

# **The Role of Radical Species in Peroxide Bleaching Processes.**



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## **Declaration**

To the best of my knowledge, this thesis contains no copy  
or paraphrase of material previously published or written,  
except where due reference is made.

Graham C. Hobbs  
September 1992

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## ABSTRACT

Analysis of expressions describing peroxide bleaching show that there are two distinct mechanisms involved in peroxide bleaching. These routes can be associated firstly with traditional bleaching by the perhydroxyl anion and the second mechanism appears to involve the action of radical species. This analysis has been used as the basis for experimental work to determine the existence and relative contribution of each of these mechanisms.

Two-stage bleaching processes under acidic followed by alkaline conditions, without an intermediate washing stage, have been investigated in order to separate the contributions of anion and radical bleaching. The addition of chromium nitrate, which is known to catalyse peroxide decomposition under acidic conditions, to such a process enhances the brightness of the pulp compared with a single stage alkaline peroxide bleaching process. The addition of small quantities of aluminium nitrate to a two-stage bleaching process also enhances the brightness of the pulp, this process depending on the presence of both aluminium and manganese. The results are explained in terms of radical concentrations in the acidic stage and the proposed mechanisms and active bleaching species in peroxide bleaching.

Many transition metal ions decompose peroxide, with some producing significant quantities of hydroxyl radicals. The effects of addition and removal of these metals on peroxide bleaching have been investigated. Unusual negative effects are observed upon chelation and the addition of manganese, copper and iron does not appear to promote darkening reactions caused by the decomposition products of hydrogen peroxide.

The effect of pulp consistency on brightness response has also been investigated.

Work at constant conditions of peroxide and alkali, while varying either the total consistency or the ratio of bleachable to inert fibre shows that consistency is not a major factor in determining final brightness under alkaline conditions and indicates that the effect of radical species is small at low consistencies.

A method of determining relative hydroxyl radical concentrations in solutions of hydrogen peroxide has been developed, using *N,N*-dimethyl-4-nitrosoaniline. Under alkaline conditions the effect of the hydroxyl radical appears to be negligible, whilst under acidic conditions the concentration of radicals can be correlated to the observed final brightness.

# CHAPTER 1

## INTRODUCTION

## **CHAPTER ONE**

### **Introduction**

#### **1.1 A Brief History of the Paper Industry**

The use of paper in society is still increasing even though the use of computers has become the major information storage medium in our society (1). Instead of the predicted reduction in paper consumption, the demand for paper, particularly bleached uncoated papers (1) has increased dramatically. The total world production of paper has increased by 20% in the past decade (1).

The papermaking process was developed in China about 100AD. Pulp was prepared by pulverising mulberry, hemp, rags and other vegetable material to separate the fibres and then allowing the formed sheets to dry (2). This process did not change for many centuries (2) and the same processes of pulping and sheet forming, although automated and mechanised to such a degree that they are hardly recognisable as the same processes, are still used today.

Printing was the next major development that effected the paper industry. Guttenburg's development of the printing press in 1450 (2) meant the first mass production of printed material was possible, and so the demand for paper would have increased dramatically. Books were now freely available, making the communication of ideas to a large audience possible, and paper was established as the primary means of information storage and communication of ideas. Paper continued in this role until the widespread use of computers and electronic communications.

To meet the growing demand, the production of paper, still made by hand, had to be improved. The development of new pulping equipment was important but the invention of the paper machine; the first patent was granted in 1798 to Nicholas-Louis



Robert (2), was the next major advancement in the paper industry. The Fourdrinier paper machine, named after the financiers of the initial machine (2), still bears the same name. About thirty machines were built in the first twenty years of the next century in England to meet the demand for paper.

The demand for raw material was now such that alternatives needed to be found. Previously rags were the main source of fibre (2), but the use of wood as the principal source of fibre was to become common practice in the 1870's. The idea of mechanical groundwood pulp (Keller 1840 (2)) and sulfite pulping (Tilghman 1857 (2)) were implemented as the technology became available and made these processes both practical and feasible. While new pulping and bleaching technologies have increased and the size and production of paper mills has increased, essentially the same processes are still used.

The future demand for paper based products is difficult to predict but the market is currently still growing (1). The world average consumption of paper products per person is 45 kg / year (3) and many developing countries are using well below this level so an increase in demand could be predicted. However, this has to be offset by the increasing awareness of the general population regarding the environment which will tend to reduce or change the demand for paper, and hence reduce the impact the production of paper has on the environment.

The major changes to the paper industry in the foreseeable future would appear to be related to environmental concerns (4,5). These can take two forms: firstly the by-products of the paper making process have been the cause of major concern and secondly the preservation of native forests. During this decade and the last decade there has been an increasing public awareness and concern regarding the waste disposal and effluent treatment from major industries. This has brought about a significant change in practice, not only in the paper industry but all major industry, which has in many cases

been expensive. This public concern has been acted on by various parliaments, due to public pressure, to legislate environmental regulations and guidelines. While existing technologies have been modified to meet the new regulations (4,5), and new processes developed (4,5) there is still a call for even stricter legislation and improved technologies. The demand for more environmentally conscious technology does not appear to have been met with a changing demand in pulp quality. The same high brightness chemical pulps are still in demand.

The second major area of concern is with the natural resources used in the manufacture of paper. There is an increasing demand in many developed countries for the preservation of the remaining native forests, but the demand for paper products is, however, still increasing (1). This has led to the development of plantations of fast growing species to meet the demand for pulpwood. For example, in Australia 85% of newsprint is produced from plantation radiata pine, and only 15% is made from native eucalypt wood (6). There has also been a shift away from low yield chemical pulps to semichemical and mechanical pulps in some applications (4,7). This means that a lower mass of wood is required to produce the same quantity of pulp. The other major development in the industry, again because of public pressure and legislation, is the increased emphasis on recycling of paper products (4-6). While this practice has been a part of the industry for many years, the requirement to increase the proportion of fibre to be recycled leads to some problems. Secondary fibre has lower strength properties than virgin fibres, and subsequent processing reduces the strength properties further, and therefore, fibre can not be recycled indefinitely. The processing, transportation and collection of recycled paper means that the cost is not significantly lower than that of virgin fibre so there is no cost advantages associated with recycling. The advantage of recycling, apart from using less wood for paper manufacture, is the reduction in landfill caused by paper products.

These issues will cause changes in the industry in the next decade, but the future of the

paper industry seems assured, although changes will be necessary, as most new communication technologies rely on paper products in many different ways.

## 1.2 The Composition of Wood

Wood consists of a variety of components including cellulose, hemicellulose, lignin and low molecular weight extractives (8-10). A typical composition is shown in Table 1.1.

**Table 1.1** The composition of wood.

Component	Softwood	Hardwood
Lignin	25-35% <sup>1</sup>	15-25% <sup>2</sup>
Extractives and ash	4-10%	4-10%
Cellulose	40-50% <sup>3</sup>	40-50% <sup>3</sup>
Hemicellulose	25-35%	25-35%

<sup>1</sup> Softwood lignin contains primarily guaiacyl units (9,10).

<sup>2</sup>Hardwood lignin contains both guaiacyl and syringyl units (9-10).

<sup>3</sup>The degree of polymerisation of cellulose is about 10 000 (10).

The composition varies between species, within species and with location in the tree. Therefore, it is difficult to characterise wood solely on its chemical composition.

The carbohydrate component of wood consists of cellulose and hemicellulose.

Cellulose is a linear polymer of 1,4- $\beta$ - bonded anhydroglucose (10) and the degree of polymerisation is about 10 000 (9-10). Hemicellulose is a polymer of various sugar units: principally glucose, mannose, galactose, xylose, arabinose, 4-O-methylglucuronic acid, galacturonic acid and rhamose (10). The molecular weight of

hemicellulose is much lower than cellulose and the polymer can be branched.

Lignin is a complex polymer of phenylpropane units (9,10). The basic precursors of lignin are [1] p-coumaryl, [2] coniferyl (guaiacyl) and [3] syringyl alcohols. In both hardwood and softwood lignin the presence of p-coumaryl units is negligible (10). Softwood lignin consists primarily of coniferyl [2] units (9,10) while hardwood lignin contains both coniferyl [2] and syringyl [3] units (9,10). The ratio of these units in hardwood lignin ranges from 4:1 to 1:2 coniferyl to syringyl units (9,10).

### **1.3 Pulping and Bleaching Processes**

There are a variety of methods for pulping and bleaching wood (11-16) with the major consideration being the end use of the paper product. Such considerations as strength properties, optical properties, printability and longevity of the paper need to be ascertained in order to determine appropriate pulping and bleaching methods for a particular application.

#### **1.3.1 Pulping**

Pulping refers to the separation of wood, in the form of logs or chips, into separate fibres. There are two basic methods of converting wood into pulp. Firstly the wood can be chemically treated to remove the lignin portion and thus separate the fibres, or secondly the wood can be mechanically treated to separate the fibres while retaining the lignin. The processes are very different and produce pulps for different end uses.

Chemical pulps are produced by chemically treating the wood such that the lignin portion of the pulp dissolves leaving mainly cellulose, hemicellulose and some residual lignin. The conditions used to prepare a variety of chemical and semichemical pulps are set out in Table 1.2

**Table 1.2** Conditions for the production of chemical and semichemical pulps (after Smook (11)).

	Kraft	Acid Sulfite	Bisulfite	NSSC <sup>1</sup>	Soda <sup>2</sup>
Chemicals	NaOH Na <sub>2</sub> S	H <sub>2</sub> SO <sub>3</sub> M <sup>4</sup> (HSO <sub>3</sub> )	M <sup>3</sup> (HSO <sub>3</sub> )	Na <sub>2</sub> SO <sub>3</sub> Na <sub>2</sub> CO <sub>3</sub>	NaOH Na <sub>2</sub> CO <sub>3</sub>
Cooking Time (h)	2-4	4-20	2-4	0.25-1	2-4
pH	13+	1-2	3-5	7-9	13+
Temperature	170-180	120-135	140-160	160-180	170-180

<sup>1</sup> Neutral sulfite semichemical, <sup>2</sup> Additive such as AQ can also be present..

<sup>3</sup> M = Mg<sup>2+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>. <sup>4</sup> M = Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>.

Mechanical pulps are produced by physically separating the fibres by mechanical force (11). There are two major types of mechanical pulps, stoneground wood (SGW) and refiner mechanical pulps (RMP) of which thermomechanical pulp (TMP) is the predominant type (11). SGW is produced by pressing a block of wood against a rotating grindstone (17). Fibres, and fragments of fibres, are torn from the surface of the wood and, after subsequent screening a pulp suitable for papermaking is obtained. Stoneground woods are the oldest type of mechanical pulps and, due to the short fibres have low strength properties (11). Refiner mechanical pulps are produced by passing wood chips, which may have been pre-steamed (TMP) or treated with chemicals to soften the wood (semi-chemical pulps), through a refiner (18). The refiner consists of counter-rotating grindstones. The resultant pulp, after several stages of refining is ready for further processing. These pulps contain a greater proportion of long fibres,

and thus have better strength properties than stoneground woods.

It is possible to produce pulps using a combination of chemical and mechanical methods (11). The properties of these pulps are intermediate to those of chemical and mechanical pulps and are gaining wider acceptance as partial replacements for chemical pulps in some applications. The production of these pulps requires less mechanical energy than mechanical pulps and lower chemical application than chemical pulps and have an intermediate yield. The properties of chemical and mechanical pulps are significantly different with respect to both physical and optical properties as outlined in Table 1.3.

**Table 1.3** Comparison of chemical and mechanical pulp properties

Pulp type	Chemical	Mechanical
Yield	low 40-55%	high 90-95%
Fibre properties	long	short
Printability	poor	good
Pulping chemical cost	high	negligible
Pulping energy	low	very high
Bleaching chemicals	high, multistage	lower, lower brightness
Cost	bleaching required	achieved
Bleachability	relatively easy to reach high brightness (85-90%ISO)	Difficult to achieve high brightness (75 %ISO)
Strength properties	high	low
Examples	Kraft, Sulfite, Soda	SGW, TMP, RMP

### 1.3.2 Bleaching

Bleaching is undertaken to improve the optical properties of the pulp, where the greatest concern is the brightness of the pulp. The aims of bleaching chemical and mechanical pulps are significantly different (11). When bleaching chemical pulps the bleaching procedure should remove essentially all of the residual lignin to leave a pulp comprising mainly cellulose and other carbohydrate components. In the case of mechanical pulps, in order to preserve the high yield, bleaching selectively removes or modifies the coloured components of lignin, which only constitute a small percentage of the lignin macromolecule, without significantly altering the yield or delignifying the pulp. For these reasons different bleaching reagents are used for chemical and mechanical pulps.

The bleaching of chemical pulps, and especially kraft pulps, is performed in several stages, the first part of the sequence being to eliminate the residual lignin and then the latter part of the sequence aims to increase the brightness of the pulp (11). The use of chlorine based bleaching reagents such as elemental chlorine, chlorine dioxide and hypochlorite is common with chemical pulps and leads to environmental concerns regarding the by-products of this treatment (11). These increasing environmental concerns are a major driving force behind development of different bleaching technologies that reduce or remove the need for chlorine based chemicals. Thus elementally chlorine free (ECF) and totally chlorine free (TCF) pulps are now being produced (19-21). To replace these chlorine based chemicals, reagents such as ozone, oxygen and hydrogen peroxide are increasingly being used in the bleaching of chemical pulps (12-15). Alkaline extraction stages with the addition of oxygen and/or hydrogen peroxide are also used and can reduce the quantity of chlorine based chemicals required (12,13). The reactions occurring in these processes are as yet ill-defined, but their understanding is of enormous potential economic importance. Under conditions where selective lignin removal is required, as in bleaching of chemical pulps, it is possible that processes involving the hydroxyl radical play a very

significant role (21). However, it is also known that attack on the carbohydrate component of the pulp by this radical species can also lead to depolymerisation (22), resulting in unacceptably low mechanical strength properties. The controlled activity of this radical species as a selective reagent could therefore be crucial in moving to chlorine free bleaching.

The use of chlorine dioxide as a partial or total replacement for chlorine is also a viable process (12), and although still using chlorine based bleaching reagents, produces significantly lower quantities of harmful by-products, such as dioxins and other polychlorinated organics (12-14). A peroxide stage can also be used as the final stage of a multi-stage bleach sequence when several extra points of brightness are required (23).

The bleaching of mechanical pulps requires less severe conditions than for chemical pulps as the aim is to preserve the high yield while improving the brightness, therefore removal of lignin is not wanted. For this reason different reagents such as sodium dithionite (hydrosulfite) and hydrogen peroxide are commonly used for bleaching mechanical pulps. It should be noted that the bleaching of mechanical pulps with hydrogen peroxide is performed under milder conditions than the bleaching of chemical pulps, and different types of reactions occur (11,13). These reagents are capable of bleaching mechanical pulps to brightnesses suitable for lower grade paper products, such as newsprint (11), while not lowering the yield of the pulp significantly. Brightnesses of 75% %ISO are quite possible with peroxide in a single stage (11). The cost of peroxide is significantly higher than that of dithionite but is capable of producing higher brightness pulps with greater thermal stability (11). The proportion of mechanical pulps bleached with hydrogen peroxide is increasing rapidly.

#### **1.4 Peroxide Bleaching of Mechanical Pulps**

Hydrogen peroxide has been used as an oxidative bleaching reagent for mechanical



pulps for many years (24-29). As with bleaching of all mechanical pulps, the process is lignin retaining, that is, the lignin is modified to reduce the colour but not removed from the fibre (11). In this way the high yield of mechanical pulps is maintained while the optical properties are improved. The major bleaching reagent for bleaching of mechanical pulps is sodium dithionite (hydrosulfite) (30,31) but the proportion of pulp bleached with hydrogen peroxide is rapidly increasing due to the benefits it offers. Peroxide is capable of achieving greater brightness gains and the pulp is less susceptible to reversion processes (28,32-34), the disadvantage being the cost of peroxide compared to sodium dithionite. Two-stage bleaching with peroxide followed by dithionite is used when high brightness mechanical pulps are required (29,32,35-38). After the peroxide stage, dithionite is capable of bleaching to several %ISO brighter at a much lower cost than peroxide. One of the major benefits of peroxide bleaching is that the decomposition products, water and oxygen, are of no environmental concern, whereas other bleaching reagents can produce by-products which are harmful to the environment.

#### **1.4.1 Peroxide Bleaching Conditions**

Hydrogen peroxide is a very versatile bleaching reagent that can be used in a variety of ways. These include use in the bleaching of chemical pulps (23), steep bleaching of mechanical pulps (28) and the more traditional bleaching of mechanical pulps (24,29). The conditions used vary depending upon the type of pulp, the final brightness required and many other factors.

Typically the following conditions are used for the bleaching of mechanical pulps:

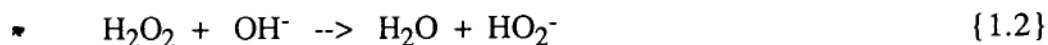
Peroxide charge	: 1-3% on o.d. pulp.
Alkali charge	: 1-2% on o.d pulp, sufficient to give an initial pH of
(Sodium hydroxide)	10.5 - 11.5.
Consistency	: 10-30%.
Time	: 1-4 hours.
Temperature	: 40-80°C.
Stabilisers	: Sodium silicate (2-5% on pulp of a 30% solution), Magnesium salts (0.05%), or Chelating agents (0.2-0.5%).

#### 1.4.2 The Chemistry of Peroxide Bleaching

The perhydroxyl anion,  $\text{HO}_2^-$ , is thought to be the species primarily responsible for bleaching of mechanical pulps (24,29). For this reason peroxide bleaching is performed under alkaline conditions to maximise the concentration of this species. Hydrogen peroxide is a weak acid with  $\text{pK}_a = 11.6$  (39), and dissociates according to equation {1.1}



Therefore under alkaline conditions the concentration of the perhydroxyl anion can be increased according to equation {1.2}

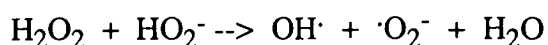


This is further complicated by the influence of alkali alone on pulp brightness. In the absence of peroxide, or at low levels of peroxide the pulp can darken. This phenomena is known as alkali darkening (29,40,41). Because pulp darkens in the presence of alkali it is usual practice to ensure that there is peroxide remaining at the completion of the bleaching process. This is typically of the order of 10% of the initial peroxide

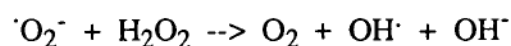
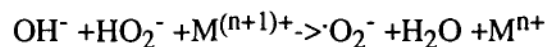
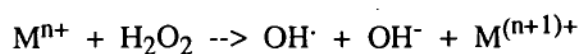
charge (29,40). In a single stage bleaching system this peroxide is normally neutralised with sulfur dioxide prior to the papermaking process (25), but the possibility of recycling this peroxide, due to the cost of the reagent, is now being considered in more cases (27,40,42-44). Furthermore, the decomposition of hydrogen peroxide increases at higher alkalinities (24), whether this is due to the influence of residual transition metal ions or the base induced reductive cleavage of peroxide. It is therefore necessary to achieve a balance between the concentration of the perhydroxyl anion and the level of peroxide decomposition reactions and alkali darkening caused by high pH. Due to these processes an optimum pH for the peroxide bleaching of mechanical pulps is observed (24,28,34,45, Figure 2.18), generally in the range pH 10.5 - 11.5.

In alkaline peroxide solution species other than the perhydroxyl anion can be formed, and some of these species can be powerful oxidants (39,46-48), capable of reacting with the lignin and cellulose portions of mechanical pulps. While these species are not usually considered useful bleaching reagents, and efforts are made to reduce their concentrations, they do need to be considered in the overall chemistry of peroxide bleaching. In the absence of pulp, alkaline peroxide solutions can decompose via mechanisms that involve the formation of species such as the hydroxyl, perhydroxyl and superoxide anion radicals,  $\text{OH}^\cdot$ ,  $\text{HO}_2^\cdot$  and  $\text{O}_2^{\cdot-}$  (39,48). Many mechanisms have been proposed to account for the generation of these species, with transition metal ions playing a significant role in the production of these radical species. Such a scheme is shown below.

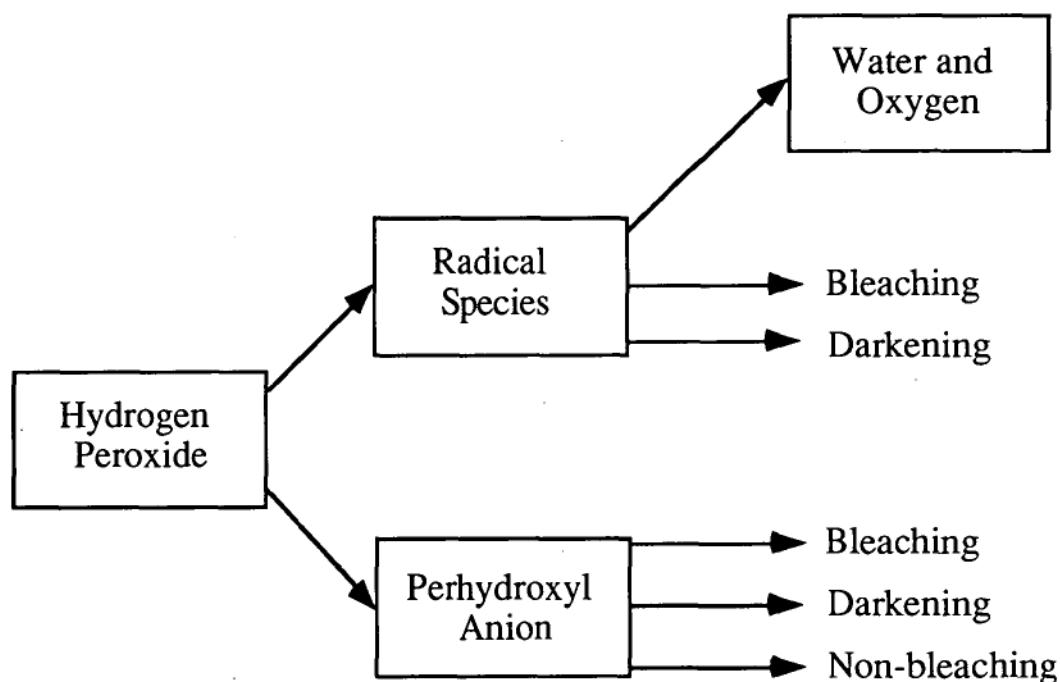
Firstly, the base induced cleavage of hydrogen peroxide (48-50);



or secondly and more importantly, by transition metal ion catalysed decomposition of hydrogen peroxide (48,49);



The rate of the third reaction is small and is governed by the presence of transition metal ions. The role of these species has traditionally been thought to be negative, causing darkening of pulp (41) and loss of pulp strength (51). However, it has also been proposed that these species may have a positive influence on peroxide bleaching. Figure 1.1 shows a possible reaction scheme for this.

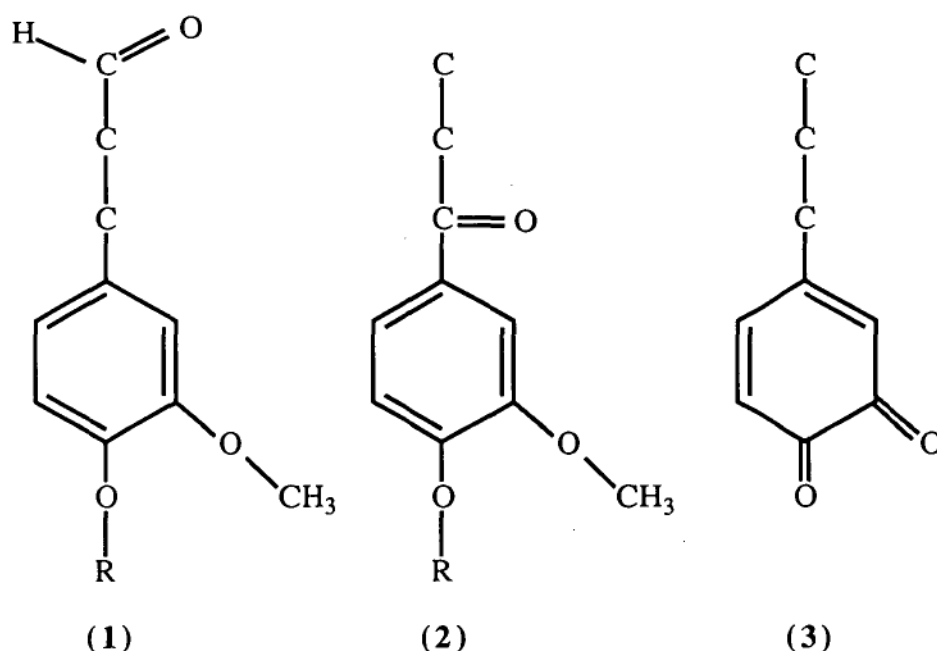


**Figure 1.1** The possible role of radical species and the perhydroxyl anion in peroxide bleaching processes (after Burton *et al.* (26)).

### 1.4.3 Chromophoric Structures in Lignin

Lignin is a polymer composed of phenyl propane units and constitutes approximately 30% by weight of the mass of wood (9). Within the wood the only coloured component is lignin (9) and only a small proportion of the lignin units are coloured or

potentially coloured. It is generally thought that there are three main types of chromophoric structure present in mechanical pulps (52-54), these can either be present in the native lignin or be introduced during pulping (46). These structures are shown in figure 1.2.

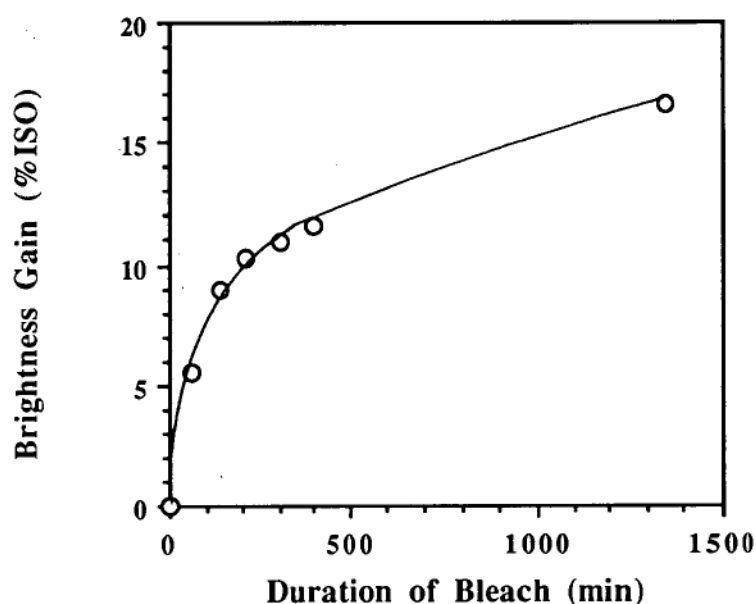


**Figure 1.2** Chromophoric structures present in mechanical pulp lignin. (1)  $\alpha$ - $\beta$  unsaturated aldehydes, (2)  $\alpha$ -carbonyls and (3) o-quinones. R = H or the lignin macromolecule.

Peroxide is thought to be capable of reacting with each of these types of structures, and in so doing, enhance the optical properties of the pulp. In the case of  $\alpha$ -carbonyls peroxide only appears to react when R = hydrogen (53), that is a p-hydroxyl group is present. The abundance of these structures in lignin is uncertain and varies with wood species and pulping processes but  $\alpha$ - $\beta$  unsaturated aldehydes are thought to constitute about 3-5% of lignin units (54,55). Quinones appear to be primarily introduced during pulping and only present in very low quantities in native lignin, but due to their high absorption coefficient can contribute significantly to the colour of pulp (55,56).

The brightness-time response of mechanical pulps to alkaline hydrogen peroxide

typically shows two distinct phases (52). An initial rapid increase in brightness being followed by a much slower brightness increase with time, as shown in figure 1.3. This response is noted under conditions where both peroxide and alkali concentrations are declining, as encountered under industrial brightening conditions, and also under conditions of constant reagent concentrations (57).



**Figure 1.3** Brightness response of *E.regnans* SGW to alkaline hydrogen peroxide. Conditions 1% consistency, 50°C, pH 11.0, 6% peroxide on o.d pulp.

Attempts have been made to try and identify the chromophore types that are reacting at various stages of peroxide bleaching and give rise to the brightness-time profile observed. It appears that  $\alpha$ - $\beta$  unsaturated aldehydes and o-quinones can react quickly with peroxide (52), and so could be related to the initial rapid increase in brightness and that  $\alpha$ -carbonyls could be responsible for the slow residual rate of brightening. However, it is well known that dithionite reacts with  $\alpha$ - $\beta$  unsaturated aldehydes and o-quinones (52), even after extended times of peroxide bleaching significant brightness increases can be observed after subsequent dithionite bleaching, indicating that some of these structures must still be present. It is clear that much work is still needed in this area to decide which structures are susceptible to elimination by alkaline hydrogen

peroxide.

#### **1.4.4 Delignification and Brightening Chemistry**

The aim of peroxide brightening of mechanical pulps and delignification of chemical pulps are significantly different. In mechanical pulp bleaching the aim is to modify chromophoric structures to increase the brightness while not significantly reducing the yield of the pulp, that is, the lignin structure is left essentially intact. In the delignification of chemical pulps the role of peroxide, whether used with or without oxygen in an oxidative extraction stage, is to help breakdown the structure of the residual lignin so it can be easily removed. Thus, mechanical pulp bleaching is yield preserving while chemical pulp bleaching aims to degrade and remove residual lignin.

The colour of mechanical pulp lignin is due to a small fraction of the lignin (54-56). Therefore, in order to bleach the pulp, a very selective reagent is required, but also a relatively mild reagent so as not to react with other structures or degrade the lignin macromolecule. Peroxide bleaching of mechanical pulps is a well established procedure while its use in delignification of chemical pulps is a relatively new process (58).

The presence of radical species in mechanical pulp bleaching has traditionally been thought to have negative effects. However, delignification requires more severe conditions than brightening and the presence of radical species are thought to play a more significant role. Hydroxyl radicals are thought to be essential for maintaining a reasonable rate of oxidative processes, as well as contributing to undesired cellulose degradation (59).

### 1.5 The Australian Industry

While the pulp and paper industry is important in Australia, it is still a net importer of paper products (60). As shown in Table 1.4, Australia is close to self sufficient in tissue and packaging grades but produces only about half its requirement for newsprint and fine writing papers (60). As can be seen from this table, approximately 800 000 tonnes of paper products are imported each year significantly influencing the economy of the country, by incurring a trade deficit of A\$1.33 billion.

