and were reagent grade. Finally, Sulfuric acid was also supplied as reagent grade from Fisher Scientific.

Metal ion solution were prepared by adding small amount of the concentrated solutions prepared with distilled water. The concentrations of metal ions were approximately 50 ppm, on pulp, unless specified. The images used in the Figures were taken using a Sony Digital Camera with 20X zoom.

RESULTS AND DISCUSSION

This research was designed to clarify some concepts about decomposition of hydrogen peroxide during alkaline mechanical pulp bleaching. We have simplified the experiments to show some basic truths and misconceptions that are found in the industry. We know that iron and manganese ions are catalysts for hydrogen peroxide decomposition¹⁻⁵. Iron(II) is a well known Fenton's reagent ⁴⁰, and manganese ion is known as the most detrimental transition metal to hydrogen peroxide⁵.

The first experiment addressed the effect of oxidation state of the metal ions. Both iron and manganese change oxidation state with changing pH, and in the presence of molecular oxygen (both air and dissolved forms)⁴¹. Figures 4.1, 4.2 and 3 show solution of Fe(II), Fe(III) and Mn(II) respectively, in acidic solution. The original metal solutions were made with deionised water, and appeared visually to be the same as the acidic Figures. The acidic solutions had pH's below 3. The Figures indicate that all three metals are soluble and stable in acidic media, and Fe(II) and Fe(III) are not reduced or oxidized, as they appear unchanged from their original solutions, at neutral pH. The results were different when sodium hydroxide was added instead of hydrochloric acid.

Starting with the original solutions made from deionised water, enough sodium hydroxide was added to increase the pH to above 10.5. The results are shown in Figures 4.4, 4.5 and 4.6, respectively, which represent Fe(II), Fe(III) and Mn(II) after caustic addition. Comparing Figures 4.1 and 4.4, there is an obvious change. The solution of Fe(II) appears to have been oxidized to Fe(III) as it appears very similar to Figures 4.2 and 5 which represent Fe(III). Further, Figures 4.2 and 4.5 appear the same, so the
- Figure 4.1 Iron (II) ions in acidic conditions.
- Figure 4.2 Iron (III) ions in acidic condition.
- Figure 4.3 Manganese ions in acidic conditions.
- Figure 4.4 Manganese ions in mild caustic conditions
- Figure 4.5 Iron (II) ions in mild caustic condition.
- Figure 4.6 Iron (III) ions in mild caustic conditions.



solution Fe(III) had remained in the same oxidation state. Finally, the solution of Mn(II) has been oxidized. The dark reddish brown suspension could mean the production of Mn(OH)₃, MnO₂, or MnO(OH), all of which are precipitates. Research has shown that manganese precipitates primarily as hydroxide when the pH exceeds 10¹⁴. However, this hydroxide species is easily oxidized to MnO(OH) and eventually to MnO₂⁴². Work by Ni et al.⁴³ have recently proposed that the Mn(III) ion, although unstable⁴², is the main reactive form of manganese for the decomposition of hydrogen peroxide during mechanical pulp bleaching. They founded part of their hypothesis on the fact that Mn(III) forms a brown precipitate, while Mn(IV) forms a primarily black precipitate¹³. Iron(III), on the other hand, precipitates at a much lower pH. Above pH 3, Fe(III) ions form hydroxides⁴³.

Another interesting observation is that although the pH was set to 10.5, it was unstable. In both Fe(II) and Mn(II) the pH dropped over a period of minutes, as the metals were precipitated. We have attributed this to the consumption of hydroxyl anions by the metals to form hydroxides [e.g. Fe(OH)₃, Mn(OH)₃].

After adding more caustic to raise the pH above 11, for the strong caustic trials, all three samples showed visible reactions. Figures 4.7, 4.8 and 4.9 represent the result of exposing Fe(II), Fe(III) and Mn(II) to high caustic charge. Both Fe(II) and Fe(III) precipitate with a low density reddish brown solid, that settled over several minutes. Both iron samples were identical. Figure 4.8 was several minutes older than Figure 4.7, which accounts for the greater accumulation of precipitate on the bottom of the vial. Manganese, Figure 4.9, showed a very distinct change in character. The precipitate, unlike Figure 4.6, was black and settles out within minutes; whereas in mild caustic, the light brown precipitate remained suspended for tens of minutes. With the increase in pH the

- Figure 4.7 Iron (II) ions in strong caustic conditions. The Iron (II) ions have been oxidized into iron (III) and they now appears the same as Figure 4.8.
- Figure 4.8 Iron (III) ions in strong caustic conditions.
- Figure 4.9 Manganese ions in strong caustic conditions. The manganese ions have been oxidized to the +IV oxidation state, which is black.
- Figure 4.10 Iron (III) ions in acidic conditions after the addition of hydrogen peroxide. The appearance of bubbles indicates the formation of oxygen from the decomposition of hydrogen peroxide
- Figure 4.11 Manganese ions in mild caustic conditions after the addition of hydrogen peroxide. Manganese is in the +III state and reacts to form oxygen gas.
- Figure 4.12 Both iron ions samples, Fe (II) and Fe(III), under strong alkaline conditions. The two samples are the same under strong caustic conditions.



manganese is most likely in its most stable form, as manganese dioxide (MnO_2) solid, which is known to be a black solid⁴⁴.

We have shown that the metal ions in solution change form when the pH is altered. The effect of the metal's form on peroxide decomposition was also tested. First, Fe(II) and Mn(II) solution under neutral or acidic conditions had no immediate reaction with hydrogen peroxide, and appeared as they did in Figures 4.1, 4.2 and 4.3. However, Fe(III), as seen in Figure 4.10, shows significant reaction with peroxide. This can be seen by the formation of oxygen bubbles which, along with water, are the products of transition metal catalyzed peroxide decomposition. Interestingly, Fe(II) is not visibly reactive while Fe(III) is, and the Fenton reaction sequence was not initiated with Fe(II) during a period of tens of minutes. The Fenton system is supposed to be initiated with the Fe(II) ion⁴⁰. This may be the result of hydrogen peroxide not being dissociated into perhydroxyl anions at low pH.

When the same experiment was performed under mild caustic conditions the manganese reacted very rapidly with peroxide, in Figure 4.11. This confirms that Mn(II) is not a catalyst for peroxide decomposition; yet other oxidation states of manganese are. This agrees with what others have reported, namely that peroxide is stable in the presence of $Mn(II)^{45, 10, 40}$.