**Table 1.4** Consumption of paper in Australia in 1989/90, all figures are in 1000 tonne units (after Sykes-Smith (60)).

Product	Production	Exports	Imports	Consumption
Newsprint	371	5	288	654
Printing and writing	406	27	439	823
Tissue	167	0	10	177
Packaging and Industrial	1067	136	221	1170
Total	2011	168	958	2824

Australia has approximately 41 million hectares of forest, 34.5 million hectares of which is native eucalypt. Of this total area 18% is managed for wood production. The employment generated in forestry, pulp and paper manufacture and related areas is approximately 184 000 (60).

There are 21 pulp and paper related mills in Australia (60) operated by six major companies. They produce a full range of pulp and paper products mainly from native eucalypt or plantation Radiata pine. Recycling is also a major part of the industry with 900 000 tonnes of paper product recycled each year (60) and the possibility of a new



recycling/deinking plant in the near future (6). This new development will be the first facility in Australia to recycle newsprint and magazine grade papers for use as newsprint. Currently approximately 45% of fibre processed in Australia is recycled.

### **1.6 Aims of the Project**

Although hydrogen peroxide has been used as an oxidative bleaching reagent for many years, recently much debate regarding active bleaching species has appeared in the literature. As outlined in the previous section (Chapter 1.3) the perhydroxyl anion is thought to be the active bleaching species, and the role of other decomposition products of hydrogen peroxide, including radical species, is uncertain.

This project aims to elucidate the role of radical species in peroxide bleaching of mechanical pulps, both under alkaline conditions and under acidic and neutral conditions not usually encountered with peroxide. In so doing, it may be possible to use conditions where radical species are major possible bleaching species and compare this with conditions under which the perhydroxyl anion is dominant. Such experiments may enable a conclusion to be reached relating to the role of different species in peroxide bleaching.

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## CHAPTER 2

# TWO-STAGE PEROXIDE BLEACHING SEQUENCES

## CHAPTER TWO

### Two-Stage Peroxide Bleaching Sequences

#### 2.1 Literature Review

As has been outlined in the previous chapter, peroxide bleaching of mechanical pulps is generally performed in a single alkaline stage (1-4). The removal or deactivation of peroxide decomposition catalysts and subsequent stabilisation of the bleach liquor is of major importance (3-16). Decomposition of hydrogen peroxide is thought to be undesirable due to the expense of the bleaching reagent and the products of this decomposition are not seen as having any significant bleaching effect (2,5,8,16-18).

Conventional single stage peroxide bleaching of mechanical pulps has been optimised to such an extent that major improvements in the process seem unlikely. The use of new bleach liquor stabilisers and increasing the consistency have been the most recent developments. Therefore, if there are to be any significant changes in the peroxide bleaching of mechanical pulps the use of multiple stages, wider ranges of conditions with respect to pH and the investigation of the role of other possible active bleaching species could be considered.

Examination of previously reported kinetic expressions describing peroxide bleaching (19-22) reveals the possible existence of two parallel paths of peroxide bleaching.

Associating these routes with the presence of the perhydroxyl anion and free radical species will allow the development of novel peroxide bleaching sequences to test these assumptions and to provide supporting evidence for the validity of the kinetic analysis performed.

##### 2.1.1 Proposed two-stage Bleaching Sequences

There have been several proposed processes for dual stage peroxide bleaching



appearing in the literature recently (23-32). These can generally be classified into two distinct groups. Firstly, the pulp is exposed to two consecutive alkaline stages (23-30), with differing ratios of bleach chemicals in the two stages and various washing and recycling procedures from one or both stages (23,24,26,29). Secondly, the pulp is exposed to peroxide at two distinctly different levels of pH, generally one of the stages being a conventional alkaline stage, but the other stage could be either neutral or acidic (25,32) or of higher pH than a conventional alkaline peroxide bleach stage (27). In some of these stages transition metal ions are added (32).

Two stage peroxide bleaching under alkaline conditions, with various recycling strategies have been studied in some detail (23,24,26,29). Generally these sequences are used when high brightnesses are required. It appears that the best strategy is to apply most or all of the total charge of peroxide in the second stage ( $P_2$ ) (23,26,29), with less in the first stage ( $P_1$ ), or recycling peroxide from the  $P_2$  stage to the  $P_1$  stage (23,24,26,29). With these strategies the optimised two stage sequence using a given total peroxide charge (25,26) gives a higher brightness than an optimised single stage bleach using the same peroxide charge. However, it should be noted that in some of these processes significantly more alkali is required compared to a single stage bleach (25,29), thus increasing chemical costs. Secondly, more capital expenditure is required for the extra bleach tower, presses and associated equipment needed for these processes (24), and this needs to be considered in the overall cost efficiency of the process.

Kinetic models of peroxide bleaching have been developed which indicate that for a given charge of peroxide a limiting brightness is achieved (33,34). Therefore, the application of a higher chemical dosage will result in a higher brightness of the pulp, but also a high peroxide residual. This can be used to explain why a higher peroxide charge is applied in the second ( $P_2$ ) stage. Because of the cost of peroxide as a bleaching chemical, there is a need to reuse this peroxide and hence, these two stage

alkaline processes usually include recycling of the residual peroxide. The addition of alkali to reestablish the pH to values normally associated with the start of a conventional peroxide bleach, pH 10-11, has also been proposed as a second stage of a two stage process (29). When there is a high peroxide residual after the  $P_1$  stage, this is an efficient method for utilising or 'reactivating' the hydrogen peroxide still present in the pulp slurry. Although no further peroxide is added the concentration of the perhydroxyl anion is increased by this addition of alkali, thus enabling further bleaching to occur.

Various processes have been developed in which dual stage peroxide bleaching is performed under conditions of pH that are not typically associated with peroxide bleaching of mechanical pulps (25,32). Systems using acidic and then alkaline conditions have been shown to give a similar or greater brightness using less peroxide. However, as the  $P_1$  stage is acidic more alkali is required to give a similar initial pH in the  $P_2$  stage compared to the single stage process (25).

A similar process, but with added transition metal ions, either tin, titanium or vanadium can be used for either chemical or mechanical pulps (35), to both increase the brightness and delignification of the pulp. This process does not reduce the viscosity of the pulp as would occur in acidic peroxide without added metal ions (35). The brightness of the pulp is only increased if the pH of the acidic stage is not lower than approximately 3. Various metal additives show these properties to differing degrees, with tin appearing to be the most active.

In another process, acidic hydrogen peroxide can be used as a pretreatment in a two stage process to attain high brightness using only peroxide (25). This, coupled with recycling of peroxide leads to a viable process. Again less hydrogen peroxide is required for a given brightness in the two stage process, but the loss of some bleaching reagent in the recycling makes the advantage small.

Another approach to two stage bleaching is to have the first stage at a much higher pH than normally used for conventional peroxide bleaching (27). This process, known as hyper-alkali peroxide bleaching, increases the strength of the pulp, and the peroxide present in the first stage appears only to prevent significant darkening from occurring. While producing a stronger pulp, additional alkali and presumably acid would be required for this process.

### **2.1.2 Separate Radical and Anion stages**

It would appear from the literature that both radical species (36-43), particularly the hydroxyl radical, and the perhydroxyl anion (39) are capable of reacting with structures typically present both in lignin and cellulose. Therefore it would be reasonable to assume that a bleaching process that exposes mechanical pulps to both of these species could be beneficial, or is at least of interest to determine the active species and mechanisms of peroxide bleaching. Furthermore, if the two processes can be separated, as much as possible, it may be feasible to determine the relative contribution of each mechanism.

Clearly, increasing the pH of hydrogen peroxide solutions increases the concentration of the perhydroxyl anion (49), and could be associated with increasing the rate of bleaching due to this species. However, at elevated pH, above approximately pH 11, darkening reactions caused by alkali occur to such an extent that the bleaching response is reduced (2,3,20). For this reason the traditional bleaching conditions of approximately pH 11.0 initially, should be used for exposure of the pulp to the perhydroxyl anion.

For radical induced bleaching other conditions need to be used. The decomposition of hydrogen peroxide in alkaline solution in the absence of pulp proceeds, at least partly via a radical chain mechanism (47,48), and presumably this also occurs in the presence of pulp to some extent. This may be due to the presence of transition metal ion

impurities (49-50) or may be a route of peroxide self-decomposition (47,48).

However, under normal bleaching conditions the pulp will be exposed to some radicals, especially pulps which have high transition metal ions contents. For this reason it is not possible to totally separate the two mechanisms.

In order to expose pulp to radical species under conditions of reduced perhydroxyl anion concentration, neutral or acidic conditions need to be employed and the addition of a peroxide decomposition catalyst to produce radical species is required as the decomposition of peroxide under acidic conditions is very slow. Another reason for this approach is that the oxidation potential of the hydroxyl radical increases in acidic media (51,52), so any effects due to this species could be enhanced in acidic solution, however, the radical is still capable of reacting under alkaline conditions.

There are few reports of beneficial effects resulting from the presence of catalytic species during bleaching (25,53-55). Introduction of manganese has been shown to accelerate delignification and reduce carbohydrate degradation in studies of oxygen delignification (54,56). Transition metal species have also been shown to be effective in catalysing oxygen delignification of residual lignin in chemical pulps (55,57,58). Recent studies have also shown that transition metal catalysts can promote peroxide bleaching efficiency during two-stage processes, initially using acidic conditions followed by a conventional alkaline peroxide stage (55,57,58).

In some cases transition metal catalysed decomposition of hydrogen peroxide is thought to proceed via free radical chain reactions, producing intermediate species such as  $\text{OH}^\cdot$  and  $\text{O}_2^{\cdot-}$ , and there has been recent interest in the possible role of these active species in chromophore elimination (38,59). The radicals formed, and particularly the hydroxyl radical, are powerful oxidants and capable of reacting with structures typically present in lignin.

Chromium is unusual in that the maximum decomposition rate for hydrogen peroxide in the presence of this transition metal occurs under slightly acidic conditions (16), while the rate of decomposition is negligible at  $\text{pH} > 8.0$ . In contrast, transition metal ions including manganese, copper and iron, which are often present in pulp samples, have maximum activity under alkaline conditions (60,61). This observation for the behaviour of chromium may allow the pulp to be exposed to radicals produced by the catalytic decomposition of hydrogen peroxide in a pH range where the concentration of the perhydroxyl anion is low, which enables the effects which occur under both acidic and alkaline conditions to be studied separately.

In the present work, parallel pathways for peroxide bleaching have been examined using a range of pH conditions. Further experimental work aimed at providing additional evidence for this dual mechanism has also been undertaken, and discussed in the context of the literature pertaining to active species in peroxide bleaching.

### **2.1.3 Kinetic Models of Peroxide Bleaching**

During the past decade there has been an increasing interest in the kinetics of peroxide bleaching (19-22). This interest probably arises from the greater use of peroxide as a bleaching reagent for mechanical pulps as a replacement for reductive treatment with hydrosulfite (2). Kinetic phenomena during peroxide bleaching of wood have been much less extensively reported than for many other important reactions, particularly alkaline pulping processes (62-64) and therefore, interpretation of these studies may lead to further understanding of the mechanisms of peroxide bleaching.

There have been two basic approaches to formulating models to simulate the kinetics of alkaline peroxide bleaching (4,19-22,65). One approach is to relate brightness increase to variables such as initial pH and peroxide charge, temperature, stock concentration etc. (4,65). This type of formulation may be useful in predicting final brightness of a pulp using a given set of parameters, particularly under mill conditions. The other type

of kinetic formulation can be closely associated with the approaches of standard chemical kinetics. In this case, too, kinetic expressions must also be regarded initially as empirical expressions. However, these expressions should reflect the net result of many concurrent elementary processes which occur during bleaching.

Many of the difficulties with interpretation of these types of kinetic expressions are identical to those encountered when considering expressions describing alkaline pulping processes (62-64). These include the heterogeneous nature of the reaction, uncertainties in the importance of diffusion processes and questions regarding the validity of defining species within the lignin macromolecules on a molar concentration basis (64). However, accepting these possible limitations, it is possible to proceed with an analysis of this kinetic expression.

However, from an analysis of such expressions, particularly if they are formulated directly in terms of the concentrations of the active species, a better understanding of mechanisms involved should be achieved. An attempt to further analyse kinetic expressions reported in the literature (19-22) to show how these can be reconciled with observations concerning bleaching mechanisms has been made.

## 2.2 The Empirical Model

Several recent studies (19-22) have considered kinetic behaviour during alkaline peroxide bleaching of mechanical pulps. Kinetic expressions obtained under conditions of constant concentrations of peroxide and alkali, usually obtained at low consistency, are most appropriate to a consideration of reaction mechanisms. Under such conditions the rate of removal of chromophores has been described by the expression:

$$\frac{-d[C_k]}{dt} = k [H_2O_2]_{tot}^a [OH^-]^b [C_k]^c \quad \{2.1\}$$

where  $[C_k]$  = concentration of chromophores  
 $[H_2O_2]_{tot}$  = total concentration of peroxide  
 $[OH^-]$  = hydroxide ion concentration

It has been reported (19-22) that the orders of the reaction had the following values: a (1.0), b (0.3 - 0.5) and c (4 - 5). Specific values were found to depend on the particular pulp studied. Although this expression has been derived for conditions of low consistency and constant concentrations of reactants, it has also been applied to typical bleaching situations found for mill conditions (26,66), the major difference being the values of the orders of reaction with respect to alkali, peroxide and chromophore concentration.

The high apparent order of reaction with respect to chromophore concentration would be expected to occur for a set of chromophores with a wide variation in susceptibility to peroxide bleaching. High apparent orders with respect to lignin concentration during pulping and bleaching processes have been discussed previously (63,64). This effect is similar to that found for other heterogeneous systems involving complex components, as often encountered for processes of industrial importance. For example, during cracking of hydrocarbons, while simple reaction orders are found for single components (67) high reaction orders are calculated applying a kinetic model to complex mixtures (gas-oils) containing a wide diversity of chemical structures with different reactivity (68).

### 2.2.1 Kinetic Analysis

The dependence on the rate of chromophore elimination in equation {2.1} is expressed in terms of the total peroxide concentration, which remains constant during the reaction and is given by

$$[H_2O_2]_{tot} = [H_2O_2] + [HO_2^-] \quad \{2.2\}$$

where  $[H_2O_2]$  and  $[HO_2^-]$  are the concentrations of undissociated hydrogen peroxide and perhydroxyl anion respectively. As these species probably differ significantly in their activity in bleaching processes, and many studies have suggested that the presence of the anion has the dominant influence, equation {2.1} has been rearranged, taking values of a, b and c as 1.0, 0.5 and 5.0 respectively, and using the relationships (21):

$$\frac{[H^+][HO_2^-]}{[H_2O_2]} = K_a = 10^{-11} \quad \{2.3\}$$

$$[H^+][OH^-] = K_w = 10^{-14} \quad \{2.4\}$$

to give the following kinetic expression:

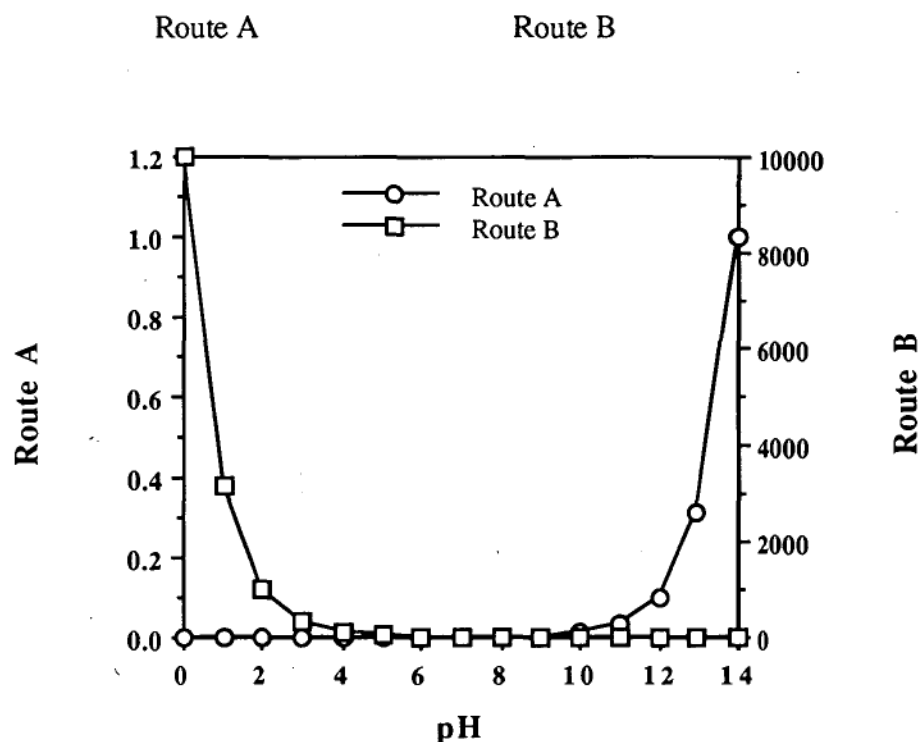
$$\frac{-d[C_k]}{dt} = k ([OH^-]^{0.5} + 10^{-3}/[OH^-]^{0.5}) [HO_2^-] [C_k]^5 \quad \{2.5\}$$

Equation {2.5} shows that the rate of chromophore elimination is directly proportional to the concentration of perhydroxyl anions. The dependence of the rate on alkalinity of the solution is a more complex function, however, consisting of the sum of two terms. The first term increases with alkalinity while the second decreases with increasing pH of the medium. Figure 2.1 shows the behaviour of the two components of this expression as the pH is changed.

This formulation can be interpreted by assuming chromophore elimination can arise through two parallel pathways following different mechanisms and hence leading to distinct kinetic behaviour, as shown in equation {2.6}.

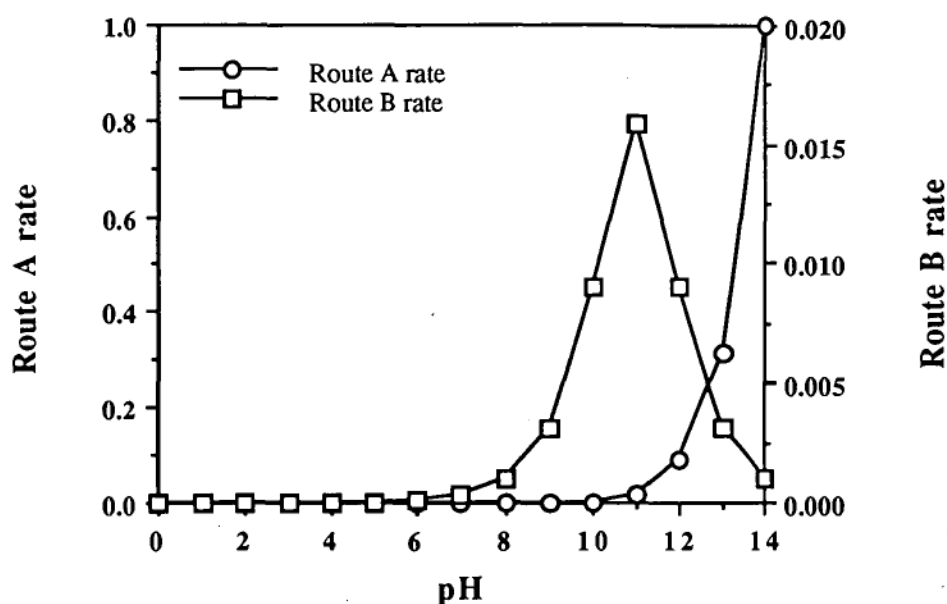


$$\frac{-d[C_k]}{dt} = k[OH^-]^{0.5} [HO_2^-] [C_k]^5 + k(10^{-3}/[OH^-]^{0.5}) [HO_2^-] [C_k]^5 \quad \{2.6\}$$



**Figure 2.1** Plots of the two pH dependent terms of the rate expression ( $[OH^-]^{0.5} + 10^{-3}/[OH^-]^{0.5}$ ) against pH. Rates have been calculated based on the appropriate concentration of hydroxide ion.

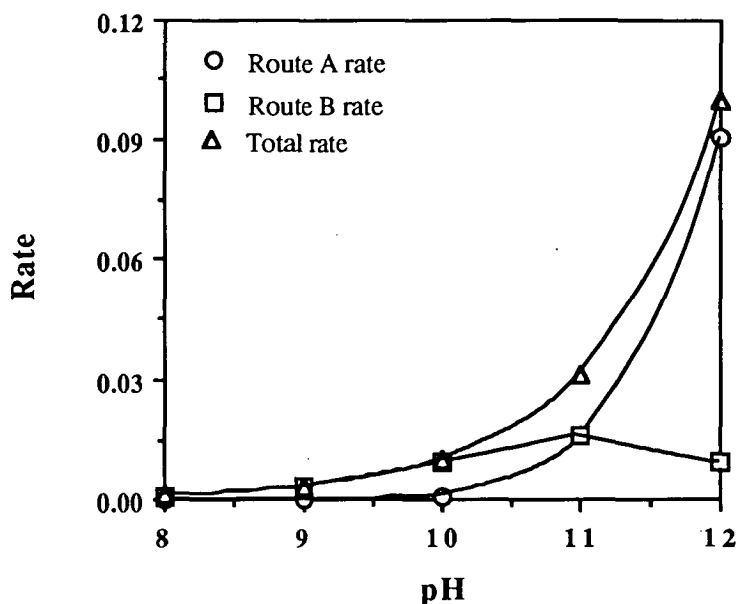
Route A is favoured by the presence of  $OH^-$  and  $HO_2^-$ , while route B is favoured by the presence of  $HO_2^-$  and  $H^+$ . Figure 2.2 shows the variation in the two components of the expression ( $[OH^-]^{0.5} + 10^{-3}/[OH^-]^{0.5}$ )[ $HO_2^-$ ] as the pH is varied. A small magnitude is associated with both components under neutral and acidic conditions. Under alkaline conditions the rate for route A increases with pH, while a maximum rate is observed for route B at approximately pH 11. It is apparent that, according to this analysis, both routes are of importance in the pH range 8 - 12 normally encountered in conventional peroxide bleaching (Figure 2.3), with route A dominant at  $pH > 11$  and route B dominant at  $pH < 11$ . At pH 11.0 which would be a typical initial pH value in peroxide bleaching the relative contribution from the two routes would be very similar.



**Figure 2.2** Plot of the two components of the rate expression ( $[\text{OH}^-]^{0.5} + 10^{-3}/[\text{OH}^-]^{0.5} [\text{HO}_2^-]$ ) as the pH is varied. Rates have been calculated based on the appropriate concentration of hydroxide ion and using  $\text{pK}_a = 10^{-11}$  for  $\text{H}_2\text{O}_2$ .  $[\text{H}_2\text{O}_2] = 1.0 \text{ M}$

### 2.2.2 Mechanisms and Active Species

The classical explanation for the action of alkaline hydrogen peroxide is given in terms of the perhydroxyl anion as the active species (2,69). This anion is thought to act as a nucleophile, preferentially attacking centres of low electron density in the lignin structure (39). These reactions would include addition of the perhydroxyl anion to a double bond in a conjugated structure derived from a quinone methide intermediate at the  $\text{C}_2$  position of the side chain, at unsubstituted positions in the ring (39) or at the carbonyl group (44). Addition to carbonyl groups in the  $\alpha$ -position of the side chain has also been suggested (43). Most mechanisms presented to illustrate these types of process involve a series of sequential steps, some of which may depend on the presence of hydroxide ions, either during formation of a quinone methide structure (43), or during breakdown of a perhydroxyl intermediate (44).



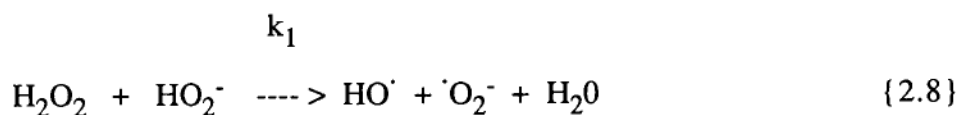
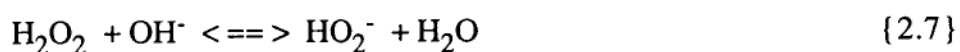
**Figure 2.3** Plots of the two components of the rate expression as in Figure 2.2, and the sum of the two rates in the pH range 8 -12. Rates have been calculated based on the appropriate concentration of hydroxide ion and using  $pK_a = 10^{-11}$  for  $H_2O_2$ .

It would appear reasonable to identify this type of mechanism with route A in our kinetic model, where the rate of chromophore elimination depends on  $[OH^-]^{0.5}$ ,  $[HO_2^-]$  and  $[C_k]^5$ . The appearance of three concentration terms in the rate expression and the non-integer order of the hydroxide ion is consistent with the proposal of a sequential mechanism, in which the perhydroxyl anion and the hydroxide ion interact with the chromophore in different steps of the overall mechanism.

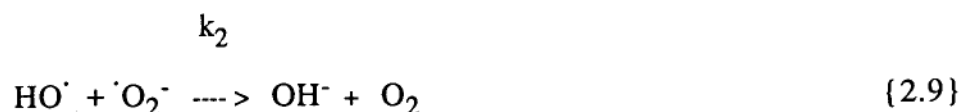
It is apparent that the predicted bleaching rate via route A would increase continuously with pH, so that the total rate of bleaching would not exhibit a maximum value. Most bleaching studies have been reported under conditions where the peroxide concentration falls as the reaction progresses, and in most cases (2) a maximum bleaching rate is found in the range pH 11-12. This could be attributed to an increased rate of peroxide decomposition at high pH levels (70). However, a maximum in

bleaching rate is also observed at approximately pH 11 when the peroxide charge is maintained at a constant level throughout (22). This has been explained by the alkali darkening effect (71), which has been attributed to competing alkali induced creation of new chromophores at high pH levels.

It has been known for many years that decomposition of aqueous hydrogen peroxide to produce molecular oxygen can occur through free radical intermediates (38), particularly when the process is catalysed by the presence of transition metal ions (38). Those processes have traditionally been regarded as detrimental to peroxide bleaching efficiency, leading to loss of the bleaching agent. Consequently, additives such as sodium silicate, DTPA and magnesium salts are routinely incorporated into bleaching systems to retard decomposition (2,16). During the past decade, however, there has been an increasing awareness that free radicals derived from peroxide decomposition may, in fact, play an important role in the bleaching reactions of wood pulp (37,39,40,72). In the absence of metal ion catalytic species, hydroxyl and superoxide radicals can be produced as follows (39,42,47):



Taking equations {2.7} and {2.8} as the principal route to generation of free radicals, and including a termination step (47):

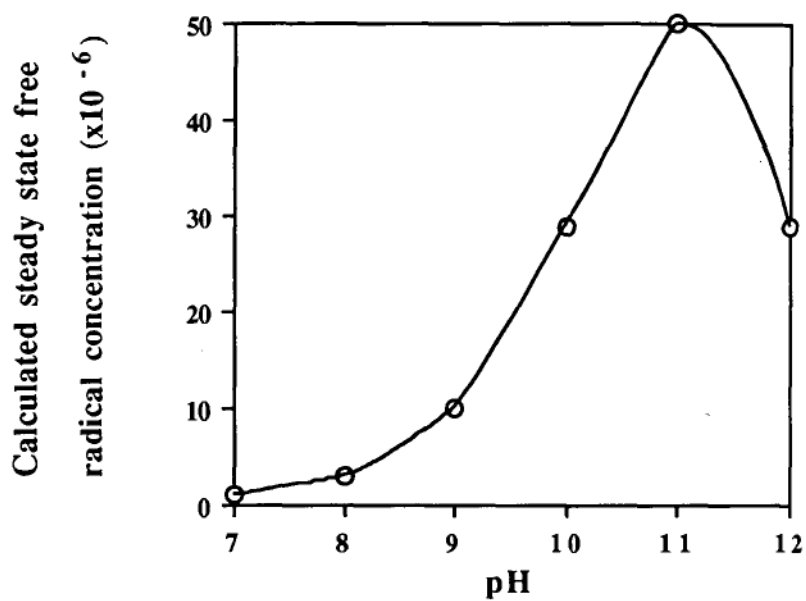


we have a simple overall mechanism for decomposition of hydrogen peroxide to

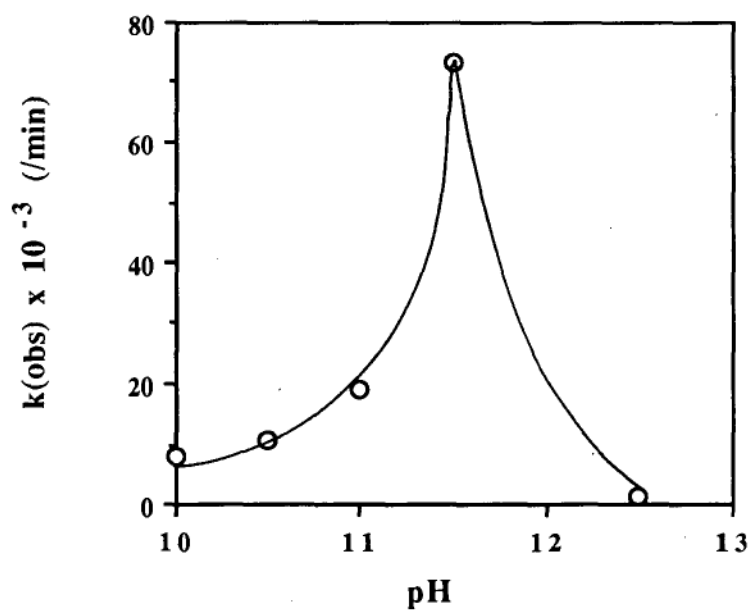
produce molecular oxygen. The final step in which two free radicals combine is very fast (73) compared to the overall rate of reaction (74). Assuming that equilibrium has been established according to equation {2.7} and  $k_2 \gg k_1$  the steady state concentration of free radicals (60) established will depend on the pH of the solution. The kinetic behaviour of this system can be modelled by computer methods (62) using a dynamic simulation program to give a profile of the variation in steady state total free radical concentration with pH as shown in Figure 2.4. It is apparent that this profile has a maximum at approximately pH 11, and is similar to that describing the magnitude of route B in Figure 2.2. These distributions can also be compared with Figure 2.5, which shows the reported (37) variation in rate constant with pH for oxidation of  $\alpha$ -methyl syringyl alcohol with hydrogen peroxide at 30°C. The rate of alkaline peroxide oxidation for this lignin model compound also exhibits a maximum at approximately pH 11, and the mechanism for this process has been discussed in terms of free radical intermediates derived from hydrogen peroxide (37).

Consequently, it is proposed that the generation of free radical species which can interact with chromophores in the lignin structure gives rise to route B in the kinetic model. A number of studies have concluded that it is the hydroxyl radical rather than the superoxide radical that is active in reactions with lignin (18,38,44,46). The hydroxyl radical is a strong oxidant (72) and is thought to add to aromatic rings in the lignin structure as an electrophile (39).

In the presence of transition metal ions which can catalyse peroxide decomposition we might expect the steady state concentrations of free radical species would be increased, and this has indeed been observed (60). Furthermore, it has been found that the position of the maximum rate occurs at a pH which depends on the metal present under both homogeneous (16) and heterogeneous (75,76) conditions. The metal ions most commonly present in wood pulp which are also active towards peroxide decomposition are manganese, copper and iron. These ions have been found to produce maxima in the

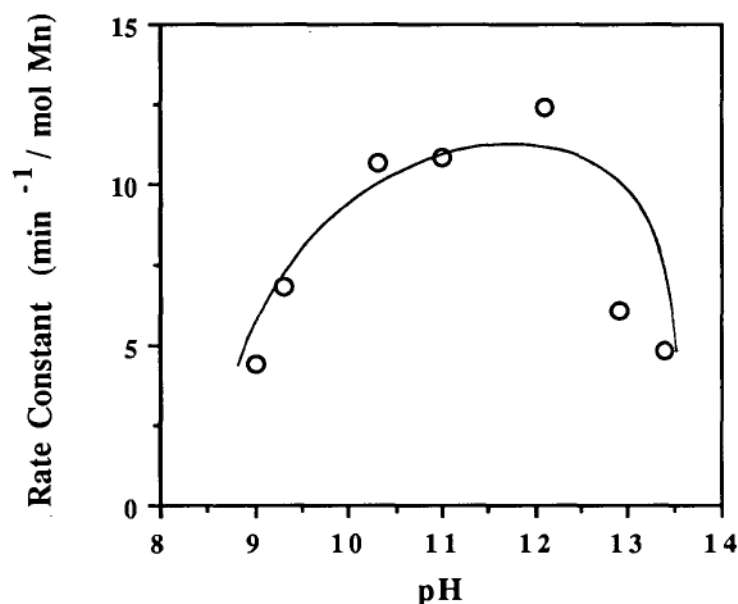


**Figure 2.4** Plot of the variation of steady state free radical concentration with pH. Values calculated using TUTSIM dynamic simulation program (62) with  $k_1 = 10^{-3} \text{ s}^{-1}$  and  $k_2 = 10^6 \text{ s}^{-1}$ .



**Figure 2.5** Variation in the rate constant for the oxidation of  $\alpha$ -methyl syringyl alcohol by hydrogen peroxide as a function of pH (44).

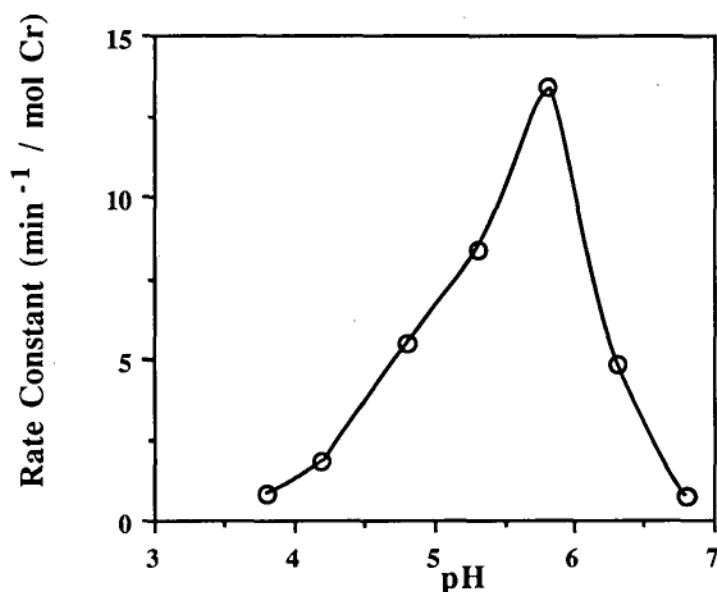
pH range 9 -12 (60) as illustrated for manganese in Figure 2.6. This range includes the pH at which maximum brightness is usually observed for peroxide bleaching (44). Other metal ions, not normally present in pulp in high concentrations, can exhibit maxima under neutral or acidic conditions as for example with cobalt and chromium (16). Figure 2.7 shows that for chromium the maximum initial activity occurs at pH 5.8. This observation is useful, as it may enable us to expose pulp samples to high concentrations of radical species under conditions where the perhydroxyl ion concentration is low, and the contribution from route A should be very small.



**Figure 2.6** Variation in the rate of decomposition of hydrogen peroxide in the presence of manganese against pH at 20°C. Initial concentration of hydrogen peroxide 0.10M; initial concentration of manganese nitrate  $4.4 \times 10^{-6}$ M.

Several recent studies have discussed the possibility of catalytic effects due to the presence of transition metal ions leading to increased rates of delignification with alkaline hydrogen peroxide (37,57). Other investigations have shown that acidic peroxide treatment of pulp can have beneficial effects (32,35,77,78), and there are indications that these may be promoted by the presence of metal ions acting as catalysts (35). These observations, coupled with the kinetic analysis leads to further bleaching

studies under both acidic and alkaline conditions. The results of these studies are described below. If the presence of radical species has a positive effect on bleaching then a stage designed to expose the pulp to radicals may be able to produce an increased brightness response compared to a single stage alkaline bleach.



**Figure 2.7** pH dependence of the rate of decomposition of hydrogen peroxide in the presence of chromium at 20°C. Initial concentration of hydrogen peroxide 0.10M; initial concentration of chromium nitrate  $2.5 \times 10^{-4}$ M.

### 2.3 Chromium Addition to two-stage Peroxide Bleaching

It has previously been reported (16), and confirmed in this work, that hydrogen peroxide is catalytically decomposed by solutions initially containing chromium (III) ions. This decomposition, unlike many other transition metal ions catalysts, occurs in slightly acidic solutions, with a maximum rate at approximately pH 6. This observation, together with the kinetic analysis reported in the previous section, will allow two stage bleaching sequences to be investigated in which the two proposed mechanisms of bleaching are separated. This is of course assuming that chromium catalysed decomposition of hydrogen peroxide proceeds via a radical mechanism. Later work (Chapter 4) indicates that a radical mechanism is evident in this decomposition.



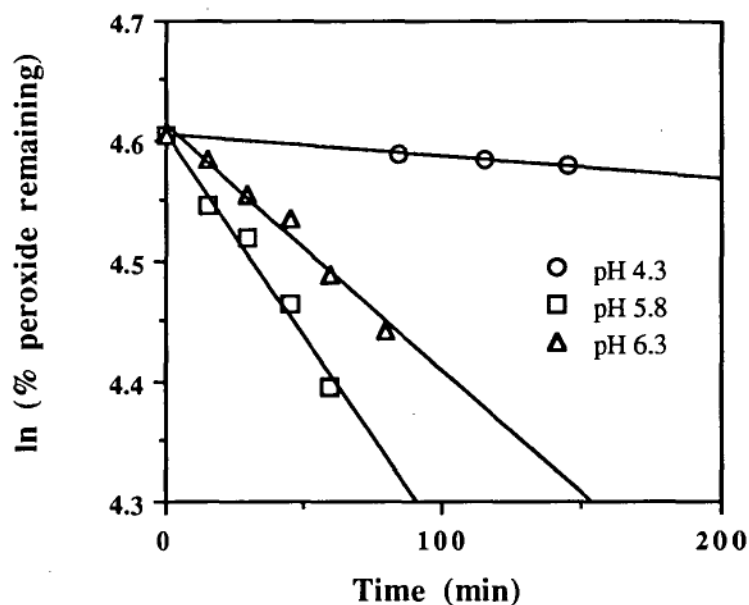
Initially the chemistry of chromium-hydrogen peroxide solutions was studied, to find appropriate conditions for later bleaching studies. Preliminary bleaching studies were performed to determine if an increased brightness response could be observed and that the response could be attributed to the presence of chromium in the acidic ( $P_1$ ) stage. This process was then optimised and studied further in comparison to a single stage alkaline peroxide bleach. The results are discussed in terms of the mechanisms and active species involved in peroxide bleaching.

### 2.3.1 Chromium-Hydrogen Peroxide Solution Chemistry

This section focuses on the catalytic decomposition of hydrogen peroxide in the presence of chromium ions and various peroxide stabilising agents. The investigation was directed at determining the pH range over which chromium decomposes hydrogen peroxide and determining the effects of various additives on this range and rate of reaction. These results were then used to determine appropriate conditions for using chromium in a two stage peroxide bleaching sequence.

The rate of decomposition of hydrogen peroxide in the absence of chromium at pH 5.8 is insignificant compared to other first-order rate constants calculated. Similar decomposition rates were observed in the presence of magnesium nitrate, aluminium nitrate and sodium silicate when chromium nitrate was not present. For this reason the residual peroxide decomposition rates were not considered when reporting rate constants.

The decomposition of aqueous hydrogen peroxide in the presence of chromium nitrate is first order with respect to total hydrogen peroxide concentration over the range of pH studied. This was found to be the case in all situations investigated except for the addition of aluminium nitrate where the rate of reaction appears to be increasing as the reaction proceeds. Figure 2.8 shows a typical decomposition in the presence of chromium.



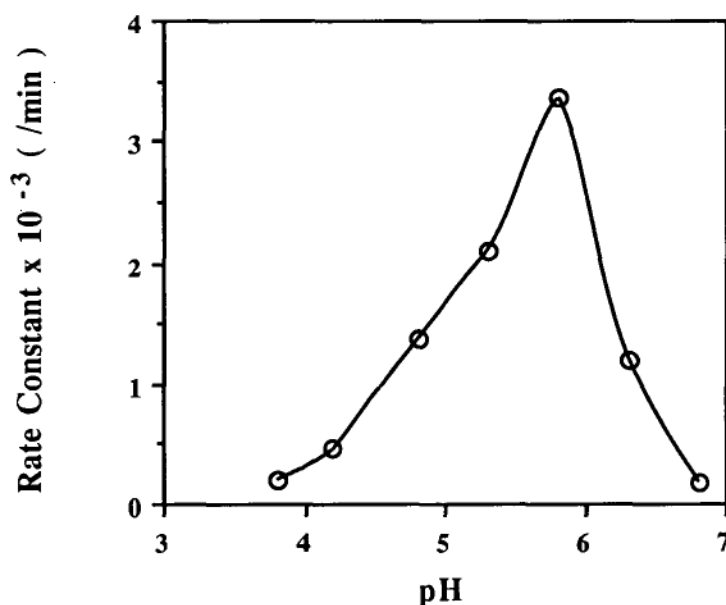
**Figure 2.8** Logarithmic plots for decomposition of hydrogen peroxide at 20°C at various pH levels in the presence of  $2.5 \times 10^{-4}$  mol/L chromium.

Hydrogen peroxide decomposition was found to be strongly dependent on the pH of the solution in the presence of chromium ions. The rate of decomposition of peroxide varied with pH as shown in Figure 2.9. A maximum rate was observed at approximately pH 5.8.

Due to the complex hydrolysis of chromium ions (79-87) and the associated change in pH, it was necessary to maintain the pH at a constant level during a decomposition experiment. If the pH was not controlled a change of up to 2 pH units was observed in some instances.

The hydrolysis of chromium ions has been extensively studied. The presence of polynuclear species (80-87), with hydroxy and oxy bridges, is now quite well established and several species have been isolated and analysed (80,83). The distribution of these species changes with both pH and concentration so it is difficult to

propose a particular species that may be actively catalysing the peroxide decomposition. However, from two separate studies (82,84) of species distribution in chromium solutions, it would appear that the predominant species could be  $\text{Cr}_4(\text{OH})_6^{6+}$ . The influence of hydrogen peroxide on the hydrolysis may, however, change the species present.



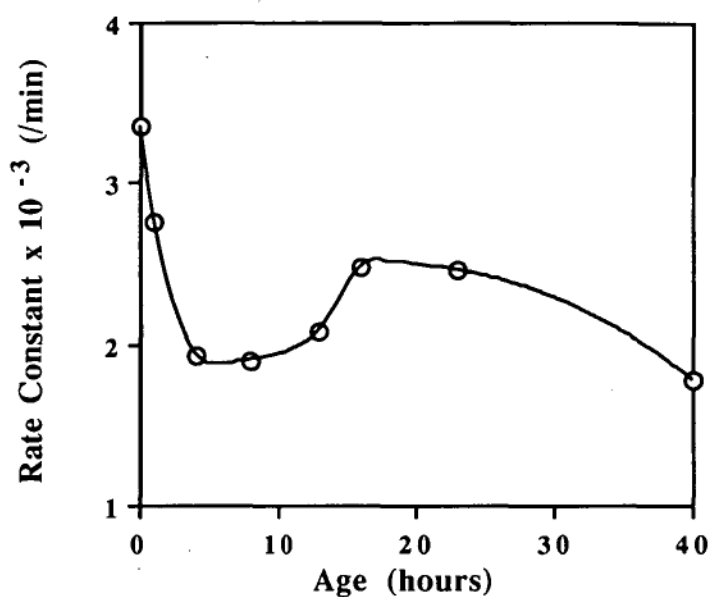
**Figure 2.9** Plot of variation of initial first-order rate constant with varying pH in the presence of  $2.5 \times 10^{-4}$  mol/L chromium.

As has been reported (88), the colour of the chromium - hydrogen peroxide solutions changed with pH. At pH values less than 5.0 the solutions were nearly colourless or slightly blue, at pH greater than 6.5 the solutions were yellow and at intermediate pH values the solutions showed a red brown colouration. The UV-vis spectra of solutions at varying pH shows a peak at 374 nm, typical of  $\text{Cr}^{6+}$  (88), for pH values greater than 6.0 indicating that the chromium ions had been oxidized by the peroxide. These colourations were only present after the hydrogen peroxide had been added, suggesting that the colour was due to either complex formed between chromium containing species and the peroxide, or oxidation of chromium caused by the peroxide.

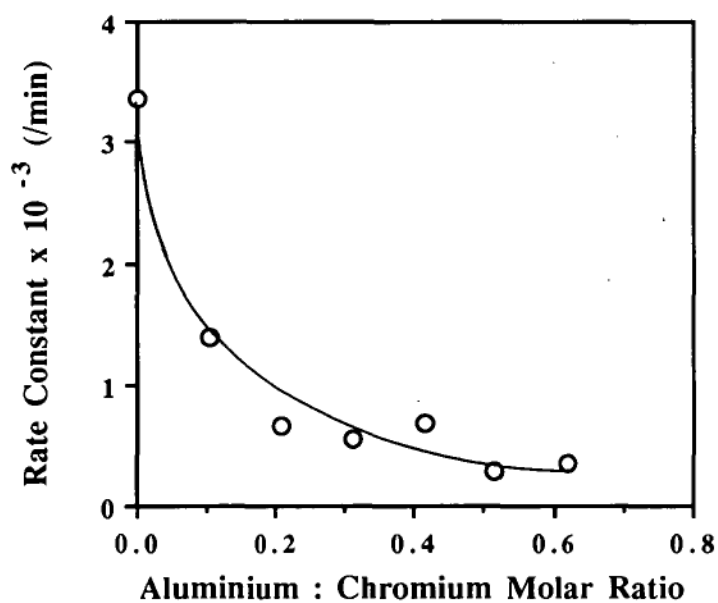
Due to the equilibrium of the hydrolysis products of chromium ions being reached slowly (80-82,84), typically taking hours to days, the effect of aging solutions of chromium before a decomposition experiment was investigated (89). This was achieved by leaving a solution of chromium nitrate and potassium hydroxide at the required pH to stand for a given time before addition of hydrogen peroxide. Similar work with iron catalysed decomposition of hydrogen peroxide has shown aging to effect the rate of decomposition (10). Figure 2.10 shows the variation in rate of peroxide decomposition with the age of the solution. The complex nature of the relationship between rate and age is not unexpected considering the complex hydrolysis occurring. The variation in rate would appear to reflect the changing concentration of the catalytically active species. Due to this change in catalytic activity of chromium solutions with age, all further experiments were performed using fresh solutions of chromium ions. The formation of the catalytically active species may also be related to the presence of hydrogen peroxide.

It has been reported that chromium catalyses the decomposition of peroxide more effectively when supported on alumina (90). It was thought that the addition of aluminium nitrate to the system may have a similar effect on the rate of reaction. Similar work with manganese (91) has shown aluminium has little effect on the rate of hydrogen peroxide decomposition even when added in large quantities. Figure 2.11 shows the effect of adding aluminium to the reaction mixture. It is found that even at low concentrations of aluminium, the rate of decomposition is dramatically reduced.

The hydrolysis of aluminium ions is complex (92-94), with polynuclear species being present in solution. Like chromium, the hydrolysis of aluminium is slow to reach equilibrium (93-95). The colour of solutions of peroxide with chromium and aluminium is not as intense as when only chromium is present. It appears that aluminium ions interfere with the formation of the catalytically active chromium species and so slow the rate of reaction.

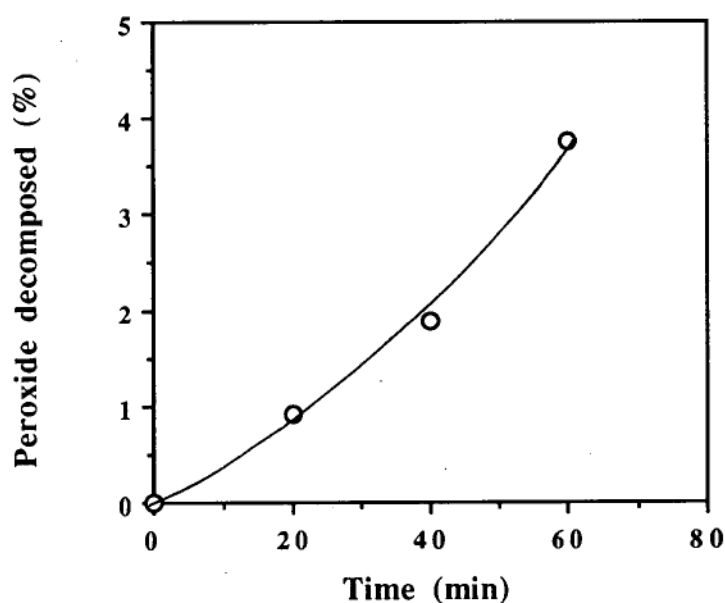


**Figure 2.10** Variation of initial first-order rate constant with the age of solution for hydrogen peroxide in the presence of  $2.5 \times 10^{-4}$  mol/L chromium.



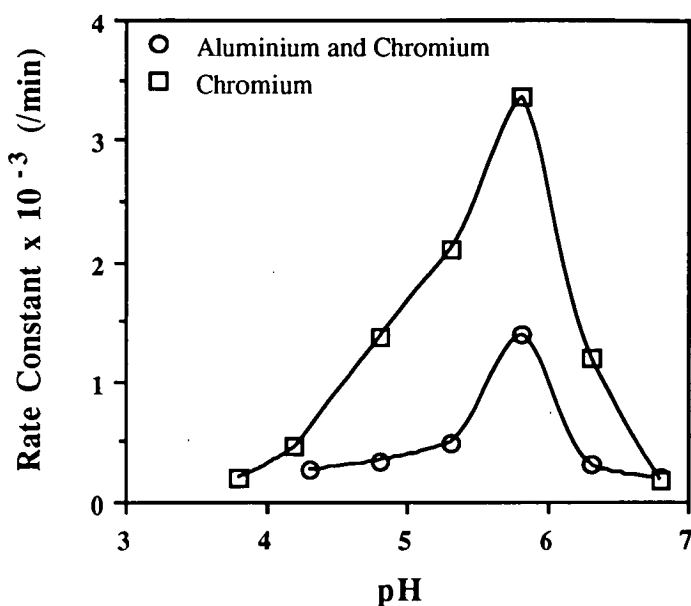
**Figure 2.11** The effect of varying the aluminium to chromium ratio on the initial first-order rate constant. Chromium ion concentration is  $2.5 \times 10^{-4}$  mol/L.

In the presence of aluminium nitrate the rate of reaction, unlike typical first order reactions that slow as they proceed, appears to accelerate. Figure 2.12. shows a typical decomposition against time plot. This may indicate that although the active species is reduced in concentration at the beginning of the reaction, due to the presence of aluminium nitrate, its concentration may be increasing as the reaction proceeds. Mixed hydrolytic species have been proposed previously for other metal ions and may form part of the explanation of this effect (91).



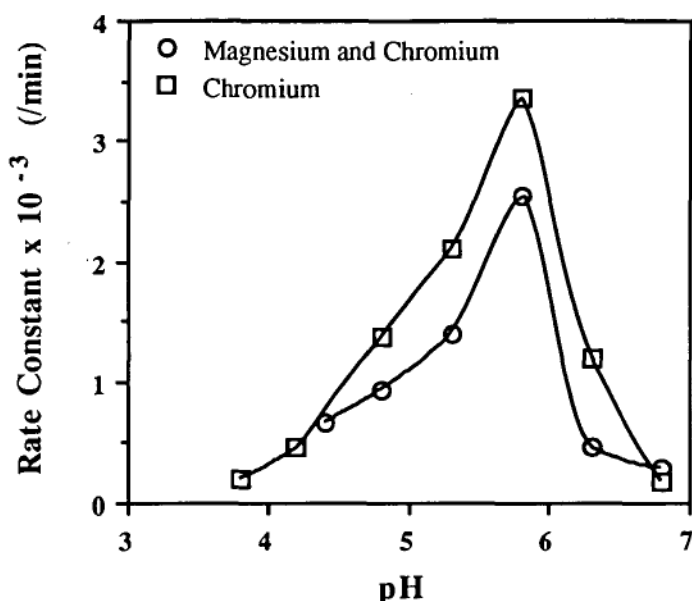
**Figure 2.12** Plot of conversion against time for decomposition of hydrogen peroxide in the presence of  $2.5 \times 10^{-4}$  mol/L chromium and  $5.0 \times 10^{-5}$  mol/L aluminium, pH 5.3.

It was thought that the addition of aluminium ions, which undergo hydrolysis in acid solutions, that the pH of the maximum rate of decomposition may change. However, as shown in figure 2.13, this was not the case. The maximum rate is still observed at pH 5.8 and the rate varies in a similar manner to when only chromium is present.



**Figure 2.13** Variation in the initial first-order rate constant with varying pH in the presence of  $2.5 \times 10^{-4}$  mol/L chromium and  $2.5 \times 10^{-5}$  mol/L aluminium.

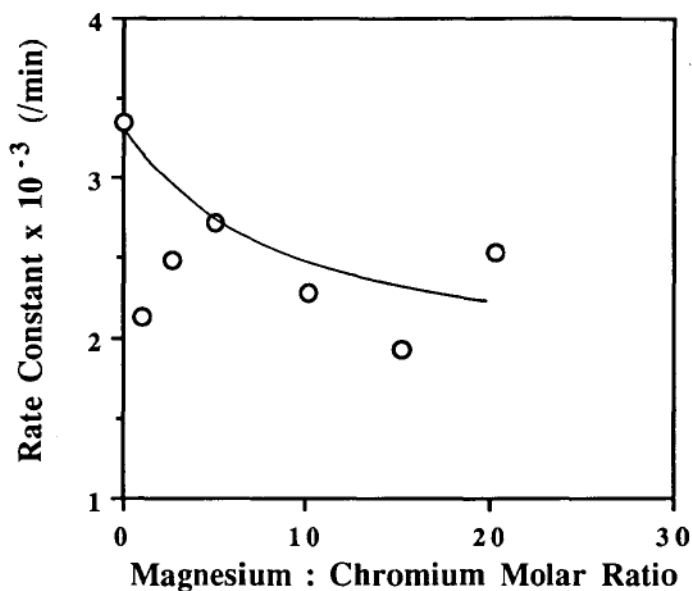
Magnesium has been reported to moderate the rate of metal ion catalysed decomposition of hydrogen peroxide solutions for a number of metal ion catalysts including copper and iron (15), especially in combination with silicate, and increase the rate of reaction when manganese is present (91). Figure 2.14. shows that the addition of magnesium ions does reduce the rate of chromium catalysed decomposition of peroxide over the range of pH studied. Various mechanisms have been reported previously for the slowing of the decomposition including magnesium acting as a trap for superoxide anion radicals (15), which are an important carrier in the radical chain mechanism. As the superoxide anion radical has a longer lifetime than the hydroxyl radical it is more likely that the superoxide radical is where the mechanism could be interrupted.



**Figure 2.14** The effect of pH on the initial first-order rate constant in the presence of  $2.5 \times 10^{-4}$  mol/L chromium and  $5.0 \times 10^{-3}$  mol/L magnesium.

The amount of magnesium added also has an influence on the rate of reaction. Figure 2.15 shows the change in the rate of decomposition as a function of the amount of magnesium added. With increasing magnesium to chromium ratio the rate generally decreases but the relationship between amount of magnesium and the rate is complex. Binuclear species containing M - O - Mg (where M is a metal ion other than magnesium) have been proposed previously to account for the action of magnesium ions (91). If this occurs in the case of chromium ions then the reduced concentration of the catalytically active species because of magnesium being incorporated into the structure would account for the gradual reduction in rate. This proposal offers no reason for the complex behaviour observed and again this could be related to the slow hydrolysis equilibrium for chromium species.





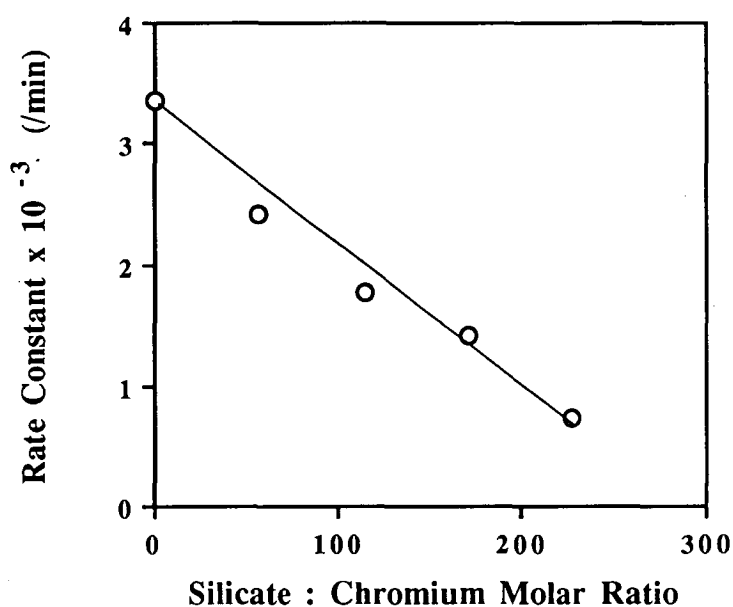
**Figure 2.15** The effect of varying the magnesium to chromium ratio on the initial first-order rate constant. Chromium concentration is  $2.5 \times 10^{-4}$  mol/L.

Silicate is another additive that has been reported to reduce the metal ion catalysed decomposition of hydrogen peroxide (48), particularly by manganese, copper and iron. Silicate was found to reduce the rate of chromium catalysed decomposition at pH 5.8. Figure 2.16. shows the effect of varying silicate dose on the rate of reaction at pH 5.8.

Several mechanisms have been proposed to account for this reduction in rate of decomposition. These include silicate acting as a free radical trap (18), the formation of stable intermediates (48) and the binding of metal ions (48).

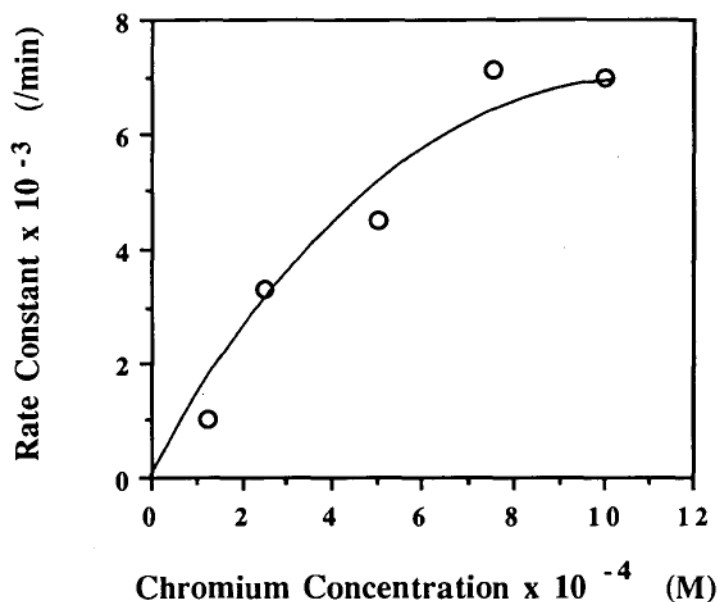
Experiments varying the concentration of chromium nitrate at pH 5.8 were conducted. Figure 2.17. shows the effect on the rate of hydrogen peroxide decomposition with increasing chromium ion concentration. The graph shows near linear behaviour until the concentration of chromium reaches  $7.5 \times 10^{-4}$  mol/L and then the rate of increase

slows. The final part of the graph may be explained by diffusion effects caused by insufficient stirring of the solution. Another consideration would be the changing species distribution as the chromium ion concentration is increased. The hydrolysis of chromium does produce different species under different conditions and the concentration may be such that proportionally less of the catalytically active species is produced.



**Figure 2.16** Plot of variation of initial first-order rate constant with varying silicate to chromium ratio. Chromium ion concentration is  $2.5 \times 10^{-4}$  mol/L.

From this work, and the results in Chapter 4, it would appear that catalytic decomposition of hydrogen peroxide proceeds via a radical chain mechanism. Such a mechanism has been proposed for basic solutions (57) and a similar mechanism would appear to be acting in this case. This will allow the separation of a radical stage from conventional bleaching processes and provide suitably constructed two stage bleaching sequence to further investigate the proposed two component mechanism of peroxide bleaching. An initial stage at approximately pH 6 in the presence of chromium, followed by a conventional alkaline stage at pH 11 should be an appropriate sequence.