Under strong alkali conditions (above pH 11), there is another turn of events. Although both manganese and iron are reactive to hydrogen peroxide, their significance has changed. Iron under strong alkali oxidizes further and forms large particles which reacted slowly with hydrogen peroxide, as seen in Figure 4.12. This Figure represents both Fe(II) and Fe(III) solutions, as they appear to be in the same form. Manganese, on the other hand, becomes more reactive; reacting violently with peroxide, while in the

- Figure 4.13 Manganese ions in strong caustic conditions after the addition of hydrogen peroxide. Manganese ions have been oxidized to the +IV state and react violently with hydrogen peroxide.
- Figure 4.14 Manganese ions in caustic condition, in the presence of cellulose fibres, after the addition of hydrogen peroxide. Cellulose increases the reactivity of manganese with hydrogen peroxide.
- Figure 4.15 Iron ions, under caustic conditions, in the presence of cellulose fibres, after the addition of hydrogen peroxide. The reactivity of iron increased in the presence of cellulose.
- Figure 4.16 Iron (II) ions, under acidic condition, in the presence of glass fibres, after the addition of hydrogen peroxide. The glass fibres increased the reactivity of iron (II) enough to be visible.
- Figure 4.17 Iron (III) ions, under acidic condition, in the presence of glass fibres, after the addition of hydrogen peroxide. The glass fibres increased the reactivity of iron (III).
- Figure 4.18 Manganese ions, under mild caustic conditions, in the presence of glass fibres, after the addition of hydrogen peroxide. The reactivity increased after the addition of glass fibres.



form of MnO_2 , as seen in Figure 4.13. Our results show that Mn(IV) is more reactive than Mn(III). However, all of the experiments discussed up to now have been performed in the absence of pulp.

Wood pulp has two major components. The first and most abundant component is cellulose followed by lignin. In the next experiment, dissolving pulp was added to the reactions. Dissolving pulp is more than 99% pure cellulose, and it will not introduce the effects of lignin to the system. Under acidic conditions, the addition of cellulose had no effect, and the reactions appeared as they did in Figures 4.1, 4.2 and 4.3; except now there was pulp in the vial. Cellulose added to the reactions under caustic conditions did have an effect. For manganese in Figure 4.14, the reaction was so severe that it foamed, and carried some of the precipitate out of the vial. Iron was also affected. With the presence of cellulose fibres the Fe(II) ions were oxidized to the same form as Fe(III). This was attributed to the increased amount of molecular oxygen carried into the solution, as entrained gas, when the fibres were added. Both solutions of iron are represented by Figure 4.15. In this case, as with manganese, the presence of cellulose fibres increases the rate of oxygen evolution. We wanted to determine if the effect of cellulose was chemical or physical, so we added an inert solid to the system to determine if the effect was physical.

We chose glass fibres as our inert substrate. Figure 4.16 shows how the glass fibres were able to increase the reaction rate of Fe(II), so that the reaction became visible, in acidic conditions. The Fenton mechanism does work in acidic solution; however a reaction site is necessary for it to be visibly producing oxygen gas. This same effect, under acidic conditions, can be seen with Fe(III). In this case, the reaction is more vigorous, as shown in Figure 4.17.

- Figure 4.19 Iron ions, under mild caustic conditions, in the presence of glass fibres, after the addition of hydrogen peroxide. The reactivity increased after the addition of glass fibres.
- Figure 4.20 Milled wood lignin solution in acidic conditions.
- Figure 4.21 Iron (II) ions, under acidic conditions, in the presence of milled wood lignin and glass fibres, after the addition of hydrogen peroxide. Milled wood lignin suppressed the reactivity of iron (II) ions with hydrogen peroxide.
- Figure 4.22 Iron (III) ions, under acidic conditions, in the presence of milled wood lignin and glass fibres, after the addition of hydrogen peroxide. Milled wood lignin suppressed the reactivity of iron (III) ions with hydrogen peroxide.
- Figure 4.23 Manganese ions, under caustic conditions, in the presence of milled wood lignin and glass fibres, after the addition of hydrogen peroxide. Milled wood lignin did not affect the reactivity of manganese with peroxide. The foaming has been attributed to the lignin.
- Figure 4.24 Iron ions, under caustic conditions, in the presence of MWL after the addition of hydrogen peroxide. Milled wood lignin prevented the further oxidation of both iron solutions to form precipitates and their reactions with hydrogen peroxide.



When glass fibres were added to mild caustic solutions, the reaction of Fe(III) was not visible, however, both manganese (Figure 4.18) and Fe(II) (Figure 4.19) were very reactive. These results explain how pulp accelerates the decomposition of hydrogen peroxide. The pulp, like the glass fibres, provides a surface for the reaction to take place, and prevents large particle precipitates from forming. The increase in surface area (fibres) binds the new precipitate particles before they can join each other to form large, low surface (less reactive area) particles.

We consider that the cellulose acts as a physical reaction point, the way boiling chips work add a rough surface for gas formation, and as a solid substrate for the precipitate to attach to. Because the reactions are much more visible in the presence of glass fibres, the remaining photos will have glass fibres present to facilitate observation.

The other major component in mechanical pulp is lignin, as mentioned earlier. Mechanical pulp contains over 25% lignin by mass⁴⁶. To determine the effect of lignin alone, we added a small amount of milled wood lignin (MWL) to the sample. Milled wood lignin is the closest one can get to native lignin in the absence of cellulose⁴⁶. The addition of MWL was made prior to pH adjustment. Figure 4.20 shows the effect of acidifying the solution. A similar cloudy colloidal suspension is formed under caustic condition; however, it is not as opaque.

In acidic conditions, MWL had no effect on manganese which remained unreactive towards hydrogen peroxide. The Fe(II) solution, which was reactive in Figure 4.16, in the absence of MWL, was now unreactive as seen in Figure 4.21. The same effect can be seen with the Fe(III) solution in Figures 4.17 and 4.22. Overall, under acidic conditions lignin prevented iron catalyzed decomposition of hydrogen peroxide.

Under caustic conditions, lignin did not slow the reaction of hydrogen peroxide with manganese. Figure 4.23 presents the severe reaction of manganese with hydrogen peroxide under caustic conditions, in the presence of MWL. This also shows that milled wood lignin acts as a surfactant, producing a stable foam. On the other hand, lignin does inhibit the reaction of hydrogen peroxide with both iron solutions. Both iron solutions are represented by Figure 4.24 as visually they appeared the same. This figure can be compared with Figure 4.19, which has the same caustic conditions, without MWL. Finally, MWL prevented the precipitation of ferric hydroxides, which can be seen in Figure 4.12. This corresponds well with our own results from Chapter 2 of this thesis, where iron's ability to catalyze the decomposition of hydrogen peroxide has been neutralized in the presence of pulp. The idea that hydrogen peroxide is stable in the presence of iron is surprising in that iron has been used as a catalyst for the decomposition of hydrogen peroxide, since before the discovery of the Fenton Reagent⁴⁰. However, in the presence of pulp, iron is no longer reactive as a catalyst for hydrogen peroxide decomposition³⁴. Certain important ideas explain why iron is not reactive in the presence of pulp. First, iron is difficult to wash out with chelating agents⁴⁷, and second, they found that iron was tightly bound to the pulp fibres². Therefore, iron is not available for reaction. Manganese is not complexed by lignin and is not inactivated in the same manner as iron. The manganese remains available for reaction.