**Figure 2.17** Plot of the initial first-order rate constant with varying chromium concentration at pH 5.8.

The addition of stabilisers such as magnesium salts, sodium silicate and aluminium nitrate will allow the reduction of peroxide decomposition catalysed by chromium, and may reduce the hydroxyl radical concentration, whilst addition of further chromium allows the radical concentration to be increased. These assumptions are confirmed in later results (Chapter 4).

This ability to vary the hydroxyl radical concentration would allow experiments to be performed that can further elucidate the role of hydroxyl radicals in peroxide bleaching. Chapter 4 will investigate the effect of varying the radical concentration in both single stage and two-stage bleaching sequences.

### 2.3.2 Initial Bleaching Studies with Chromium Addition

Experimental studies were undertaken with *Eucalyptus Regnans* groundwood.

Bleaching was carried out at 50°C at constant pH levels using 1% consistency and 30%

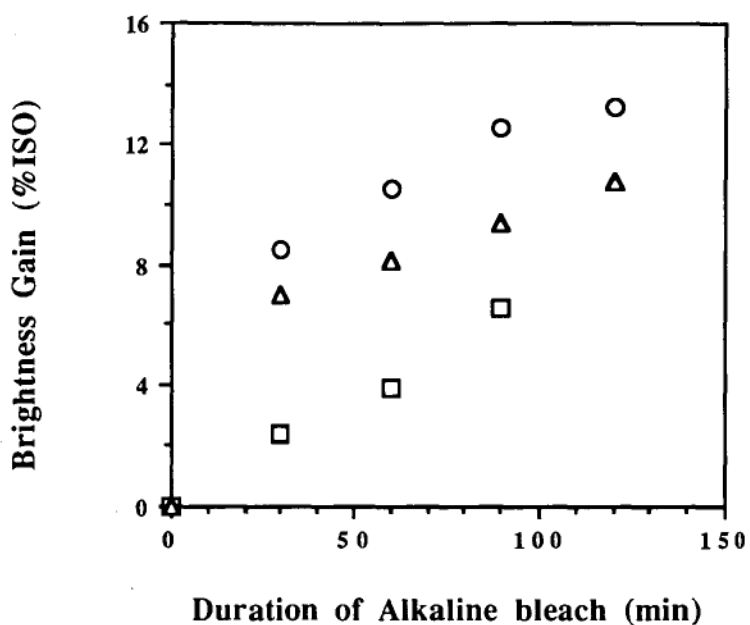
hydrogen peroxide (on o.d. pulp). Under these conditions the peroxide concentration did not decrease to low residual levels during the bleaching runs, but it was possible to measure the amount of peroxide consumed. As has been discussed previously, at higher pH levels the increased concentration of perhydroxyl anion does not lead to increased brightness due to reactions of the hydroxide ion causing darkening of the pulp and increased transition metal ion catalysed decomposition of hydrogen peroxide leaving less chemical available for bleaching. For single stage bleaching at pH 6.0 there was no increase in brightness of the pulp, even after 10 hours. At this pH any brightness gain would be due to radical reactions due to the presence of chromium and not the perhydroxyl anion which is only present in very low concentrations.

Figure 2.18 shows the increase in brightness of the groundwood pulp under alkaline conditions (initial pH 11.0) over a period of 2 hours for three different bleaching processes. The brightness increase for a standard one stage alkaline bleaching process gives the lowest brightness improvement at any particular time. The figure also shows the effect on brightness increase for two-stage processes with prior acid treatment of the pulp at pH 6.0, both with and without addition of a catalytic amount of chromium nitrate (1.0% on o.d. pulp). For these two stage bleaching experiments the duration of the acid treatment was 30 minutes in each case, after which the pH of the solution was adjusted to 11.0 by addition of potassium hydroxide. Figure 2.18 shows that the rate of brightness enhancement is increased by an acid treatment prior to alkaline peroxide bleaching at pH 11.0. The addition of chromium to the system at pH 6.0 increases the effect of the first stage acid treatment. Our results can be compared to a previously reported study in which a two stage peroxide bleaching sequence was used for brightening an oxygen bleached hardwood kraft pulp (35). While the chemistries of the delignification of kraft pulps and the brightening of mechanical pulps are different some similarities exist and comparisons can be made. In that study compounds of tin, vanadium or titanium were introduced during the first stage under acidic conditions at pH 4-6, followed by an alkaline bleaching stage. Another study (32) has described an

improved bleaching response with a two stage acid/alkali peroxide treatment without addition of a catalyst.

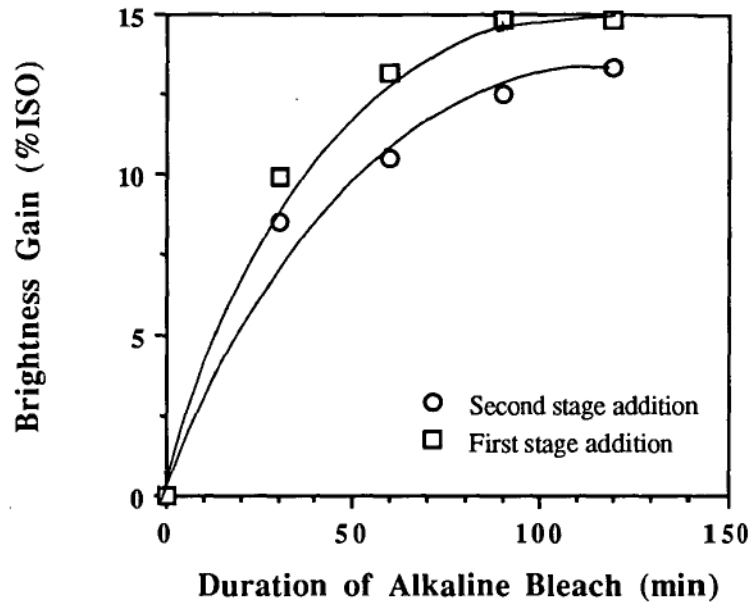
Figure 2.19 shows that the chromium is active in the first stage of the two stage bleaching sequence. When chromium is added to the alkaline stage of a two stage bleaching sequence significantly less brightness gain is achieved. Comparing these curves with figure 2.18, it is apparent that when chromium is present only in the alkaline stage, the response is approximately the same as when no chromium is added, thus further supporting the view that the chromium is having an effect during the first stage of the bleaching sequence. This can be related to the solution studies (Chapter 2.3.1) which indicated that chromium only decomposes peroxide under mildly acidic conditions.

Figure 2.20 shows the influence of chelating and washing the pulp with DTPA prior to a two stage acid/alkali bleaching sequence in the presence of chromium. The metal ion analysis of the pulp is reported in Table 5.1 (Chapter 5). By comparison with Figure 2.19 the results show that there is a reduced brightness enhancement when metal ions are removed from the pulp, and it appears that the effects of chromium and the other transition metal ions in the pulp are additive. It has also been shown that the removal of transition metal ions from *Pinus Radiata* TMP by chelation and washing reduces the effectiveness of two stage acid/alkali peroxide bleaching (96).

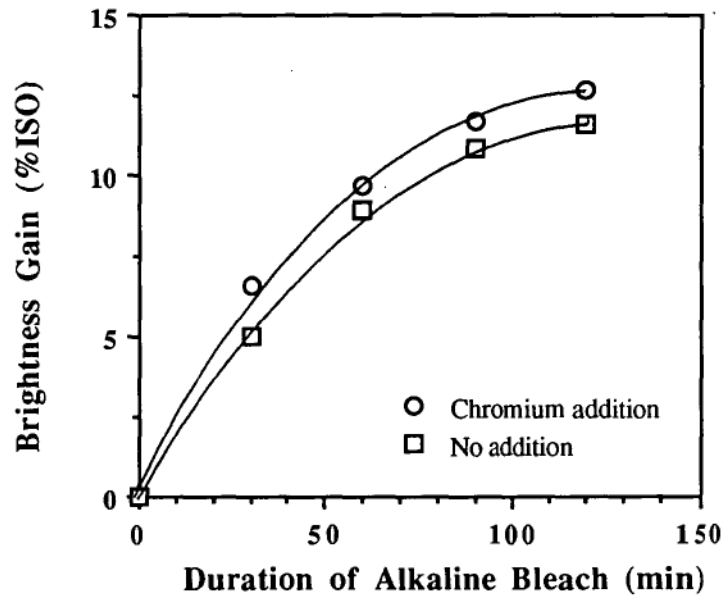


**Figure 2.18** Comparison of one and two stage bleaching processes showing the brightness gain for *E.Regnans* SGW bleached at 1% consistency, 50°C, with 30% peroxide (on o.d. pulp) under various conditions.

- ) 30 minute acid bleach with  $2.5 \times 10^{-4}$  mol/L chromium nitrate followed by an alkaline bleach at pH 11.0.
- Δ) 30 minute acid bleach with no added chromium followed by an alkaline bleach at pH 11.0.
- ) alkaline bleach at pH 11.0 (no acidic treatment).



**Figure 2.19** The influence of addition of chromium during the first and second stages (conditions as in figure 2.18).  $2.5 \times 10^{-4}$  mol/L chromium nitrate.

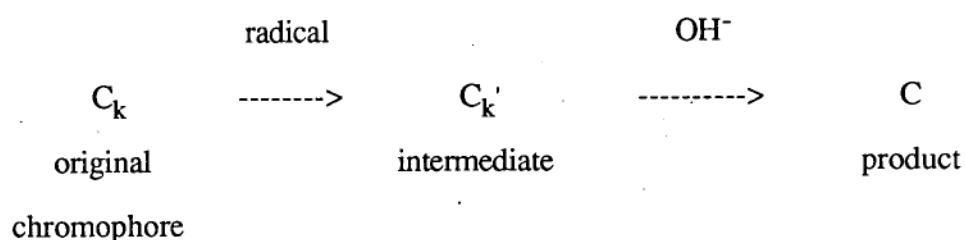


**Figure 2.20** The influence of pulp chelation on two stage acid/alkali bleaching sequence in the presence of chromium (conditions as Figure 2.19).

It would appear that the acidic peroxide treatment results in changes in the lignin

structure promoted by the species formed during the catalytic decomposition of hydrogen peroxide (42,55). This can happen even when no catalyst is introduced (97), as metal ions from the wood itself may be active or the acidic conditions may cause changes that enhance peroxide bleaching in a subsequent alkaline stage. A number of studies have indeed shown that lignin structures are reactive under acidic conditions (39,77,78,98), most likely through processes involving free radicals (39), although little enhancement in brightness may be achieved (99) as expected from the kinetic analysis. The initial product of reaction between a radical species and a lignin chromophore can be regarded as an intermediate, the formation of which does not itself improve pulp brightness. The rate of formation of the intermediate will depend primarily on the concentration of free radical species as shown previously in Fig 2.5.

In order to observe an increase in brightness a second step is required in the overall mechanism to eliminate the chromophore, which depends directly or indirectly on the presence of the hydroxide ion :

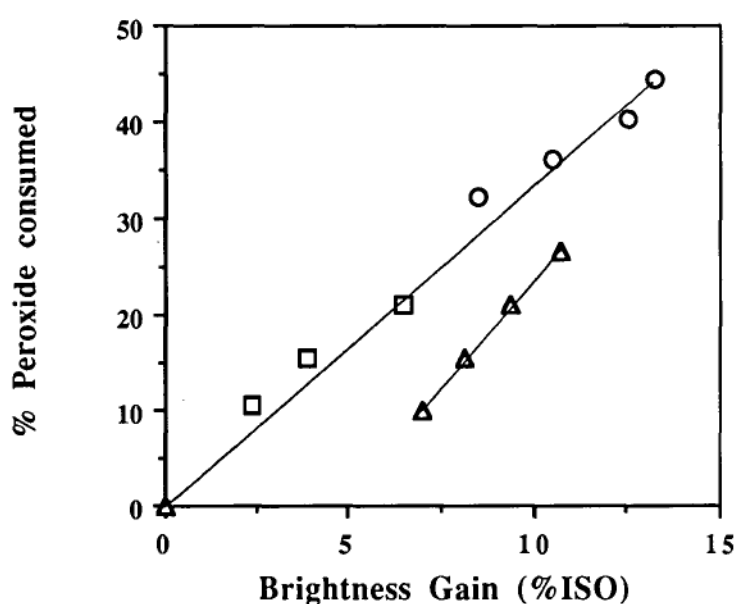


Under acidic conditions where hydroxide ion concentration is low the intermediate is formed, and its production is enhanced by the presence of catalysts which promote radical formation. Under alkaline conditions, this intermediate species may again be produced, but it rapidly reacts with the perhydroxyl anion in the presence of hydroxide ions leading to the elimination of the chromophore.

Fig 2.21 shows the consumption of hydrogen peroxide plotted against the increase in pulp brightness for pulps bleached by a single stage alkaline process (initial pH 11.0)



and the two stage acid/alkali process both in the presence and absence of chromium. Comparing the single stage alkaline bleach and the two stage bleach in the presence of chromium, it is apparent that the brightness gain achieved in each case is approximately proportional to the amount of peroxide consumed. It is also clear that use of a two stage process without added chromium can increase the efficiency of bleaching under the conditions employed in this study.



**Figure 2.21** Plot of the peroxide consumption against brightness gain for pulps bleached at 1% consistency, 50°C and 30% peroxide (on o.d.pulp) under various conditions:

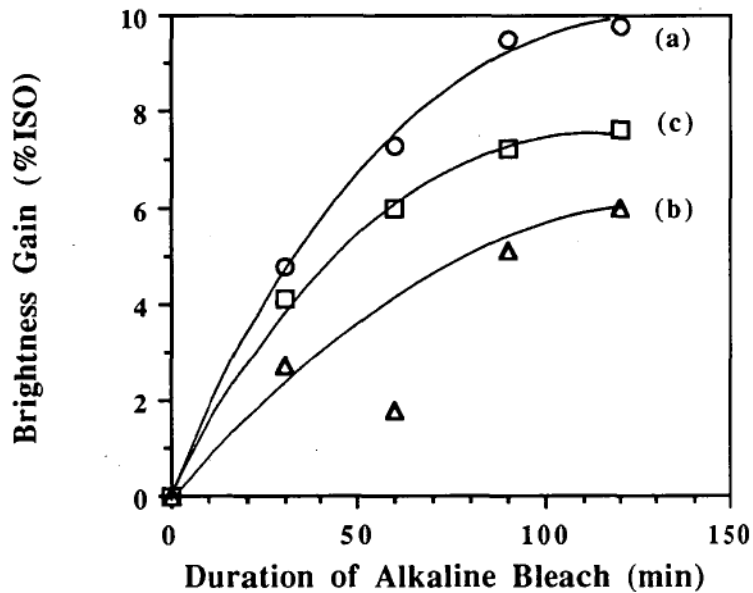
- ) 30 minute acid bleach with  $2.5 \times 10^{-4}$  mol/L chromium nitrate followed by an alkaline bleach at pH 11.0.
- ) alkaline bleach at pH 11.0 (no acidic treatment).
- Δ) 30 minute acid bleach with no added chromium followed by an alkaline bleach at pH 11.0.

### 2.3.3. Optimisation of two-stage Bleaching with Chromium Addition

Figure 2.22 shows the effect of a two-stage peroxide treatment with chromium nitrate initially introduced and with an initial charge of 6% peroxide (on o.d. pulp). This

shows the same trends as in figure 2.18 where a higher peroxide charge was used. In the first stage, the pH was maintained at 5.8. After 30 minutes the concentration of hydrogen peroxide was restored to its initial level before adding alkali to raise the pH to 11.0 in the second stage of the bleaching sequence. This was in order to be comparing alkaline stages with a similar peroxide charge. Curve (a) shows the increase in brightness with time during the second stage of the bleaching process, at a constant pH under alkaline conditions. This can be compared with curve (b), which corresponds to bleaching under the same conditions, but without pre-treating the pulp with acidic peroxide or introducing chromium. It is apparent that chromophore elimination occurs more rapidly for the pulp which has been subjected to the two-stage bleaching sequence. It is important to point out that no brightness gain could be detected for these pulps after the first (acidic) stage. It would appear that even though chromophores are not eliminated by acidic peroxide treatment in the presence of chromium, the chromophores present are rendered more susceptible to subsequent removal by alkaline peroxide bleaching. Previous work (32,35) has shown that a two-stage hydrogen peroxide bleaching sequence involving an acidic stage followed by alkaline treatment can give an enhanced brightness over a conventional one stage alkaline bleach. Curve (c) in Figure 2.22 shows the effect of an acidic treatment followed by an alkaline treatment without initial introduction of chromium. It is apparent that the bleaching response for this pulp under alkaline conditions is intermediate between the case where no acidic pre-treatment is applied, and that in which chromium is introduced with acidic peroxide. These effects can be explained on the basis of other metal ions which occur naturally in the wood, or have been introduced during pulp production. The acidic conditions may also contribute to these observations. It appears that the presence of these transition metal ions can induce effects on the chromophores in the presence of acidic peroxide similar to those produced in the presence of chromium. The total effect seen (curve (a)) in Figure 2.22 can therefore be attributed to the combined effects of chromium, the other metal ions in the pulp and the acidic conditions.

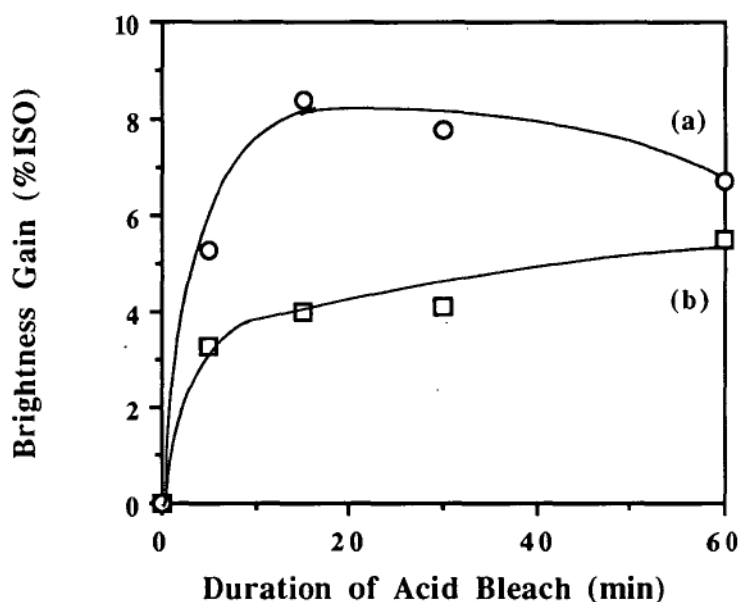
Figure 2.23 shows that the brightness gain for two-stage acid/alkali bleaching in the presence of chromium is significantly reduced using the chelated pulp compared to an unchelated pulp. It can be concluded that the presence of manganese and copper, and possibly other metal ions initially present in the pulp, contribute to the observed effects on brightness enhancement for the two-stage bleaching sequence.



**Figure 2.22** Brightness gain plotted against time of alkaline bleach (pH 11.0). (a) acidic treatment (pH 5.8) for 30 minutes with  $2.5 \times 10^{-4}$ M chromium nitrate; (b) no acidic treatment; (c) acidic treatment (pH 5.8) for 30 minutes with no added chromium.

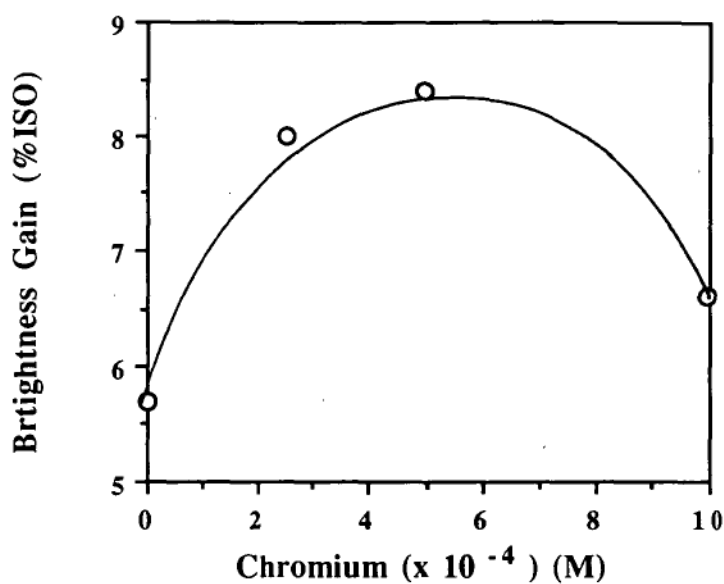
Figure 2.24 shows the effect of varying the amount of chromium introduced prior to the two-stage acid/alkali peroxide bleaching sequence. It is clear that there is an optimum range for addition of chromium to achieve maximum brightness gain of the eucalypt pulp. This effect may be attributed to the additional reduction in peroxide concentration under acidic conditions as the chromium concentration is increased (Figure 2.25). At the highest level of chromium addition shown, about 25% of the initial peroxide charge was consumed by the end of the first stage. The presence of high levels of chromium also leads to excess total consumption of peroxide to reach a given level of brightness after the alkaline bleaching stage. Figure 2.26 shows that

addition of chromium beyond the optimum range results in increased total consumption of peroxide without a proportional increase in pulp brightness. At lower chromium levels, peroxide consumption is approximately proportional to brightness gain for both the two-stage acid/alkali bleaching sequence and single-stage alkali treatment (see also figure 2.21).

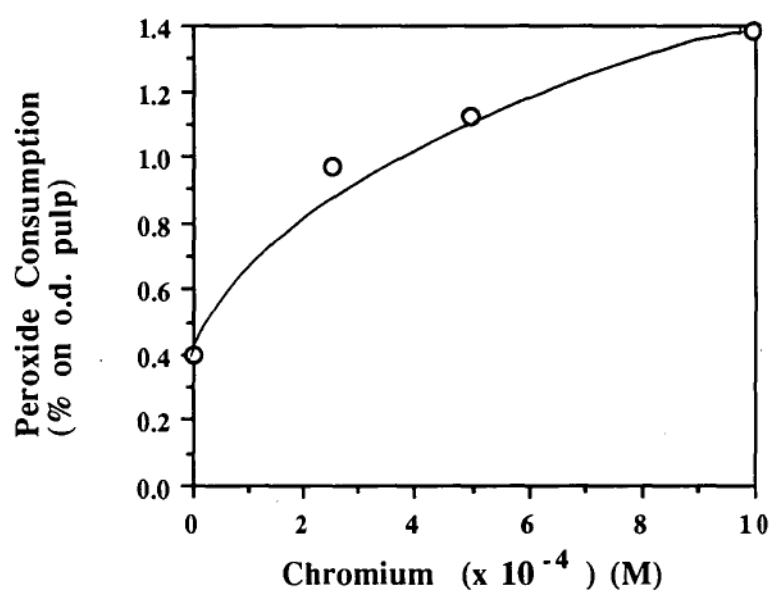


**Figure 2.23** Effect of removing metal ions from the pulp prior to bleaching: (a) unchelated pulp; (b) chelated pulp. Acid stage: pH 5.8; alkaline stage: pH 11.0, 120 minutes.

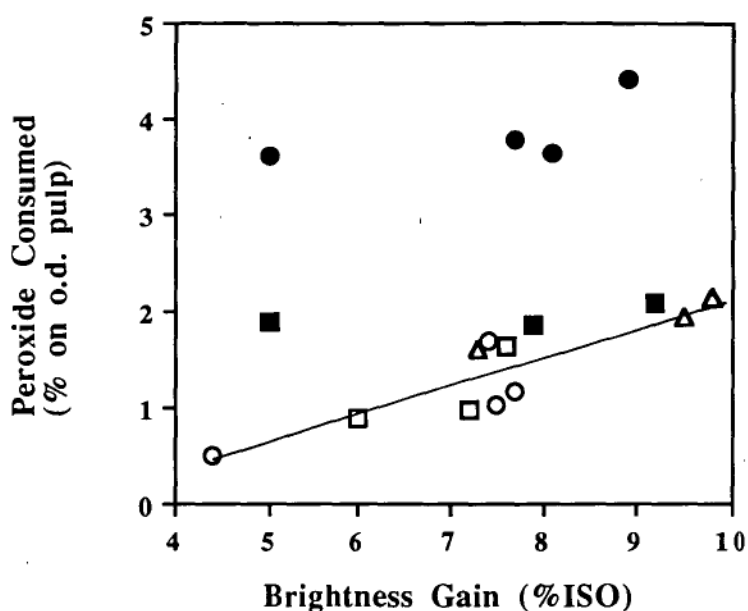
With the conditions used in this study (1% consistency, 6% hydrogen peroxide on o.d. pulp, 50°C, no stabilisers) the experiments showed that a maximum brightness gain of approximately 10 %ISO can be achieved for this eucalypt pulp. The more rapidly this level is reached, and the smaller the amount of peroxide consumed, the more efficient the process will be. Table 2.1 shows that the two-stage acid/alkali treatment enables a target brightness increase of 8 units to be reached in less time compared to a single stage alkali process while consuming a similar amount of peroxide.



**Figure 2.24** The effect of varying the dose of chromium nitrate on the brightness gain. Acid stage: 15 minutes, pH 5.8; Alkaline stage: pH 11.0. 0.13% on o.d. pulp =  $2.5 \times 10^{-4}$ M chromium nitrate.



**Figure 2.25** Effect of varying the amount of chromium on the peroxide consumption after the first (acidic) stage. Acid stage: pH 5.8, 15 minutes.



**Figure 2.26** Plot showing the correlation between peroxide consumed and the brightness gain. Acid stage: 30 minutes, pH 5.8; alkaline stage: pH 11.0. ; 0% Cr added, ;  $2.5 \times 10^{-4}$  M Cr, ;  $5.0 \times 10^{-4}$  M Cr, ;  $1.0 \times 10^{-3}$  M Cr, ; single stage alkaline bleach only, no added Cr.

Figure 2.27 shows the effect on brightness gain resulting from varying the pH of the first stage of the two-stage bleaching sequence. Both in the presence and absence of chromium a minimum response is observed in the pH range 4-5, whereas at pH 7 the response is similar both with and without chromium. The lower curve (b) can be attributed to the effects of metal ions in the original pulp (e.g. manganese and copper) and the acidic conditions. Figure 2.28 shows the effect of chromium alone, obtained by taking the difference between the two curves in Figure 2.27. Figure 2.28 shows a maximum in the pH range 5-6, and this may be compared with Figure 2.9, which also shows a maximum in this range for peroxide decomposition catalysed by chromium. This apparent correlation between catalysing peroxide decomposition under acidic conditions and inducing brightness gain in the subsequent alkaline step may be significant. The result may show that it is the products from catalytic decomposition of

hydrogen peroxide (i.e free radicals) which are active under acidic conditions in causing changes in the susceptibility of chromophores to subsequent alkaline peroxide treatment, where there are much higher concentrations of the perhydroxyl anion (46).

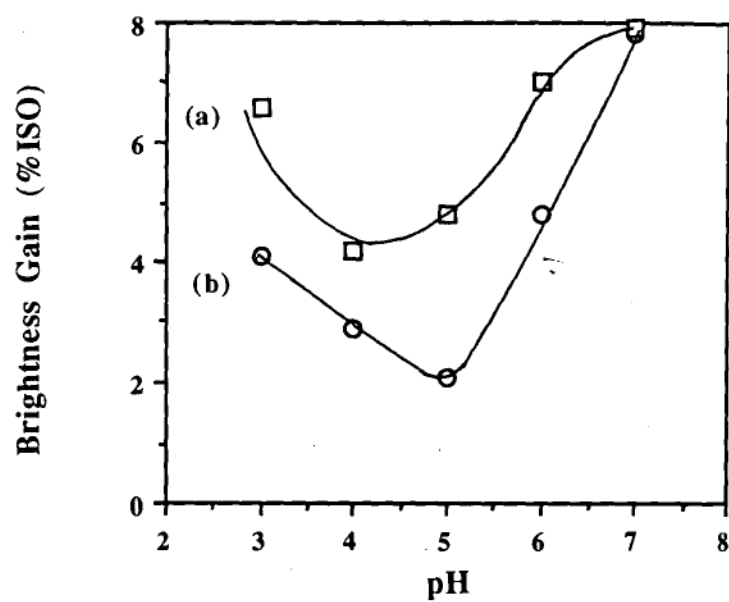
**Table 2.1** Time to Reach a Brightness Gain of 8 Points.

[Cr]	Time (min)			Peroxide <sup>+</sup>	Brightness Gain/	Bleaching
	acid	alkali	total	Consumed (% on pulp)	Peroxide (ISO/%)	Efficiency* (ISO%/hour)
0	-	170	170	2.08	3.83	1.35
0	30	120	150	1.74	4.59	1.84
$2.5 \times 10^{-4}$	15	120	135	1.58	5.03	2.24
$5.0 \times 10^{-4}$	30	60	90	1.86	4.30	2.87
$1.0 \times 10^{-3}$	30	60	90	3.64	2.19	1.46

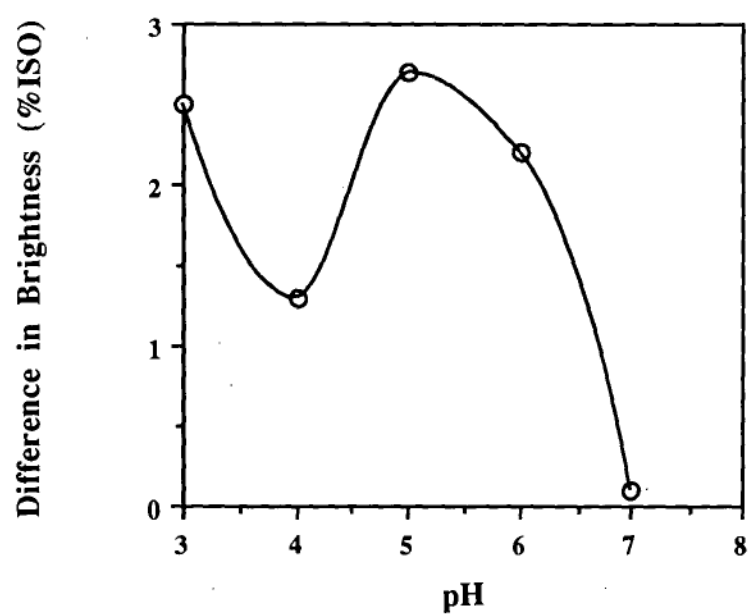
Bleaching experiment at 50°C, 1% consistency. Acid stage: pH 5.8, initial peroxide charge 6.0% on o.d. pulp. Alkaline stage: pH 11.0, initial peroxide charge 6.0% on o.d. pulp. Initial brightness of eucalypt pulp 54.0.