Diethylenetriaminepentaacetic acid (DTPA) is used by the paper industry to chelate transition metals⁴⁸. When DTPA was added to a caustic solution of manganese, the solution was reactive towards hydrogen peroxide, as seen in Figures 4.13 and 4.18. What is interesting is that if the DTPA was added to the acidic or neutral solution of manganese, and then the pH was adjusted, to more caustic conditions, the solution

- Figure 4.25 Iron (II) ions under caustic conditions after the addition of DTPA, and following the addition of hydrogen peroxide. Iron (II) reacted with DTPA and then the DTPA-complex reacted with hydrogen peroxide.
- Figure 4.26 Iron (III) ions under caustic condition, after the addition of DTPA, and following the addition of hydrogen peroxide. Unlike iron (II), the vials remained unchanged.





remained clear and non-reactive. This would imply that Mn(II) was bound by DTPA, but the higher oxidation states of manganese in aqueous media are not. Once the Mn(II) is bound to DTPA the complex is stable even at very high caustic charge.

Other researchers have presented similar results¹⁴. This explains why the optimal treatment of pulp with DTPA was found to be pH 5, when manganese would still be in the Mn(II) state³⁵.

Iron was characterized by different behaviour in the presence of DTPA. Figure 4.25 is a series of three pictures of Fe(II) solution. The second vial shows the effect of adding DTPA. Obviously, there was a reaction with the iron as the colour of the solution changed. Finally, the third vial presents the effect of adding hydrogen peroxide. Although the system is not visibly reactive in decomposing hydrogen peroxide, the DTPA iron complex reacted with peroxide to form a purple solution. Although this complex does not react vigorously enough to produce visible bubbles of oxygen gas, researchers have demonstrated that it is still reactive towards the decomposition of hydrogen peroxide^{32, 33}. The Fe(III) solution, Figure 4.26, showed almost no effect, and can be attributed to the formation of iron hydroxo-species $[Fe(OH)_4^-(aq)]^{14}$, which is not compatible for DTPA chelation.

Silicates (SiO₂) are another additive used to stabilize the bleaching liquor against peroxide decomposition. An average bleaching reaction has 4 to 5% silicates added relative to pulp mass. As an example, we have calculated the molar ratio of silicates to manganese in a pulp that has 10 ppm manganese ion content. With a 5% addition of silicates, the molar ratio was in excess of 450:1 silicates to manganese. The original silicate solution, which contains sodium hydroxide, was not alkaline enough to oxidize the manganese ions, and therefore the silicate manganese solution remained clear and

- Figure 4.27 Manganese ions under caustic conditions in the presence of silicates. The silicates resisted the oxidation of manganese.
- Figure 4.28 Manganese ions, under caustic conditions, in the presence of silicates, after the addition of hydrogen peroxide. The reactivity of manganese was reduced by the presence of silicates.
- Figure 4.29 Manganese, under acidic conditions in the presence of magnesium ions. There was little or no apparent reaction.
- Figure 4.30 Manganese, under caustic conditions, in the presence of magnesium ions. Under caustic conditions magnesium precipitates as Mg(OH)₂.
- Figure 4.31 Manganese, under caustic conditions, in the presence of magnesium ions, after the addition of hydrogen peroxide. Magnesium did not inhibit the reaction of manganese with hydrogen peroxide.



colourless as recorded in Figure 4.1. When caustic was added the oxidation of manganese did occur. Figure 4.27 presents the effect of caustic addition. The addition of silicate did not prevent the manganese from changing oxidation states. Following the addition of silicate, the introduction of hydrogen peroxide brought a surprise, as the reactivity of manganese was reduced appreciably by the presence of silicates under caustic conditions. Figure 4.28 shows the minor reactions of manganese with peroxide in the presence of silicates. Silicate also slows the formation of large particles of Mn(IV); the solution remains light brown and the reactivity is reduced. Although Mn(IV) has the form of a black precipitate, it was not visible⁴⁹. Most likely the Mn(IV) were prevented from forming larger more visible particles due to the surface of the glass fibres.

Magnesium sulphate (MgSO₄) is added to a bleaching system as a stabilizer. Under normal alkaline peroxide bleaching of TMP and with a manganese concentration of 10 ppm, the molar ratio of magnesium to manganese would be roughly 20 to 1. In our experiments, the ratio was set higher at roughly 50 to 1 moles of magnesium to moles of manganese. Magnesium and manganese showed no signs of reaction under acid and neutral conditions, and the solution remained clear as shown in Figure 4.29. Magnesium alone under alkaline conditions did react with hydroxide ions to form a white precipitate [Mg(OH)₂] as seen in Figure 4.30. When the same alkaline solution was prepared with manganese the white precipitate and the brown oxidized forms of manganese were both present, and the reaction with hydrogen peroxide was not inhibited. However, manganese did not form visible black particles in the presence of pulp or glass fibres. This was attributed to the presence of a surface in which Mn(IV) would deposit before it could aggregate into larger particles. Figure 4.31 shows how the alkaline solution of magnesium, manganese and peroxide appeared.

CONCLUSIONS

MANGANESE

Manganese in the (II) oxidation state is not reactive to peroxide. After increasing the pH to 10.5 manganese oxidizes to the Mn(III) oxidation state by forming either Mn(OH)₃ or MnO(OH). The manganese in the +III oxidation state reacts vigorously with hydrogen peroxide. Further addition of caustic promoted the oxidation of manganese to its most stable alkaline form of MnO₂. Although the Mn(III) forms of manganese were reactive to decomposition of hydrogen peroxide, the Mn(IV) forms are much more reactive. In the presence of pulp or glass fibres, Mn(IV) particles are most likely too small to be seen with the naked eye, and therefore were not visible. The pulp and glass fibres act as a surface on which the precipitate will deposit before large aggregates can be formed.

IRON

Under acidic and neutral conditions Fe(II) reacted slowly with hydrogen peroxide, whereas Fe(III) reacted more vigorously. The addition of caustic caused the oxidation of Fe(II) to Fe(III) and the resulting solutions were indistinguishable. The caustic solution of iron was reactive to hydrogen peroxide.

THE EFFECT OF CELLULOSE

The addition of cellulose increased the rate of hydrogen peroxide decomposition in all cases. However, the same effect could be seen when glass fibres were added to the reactions. Cellulose and glass fibres act as a reaction sites for the formation of oxygen, similar to boiling chips. The other more appreciable effect is the ability of cellulose and glass fibres to inhibit the formation of large low surface area precipitates. The precipitate materials became bound to the substrate before they could interact to form larger particles.

THE EFFECT OF LIGNIN

Lignin neither enhanced nor inhibited the reaction of manganese with hydrogen peroxide. On the other hand, the presence of lignin completely inhibited the reactions of iron with hydrogen peroxide. Unlike manganese, iron can be complexed by lignin, thus rendering it non-reactive.