\* Efficiency = Brightness Gain / % peroxide consumed (on o.d. pulp) / time (hours).

<sup>+</sup> It should be noted that, due to the restoration of the peroxide charge to its initial level after the first stage of the two stage bleaching process, the peroxide charge is higher than 6.0% in some cases.



**Figure 2.27** The effect of varying the pH of the acidic stage for (a)  $5.0 \times 10^{-4}\text{M}$  chromium nitrate added; (b) no added chromium. Acid treatment: 30 minutes; alkaline stage: pH 11.0, 120 minutes.



**Figure 2.28** Difference in the brightness gain after the alkaline stage (pH 11.0, 120 minutes) for the pulps bleached in Figure 2.27.



There has been recent interest in the idea that free radical species, particularly the hydroxyl radical ( $\text{HO}^\bullet$ ), may indeed play an important role in peroxide bleaching, under conventional alkaline bleaching conditions as well as under acidic conditions (39,100). The idea that free radicals as well as the perhydroxyl anion may be active in brightness development during peroxide bleaching suggests that there may be more than one mechanism for chromophore elimination. As shown previously (Chapter 2.2) an analysis of kinetic phenomena during peroxide bleaching at various pH levels was based on the assumption of two distinct mechanisms of chromophore removal, one dependent on the perhydroxyl anion concentration and the other depending on participation of free radicals. The results of the present study also provide support for the concept of a dual mechanism for chromophore elimination. Studies involving changing the concentration of radical species during two-stage acid/alkali peroxide bleaching processes are reported later (Chapter 4.4), where a more thorough analysis of hydroxyl radical concentration is included.

The addition of aluminium ions significantly reduces the rate of chromium catalysed hydrogen decomposition in the pH range 4-7 (figure 2.13). If aluminium is used to modify the rate of chromium catalysed hydrogen peroxide decomposition during bleaching experiments unexpected results were obtained. For a single stage alkaline peroxide bleach it has previously been reported (101,102) that the brightness gain is lowered with the addition of aluminium. Using a two stage acid/alkali bleaching sequence with the addition of aluminium, in the presence and absence of chromium, two observations are made. Firstly, significantly higher brightness gains are achieved after the alkaline stage, even in the absence of chromium, and secondly, the peroxide consumption is greatly reduced compared to the process in the presence of chromium. This was an unexpected result, as presumably less radicals are produced when the decomposition of hydrogen peroxide is slowed, and the increased brightness had previously been attributed to the presence of these reactive species. Secondly, aluminium in a single stage alkaline peroxide bleach has an adverse effect on

brightness (101,102). The implications of this result, further experimental results and explanations will be attempted in the following sections.

## **2.4 Aluminium Addition to two-stage Peroxide Bleaching**

The previous section (Chapter 2.3) showed that two stage acid/alkali bleaching in the presence of added chromium could result in higher brightness than single stage alkaline peroxide bleaching. In the course of that work it was shown that the addition of aluminium nitrate in the absence or presence of chromium ions could produce similar brightness gains but with a significantly lower peroxide consumption. This result, initially only attained by way of checking that the presence of aluminium ions alone did not influence the two stage bleaching sequence, leads to the possibility of another two stage bleaching process. This investigation will allow further examination of the proposed two mechanisms of peroxide bleaching.

### **2.4.1 Solution Chemistry of Aluminium ions**

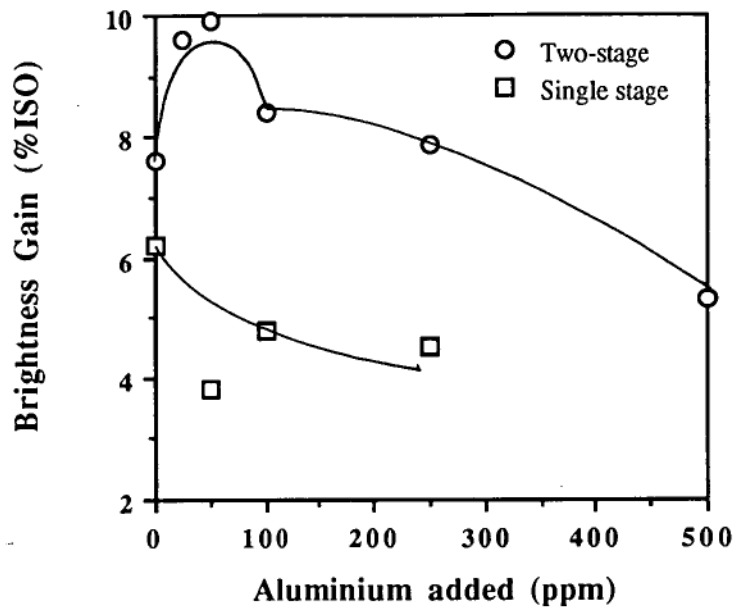
The hydrolysis of aluminium (III) has been studied extensively (92-95,103-110) with significant disagreement on the species present. Some points are, however, quite clear. The hydrolysis is very complex (92-95,103-110), and slow to reach equilibrium (94,95). With time large polynuclear species are formed (92,95) although the composition of these species is not clear. There have been some attempts to measure equilibrium constants for some of the initial hydrolysis products (104,105). A 'Core + Links' model (107,108) has been proposed to try and further unravel the complexity of the system, but this is also disputed (105). Overall, the hydrolysis is complex, and no attempt will be made here to further investigate the system.

### **2.4.2 Optimisation of two-stage Bleaching with Aluminium Addition**

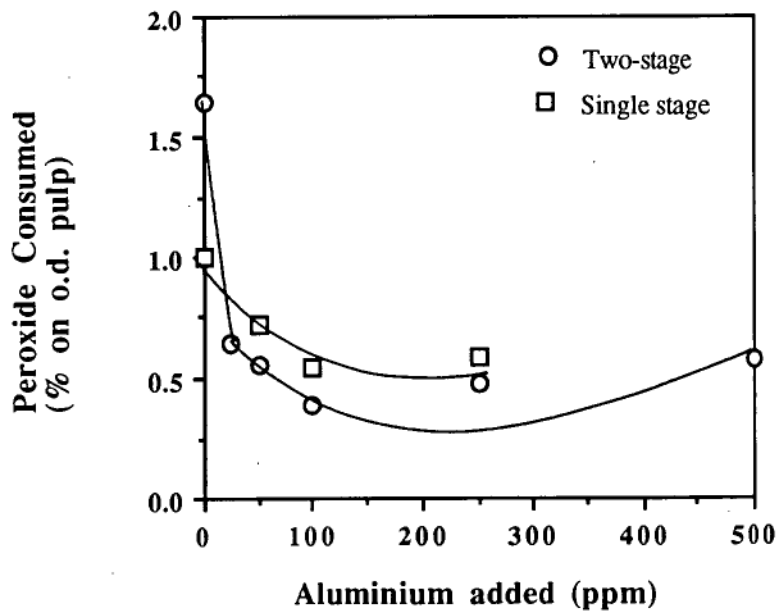
Generally it has been found that the presence of aluminium is undesirable in conventional alkaline peroxide bleaching of mechanical pulps, as it results in a lower final brightness of the pulp (101,102). This is illustrated for a *Eucalypt* SGW pulp,

in Figure 2.29 for a conventional single stage alkaline peroxide bleach. Figure 2.30 shows that although there is a reduction in peroxide consumption with increasing addition of aluminium, this does not result in a higher brightness gain, that is, the effect is not simply a case of peroxide stabilisation, as appears to be the case for magnesium and other peroxide stabilising agents. However, Figure 2.29 also shows that when a two stage, acid-alkali peroxide bleaching sequence is employed the addition of aluminium to the bleaching liquor can enhance the brightness of the pulp beyond that achieved in a single stage bleach, with a concurrent reduction in the amount of peroxide consumed. From Figure 2.29 it can be seen that the dose of aluminium added is critical in achieving maximum brightness gain in the two stage process. Increasing the dose of aluminium above that required to give the maximum brightness enhancement still leads to stabilisation of the bleach liquor although the brightness gain is decreased. Most of the peroxide consumption occurs during the first (acid) stage of the bleaching sequence as shown in Table 2.2. However, as shown in Figure 2.31, the brightness gain achieved during this stage is negligible, as previously reported for other two stage processes of this type (Chapter 2.3) and for the addition of chromium.

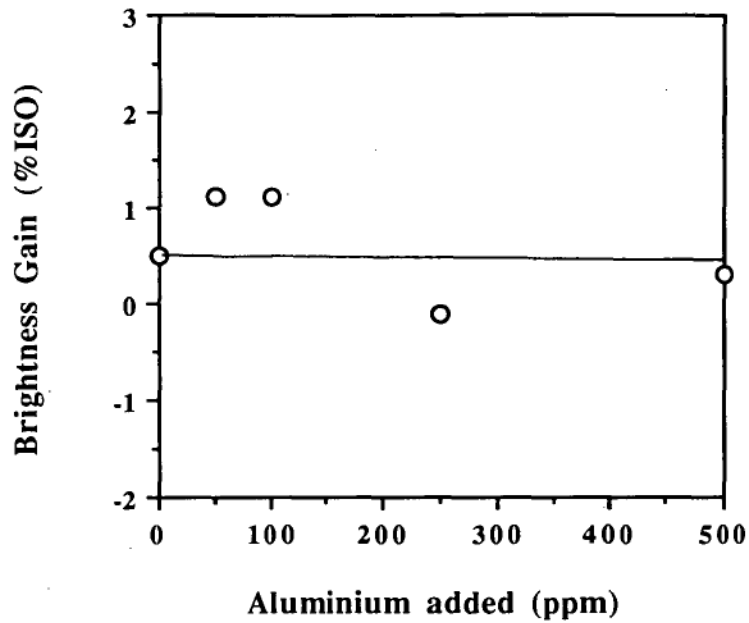
Figure 2.32 shows that the duration of the first stage of the acid/alkali bleaching sequence is important in achieving maximum brightness gain, with the optimum time approximately 15 minutes under the conditions used. Longer times appear to result only in increased consumption of peroxide during the acid stage, leaving less peroxide available for bleaching in the alkaline stage. Shorter times result in reduced brightness enhancement and increased consumption of peroxide. Figure 2.33 shows that the pH of the first stage of the bleaching sequence does not significantly change the final brightness of the pulp after the alkaline stage. Therefore, it would appear that using neutral conditions would be most economical as this will eliminate the need to add acid to the initial liquor and subsequently reduce the amount of alkali required to be added to reach sufficiently alkaline conditions for the second stage of the bleaching sequence.



**Figure 2.29** Brightness response of pulp to both a single stage and two stage bleach with varying levels of aluminium. 1% consistency; Acidic stage: pH 6.0, 30 minutes; Alkaline stage: pH 11.0, 120 minutes.



**Figure 2.30** Variation in peroxide consumption during a single stage and two stage bleaching sequence in the presence of various levels of aluminium. Conditions as in Figure 2.29

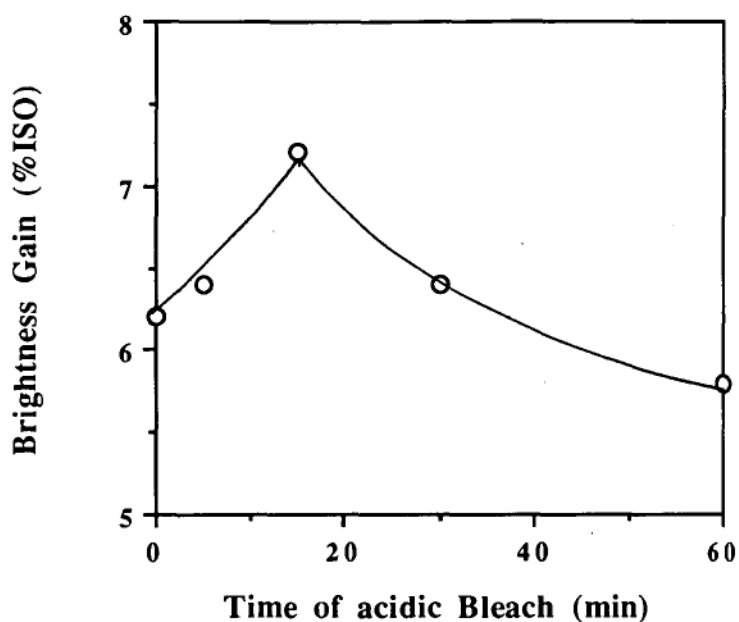


**Figure 2.31** Brightness response of pulp to an acidic peroxide treatment in the presence of various levels of aluminium. 1% consistency, pH 6.0, 60 minutes.

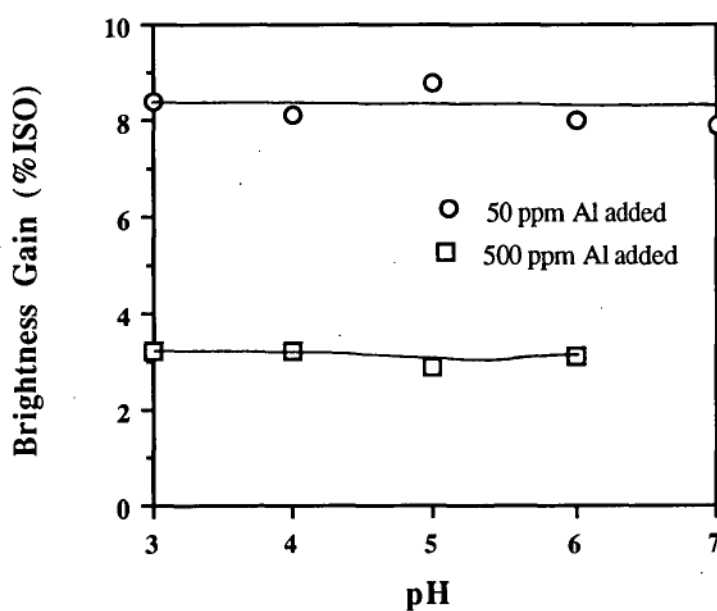
**Table 2.2** Comparison of peroxide consumption in acid and alkaline stages of a two stage bleaching sequence.

Aluminium dose (ppm on o.d.pulp)	Peroxide consumed(% on o.d. pulp)		
	Acid stage	Alkaline stage	Total
0	0.51	1.65	2.16
50	0.41	0.08	0.49
100	0.24	0.15	0.39
250	0.33	0.15	0.48
500	0.43	0.15	0.58

Conditions: 1% consistency, 50°C, Initial charge peroxide 6.0% on pulp. Acid stage: 30 minutes, initial pH 6.0. Alkaline stage: 120 minutes, initial pH 11.0.

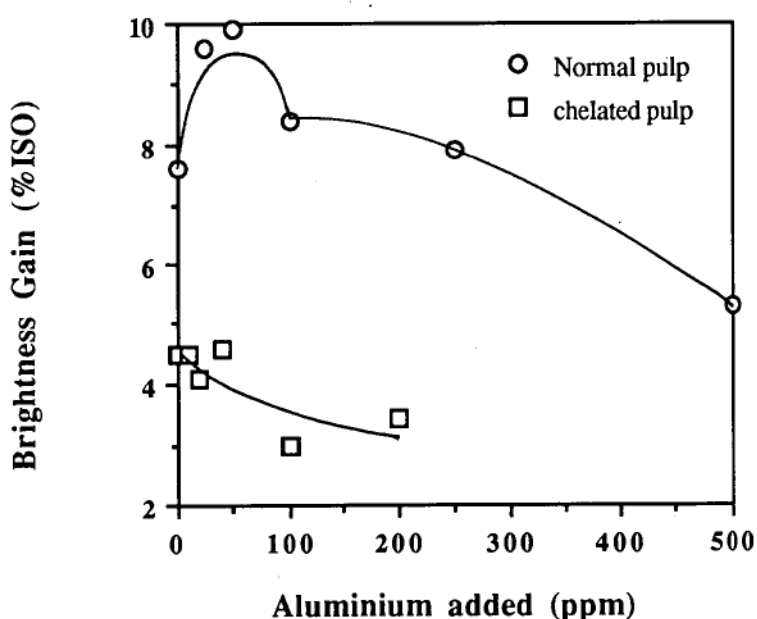


**Figure 2.32** The effect of varying the time of the acidic treatment on the brightness gain of the pulp during a two stage peroxide bleaching sequence. 1% consistency; 50 ppm aluminium, Acidic stage: pH 6.0; Alkaline stage: pH 11.0, 120 minutes.



**Figure 2.33** The effect of varying the pH of the first stage of a two stage treatment. 1% consistency; First stage: 30 minutes; Second stage: pH 11.0, 120 minutes.

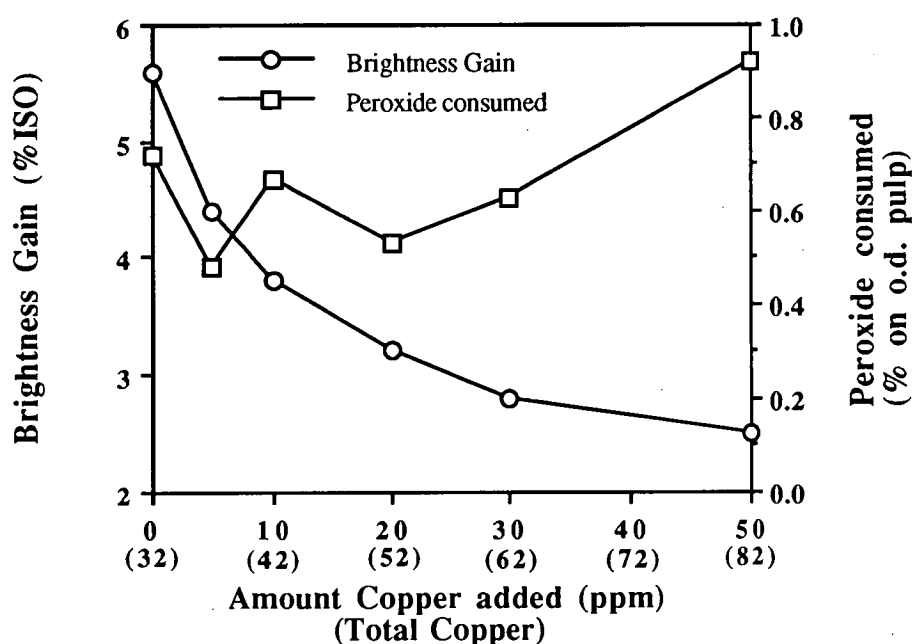
If the presence of transition metal ions in the pulp is important in producing enhanced brightness, removal of the metal ions by chelation and washing prior to bleaching may result in a different brightness response. Table 5.1 (Chapter 5) shows a typical metal ion analysis for the pulp. Figure 2.34 shows the effect on brightness gain of removing metal ions from the pulp prior to bleaching. Clearly the brightness response of the chelated pulp is greatly reduced compared to that of the untreated pulp, indicating that the presence of transition metal ions is indeed important in this process. From the table of metal ion contents of the untreated and chelated pulps (Table 5.1) it can be seen that the levels of manganese and copper, are changed significantly by chelation, whereas the iron content remains unchanged.



**Figure 2.34** Plot showing the different brightness response of normal and chelated pulps to a two stage bleach. 1% consistency; Acidic stage: pH 6.0, 30 minutes; Alkaline stage: pH 11.0, 120 minutes.

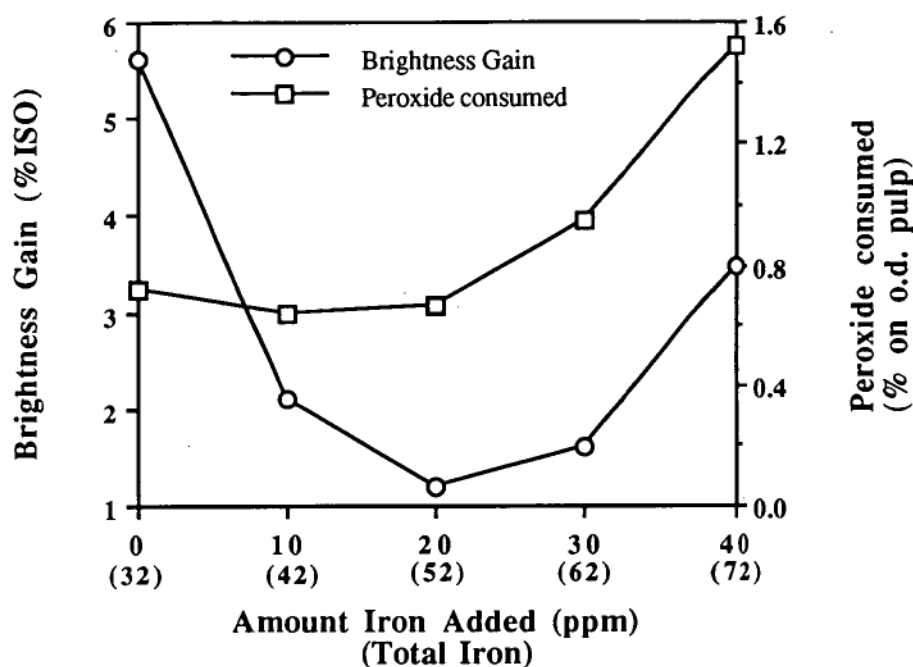
As chelated pulps produce a lower brightness response than normal pulps, it may be possible to determine which transition metal ions are involved in promoting brightness development during the two stage process. For a fixed addition of aluminium to the chelated pulp, the brightness gain was reduced with increasing doses of copper as

shown in Figure 2.35. The peroxide consumption does not change significantly with copper addition in the presence of aluminium, even though copper is known to catalytically decompose hydrogen peroxide under typical alkaline bleaching conditions (16). At low levels of addition the peroxide consumption does not increase significantly, which could indicate some stabilisation of the bleaching liquor under these circumstances. Figure 2.36 shows the effect of addition of iron. This again shows that the peroxide consumption increases with addition of iron and that the brightness of the pulp initially decreases. However at higher levels of iron addition the brightness gain increases, possibly indicating a role in bleaching for the products of catalytic decomposition of hydrogen peroxide.



**Figure 2.35** Correlation between the brightness gain and the peroxide consumption for chelated pulp treated with various levels of added copper. 1% consistency, 40 ppm aluminum; Acidic stage: pH 6.0, 15 minutes; Alkaline stage: pH 11.0, 180 minutes.

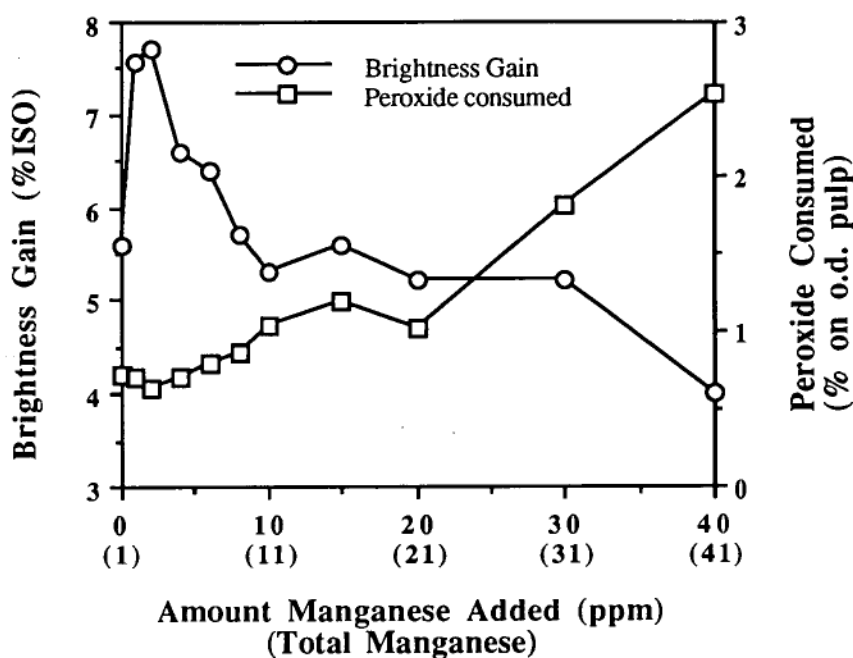




**Figure 2.36** Correlation between the brightness gain and the peroxide consumption for chelated pulp treated with various levels of added iron. Conditions as in Figure 2.35.

The addition of manganese in the presence of a constant amount of aluminium exhibits a different effect compared to the addition of either iron or copper. Figure 2.37 shows that the addition of less than 10 ppm manganese, which is approximately the level normally present in the pulp used in this study (see Table 5.1), in the presence of 40 ppm aluminium enhances the brightness gain during the two stage acid/alkali process. The optimum level of manganese addition was found to be 2 ppm, corresponding to an aluminium to manganese molar ratio of 35. This can be compared with a molar ratio of 16 corresponding to maximum brightness gain in Figure 2.29. It is not clear whether these ratios reflect the chemical composition of particularly active catalytic species formed through interactions between aluminium and manganese. Mixed binuclear species formed through oxy or hydroxy bridges between transition metal ions and other centres capable of undergoing hydrolysis have been postulated, as for example in Mg-O-Fe structures implicated in the stabilisation of iron catalysts by magnesium in the

presence of alkaline peroxide (111,112). Both magnesium (91) and aluminium (92) are known to undergo hydrolysis to produce dimers and higher polymers, even in acidic and neutral solution, so the possibility of a mixed hydrolytic species being responsible for the observed effect is significant.



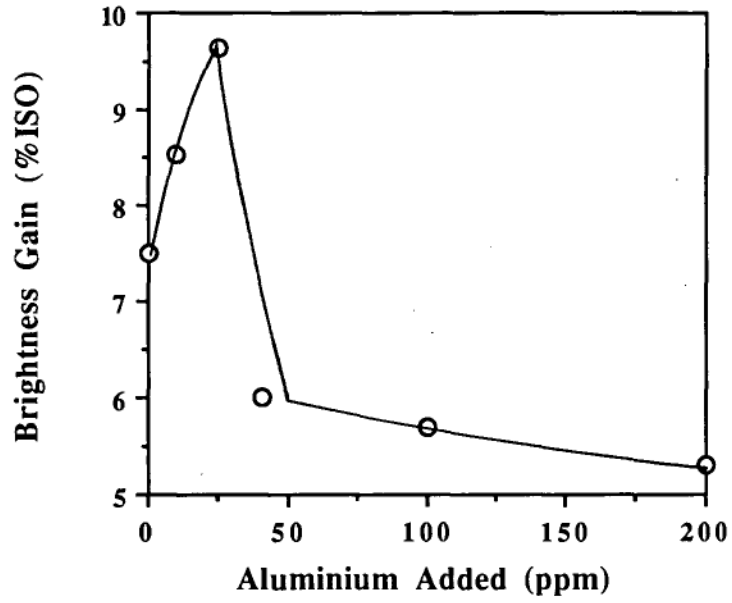
**Figure 2.37** Correlation between the brightness gain and the peroxide consumption for chelated pulp treated with various levels of added manganese. Conditions as in Figure 2.35.

It has previously been reported (35) that the addition of transition metal ions such as chromium, titanium and vanadium during two stage peroxide bleaching processes can enhance the brightness development of mechanical pulps. It has also been shown (32) that the metal ions occurring naturally in the pulp can give rise to enhanced brightness gains when a two stage acid/alkali sequence is used instead of a conventional single stage alkaline bleach. This has been demonstrated by observing the effects of removing the naturally occurring metal ions by chelation and washing prior to two stage peroxide bleaching as previously shown in Chapter 2.3. When aluminium is added to the pulp changes occur in the nature of the catalytic species present under acidic or neutral conditions. Reactions occurring in acidic or neutral peroxide in the presence of these

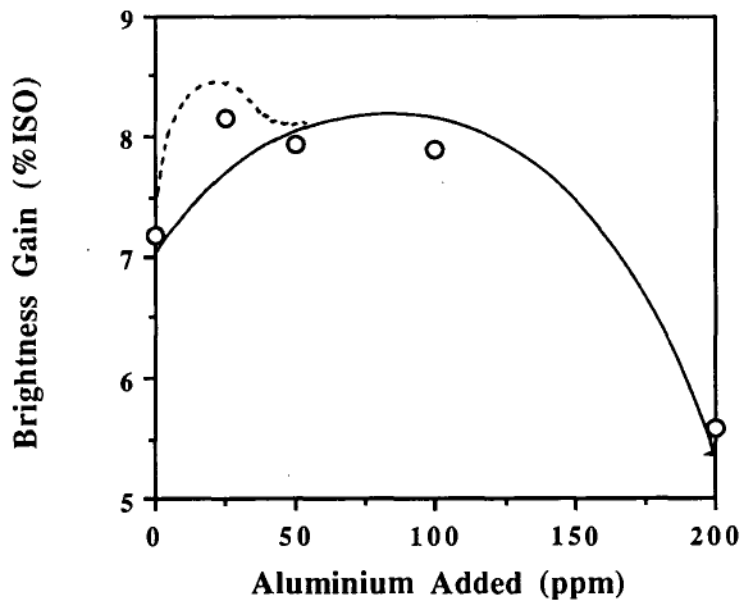
catalysts render the chromophores present in the pulp more susceptible to elimination in the subsequent alkaline stage. It has been suggested that generation of free radical species in the presence of these catalysts may play a significant role in these processes. Recent studies in the absence of pulp have shown that the presence of aluminium has little effect on the catalytic activity of manganese during peroxide decomposition under alkaline conditions (91). However other studies have shown that catalytic behaviour of transition metal species may be significantly modified in the presence of pulp or lignin model compounds (113). This can result in an enhancement of peroxide stability as illustrated in Figure 2.30.

At 1% stock consistency the addition of small quantities of aluminium to a two stage acid/alkali peroxide bleaching sequence can enhance the brightness gain with a simultaneous decrease in the amount of peroxide consumed. Figures 2.38 and 2.39 show the brightness response at 4% and 8% stock consistency respectively. On moving to higher stock consistencies the same brightness enhancement is observed. Aluminium levels of 25-100 ppm on pulp lead to an increased brightness irrespective of the stock consistency. The reduced peroxide consumption observed at 1% stock consistency is not observed at higher consistencies as shown in figures 2.40 and 2.41.