THE EFFECT OF DTPA

If manganese is chelated in the Mn(II) form, the complex formed with DTPA is stable towards oxidation and reactions with hydrogen peroxide even with the addition of caustic. Iron II is also complexed with DTPA. However the complex reacts with both caustic and the presence of hydrogen peroxide. Although the reaction is not visibly reactive with hydrogen peroxide, researchers have shown that it remains reactive. ^{31, 32, 33} Iron III complexes with DTPA. The solution does not change after the addition of caustic or hydrogen peroxide. In both iron solutions precipitation is prevented by the presence of DTPA.

THE EFFECT OF SILICATES AND MAGNESIUM WITH MANGANESE

Manganese in the presence of silicates was less reactive. Not only was manganese less reactive, silicate prevented large visible precipitate particles from forming. The addition of magnesium sulfate to the system produced a white precipitate of $Mg(OH)_2$ when the solution was made caustic. In the presence of magnesium, the reaction of manganese and hydrogen peroxide was not inhibited.

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CHAPTER 5

KINETICS OF CO₂ EVOLUTION DURING H₂O₂ BLEACHING OF MECHANICAL PULP

ABSTRACT

We have demonstrated that CO_2 is produced during the bleaching reactions with alkaline hydrogen peroxide, and that the caustic environment of the bleach liquor fixes the carbon dioxide as carbonate in solution. This paper describes a novel method for the analysis of carbon dioxide in bleach liquor, using delignified pulps and milled wood lignin as model systems. The dependence of lignin concentration on the amount of carbon dioxide produced is explored. Unlike the brightening response, the amount of carbon dioxide produced was not affected by the consistency of the bleach. Our data demonstrates that lignin carboxyl groups react with hydrogen peroxide to produce CO₂. The rate of CO_2 production changes after two hours, as the amount of rapidly oxidized lignin groups are consumed, and slower oxidative reaction pathways increasingly dominate the reaction. Furthermore, the residual lignin in Kraft pulp shows a higher initial production of CO₂ than milled wood lignin impregnated dissolving pulp. Equations for the reaction kinetics for CO₂ production have been developed. The rate constants for CO_2 production as well as peroxide consumption are presented for the initial rate of reaction for up to two hours of reaction time. Finally, sources of CO₂ production are proposed.

INTRODUCTION

Alkaline hydrogen peroxide is widely used to bleach both chemical pulp and mechanical pulp¹. Two competitive pathways consume peroxide: brightening of pulp through oxidation of chromophores, and transition metal catalyzed decomposition to oxygen and water². Peroxide reacts with the hydroxyl anion as summarized in Equation 5.1 to form the perhydroxyl anion and water. Subsequently, hydrogen peroxide reacts with the hydroperoxide anion, (Equation 5.2), to form water and oxygen. This reaction mechanism has been accepted for more than ten years²⁻⁴. In the presence of Fe, Cu, and Mn ions, one mole of oxygen is formed for every two moles of peroxide consumed⁵⁻⁷.

$$H_2O_2 + HO^- \leftrightarrow HOO^- + H_2O \tag{5.1}$$

$$H_2O_2 + HOO^- \leftrightarrow O_2 + H_2O + OH^-$$
(5.2)

Equations 5.3 and 5.4 demonstrate the catalytic decomposition of peroxide in the presence of manganese⁸.

$$Mn(OH)_2 + H_2O_2 \leftrightarrow MnO_2 + 2H_2O \tag{5.3}$$

$$MnO_2 + H_2O_2 \leftrightarrow Mn(OH)_2 + O_2 \tag{5.4}$$

Early work on the decomposition of peroxide demonstrated that oxygen is the only detectable gas evolved into the headspace of the peroxide bleach^{2, 9, 10}. The only related

study, which mentions CO_2 evolution, is the work on peracetic acid decomposition in the presence of manganese, and in this case, the carbon dioxide was demonstrated to come from the decomposition of acetic acid in solution¹¹. Since this study was done at an acidic or neutral pH and the CO_2 was measured as the gaseous product, CO_2 was not converted into a carbonate. There is no mention in the literature of carbon dioxide detection, in the bleach liquor, during alkaline peroxide bleaching. The detection of carbon dioxide and a method for analysis, in the liquor, would extend the proposed mechanisms that are currently accepted. The current mechanism involves the decomposition of carboxylic acid groups¹.

Mechanical pulp is a complex system of fibres, fines, extracts, metals, and lignin. Adding the complexity of mechanical pulp to the many parameters of alkaline peroxide bleaching would be very tedious in determining trends. Therefore, in this paper, instead of mechanical pulp, dissolving pulp was substituted. Dissolving pulp is well characterised by the supplier, and has very low metal and lignin content. Milled wood lignin was used to predict the effect of mechanical pulp lignin on the production of CO₂. Finally, Kraft pulp was used to determine how close milled wood lignin represented native lignin in pulp. The bleaching parameters were chosen to represent the same additions used in the bleaching of mechanical pulps.

EXPERIMENTAL

Dissolving pulp was supplied by an eastern Canadian mill to be used as the cellulose model to which milled wood lignin was added. Another eastern Canadian mill provided black spruce thermomechanical pulp (TMP). The Kraft pulp was prepared in our laboratory, from black spruce chips.

All bleaching reactions were designed to mimic the parameters found in bleaching of mechanical pulp. Samples were bleached for two hours at 60 °C. The chemical charge based on pulp mass was 4% peroxide, 5% sodium hydroxide, 0.2% DTPA, 3% sodium silicates and 0.25% MgSO₄, unless otherwise specified.

Chemical addition was kept constant throughout the experiments, to ensure that the reactivity remained constant. Experimental preparations were carried out in polyethylene bags heat-sealed under a nitrogen atmosphere, unless otherwise specified. After the bags had been sealed, samples were kneaded by hand to ensure thorough mixing.

Milled wood lignin (MWL) was prepared from black spruce chips using the method of Brownell¹². Dioxane was used to dissolve the MWL prior to its addition to the dissolving pulp. The resulting MWL impregnated dissolving pulp samples were dried overnight under vacuum to remove all traces of dioxane.

Kraft pulp was prepared in the laboratory with H-factors ranging from 800 to 2050, which resulted in kappa numbers ranging from 28 to 62 (4.1%- 9.2% residual lignin by mass).

Following the bleaching reactions, samples of bleach liquor were separated from the pulp before analysis. The CO_2 analysis was performed on a Tekmar-Dohrman total organic carbon analyzer model DC-80, with the UV lamp turned off, to ensure that the decomposition of organic material did not contribute to the CO_2 analysis. When MWL is acidified, it becomes a strong surfactant, and causes severe foaming while being aerated inside the total inorganic analyzer. Therefore, during the trials with MWL, octanol, which acts as an anti-foaming agent, was added to both the bleach liquor samples and blanks.