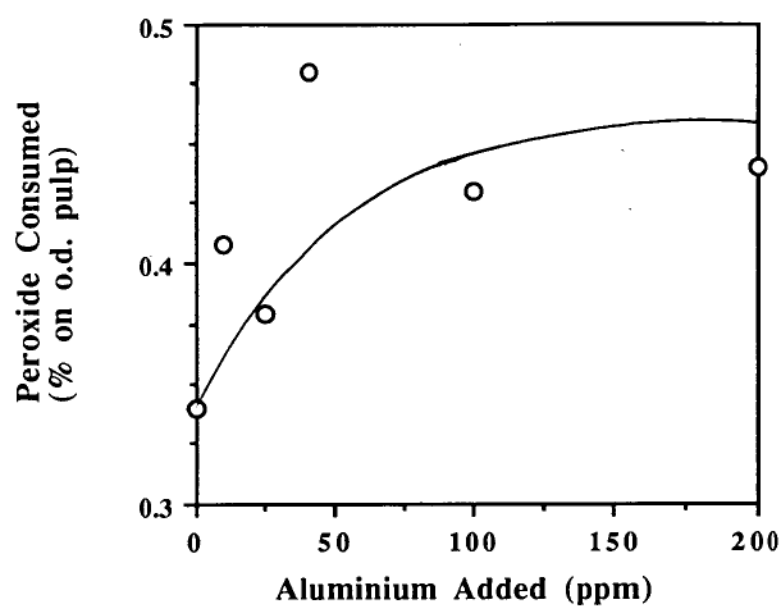
It appears, therefore, that the same mechanisms are occurring in all cases, independent of the stock consistency. Further studies will be required to identify species responsible for enhancement of bleaching response during two stage processes, although the presence of hydroxyl radicals have been postulated as having a significant role in peroxide bleaching of mechanical pulps (92).



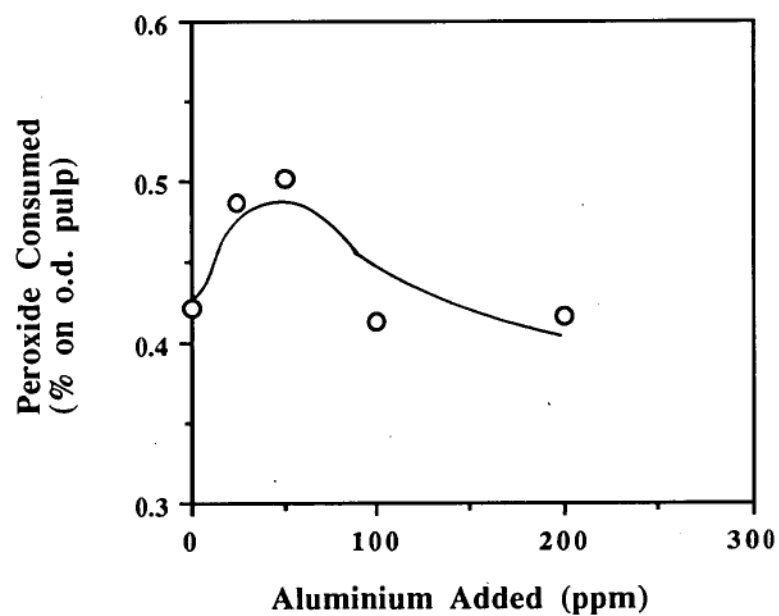
**Figure 2.38** Brightness response of pulp to two stage bleach with various levels of aluminium. 4% consistency, 1.5% peroxide charge; Acidic stage: pH 6.0, 15 minutes; Alkaline stage: pH 11.0, 150 minutes.



**Figure 2.39** Brightness response of pulp to two stage bleach with various levels of aluminium. 8% consistency, 0.75% peroxide charge; Acidic stage: pH 6.0, 15 minutes; Alkaline stage: pH 11.0, 120 minutes.



**Figure 2.40** Peroxide consumption of pulp during a two stage bleach with various levels of aluminium at 4% consistency. Conditions as in Figure 2.38.



**Figure 2.41** Peroxide consumption of pulp during a two stage bleach with various levels of aluminium at 8% consistency. Conditions as in Figure 2.39.

## 2.5 Conclusions

This study has provided further evidence for a dual mechanism for chromophore elimination during peroxide bleaching. Analysis of previously reported kinetic expressions leads to the conclusion that two parallel routes exist for peroxide bleaching corresponding to [1] a reaction which depends upon the direct participation of the perhydroxyl anion; and [2] a reaction in which free radical species participate in chromophore elimination. This analysis suggests that both routes are important at pH levels normally encountered in conventional bleaching of wood pulp with hydrogen peroxide. Although the rate of chromophore elimination is very slow under acidic conditions, reactions which occur render the chromophores present more susceptible to subsequent reaction under alkaline conditions. Formation of these reactive intermediates is promoted by the formation of free radical species produced through catalytic decomposition of peroxide by transition metals such as chromium.

It has been shown that chromium is an active catalyst for the decomposition of hydrogen peroxide in the pH range 3.8 to 7.3 with a maximum rate observed at pH 5.8. The rate of decomposition can be reduced by addition of aluminium, magnesium or silicate, possibly due to the formation of mixed hydrolytic species which reduces the concentration of the catalytically active chromium species. Silicate may also act as a free radical trap, thus slowing the radical chain reaction proposed for metal ion catalysed decomposition of hydrogen peroxide. The complex behaviour observed in the case of aged chromium solutions and when magnesium is present in various quantities at pH 5.8 reflects the complicated hydrolysis of chromium solutions.

The solution work is important in that it has allowed the development of a two-stage acid/alkali peroxide bleaching sequence in which the radical stage is separated from conventional peroxide bleaching and the rate of radical generation can be altered. This allows an examination of the role of various species in peroxide bleaching processes. The presence of certain transition metal ions during a two-stage hydrogen peroxide

bleach of *Eucalypt* SGW has been found to enhance the brightness of the pulp. The total effect produced appears to be derived from the influence of chelatable ions naturally present in the pulp, introduced chromium species and the prevailing acidic conditions. The influence of these metal species during acidic peroxide treatment renders the chromophores present in the pulp more easily removed during subsequent bleaching under alkaline conditions. This effect may be related to generation of active radical species through catalytic decomposition of hydrogen peroxide at low pH. Using such a process, optimised for dose of catalyst and time of acidic treatment, brightness gains can be achieved in less time while consuming no additional peroxide.

The two-stage peroxide bleaching process involving the addition of aluminium shows that under certain conditions the transition metal ions present in mechanical pulps can play a positive role in peroxide bleaching. At low and medium consistency the addition of aluminium nitrate to a two stage acid/alkali peroxide bleaching sequence can enhance the brightness gain of the pulp. A reduction in the amount of peroxide consumed compared to a conventional single stage alkaline peroxide bleach was also observed at 1% consistency. The effect appears to be due to an interaction between the manganese present in the pulp and the added aluminium. The properties of transition metal ion catalysts naturally present in the pulp appear to be modified by the addition of aluminium so that greater stabilisation of peroxide is achieved with enhanced brightness response. This is further evidence that transition metal ions can indeed play an important role in peroxide bleaching and are not universally undesirable as traditionally thought. The results of this study demonstrate the potential for utilizing the catalytic properties of naturally occurring transition metal ions in the pulp, and shows that these positive effects can be promoted through addition of trace amounts of catalytically inactive elements such as aluminium. The use of these types of catalytic systems are more likely to be given commercial consideration than other previously reported systems which rely on the addition of transition metals such as chromium or titanium.

From a mechanistic viewpoint, no brightness gain is observed in the acidic stage in either process but changes clearly occur in the pulp that enable the perhydroxyl anion to eliminate the chromophoric material more easily. Also of interest is the low level of peroxide consumption in the second stage ( $P_2$ ) of the aluminium process, as shown in table 2.2, compared to a single stage alkaline peroxide bleach. The role of radical species in this case again appears to be essentially in the  $P_1$  stage, although the nature of the catalytically active species is uncertain.

The two-stage bleaching with added chromium or aluminium has shown that there is potential scope for development of beneficial catalytic processes for the enhancement of peroxide bleaching. Such processes may utilize the presence of metal ions naturally present in the wood pulp, or species which may be introduced prior to peroxide treatment. The development of such processes would appear to depend on recent concepts of peroxide bleaching in which species other than the perhydroxyl anion are implicated in chromophore removal. This may in turn revise the traditional view that the presence of transition metal ions in wood pulp should only be associated with adverse effects in bleaching sequences.

Two-stage peroxide bleaching sequences with separate radical and anion stages have been investigated. From these studies it is clear that both hydroxyl radicals and the perhydroxyl anion are both involved in the elimination of chromophoric material. Although no brightness gain is observed for acidic bleaching stages there appears to be evidence that changes occur in the pulp that make subsequent removal in alkaline stages easier.

The addition of metal ions to produce radical species is therefore beneficial in the peroxide bleaching of mechanical pulps. Although such factors as overall peroxide consumption and capital costs need to be considered on an industrial scale, this work has shown that the initial kinetic analysis is essentially correct in predicting two



separate mechanisms of peroxide bleaching.

While the processes investigated here may be of no commercial significance, what has been achieved is a further understanding of the mechanisms of peroxide bleaching. In all peroxide bleaching processes it would appear necessary to ensure that both radical and anion induced bleaching can occur, whether this be in separate stages, or more conveniently, in a single stage.

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## CHAPTER 3

# THE EFFECT OF METAL IONS ON PEROXIDE BLEACHING

## CHAPTER THREE

### The Effect of Metal ions on Peroxide Bleaching

#### 3.1 Literature Review

The presence of transition metal ions, particularly iron, manganese and copper, have generally been considered undesirable during peroxide bleaching of mechanical pulps (1-5) as they are thought to reduce the effective charge of bleaching chemical. These metals can arise from the wood itself, the process water or be introduced during pulp processing (5). The decomposition products of transition metal ion catalysed decomposition of hydrogen peroxide, including radical species such as the hydroxyl and superoxide anion radicals,  $\text{OH}^\cdot$  and  $\text{O}_2^\cdot$ , are traditionally thought to play no positive role in bleaching (5-9) or even darken the pulp (3,9). Much effort is usually expended on either trying to remove these metal ions prior to bleaching by using complexing agents such as DTPA, EDTA or DTMPA (6,8-12), or rendering the metal ions inactive by addition of stabilisers such as sodium silicate or magnesium salts (8,10-11,13).

During the past decade interest has been shown in the use of hydrogen peroxide under conditions not previously employed. Usually peroxide bleaching is performed in a single alkaline stage at pH 9-11 to maximize the concentration of the perhydroxyl anion,  $\text{HO}_2^-$  (2,8-10,14-15) as outlined previously (Chapter 1.3). However, some recent studies have shown that two stage bleaching processes with the pulp initially under acidic or neutral conditions, followed by a conventional alkaline stage can give greater brightness enhancement. It has also been demonstrated that the addition of various transition metal ions can, in fact, enhance the brightness development during these two-stage processes (16-18). This chapter presents further results which show the importance of metal ions in peroxide bleaching for both conventional single stage

alkaline processes and two stage acid/alkali peroxide bleaching sequences.

### **3.1.1 Transition Metal ion Catalysed Peroxide Decomposition**

It has been known for many years that certain transition metal ions can catalytically decompose hydrogen peroxide. Many studies have been undertaken in the absence of pulp in order to determine the mechanism of transition metal ion catalysed hydrogen peroxide decomposition and subsequent stabilisation by known stabilising agents such as magnesium salts and sodium silicate (1,19-26).

Generally the effects of transition metal ions are most apparent under alkaline conditions (1,2,20-22,25,26), similar to those employed in the bleaching of mechanical pulps (2,6,8-10), although some metals can decompose hydrogen peroxide under acidic conditions (1,23). Various decomposition mechanisms have been proposed, with some metals appearing to act via a radical mechanism (21,24), involving the hydroxyl and superoxide anion radicals, and others proceeding by mechanisms not involving radicals species (24).

In the absence of pulp, mechanistic studies have been performed to elucidate the mechanism of stabilisation of transition metal catalysed decomposition of hydrogen peroxide (19,22,24-26). While these studies are of significant interest, it appears that the presence of pulp significantly alters the mechanism and catalytic activity (1,27). For example, at low concentrations iron (III) does not significantly decompose peroxide in alkaline media, but in the presence of pulp a much greater catalytic effect is observed (27).

There are three possible means by which the presence of transition metal ions can influence the response of mechanical pulps to peroxide bleaching. Firstly, the major consideration is that increased consumption of peroxide via catalytic decomposition leaves a reduced amount of peroxide available for bleaching reactions (1,5,19,20,28-

30). It is essentially for this reason that stabilisers are added to peroxide bleach liquors. Secondly, the metal ions themselves, especially iron, can form coloured complexes with the lignin portion of the pulp (31,32). Finally, the products of the decomposition can include reactive species that are themselves capable of reacting with pulp (2,33,34). These reactions are the subject of much debate and will be discussed further in this chapter (3.3). A more thorough examination of the role of the hydroxyl radical will be undertaken in the next chapter (4.1.1). For these reasons, transition metal ions are either removed or deactivated to enhance the bleaching response of the pulp.

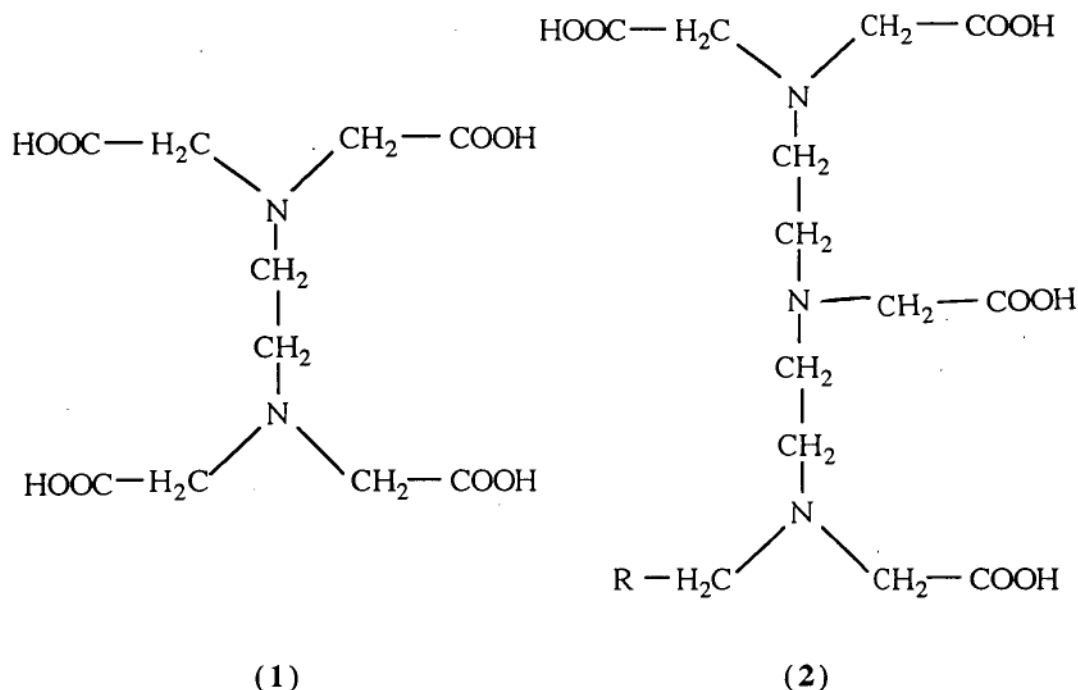
### **3.1.2 Common Stabilisation Practices**

Pulp samples typically contain transition metal ions that are capable of decomposing hydrogen peroxide under the alkaline conditions employed for the bleaching of mechanical pulps. Of major significance to peroxide bleaching are manganese, copper and iron (2,5,8,19)).

Because of the presence of these metal ions and the cost of hydrogen peroxide, an effort is made to reduce this wastage, and thus leave more peroxide available for bleaching reactions. This can be achieved in two main ways. Either the metal ions can be partially removed, or the activity of the transition metal ions catalysts can be reduced in some way.

The use of chelating agents is a common practice in the peroxide bleaching of mechanical pulps. Soluble salts of diethylenetriaminepentaacetic acid (DTPA) and ethylenediaminetetraacetic acid (EDTA) are the most commonly used chelating agents (1,6,8,10,11,35). Figure 3.1 shows the structures of these chelating agents. Generally this process is performed as a pre-treatment before exposure of the pulp to bleach liquors, where 0.2-0.5% of chelating agent is added to the pulp at low consistency (6,8,9,11) and after 5-30 minutes the pulp is filtered (6,9) and washed (35) to remove

the complexed metal ions. This process is capable of removing significant quantities of copper and manganese from pulp samples (9,35), but the removal of iron is not so effective (See Table 5.1). With extended time of chelation and acid washing of the pulp (9) further removal of metal ions is possible but this would appear not to be practical on an industrial level.



**Figure 3.1** The structure of chelating agents EDTA (1) and DTPA (2).

Environmental concerns regarding the effects of chelating agents such as DTPA, specifically with regard to metal ion solubility (36), may reduce or stop the use of these and similar reagents in the future so new stabilising reagents are being sought by the industry.

Secondly, reagents that partially deactivate the residual metal ions such as sodium silicate (1,8,10,12,24,25,28,29) and magnesium salts (8,10,19,25) can be added to peroxide bleach liquors to prevent or reduce transition metal ion catalysed decomposition of hydrogen peroxide.

The addition of sodium silicate solution (2-5% on o.d. pulp) to pulp during peroxide bleaching is a common practice. The addition of these solutions also provides some of

the alkali required for peroxide bleaching. The mechanism by which sodium silicate acts to stabilise peroxide solutions and so increase brightness gains is not clearly understood with many conflicting views appearing in the literature. Suggestions include the binding of silicate to transition metal ions (10,24,28,37,38), buffering action (8,28,38), surface coating (37), a radical trap (24,28) and peroxysilicate formation as an active bleaching species (13,24,37,39,40)

Studies by Burton (40) show that there is no advantage in forming a peroxysilicate complex prior to the addition of pulp, thus indicating that this species has no advantage over peroxide in the presence of silicate. Colodette *et al.* (24) have also shown no significant difference in the rates of peroxide reaction with lignin like structures in the presence and absence of silicate, again indicating that the peroxysilicate complex is not a more active bleaching species than the perhydroxyl anion.

Colodette *et al.* (24) have shown that, in the absence of pulp there is no significant change in either the hydroxyl or superoxide anion radical concentration with silicate addition, therefore indicating that silicate does not act as a free radical trap.

The interaction of silicate with transition metal ions has been extensively studied (24,28). In the absence of pulp, silicate is capable of reducing the effects of iron and manganese catalysed decomposition of hydrogen peroxide, but silicate addition to copper enhances the catalytic activity. Therefore it appears that silicate does interact and bind with transition metal ions but the effect on peroxide decomposition is not always similar, and does not appear to be related to the coating of the metal with silicate (24).

The buffering action of silicate appears only to be present at levels that are much higher than normally encountered in bleach liquor preparation, of the order of 16% on pulp (40).

Therefore, it would appear that the main method of stabilisation by silicate is due to binding between silicate and transition metal ions, and a subsequent change in the activity of the metal species. If iron and manganese are the major metal ions present then stabilisation would be predicted from the solution studies. In the case of high copper levels, silicate addition would be not so beneficial and the use of other stabilisers in conjunction with silicate would be necessary.

Magnesium salts are less commonly added to bleaching liquors but can also have a stabilising effect on peroxide solutions (8,10,19,25). Magnesium sulfate (Epsom salt) is added in much smaller quantities (~0.05% on o.d. pulp) than silicate (8,10). The method of stabilisation is again unclear with several suggested mechanisms. The formation of binuclear complexes involving magnesium and other transition metal ions (22,25) has been suggested as a method whereby magnesium can stabilise peroxide solutions in the absence of pulp by binding the active transition metal ions. Reaction of magnesium ions with the superoxide anion radical has also been proposed as a possible stabilisation mechanism (19,28). This radical is an intermediate in radical chain processes (33,41,42) that produce hydroxyl radicals and finally leads to peroxide decomposition to water and oxygen (33,41,42). By trapping the relatively stable superoxide anion radical this chain process can be either slowed or stopped. Co-precipitation of transition metal ions with magnesium oxides and hydroxides is also a possible explanation for the behaviour of magnesium salts in peroxide solutions (22,25).

These methods of stabilisation can either be used separately or in various combinations. The reagents selected for a given situation are chosen to give the best results for the particular pulp type and transition metal ion profile. The major consideration being the maximum stabilisation, thus allowing a lower initial peroxide charge, and the brightness response of the pulp compared to the cost of the stabilising agents.



### 3.1.3 Hydrogen Peroxide Decomposition Products

The products of hydrogen peroxide decomposition include very reactive species capable of reacting with both the lignin and cellulose portions of mechanical pulps. The influence these species have on the optical and physical properties of these pulps are the subject of much debate. A more thorough review of the literature pertaining specifically to the hydroxyl radical, considered to be the most likely species to effect pulp properties, will appear later (Chapter 4.1.1) and experimental studies in this chapter (3.3) will show results related to the effect of peroxide decomposition products on pulp brightness.

### 3.1.4 Alkali Darkening

Under alkaline conditions, in the absence of peroxide, or at low peroxide concentrations, darkening can occur (2,43,44). Alkali darkening has previously been described in Chapter 1.3. While the effect of alkali alone is well documented, less work has been performed to determine the influence of transition metal ions and radical species derived from hydrogen peroxide decomposition. Work by Kutney *et al.* (2) suggests that transition metal ions can either retard or accelerate darkening reactions in the presence of alkali and that the darkening occurring at the end of a peroxide bleaching sequence cannot be attributed to alkali alone (2,43). From this work it has been concluded that the decomposition products can accelerate darkening and hence, support the traditional view that removal of transition metal ions is essential. This work will be discussed further (Chapter 3.3) and additional experimental work performed to attempt to determine the effect of radical species on both alkali darkening and peroxide bleaching.

## 3.2. Metal ion Removal

The effect of metal ion removal by chelation on the bleaching response of *E.regnans* SGW has been investigated. Comparisons have been made between the bleaching response of chelated pulps and untreated pulps, and also the effect of different

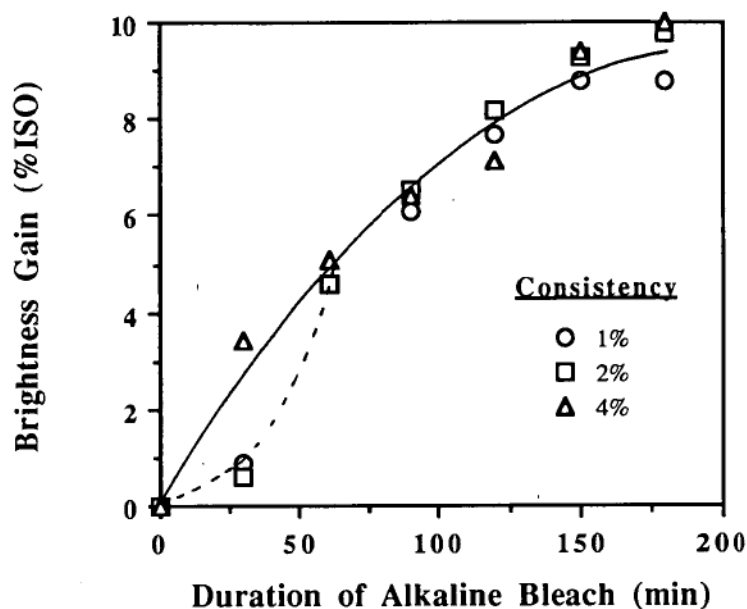
chelating agents. The effect of addition of transition metal ions to chelated pulps has also been studied to determine if the change in brightness response can be related to the removal of metal ions, and which metal ions are involved in these processes. The effect of two-stage acid alkali peroxide bleaching processes on chelated pulps has also been investigated to determine if chelation has an influence on the phenomena reported in the previous chapter.

### **3.2.1. Single Stage Bleaching under Alkaline Conditions**

Figure 3.2 shows the increase in brightness with time for the Eucalypt pulp at 4% consistency during alkaline peroxide bleaching at 50°C. The type of response observed is typical of many reported bleaching experiments using alkaline hydrogen peroxide, with the rate of brightness gain declining continuously as time progresses. For experiments at lower consistency, however, this figure also shows an interesting effect during the initial stages of bleaching. At both 1% and 2% consistency, the initial rate of brightness gain is very low, and the typical bleaching profile is observed only after an extended bleaching period. This type of "induction effect" can also be observed for pulps which were chelated with EDTA and washed prior to alkaline peroxide bleaching, as shown in Figure 3.3. This shows that at very low consistency, an induction effect is also observed, in which the brightness of the pulp actually decreases below the initial level of the unbleached pulp, that is, darkening reactions initially predominate over bleaching reactions.

This evidence indicates that removing metal ions from a pulp can, under certain conditions, adversely effect the bleaching of the pulp during single stage alkaline peroxide treatment. If the metal ion concentration is reduced to very low levels the brightness response of the pulp can actually be retarded. From the analysis of the metal ions in the pulp (Table 5.1) it would appear that removal of manganese or copper is probably responsible for this effect, as iron levels do not change significantly with chelation and washing. Manganese has previously been reported to have the most

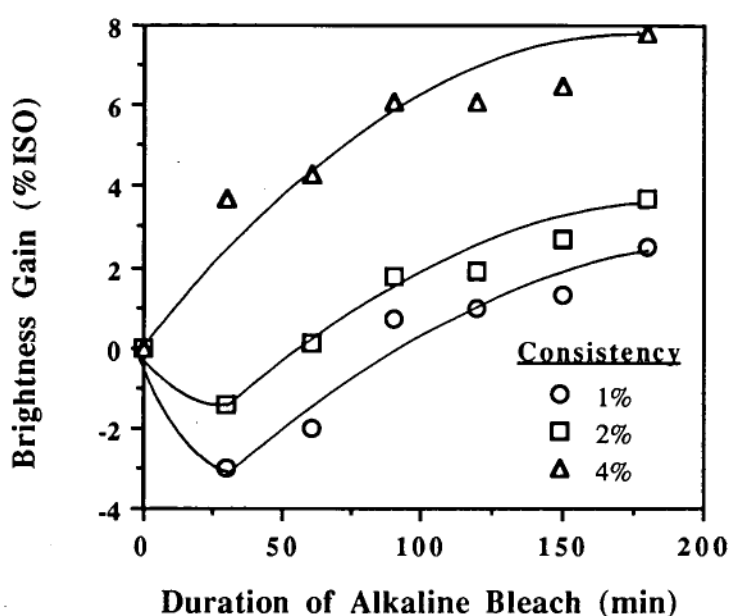
significant influence on peroxide bleaching of mechanical pulps (35), so the influence of manganese was investigated.



**Figure 3.2** Brightness response of untreated pulps to alkaline peroxide bleaching at 1%, 2% and 4% consistency, initial pH 11.0, 50°C, initial peroxide charge 1.2 g/L.

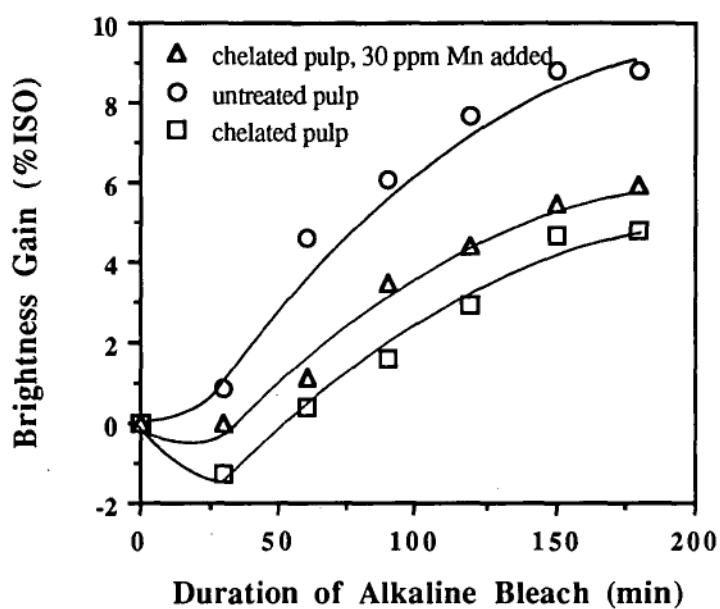
Figures 3.4 and 3.5 show the influences of adding various levels of manganese to an untreated pulp and a pulp which has been chelated with DTPA and then washed. In each case, the pulp was allowed to remain in contact with a solution containing the appropriate quantity of manganese nitrate for 20 minutes at pH 7 prior to bleaching at 1% consistency. The concentration of manganese reported indicates the amount of manganese added, this does not include the residual level in the pulp after chelation (1 ppm). It is clear that as the total amount of manganese is increased, the response to brightness gain in alkaline peroxide is enhanced, and the effect of the induction process is reduced. However, addition of manganese in excess of the levels normally encountered in the pulp does not continue to give increased brightness. From this it appears that a certain quantity of transition metal ions may need to be present to give the most effective bleaching. Figure 3.5 shows that this corresponds to approximately 8 ppm manganese for bleaching at 1% consistency. If insufficient metal ions are

present then an induction period is observed, while if excess metal ions are present peroxide decomposition leads to loss of active bleaching species, resulting in a lower final brightness.

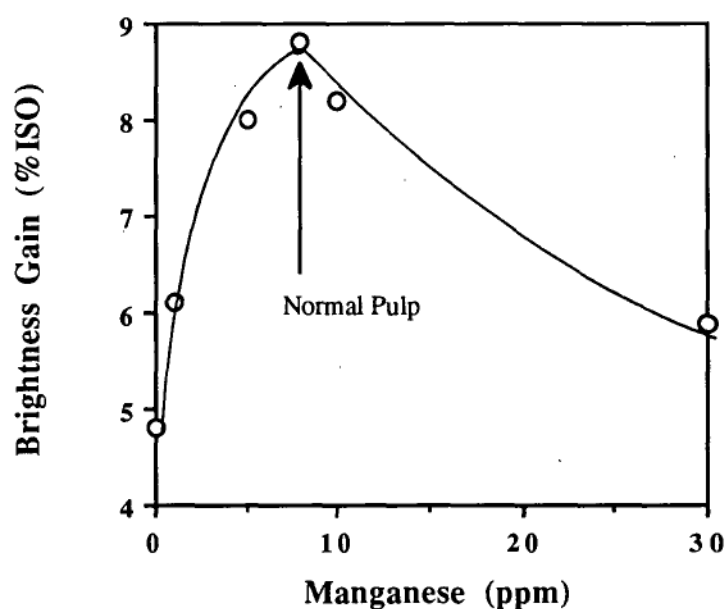


**Figure 3.3** Brightness response of chelated pulps to alkaline peroxide bleaching. Other conditions as in Figure 3.2

Figure 3.6 shows the effect of treating pulps with alkali (pH 11.0) in the absence of peroxide at 1%, 2% and 4% consistency. For both chelated and untreated pulps alkaline treatment produces a darkening of the pulp. For the chelated pulps much greater brightness losses are observed than for untreated pulps. This indicates that metal ions in some way prevent the reactions that give rise to alkali darkening from occurring. This again indicates that the presence of metal ions may be useful in peroxide bleaching in reducing darkening of pulps. This is in accordance with other results (43) which indicate that some metal ions can indeed inhibit darkening reactions.

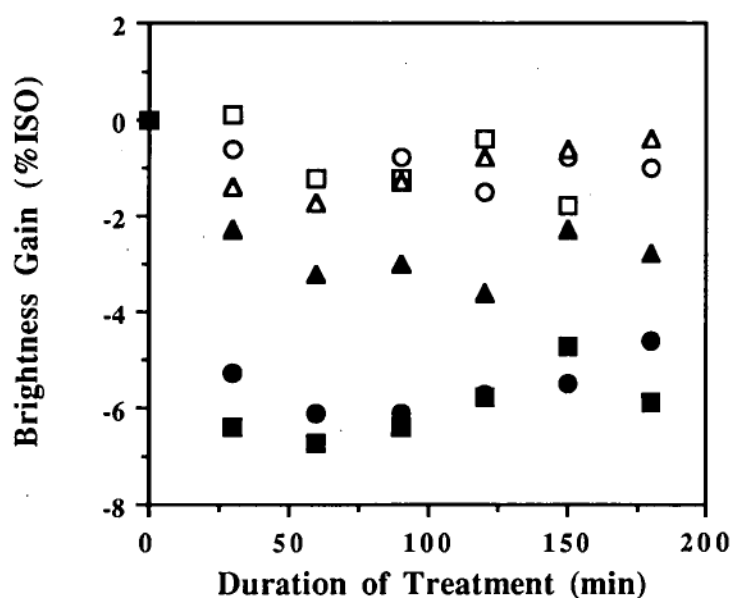


**Figure 3.4** Brightness response of pulps to a single stage alkaline bleach in the presence of manganese. 1% consistency, other conditions as in figure 3.2.



**Figure 3.5** Brightness gain plotted against amount of manganese added. Chelated pulp, 180 minutes, other conditions as in figure 3.4.

Iron, manganese and copper, however, are reported to accelerate darkening (43). Other metal ions which are present in the normal pulp could be responsible for this reduced darkening observed for normal pulps compared to chelated pulps. The darkening reactions appear to be near completion after 30 minutes at 50°C, which is similar to results previously reported (43). It is not clear from this data whether the metal ions protect potential chromophore sites in the lignin or act in some other way. It should also be noted that the situation in the absence of peroxide may be different from that in the presence of peroxide. If the pH in a bleach is too high, or the peroxide residual at the end of a bleach is too low, darkening reactions may still occur.



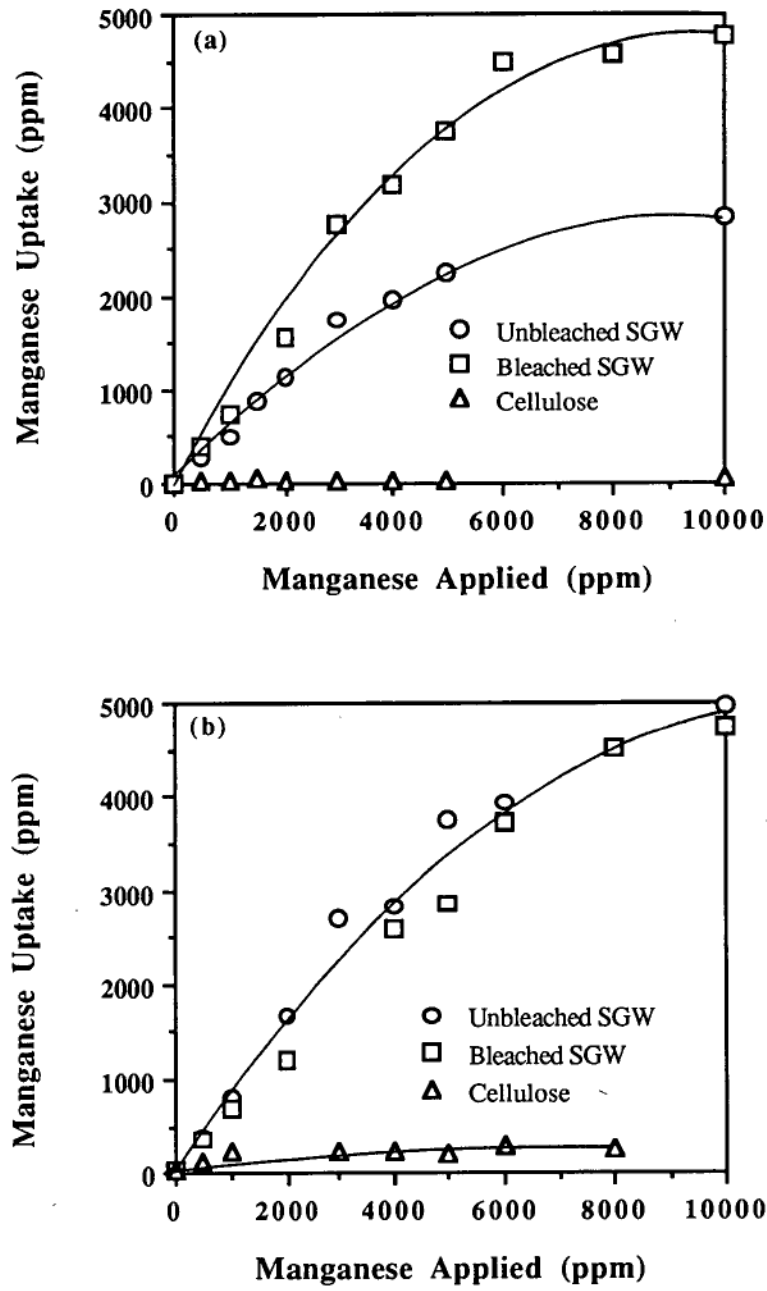
**Figure 3.6** Brightness response of various pulps to treatment with alkali in the absence of peroxide, pH 11.0. Normal pulps at various consistencies: Δ, 1%; ○, 2%; ◻, 4%. Chelated pulps: ▲, 1%; ●, 2%; ■, 4%.

### 3.2.2. Location of Manganese During Bleaching Processes

The manganese ions present in mechanical pulps are generally considered to originate in the wood itself, rather than from processing equipment, as in the case of iron (5). Having shown that under certain conditions the presence of manganese can have beneficial effects during conventional single stage alkaline peroxide bleaching, it is

useful to consider the location of the manganese within the pulp and during the bleaching process, as this may influence the observed effects of the presence of transition metal ions. The uptake of manganese ions from solution by various pulps after allowing the system to equilibrate for 16 hours at 20°C is shown in Figure 3.7. These figures show that manganese does not bind to any significant degree to pure cellulose either at pH 7 or 9. In contrast, levels of up to 5000 ppm of manganese were observed for the unbleached SGW, thus indicating that the manganese is bound to either the lignin portion of the pulps as has been previously reported (26) or the hemicellulose. It appears that manganese is bound to specific sites within the lignin and hemicellulose portions of the pulp. Both hemicellulose and lignin react under the conditions encountered in alkaline peroxide bleaching (45). The main reactions of hemicellulose are deacetylation, dissolution and hydrolysis (45). At pH 9 for both bleached and unbleached pulps manganese is associated with approximately 5% of lignin units. These results indicate that the manganese ions are bound at specific sites in the pulp structure. However, the ratios of manganese to lignin C<sub>9</sub> units do not appear to correlate with the amount of any simple functional group such as carbonyl or phenolic hydroxyl, as the measured ratios are too low (46). However, the manganese may be linked with some specific combination of groups within the lignin, of which there are more in bleached pulp, such as an adjacent carbonyl and free phenolic hydroxyl group in some particular stereochemical configuration.

If the presence of manganese in pulp can give rise to beneficial effects during peroxide bleaching, then it would be reasonable to suggest that the manganese bound to chromophores would be the most effective. Once the chromophore has been eliminated the manganese could either remain attached to the lignin or be released into solution. Figure 3.8 shows that during bleaching of the SGW pulp, manganese is released into

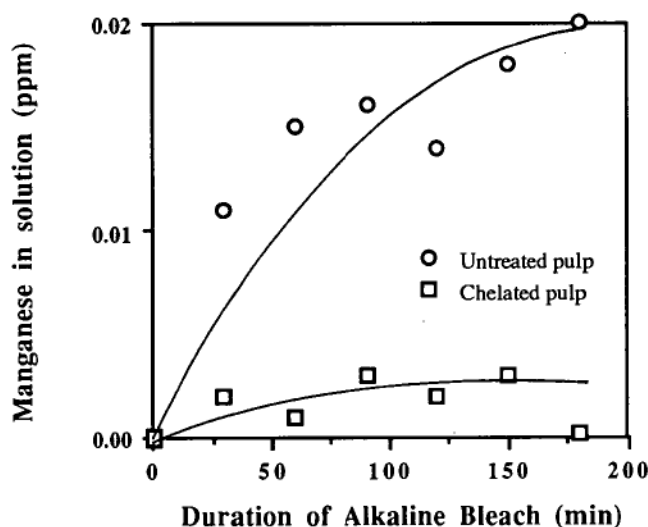


**Figure 3.7** The uptake of manganese by various pulps as a function of manganese concentration in solution. 0.5% consistency, room temperature a) pH 7.0, b) pH 9.0.

the solution, with more manganese released from the untreated pulp compared to the chelated pulps as would be expected due to the higher level manganese associated with the untreated pulp. In the presence of alkali alone, the levels of manganese in solution



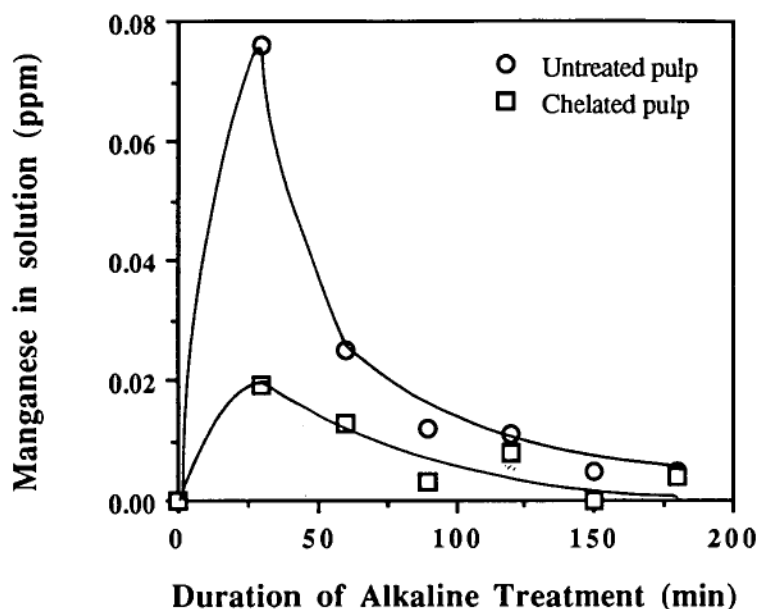
vary as shown in Figure 3.9. It appears that the manganese is initially released from the sites to which it is bound. However with time, the levels decrease possibly due to precipitation of manganese as insoluble oxides and hydroxides. This maximum, at approximately 30 minutes, also corresponds to the time over which alkali darkening reaction occur (see Figure 3.6).



**Figure 3.8** The variation of manganese concentration in solution with time during bleaching of pulps. 1% consistency, pH 11.0, 50°C, 12% peroxide on o.d. pulp.

### 3.2.3. Two-Stage Bleaching Processes

Two stage bleaching sequences using acidic and alkaline conditions have been reported previously (16-18). In many of these processes (16,18) the addition of transition metal ions to the first stage of the sequence is an important part of the process. In the other studies (17) it would appear that the metal ions occurring naturally in the pulp are sufficient to give the enhanced brightness observed. Other results reported here (Chapter 2) suggest that the presence of transition metal ions, whether naturally occurring or artificially introduced, are important in the first stage of such two stage processes, and may be associated with the production of free radical species. Although it is not possible to observe any increase in brightness after acidic peroxide treatments

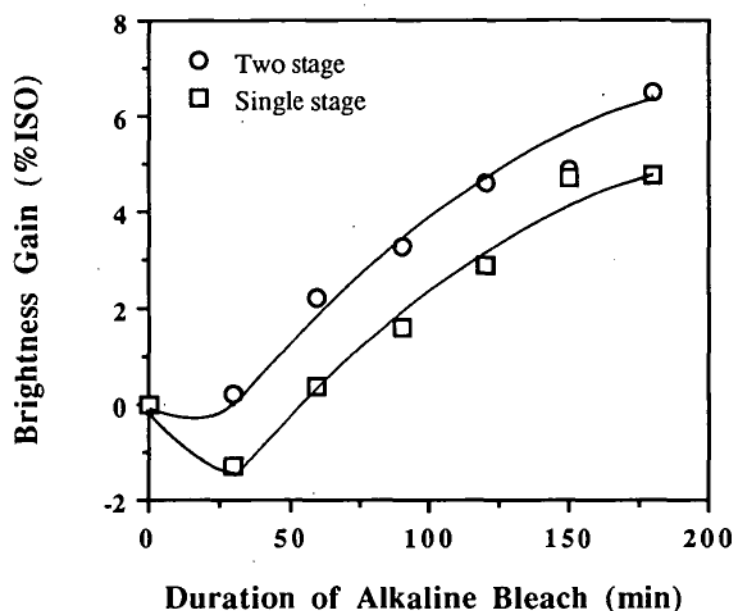


**Figure 3.9** Variation of manganese concentration in solution with time during treatment of pulps with alkali in the absence of peroxide, 1% consistency, pH 11.0.

of *Eucalypt* SGW pulps, it has been suggested that free radical species generated through decomposition of hydrogen peroxide in the presence of certain transition metal ions may render the chromophores present in the pulp more susceptible to subsequent alkaline peroxide bleaching.

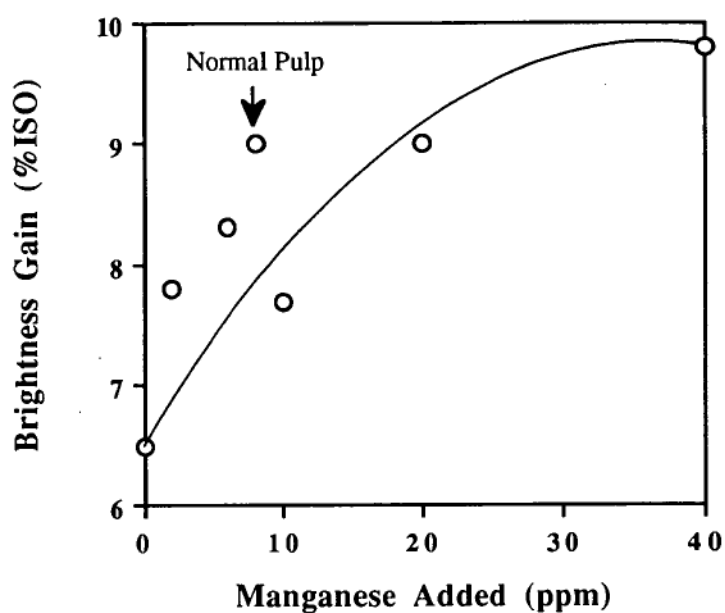
Figure 3.10 shows the brightness response of pulps (chelated with DTPA and washed) comparing a conventional single stage alkaline peroxide treatment with a two stage, acid-alkali treatment, both at 1% pulp consistency. At any time during the alkaline stage the brightness of the pulp bleached using the two stage process is greater than that using only a single stage bleach. It can also be seen that the initial brightness loss observed in the single stage process is not present in the two stage process, although there is still an induction period. The total peroxide consumption after three hours for the single stage bleach (0.29% on o.d. pulp) and the two stage process (0.33% on o.d. pulp) are comparable. However, the brightness gain for the two stage process (6.5 %ISO) is greater than for the single stage bleach (4.8 %ISO), indicating an increased

efficiency for the two stage process.

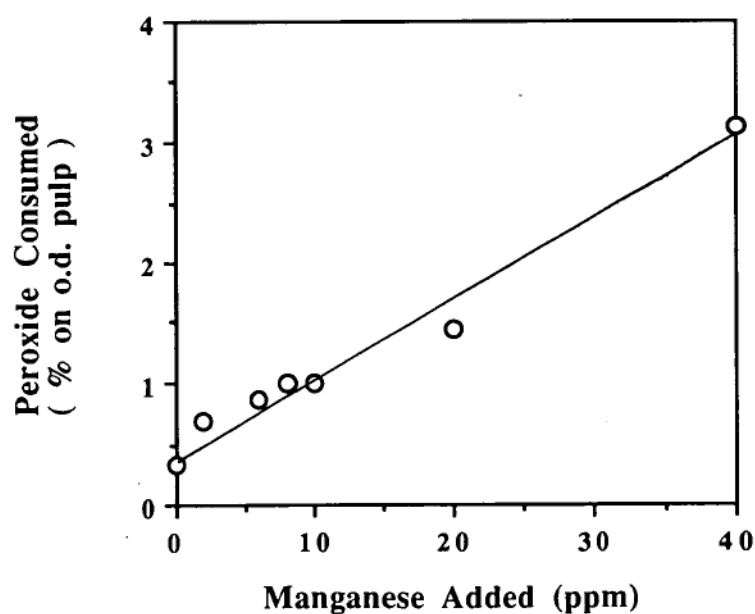


**Figure 3.10** Brightness response of a chelated pulp to single stage and two stage bleaching. Two stage: Acidic stage: pH 6.0, 15 minutes; Alkaline stage: pH 11.0. Single stage: pH 11.0. 1% consistency, 6% peroxide on o.d. pulp.

Figure 3.11 shows the effect of adding various levels of manganese to a pulp which has been chelated with DTPA and washed prior to a two stage bleaching sequence. The pulp was allowed to stand in contact with the manganese solution for 20 minutes before commencement of the bleach. The amount of manganese reported corresponds to that added to the pulp and does not include that already present (1ppm). This added manganese may be in a different form to that already present in the pulp. It is clear that increasing the total amount of manganese present enhances the brightness response of the pulp. However, as shown in Figure 3.12, it is clear that this enhanced brightness is achieved by consuming considerably more hydrogen peroxide.

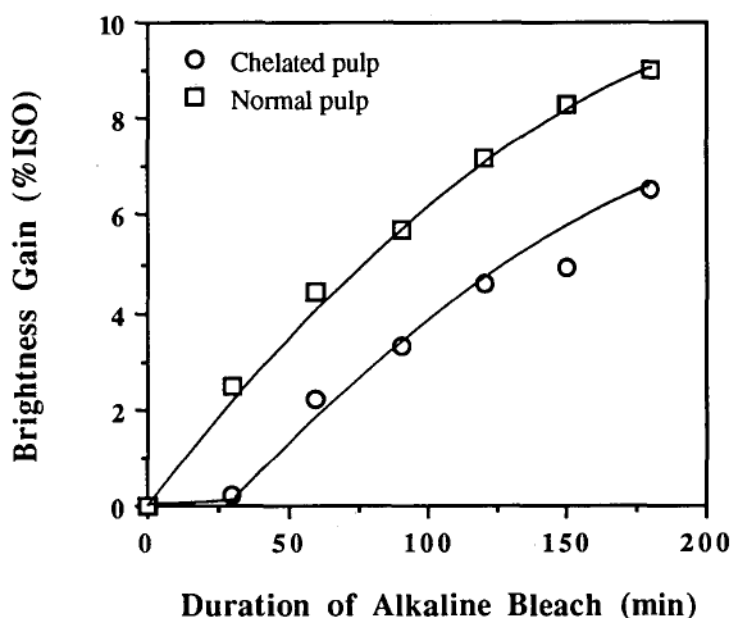


**Figure 3.11** Final brightness of chelated pulps after a two stage bleaching sequence with manganese addition. Acidic stage: pH 6.0, 15 minutes; Alkaline stage: pH 11.0, 180 minutes. 1% consistency, 6% peroxide on o.d. pulp.



**Figure 3.12** Peroxide consumption against the amount of manganese added. Conditions the same as in figure 3.11.

Figure 3.13 shows the brightness response of both chelated and untreated pulps to a two stage, acid-alkali bleaching sequence at 1% consistency. Clearly the presence of additional metal ions in normal pulp gives an increased brightness and also removes the induction period.



**Figure 3.13** Brightness response of normal and chelated pulps to a two stage bleaching sequence. Conditions as in Figure 3.11.

Chromium ions are known to catalytically accelerate decomposition of hydrogen peroxide in the pH range 4 to 7. The addition of chromium to a two stage bleaching sequence can be used to give brighter pulps, as has been shown previously (Figure 2.19, 2.23)

### 3.3. Effect of Decomposition Products on Pulp Brightness

Decomposition of hydrogen peroxide is not only reduced to conserve the expensive bleaching reagent, but also because the products of this decomposition are thought to have a detrimental effect on pulp properties (2,47). Both darkening (2) and loss of strength (47) have previously been attributed to these decomposition products. The role of the hydroxyl radical, which is considered primarily responsible for these

adverse affects, will be discussed in greater detail in Chapter 4 (4.1.1).

Some recent work (2) has shown that in the presence of peroxide, alkali and added metal ions, pulp can be darkened rather than bleached. The explanation being that the decomposition products of hydrogen peroxide cause darkening reactions which outweigh any brightening reactions. The major aim of the work was to investigate the amount of darkening that is attributable to peroxide decomposition products and to alkali.

In this work (2) a mechanical pulp was bleached to a moderately high brightness (~76 %ISO) and then after filtering and washing, it was re-exposed to either alkali or alkaline peroxide, with or without added transition metal ions.

It would appear that one major problem with this work was that the initial bleaching was carried out with a higher peroxide charge than the subsequent bleaching stage. Results from work by Ginting *et al.* (48) show that, under constant conditions of alkali and peroxide concentration, darkening can occur when the peroxide concentration is lowered. This has been discussed in terms of a proposed equilibrium kinetic model. This model assumes an equilibrium exists between chromophores and colourless leucochromophores (48), and the position of the equilibrium, which determines the colour of the pulp, is dependent upon the peroxide and alkali concentrations. This work has shown that, under conditions of constant concentration of alkali and peroxide, reducing the peroxide charge can lead to darkening of the pulp. To overcome this potential problem, all the work in this section was performed at a peroxide charge of 3.0% on o.d. pulp and 4% consistency with reducing concentrations of peroxide and alkali. Under these conditions the problems mentioned above should be overcome.

In respect of previous work with two-stage acid-alkali peroxide bleaching sequences, which suggest hydroxyl radicals have a positive role in peroxide bleaching, this

appears to be contradictory to other results results obtained here so further investigations were carried out.

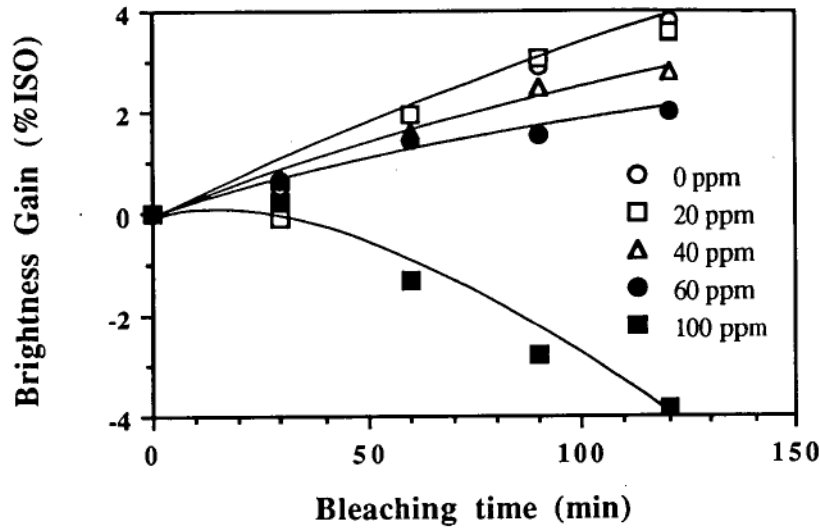
### 3.3.1 Effects of Manganese, Iron and Copper

For this work several pulps were bleached prior to further treatment, as shown in Table 3.1. Samples of both *E.regnans* SGW and *P.radiata* TMP were used in order to determine if the effects observed were specific to certain species or pulp types.

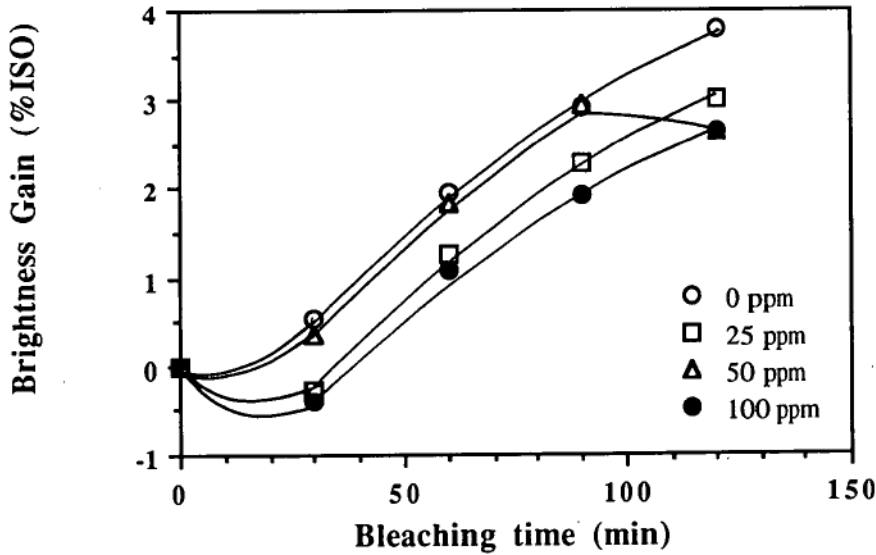
**Table 3.1** Pulps used in this study. Bleaching conditions: 240 minutes, pH 11.0, 50°C, 4% consistency, 3% peroxide (on o.d. pulp).

Pulp	Pulp Type	Brightness (%ISO)
A	SGW	72.1
B	SGW	71.1
C	SGW	70.8
D	TMP	69.7

A series of experiments were performed involving the addition of various quantities of manganese, iron and copper during peroxide bleaching of the pulps described in Table 3.1 and determining changes in brightness. These transition metal ions are known to decompose peroxide in alkaline solutions (1,2,5,10,19,22,28) and copper and manganese are thought to decompose peroxide via a radical mechanism (49-51, Chapter 4). Figure 3.14, 3.15 and 3.16 show the results of adding various amounts of these transition metal ions to such a peroxide bleaching procedure.

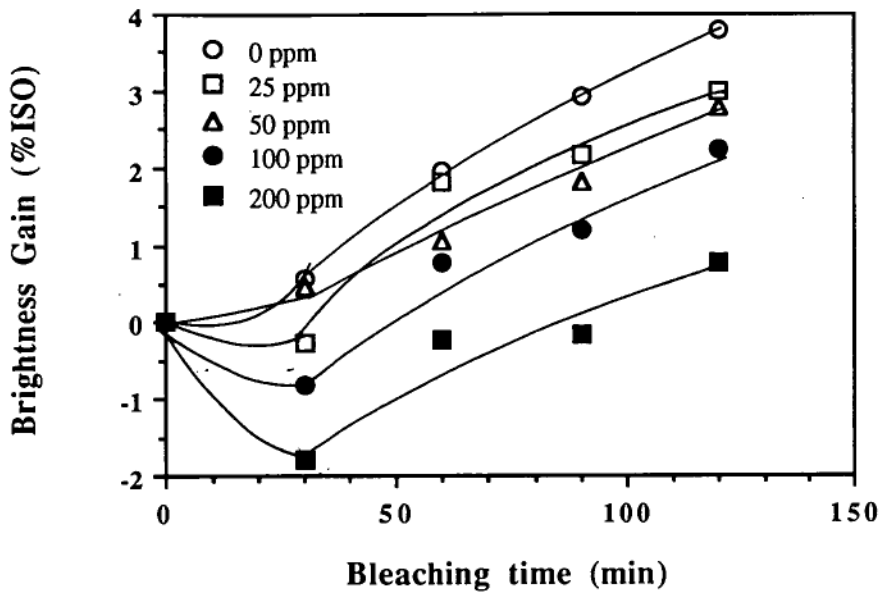


**Figure 3.14** Brightness response of Pulp A to alkaline peroxide bleaching in the presence of various levels of manganese. 50°C, 4% consistency, 3.0% peroxide on o.d. pulp, initial pH 11.0.



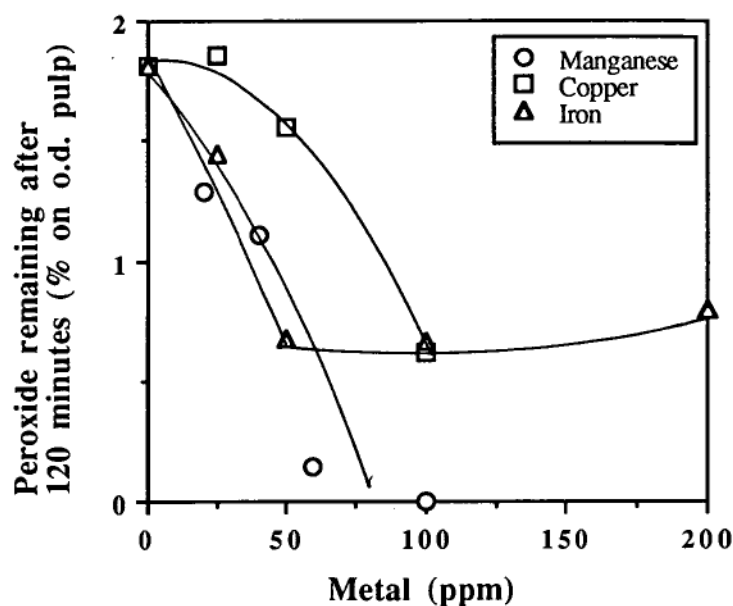
**Figure 3.15** Brightness response of Pulp A to alkaline peroxide bleaching in the presence of various levels of copper. Conditions as in figure 3.14





**Figure 3.16** Brightness response of Pulp A to alkaline peroxide bleaching in the presence of various levels of iron. Conditions as in figure 3.14.