RESULTS AND DISCUSSION

Analysis of the headspace gases using a gas chromatograph (Figure 5.1), demonstrated that only oxygen was evolved during alkaline peroxide bleaching of thermomechanical pulp. We suspected that carbon dioxide production might occur as well. However, carbon dioxide is a weak acid in aqueous media. It dissolves in water to form carbonic acid, in a Lewis acid base reaction in which an H₂O molecule is the Lewis base¹³:

$$CO_{2(aq)} + H_2O_{(l)} = HCO_3^{-}(aq) + H^{+}(aq)$$
(5.5)

Our bleaching system starts and finishes at alkaline pH. By using the same parameter settings that would be used to bleach high yield pulp, and having only a fraction of the lignin found in high yield pulps present, the initial pH exceeded 12, and remained well above 11.7 throughout the reaction. Thus, any carbon dioxide evolved would have reacted with the alkali to form sodium carbonate as soon as it was produced. The analysis for carbonate, or fixed carbon dioxide was performed by acidifying the solution in the total inorganic analyzer to roughly pH 3. Acidification would push the equilibrium of Equation 5.5 to the left to release free CO₂.

The analysis of bleach reaction liquor with and without the addition of hydrogen peroxide is presented in Figure 5.2. The addition of peroxide to the bleaching liquor produces a total of 13.5 μ mol of CO₂, whereas the addition of all chemicals used in bleaching except hydrogen peroxide to the dissolving pulp produces about 6.5 μ M/g of pulp of CO₂.



Figure 5.1 The output from the gas chromatograph of a sample of the headspace above an alkaline hydrogen peroxide bleach of mechanical pulp is shown.


Figure 5.2 The effect of adding peroxide to a dissolving pulp bleach on the amount of carbon dioxide produced. The no addition bar represents all chemicals and pulp with no peroxide. Caustic bar includes both sodium hydroxide and silicates with dissolving pulp. Finally, the peroxide bar is the result of bleaching dissolving pulp with all chemicals including peroxide. Sodium hydroxide and silicates appear to be the source of carbon dioxide contamination.

Treatment of the dissolving pulp with sodium hydroxide and sodium silicate also produced the same amount of CO2. In the absence of pulp, the combination of sodium hydroxide, sodium silicate, DTPA and magnesium sulphate produced a similar amount of CO_2 . Analysis of the sodium hydroxide and silicates alone indicated that sodium hydroxide and silicates appear to be the source of CO_2 contamination. Sodium hydroxide solutions used for the experiments adsorbed CO_2 from the lab atmosphere during their preparation. We accounted for this systematic error by running blank samples for all experiments. To prevent further contamination of the bleaching liquor, samples were prepared under nitrogen atmosphere.

Gonzalez-Sierra et al.¹⁰ stated that the oxygen produced during peroxide bleaching of mechanical pulp does not contribute to the brightening reactions. However, work by Gierer et al.¹⁴ have shown in model lignin studies that oxygen produced did oxidize phenolic groups. To determine the role of oxygen in the production of CO₂, alkaline peroxide bleaching was carried out using an ambient atmosphere instead of nitrogen. Figure 3 demonstrates that the increase in oxygen concentration above the reaction at atmospheric pressure did not increase the amount of CO₂ being produced, and therefore can be considered ineffective in increasing the oxidative nature of the CO₂ producing reaction.

Temperature and pressure are the key elements that affect the reactivity of oxygen with lignin. However, our alkaline peroxide bleaching was performed at 60°C under atmospheric pressure, where oxygen is sparingly soluble. Higher pressure and temperature would increase the reactivity of oxygen during the bleaching processes.



Figure 5.3. The effect of oxygen atmosphere. There appears to be no effect when using oxygen as the atmosphere when bleaching dissolving pulp.

Equation 5.6 represents the equilibrium between oxygen and the superoxide ion radical, which has a higher oxidative strength than either oxygen or hydrogen peroxide¹⁴. If the concentration of oxygen in solution were to increase, an increase in the amount of superoxide ion radical would also increase, therefore increasing the oxidative strength of the system. Since CO_2 formation is the same in N_2 and O_2 , the superoxide radical plays no role in the CO_2 formation (Figure 5.3)

$$O_{2(g)} + HO_2^- + OH_{(aq)}^- \leftrightarrow 2O_{2(aq)}^{\bullet} + H_2O_{(l)}$$
(5.6)

Consistency is another important parameter in alkaline peroxide bleaching. In industrial practise the mixing equipment limits how high a consistency pulp can be processed. At a given hydrogen peroxide charge, increasing the pulp consistency produces pulp with higher brightness. This effect has been attributed to an increase in hydrogen peroxide concentration. The rate of bleaching increases while the rate of decomposition remains about the same¹. Over the past decade, the availability of better mixing and dewatering equipment has led to the incorporation of medium (15%) to high (35%) consistency bleaching. It was expected that more carbon dioxide would be produced at higher consistencies. Figure 5.4 indicates that increasing both the pulp consistency and mass do not increase the amount of CO₂ produced. This represents an increase in consistency and a change in the chemical charge, but not the total amount of chemicals. When the amount of CO₂ was calculated on per-gram of pulp basis, the amount of CO₂ evolved remained constant. This indicates that neither consistency nor the amount of pulp present influences the amount of CO_2 evolved per gram of pulp. The only variables that remain constant are the chemical charges.



Figure 4.4 The effect of pulp mass on carbon dioxide production. The effect of increasing the consistency (shown as percentage) and pulp mass with a constant chemical addition, for bleaching dissolving pulp showed little

However, we do know from Figure 5.2 that the presence of pulp is needed to produce CO_2 .

Dissolving pulp has a low lignin content of about 0.25%. To determine whether lignin may be a source of CO_2 , milled wood lignin (MWL, 5% and 10%) was added to the dissolving pulp. Figure 5.5 shows that the amount of lignin present is proportional to the amount of CO_2 produced. The pulp matrix is complex, and lignin may not be the only source of CO_2 evolution; cellulose may also be a source of CO_2 evolution. Dissolving pulp was added to pure lignin in a series of experiments to determine whether cellulose participated in the production of CO_2 . Figure 6 shows that cellulose does not contribute to or inhibit the production of CO_2 . Although the dissolving pulp does contain a small amount of lignin, the plot still shows very little change.

Milled wood lignin has limitations as a model compound. The molecular weight is only a few thousand molecular weight, as opposed to natural lignin, which has molecular weights in the millions. Secondly, the MWL addition might not reproduce all of the natural bonds found in wood. To test the effectiveness of using milled wood lignin as a model compound, we needed a pulp source with known lignin concentrations on the order of the milled wood lignin additions to dissolving pulp. Kraft bleaching produces residual lignin concentrations between 4 and 9%, and the milled wood lignin additions were below 10%.

Figure 5.7 shows that the amount of CO_2 produced during alkaline peroxide bleaching of Kraft pulp varies linearly with the amount of residual lignin present. The open circle is the point for dissolving pulp.

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Figure 5.5 The effect of milled wood lignin addition to dissolving pulp. This graph demonstrates the direct relationship between the amount of lignin present with the amount of CO₂ evolved.



Figure 5.6 The effect of adding cellulose to lignin. There is no change in CO₂ evolution from bleaching lignin when dissolving pulp is added.



Figure 5.7 The effect of Kraft residual lignin. The open circle represents the value of dissolving pulp. The dotted line represents our hypothesis that the residual lignin contains a certain amount of highly reactive lignin for producing CO₂. The amount of CO₂ evolved is proportional to the amount of residual Kraft lignin.

The slope of the Kraft pulp data does not cross the origin, and the intercept can be interpreted as the amount of easily oxidized lignin that is found in the Kraft pulp, which would amount to almost 50% of the extra CO₂ produced from a 4% residual Kraft lignin concentration. The point for dissolving pulp was added, as this can be interpreted as the result of a more thorough Kraft pulping removal of lignin. The dashed line shows the proposed idea that the Kraft pulp has a large amount of easily oxidized groups on the exposed layer of its residual lignin. Research has been done on both model compounds and mechanical pulp to determine if alkaline peroxide bleaching is capable of dissolving some of the lignin. In both cases the results show that peroxide did not cleave aryl ether bonds that maintain the molecular weight in lignin; thus mechanical pulp maintains its high yield. The residual lignin in Kraft pulp is more condensed, and there are no easily cleavable ether bonds available¹. There is enough evidence to suggest that the lignin in Kraft pulp should produce a lower amount of CO₂. However, work by Lachenal¹⁵ et al. has shown that delignification of Kraft residual lignin during alkaline peroxide bleaching does take place, even though delignification of mechanical pulp was not detected. Before any significant delignification takes place, in Kraft pulp, the temperature must be above 90 °C; whereas temperatures above 110 °C will produce results similar to those found with conventional oxygen bleaching¹⁵. Studies also show that some depolymerization occurs and carboxyl groups are formed¹. This last statement confirms that a small percentage of the residual lignin in Kraft pulp has different properties compared to mechanical pulp lignin, or MWL. Figure 5.8, shows that some small fraction of Kraft pulp is responsible for the initial increase in the rate of CO_2 production, yet, the remaining lignin reacts to the same extent as MWL, as seen by the similar slopes.

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Figure 5.8 A comparison between residual Kraft lignin and MWL addition. Both plots follow the same slope, but the Kraft lignin appears to have a number of easily oxidized carboxylic acid groups.

Carbon dioxide has never been reported in papers as a product of alkaline peroxide bleaching, only as a product peracetic acid bleaching. It was proposed that the CO_2 came from decomposition of acetic acid¹¹. Therefore, carbon dioxide as a product of alkaline peroxide bleaching was not considered¹⁶. What is apparent from the mechanisms is the oxidation of carbonyls and alcohols to carboxylic acids. With one more oxidative step decarboxylation would occur: producing CO_2 as a product. Therefore, the most probable source of CO_2 would be decarboxylation of lignin carboxylic acid groups via oxidative reactions. One example of this would be the reaction of peroxide with aromatic rings in lignin to produce muconic acids which are then susceptible to decarboxylation.

Figure 5.9 presents the relationship between the rate of CO_2 production and peroxide consumption. Since the amount of pulp present is not a major factor (Figure 5.4) the reaction must be dependent on the amount of peroxide in solution. Two distinct reaction rates are evident: for the first 1 $\frac{1}{2}$ hrs, the rate of CO_2 production and H_2O_2 consumption is fast, and after two hours these reactions slow. The production of CO_2 follows the concentration of peroxide, and not the amount of pulp present, as the lignin concentration remains high enough not to be the limiting factor. The proposed peroxide attack on the carboxyl groups was interpreted as the dominant CO_2 producing reaction during the initial 2 hours of the bleaching reaction. After 2 hours, the easily accessible groups are consumed, and peroxide attack on the slower reacting lignin moieties dominates the kinetics.

Although several reaction mechanisms for hydrogen peroxide attack on lignin chromophores have been suggested, carbon dioxide or carbonates as products have not been measured during hydrogen peroxide bleaching. It is accepted that certain carboxylic acids, when exposed to heat and alkaline environments, will decarboxylate to form carbon dioxide. Some groups include: acetic acid, α -aryl carboxylic acids, α -keto carboxylic acids, β -keto carboxylic acids and β , γ -unsaturated carboxylic acids¹⁷. Kempf and Dence¹⁸ have proposed the production of CO₂ from reactions of hydrogen peroxide with orthoquinones. Using acetovanillone, Sun et al.¹⁹ have theorized the production of CO₂ following the rupture of the aromatic ring. Researchers have found that while reacting model compounds with alkaline hydrogen peroxide they produced (2-hydroxy-3methoxy-5-methyl- phenyl)-oxo-acetic acid, which contains an α -keto carboxylic acid. They continued by showing the production of CO₂ as a result of decarboxylation.

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Figure 5.9. Carbon dioxide evolution and peroxide consumed over time. It should be noted that both data sets respond along the same time scale in the same fashion. The dashed line represents the initial fast slope, and the solid line represents the slow rate.

KINETICS

Hydrogen peroxide and lignin must be present in order to produce CO_2 . Although the production of CO_2 is directly related to the amount of lignin present, the relationship between CO_2 production and peroxide consumption is not clear. Since the ratio of carbon dioxide produced to peroxide consumed after two hours is roughly 6:1, another more dominant reaction is consuming the majority of the peroxide. Dissolving pulp has undergone severe delignification, which resulted in the removal of most lignin and hemicellulose molecules. The only remaining component, available to react with peroxide is cellulose. Although cellulose undergoes oxidation, Figure 5.6 shows that it is not responsible for the production of carbon dioxide. A kinetic model has been developed to account for the initial rate that is observed in Figure 5.10. Equations 5.7 and 5.8 represent the model proposed, with the reaction having rate constants k_1 and k_2 respectively.

$$C + H \to P \tag{5.7}$$

$$L + H \to L^* + CO_2 \tag{5.8}$$

Here C, H, P, L and L^{*} represent cellulose, hydrogen peroxide, bleaching products, lignin, and lignin products formed during the CO_2 producing reaction respectively. Equation 5.7 represents the major peroxide consuming reaction during peroxide bleaching of dissolving pulp. Equation 5.8 represents the reaction of peroxide with lignin to produce carbon dioxide. The rate equation for peroxide in Equation 5.7 is represented here as Equation 5.9.



Figure 5.10. The initial slope calculated from the value of k₂/M, obtained from figure5.5, matches closely with the experimental data

$$\frac{H}{H_a} = 1 - k_1 ct \tag{5.9b}$$

For short times, this reduces to:

$$H = H_o e^{-k_1 ct} \tag{5.9a}$$

Here H_0 represents the initial concentration of peroxide added to the bleach. Equation 5.9a shows that the initial slope in Figure 5.9 is equal to the value of k_1c . Assuming dissolving pulp is greater than 99% cellulose, the value of c can be represented as one. Thus, the value of k_1 determined from Figure 5.9, is approximately 5 hr⁻¹. For t less than two hours, t is proportional to L and this explains why Figures 5.5, 5.7 and 5.8 are linear. The rate consumption of hydrogen peroxide is linear during the first two hours of the oxidation. The initial rate of carbon dioxide production obtained from Equation 5.8 and 5.9 is given by Equation 5.10.

$$[CO_2] = \frac{k_2 H_o L}{M} t \tag{5.10}$$

Here M represents the mass equivalent of one lignin unit associated with each CO₂ molecule produced, which is a constant combined with k_2 . Using the slope obtained from the data in Figure 5.5, and setting t = 2hrs, and knowing the initial mass of peroxide added per gram of pulp, the value of k_2 /M was found to be 12 hr⁻¹. Figure 5.10 demonstrates how the initial slope calculated from the value of k_2 /M closely fits the experimental data for carbon dioxide production over time.

CONCLUSIONS

Carbon dioxide evolution from lignin containing pulp was measured. The addition of peroxide is necessary for the production of CO₂. Preparation of samples under an oxygen atmosphere did not affect the amount of CO₂ produced. Pulp consistency does not appear to affect the rate of CO₂ production. The addition of milled wood lignin (MWL) increased the amount of CO₂ produced. The results from MWL additions and Kraft pulp trials indicate that the amount of CO₂ evolved is proportional to the lignin content of the pulp. The addition of cellulose does not affect the amount of CO₂ produced; therefore, peroxide attack on lignin is the primary source of CO₂. Our results indicate that Kraft pulp initially contains a small amount of easily oxidized carboxyl groups not found in MWL. The source of carbon dioxide is the decarboxylation of carboxylic groups in lignin molecules. The rate of CO₂ production can be represented by Equation 5.11 for times less than two hours, under the parameters used during our experiments. The rate constants for the consumption of hydrogen peroxide and carbon dioxide production were determined as $k_1=5 hr^{-1}$, and $k_2/M=12 hr^{-1}$ respectively.

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CHAPTER 6

GENERAL CONCLUSION

OXYGEN EVOLUTION

A novel method to follow the decomposition of hydrogen peroxide during alkaline bleaching of mechanical pulp was developed. Using this method, the only gas that is evolved into a hydrogen peroxide bleaching headspace is oxygen. This confirms earlier work by Martin⁰⁷².

We have shown that the seams of the bleaching bags and not the material is of greater concern to permeability. The 2 mm polyethylene bags were less permeable than the 4 mm bags, because the 4 mm bags have three factory heat seals.

Although our procedure requires the addition of all chemicals, save peroxide, to the pulp, the effect of alkali darkening is reversible, and is not detected in brightness measurement following the bleach. This darkening has been attributed to the ionization of phenolic groups in lignin. Further, the brightness seen following a DTPA wash may not be the effect of metals removal, but of a similar change in pH. All three pulps used in our experiments with different degrees of washing showed similar brightness after the pH's were set to the same values.

We have shown that the amount of oxygen evolved into the headspace during hydrogen peroxide bleaching of mechanical pulp decreases when the metals chelation increases. When the chelation of the pulp was sufficient enough to eliminate the oxygen producing reactions, the consumption of peroxide was attributed to the oxidative reactions associated with brightening the pulp. This was demonstrated when bleaching lab washed pulp.

Although iron is a catalyst for peroxide decomposition, in the presence of lignin, either as milled wood lignin or in mechanical pulp, this transition metal is not active in decomposing hydrogen peroxide during alkaline bleaching of mechanical pulp.

The decomposition of alkaline hydrogen peroxide was proportional to manganese concentration. We have shown that Mn(II) is not reactive towards peroxide decomposition. However, peroxide bleaching is performed under alkaline conditions, and manganese precipitates as MnO₂, which is the reactive species in the decomposition reactions with hydrogen peroxide under alkaline bleaching conditions. We have shown that Mn(IV) compounds are produced in the absence of pulp and stabilizer. However, in the presence of pulp Mn(IV) is not visible as a black precipitate, because the presence of pulp prevents the formation of large precipitate particles, which in turn would have been visible.

BLEACHING ADDITIVES

The addition of DTPA as a chelating agent works with Mn(II). However, in the absence of pulp and stabilizers, DTPA does not complex manganese in alkaline media. Manganese is oxidized in the presence of hydroxide ions, and the Mn(III) and Mn(IV) are not complexed by DTPA. When DTPA is added to the pulp along with the other bleaching chemicals, the results were different. The rate of peroxide decomposition of hydrogen peroxide varied proportionally in DTPA addition with the presence of manganese. When the molar ratio was 24 to 1 (DTPA to manganese), the decomposition reactions were inhibited. The presences of magnesium and calcium have been attributed to this high ratio, as they compete with manganese for complexing sites on DTPA. Further, the DTPA manganese complex is in equilibrium, as shown in Equation 6.1, and the high molar ratio would be necessary to shift the equilibrium.

$$Mn(OH)_2 + DTPA \to Mn(DTPA) + 2OH^-$$
(6.1)

Silicates, even in the absence of pulp, help to reduce the reactivity of manganese. In the presence of silicates, the rate of decomposition of hydrogen peroxide by manganese is reduced and manganese oxidation from Mn(III) to Mn(IV) is also slowed.

Magnesium, on the other hand, in the absence of pulp, had no effect on the rate of decomposition of hydrogen peroxide, in the presence of manganese. Although, the $Mg(OH)_2$, white precipitate of $Mg(OH)_2$ formed the prevention of manganese oxidation was not inhibited by coprecipitation.

CAUSTIC CHARGE

In the absence of pulp, the addition of caustic oxidizes Fe(II) to Fe(III), and this increases the catalytic reactivity of Fe for decomposing hydrogen peroxide. However, in the presence of pulp or milled wood lignin, a caustic solution of iron does not react with hydrogen peroxide. Since iron and caustic are not able to produce oxygen from the

decomposition of hydrogen peroxide, then caustic alone is not a catalyst for the decomposition of hydrogen peroxide. On the other hand, caustic does play a key role in the reactivity of manganese.

Manganese in acidic or neutral pH is not reactive with hydrogen peroxide. In other words, Mn(II) is unreactive. When the pH is increased above 9 manganese oxidizes to Mn(III) and further to Mn(IV); both of which are very reactive to hydrogen peroxide decomposition. Furthermore, not only does adding caustic increase the reactivity of manganese to hydrogen peroxide, but it also increases the reactivity of hydrogen peroxide to manganese. The dissociation of hydrogen peroxide to perhydroxyl anions has a pKa of 10.5. From our work we have demonstrated that the reactivity of hydrogen peroxide for decomposition corresponds to the dissociation to perhydroxyl anions.

PULP

The addition of cellulose to an alkaline solution of manganese or iron increases the reactivity. This has been attributed to the additional surface area available for the transition metal precipitates to adhere to. The precipitated transition metals will deposit on the cellulose surface, forming larger, low surface area particles. The cellulose also provide rougher surface or contact points at which gases can form from the reaction. The effects of cellulose can be mimicked by glass fibres, and thus the effect of cellulose is physical and not chemical. The effect of lignin on the other hand is chemical. The presence of lignin, either in mechanical pulp or as milled wood lignin, deactivates the transition metal iron. Both iron added to mechanical pulp and iron in the presence of milled wood lignin were not reactive to hydrogen peroxide decomposition. In all, for alkaline hydrogen peroxide bleaching of mechanical pulp, iron is not a factor in catalytic decomposition reactions when it is bound to the pulp.

OXYGEN EVOLUTION KINETICS

We have shown that the rate of oxygen production varies proportionally with the concentration of manganese, and is not affected by the presence of iron. Caustic also affects the rate of oxygen evolution: the more caustic present, the faster the rate of decomposition of hydrogen peroxide. Equations 6.2 and 6.3 represent a proposed mechanism for the manganese catalyzed decomposition reaction with hydrogen peroxide.

$$Mn(OH)_2 + HO_2^- \to MnO_2 + H_2O + OH^-$$
(6.2)

$$MnO_2 + H_2O_2 \to Mn(OH)_2 + O_2 \tag{6.3}$$

$$\frac{d[O_2]}{dt} = k^* [Mn(OH)_2] \left(\frac{[HOO^-]}{[OH^-]} \right)^2$$
(6.4)

Equation 6.4 represents the initial rate of oxygen evolution from manganese catalyzed decomposition of hydrogen peroxide under alkaline bleaching conditions.

CARBON DIOXIDE EVOLUTION KINETICS

The amount of carbon dioxide evolved during alkaline hydrogen peroxide bleaching is proportional to the amount of lignin present. Although the consumption of hydrogen peroxide is not clearly linked to the amount of carbon dioxide produced, the initial concentration of hydrogen peroxide is. With this information and the data that has been presented in the thesis, the kinetics of carbon dioxide production have been evaluated. Equation 6.5 represents the kinetics for the production of carbon dioxide.

$$\left[CO_{2}\right] = \frac{k_{2}H_{o}L}{M}t \tag{6.5}$$

Here M represents the mass equivalent of one lignin unit associated with each CO_2 molecule produced, which is a constant and can be combined with the equation constant k_2 . The other variables are the initial hydrogen peroxide concentration (H_o), the lignin concentration (L), and time (t). From the data presented in chapter 4, the value of k_2/M was determined to be 12 hr⁻¹.

LIMITATIONS

- Our work with measuring gas evolution is limited to hand mixing consistencies.
 This limitation could easily be overcome through engineering of a closed system with a high consistency mixer, like the one in Pointe Claire for bleaching.
- 2. Our work with pictures was limited to the ability to photograph oxygen bubbles being formed. However in most of the experiments the distinction was clear.
- 3. In the CO₂ work, the amount of data collected for MWL additions is low. The work was halted because the foaming was not controlled sufficiently by octanol.
- 4. Further work should be done to determine if MgSO₄ would inhibit decomposition in the presence of organic polymers as has been suggested by the literature.

POSSIBLE APPLICATIONS

Bleaching towers can be monitored for pressure and the volume is known. Therefore, gas chromatography could be used to monitor the concentration of oxygen and therefore monitor the decomposition of hydrogen peroxide. This would be a real time tool to determine if the system is optimized and, if not, what could be done to correct the optimization.

The first thing would be to apply this technique to model compounds to determine if the proposed mechanisms that claim to produce carbon dioxide actually do. Future work includes the determination of which carboxylic acids would react to produce carbon dioxide under bleaching conditions. The carbon dioxide measurements could be used to determine if the bleaching process is optimized for oxidative power. The more optimized the system is the faster and more decarboxylation would be observed.

FUTURE WORK

- Model compound studies, to determine which carboxylic acids are decarboxylated to CO₂.
- 2. The determination of the effect of organic polymers on the ability of magnesium sulfate to prevent transition metal catalyzed decomposition of hydrogen peroxide.
- Development a closed system that would allow the mixing of high consistency pulp and monitoring of the headspace. This would be the final parameter necessary for duplicating industrial conditions.
- 4. To determine the effect of organic polymers on the ability of magnesium sulfate in inhibiting transition metal catalyzed decomposition of hydrogen peroxide.
- 5. Since MWL inhibits the reactivity of iron, using model lignin compounds to determine which part of lignin or hemicellulose is responsible for this inhibiting effect. The most likely groups are catechol in lignin and uronic acid groups in hemicellulose, as the literature has suggested that they are responsible for complexing iron.

CONTRIBUTIONS TO ORIGINAL RESEARCH

- A new application has been developed for monitoring the oxygen evolution from an alkaline hydrogen peroxide bleach of pulp. This method does not influence the brightening reactions, and can and was used for kinetic studies.
- 2. Our work has determined that manganese is the main influence on peroxide decomposition during alkaline mechanical pulp bleaching. The effect of chelation on reducing hydrogen peroxide decomposition was shown to be the result of lowering the concentration of available manganese for reactions.
- 3. We have confirmed that decomposition of hydrogen peroxide due to alkalinity does not occur to an extent to produce detectable oxygen gas within the 2 hrs bleaching time. However, the caustic charge during peroxide bleaching plays a key role in the decomposition reactions. This role is expressed in the dissociation of hydrogen peroxide into perhydroxyl anions which in turn react with manganese during the decomposition reactions.
- 4. We have demonstrated that the kinetics of oxygen evolution is proportional to both manganese concentration and the caustic charge, when bleaching mechanical pulp. Further, we have proposed Equations 3.12 and 3.13 to account for the observed results. Finally, we present the kinetic equation 3 based on the proposed reaction mechanism.

$$Mn(OH)_2 + HO_2^- \to MnO_2 + H_2O + OH^-$$
(3.12)

$$MnO_2 + H_2O_2 \to Mn(OH)_2 + O_2 \tag{3.13}$$

$$\frac{d[O_2]}{dt} = k^* \left[Mn(OH)_2 \right] \left(\frac{\left[HOO^- \right]}{\left[OH^- \right]} \right)^2$$
(3.16)

- 5. We have developed a method for measuring the amount of carbon dioxide formed during hydrogen peroxide bleaching of mechanical pulp. Using this method the production of carbon dioxide has been attributed to reactions of hydrogen peroxide on lignin.
- 6. The kinetics of carbon dioxide formation have been proposed in Equation 5.10. This equation takes into account the dependence of carbon dioxide formation over time (t) on lignin concentration (L) and the initial hydrogen peroxide charge (H_o). The variable M is the mass equivalent of one lignin unit associated with each CO₂ molecule produced, which is a constant and can be combined with the equation constant k₂. The value of k₂/M has been determined as 12 hr⁻¹.

$$\left[CO_{2}\right] = \frac{k_{2}H_{o}L}{M}t$$
(5.10)

 In contrast to previous work, we have shown that MnO₂ is more reactive to hydrogen peroxide decomposition than Mn(OH)₃ or MnO(OH).