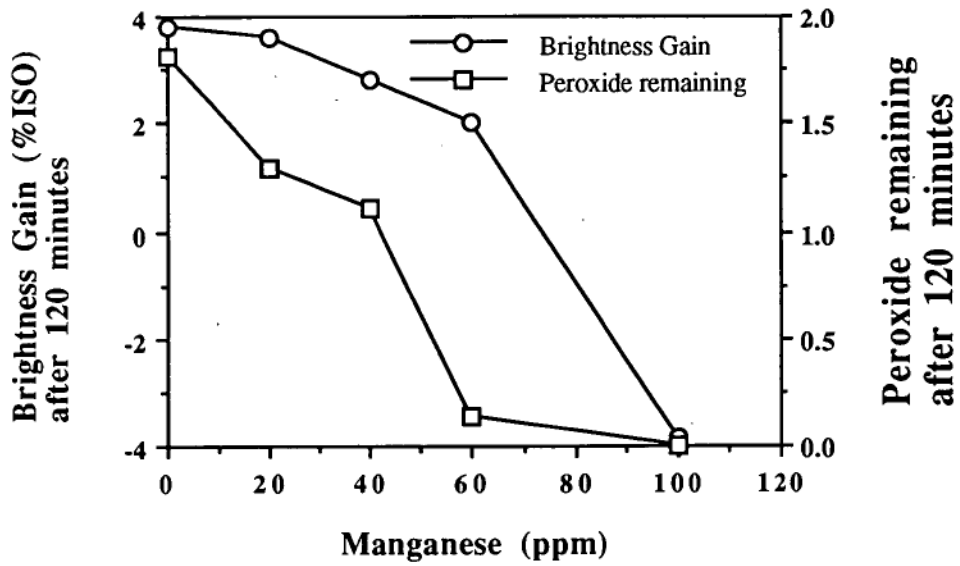
It can be seen that in all of these cases, except 100 ppm manganese, some brightening of the pulp is observed. For the addition of 100 ppm manganese all the peroxide is consumed before the end of the bleach and a subsequent brightness loss is observed. This indicates that the darkening is most likely due to the action of alkali alone, rather than any contribution from the decomposition products of hydrogen peroxide. All three metals give similar trends with increasing metal concentration, the peroxide consumption increases and a resultant reduction in brightness is observed due to the decreased quantity of bleaching reagent available for brightening reactions, as shown in figure 3.17. It shall be shown later (Chapter 4) that in solution the level of hydroxyl radicals produced is significantly different for these three metals. Therefore, as no significant differences are observed in the bleaching response in the presence of these transition metal ions, the role of hydroxyl radicals appears not to be the cause of the brightness changes.



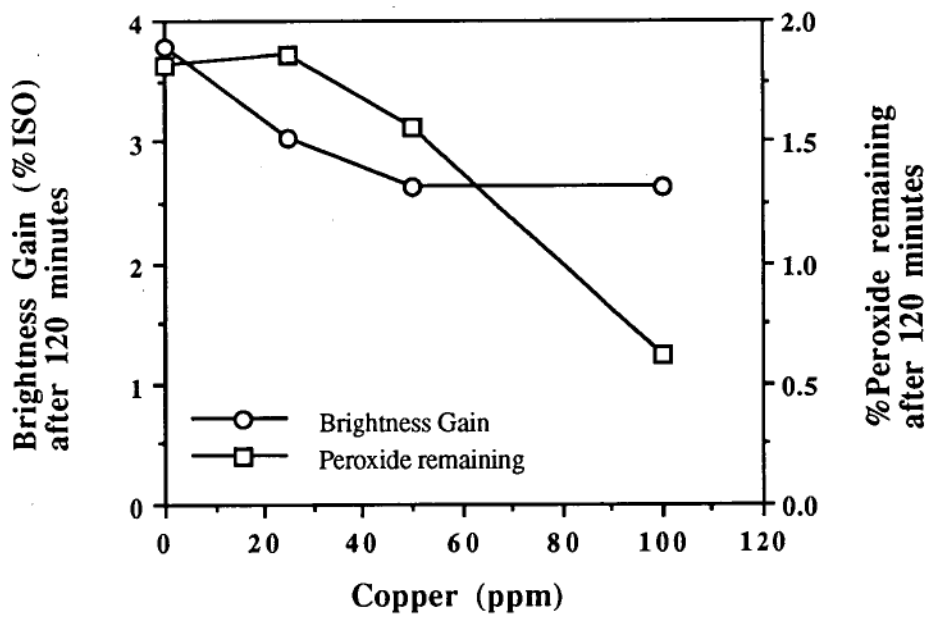
**Figure 3.17** Peroxide residual after 120 minutes. Conditions as in figure 3.14.

There appears to be a correlation between the brightness gain and the quantity of peroxide remaining for all of the metals studied, as shown in figure 3.18, 3.19 and 3.20 for manganese, copper and iron. This is due to the fact that in the cases where greater consumption of peroxide occurs due to the added transition metal ions, less peroxide is available for bleaching and, hence, a lower brightness is achieved. This again indicates that the decrease in brightness response or darkening is due primarily to peroxide consumption rather than the effect of peroxide decomposition.

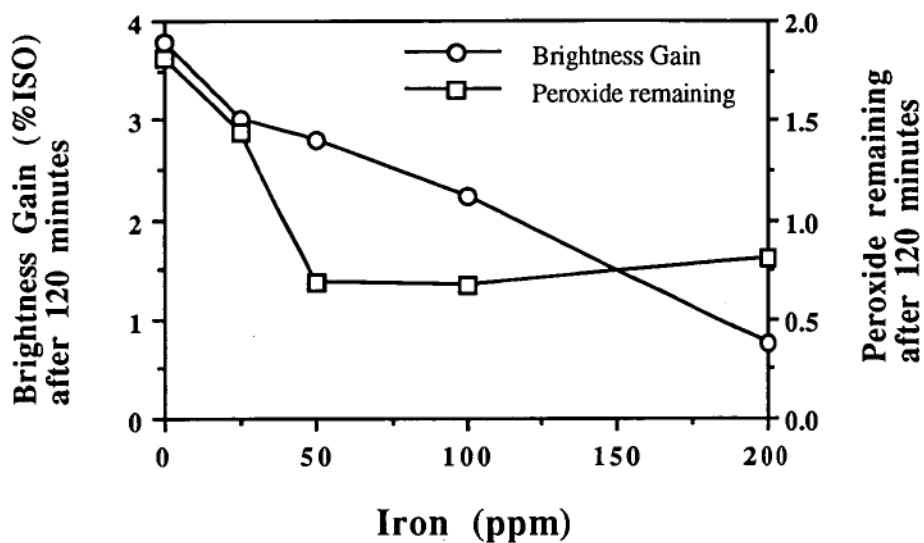
A correlation between the brightness gain and the amount of metal is also possible as shown in figure 3.21. This seems to indicate that the addition of these three metal ions all have a similar effect on the brightness development and the peroxide consumption. The only deviation from this behaviour being when all the peroxide charge is consumed and alkali darkening occurs.



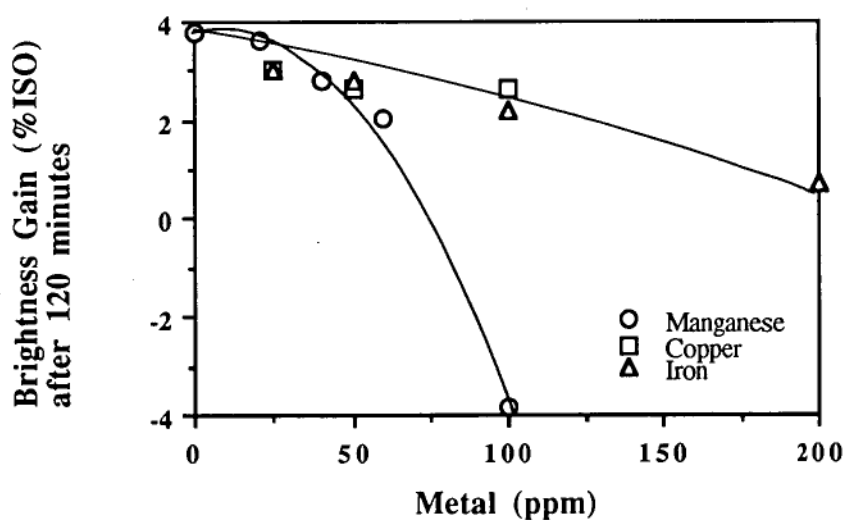
**Figure 3.18** Correlation between peroxide remaining and brightness gain after 120 minutes for bleaching with added manganese. Conditions as in Figure 3.14.



**Figure 3.19** Correlation between peroxide remaining and brightness gain after 120 minutes for bleaching with added copper. Conditions as in Figure 3.14.



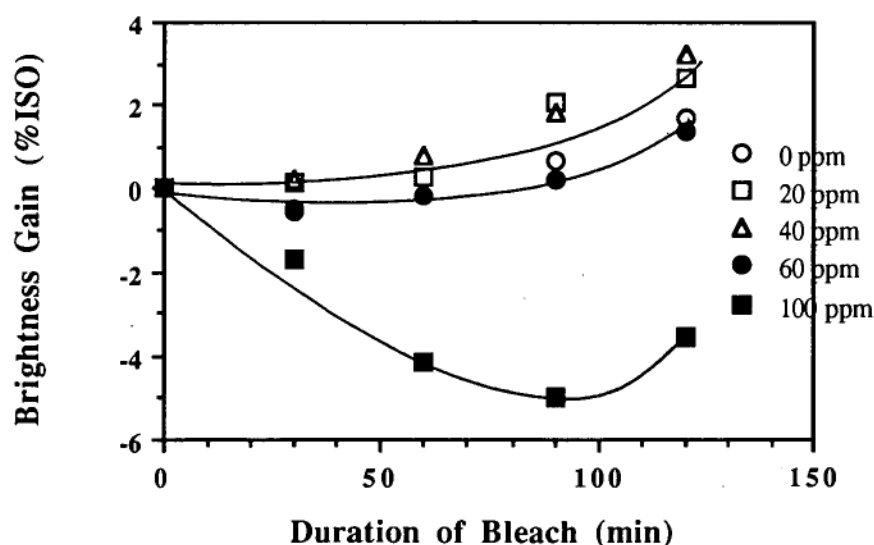
**Figure 3.20** Correlation between peroxide remaining and brightness gain after 120 minutes for bleaching with added iron. Conditions as in Figure 3.14.



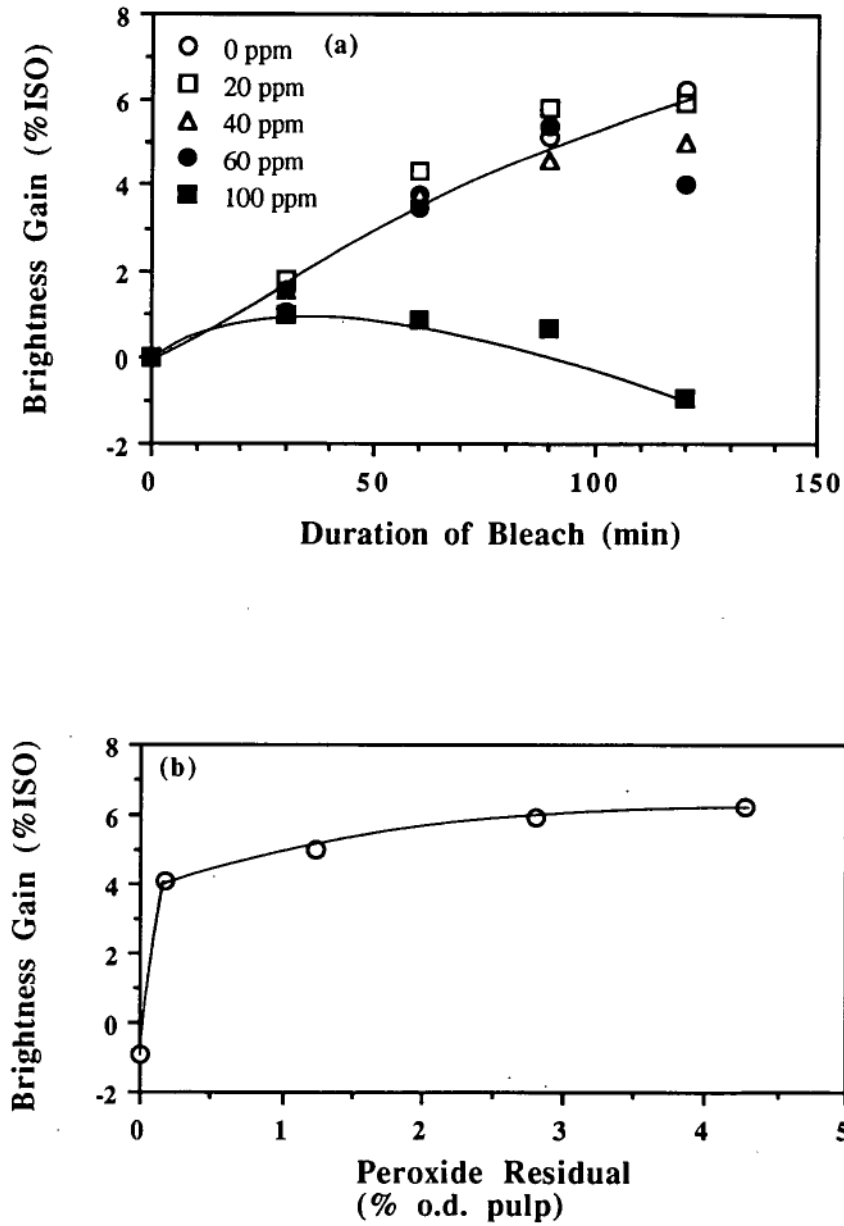
**Figure 3.21** Correlation between total metal ion concentration and the brightness gain after 120 minutes. Conditions as in figure 3.14.

### 3.3.2 Varying the Peroxide Charge.

A series of experiments were performed at peroxide charges of 1.5, 3.0 and 6.0% in the second stage of bleaching with the addition of various levels of manganese after the first stage was bleached at 3.0% peroxide as described in Table 3.1. Manganese appears to be the most active peroxide decomposition catalyst of the three metals studied and, as all three metals behave in a similar manner, as shown in figure 3.21, only manganese was used in this series of experiments. Figures 3.22 and 3.23a show the brightness response with time for various levels of peroxide. The results for 3.0% peroxide are reported in the previous section (Figure 3.14). In all cases it can be seen that there is a brightness increase after 120 minutes, except in the cases where no peroxide remains (100 ppm manganese). In the case of bleaching with 1.5% peroxide an initial loss of brightness is observed in some cases, with the decrease being greatest for higher levels of manganese. Figure 3.23b shows the relationship between the peroxide residual and the brightness achieved. Above a certain level of residual peroxide only minor increases in brightness are observed, indicating that this is not a significant factor in determining final brightness.



**Figure 3.22** Brightness response of Pulp B to second stage treatment with 1.5% peroxide. Other conditions as in figure 3.14.

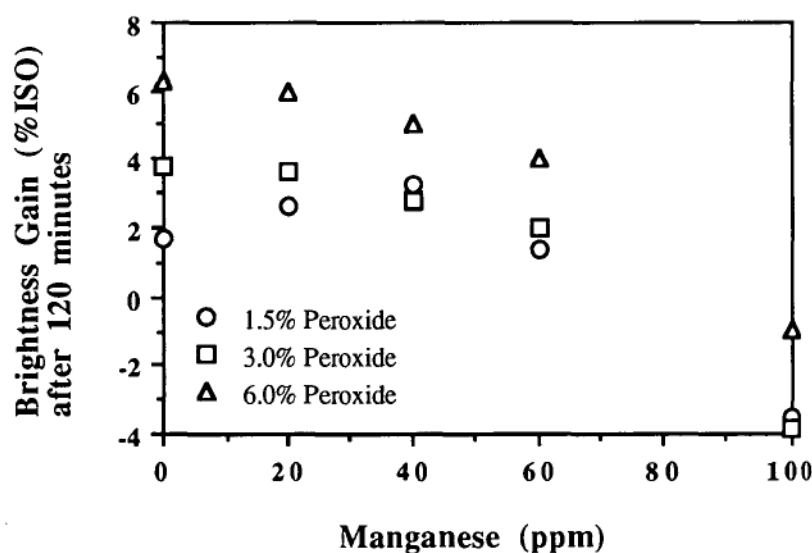


**Figure 3.23** (a) Brightness response of Pulp B to second stage treatment with 6.0% peroxide. (b) Relationship between 120 minute brightness gain and the peroxide residual. Other conditions as in figure 3.14.

Figure 3.24 shows a comparison of the brightness gain with metal ion concentration for the three levels of peroxide addition. As expected a greater brightness gain is

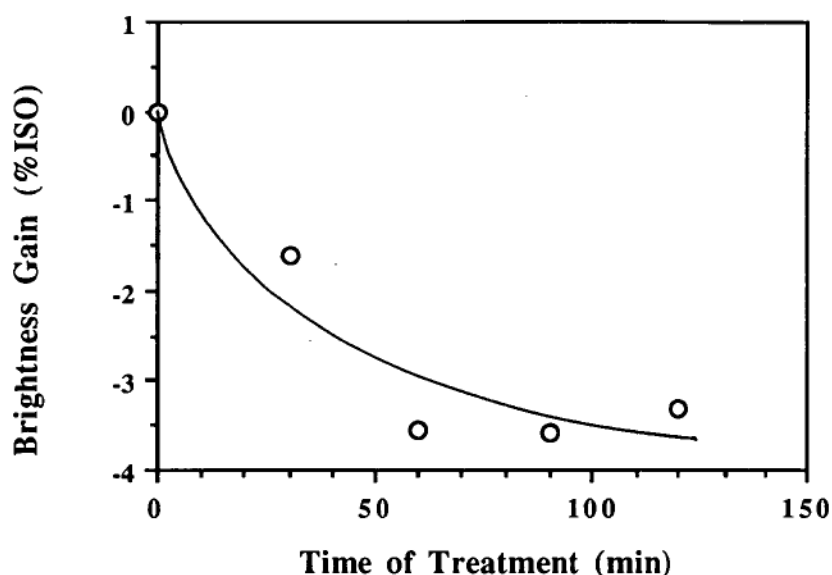
achieved in the case of the highest peroxide charge. The curve for 1.5% peroxide is different in that the addition of manganese up to approximately 40 ppm appears to give an enhanced brightness response, although this effect is small, after which further addition causes reduced brightness increase. Similar results have been obtained previously (Chapter 3.2) indicating that the presence of a certain level of transition metal ions, and particularly manganese, is at times beneficial to bleaching. The general trend is however, at increasing manganese addition, the brightness gain is reduced due to the increased peroxide consumption.

The effect of alkali treatment on SGW is shown in Figure 3.25. It can be seen that the brightness loss after 60 minutes is approximately 3 %ISO and further exposure to alkali does not result in additional darkening. Similar results have been reported previously (43, Figure 3.6), indicating that darkening reaction are essentially complete after a short exposure to alkali.



**Figure 3.24** Correlation of brightness gain to amount of manganese added.

Condition as in Figure 3.14, except 1.5% and 6.0% peroxide results are for Pulp B, 3.0% results are for Pulp A.



**Figure 3.25** Alkali darkening of Pulp C. pH 11.0, 50°C, 1% consistency.

These results are different from those obtained by Kutney *et al.* (2), but this could be related to the type of pulp used. Therefore, a similar series of experiments were performed using a different pulp type.

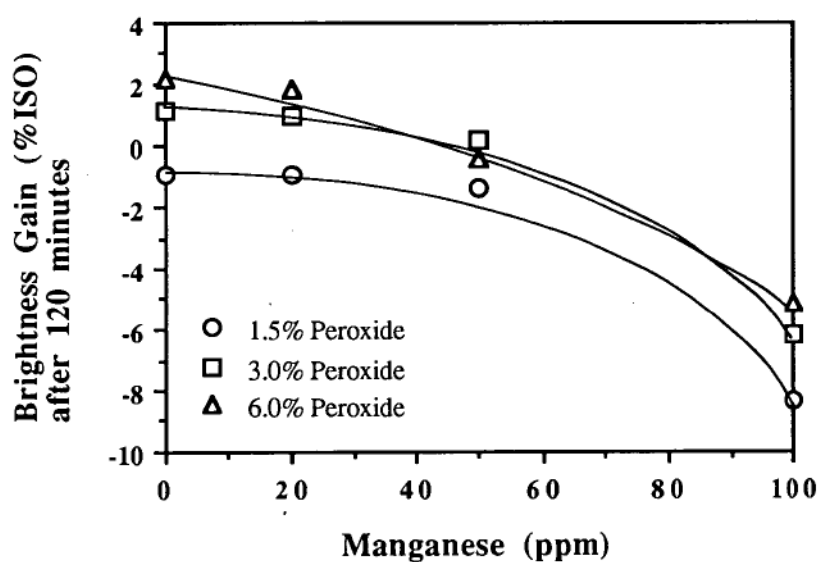
### 3.3.3 TMP Bleaching

A similar series of experiments were carried out using Pulp D, that had been chelated with 0.5% DTPA for 30 minutes at 20°C prior to the first bleaching stage, to determine if the species or type of pulp gave different results. Figures 3.26, 3.27 show the final brightness and peroxide consumption of the pulp after further bleaching in the presence of manganese.

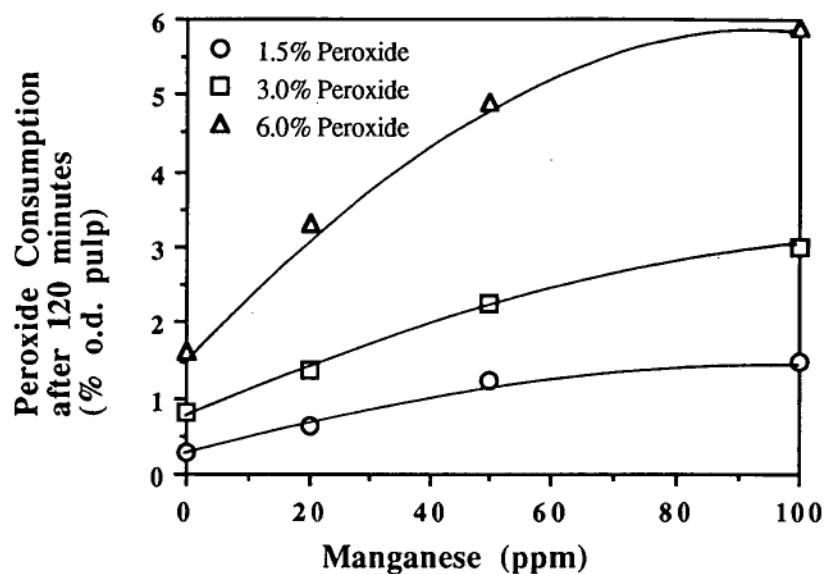
These figures show that a similar response is achieved for the TMP as was observed for SGW (Figures 3.14 and 3.17), although there are several differences that should be noted. Firstly, the brightness gains are significantly lower than observed for the SGW and that a brightness loss is observed at lower peroxide charges even when



peroxide remains at the completion of the bleach. Secondly, greater darkening is observed with the TMP when the peroxide is totally consumed compared to SGW. Although lower brightness gains are achieved, provided that the peroxide charge is as high as the first stage, further brightening is possible even in the presence of added transition metal ions. The darkening observed at 1.5% peroxide can be explained in terms of the proposed equilibrium kinetic model described previously (Chapter 3.3) (48,52).

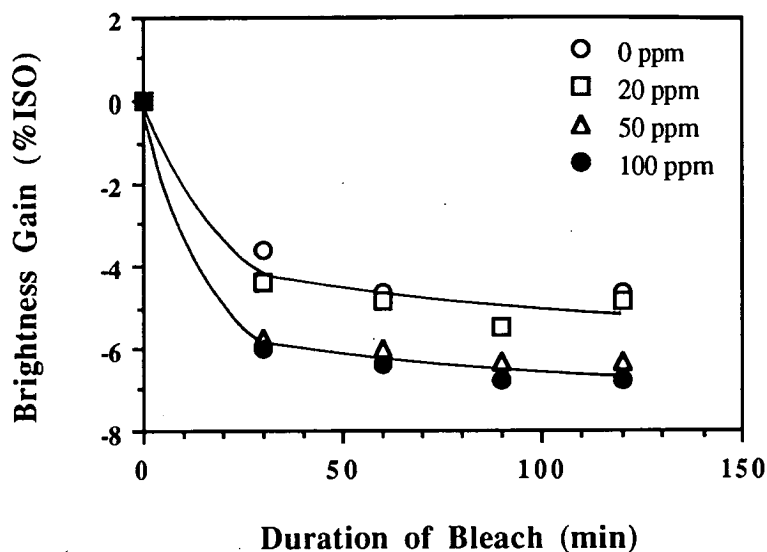


**Figure 3.26** The effect of manganese concentration on the brightness development of Pulp D. Conditions as in Figure 3.14.



**Figure 3.27** The effect of manganese concentration on the peroxide consumption during bleaching of Pulp D. Conditions as in Figure 3.14.

Alkali darkening of TMP results in a brightness loss of 5-7 %ISO as shown in Figure 3.28. The addition of manganese in the presence of alkali alone increases the amount of darkening. Similar results have been reported previously (43). The effect of alkali on SGW is slightly less than for TMP with brightness losses of 3-5 %ISO.



**Figure 3.28** Alkali darkening of TMP in the presence manganese at pH 11.0, 4% consistency, 50°C.

### 3.4 Conclusions

The effects of chelating agents, DTPA and EDTA, on the peroxide bleaching of *E.regnans* SGW are unusual. A lower brightness response is achieved when chelated pulps are bleached with hydrogen peroxide. Generally the effect of chelation is to reduce the peroxide consumed in side reactions, thus leaving a higher level of bleaching chemical available for reaction with the pulp and so achieving an increased brightness.

The reasons for this are unclear but various methods can be employed to overcome some of the decreased brightness response. The addition of manganese, which is known to catalytically decompose hydrogen peroxide, can improve the brightness response of the chelated pulp to levels approaching that for an untreated pulp, but this is offset by an associated increase in peroxide consumption. The use of a two-stage acid/alkali peroxide bleaching process has also been shown to reduce the adverse

effects of chelation. This has previously been discussed (Chapter 2) in terms of a dual mechanism of peroxide bleaching involving radical species as well as the perhydroxyl anion.

While the effect of DTPA in this case is unusual the role of transition metal ions, particularly manganese, is also worthy of consideration. It has been previously shown that the addition of transition metal ions can be beneficial during two-stage acid/alkali peroxide bleaching sequences (Chapter 2), while these results indicate that under alkaline conditions some benefit in terms of brightness response can also be achieved, even if this is at the expense of peroxide consumption.

The effect of DTPA and EDTA under these conditions is unusual and can not be explained using the traditional approach to peroxide bleaching of stabilising peroxide by the removal of transition metal ions. There appears to be some interaction between the chelating agent, the pulp and possibly transition metal ions that results in a reduced bleaching response of the pulp. Further work (Chapter 4) will show that this result does not appear to be related to radical concentration and that the effect of DTPA is anomolous compared to other peroxide stabilisers and decomposition catalysts. The effect of manganese addition to this system also appears not to be related simply to the presence of radical species as will be shown later (Chapter 4).

The effect of the products of transition metal ion catalysed decomposition of hydrogen peroxide has been investigated and shown to be minimal. Regardless of the pulp type or wood species it appears that brightness gains can be achieved in the presence of added transition metal ions. The major factors affecting the the final brightness of the pulp are the peroxide charge, especially in relation to the charge applied in the pre-treatment stage, and the transition metal ion concentration.

Provided that the peroxide charge in the presence of added transition metal ions is at

least equal to that applied in the pre-treatment stage, bleaching will occur. This is in accordance with the previously mentioned equilibrium kinetic model of peroxide bleaching that suggests that pulp brightness is determined by an equilibrium between chromophores and colourless leucochromophores. Lower brightness gains are achieved at higher levels of transition metal ion addition and this is related to the increased peroxide decomposition associated with the high levels of peroxide decomposition catalyst present, thus leaving less peroxide available for bleaching.

Therefore, in a situation where the peroxide charge is of a sufficiently high level, bleaching will occur until such time as the peroxide is totally consumed when the influence of alkali will result in a darkening of the pulp. This is found to be the case for both *E.regnans* SGW (Pulps A,B and C) and *P.radiata* TMP (Pulp D).

While the presence of transition metal ions has an effect on the rate of alkali darkening, with some metals increasing and some reducing the effect of alkali, there appears to be no evidence from this work for the products of hydrogen peroxide decomposition adversely or beneficially altering the brightness of mechanical pulps under alkaline conditions.

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## CHAPTER 4

# THE ROLE OF HYDROXYL RADICALS IN PEROXIDE BLEACHING SYSTEMS

## CHAPTER FOUR

### The Role of the Hydroxyl Radical in Peroxide Bleaching Systems

#### 4.1 Literature Review

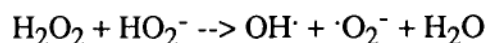
The role of radical species, and particularly the hydroxyl radical has been the topic of much debate recently (1-6). Traditionally the perhydroxyl anion,  $\text{HO}_2^-$ , has been considered the active bleaching species in alkaline peroxide bleaching of mechanical pulps (1,7), but recent work (1-6) suggests that hydroxyl radicals can play a major role in bleaching with oxygen containing species. However, it is not clear whether radical species have a positive or negative effect.

Hydroxyl radicals have also been linked with the phenomena of photoyellowing of pulp (8), alkali darkening of pulps in the presence of transition metal ions and hydrogen peroxide (9) and carbohydrate degradation (4). Model compound studies have shown that the hydroxyl radical can react with certain types of lignin groupings (10-14). In many of these cases the radicals are produced by photolysis of hydrogen peroxide solutions (15) or the use of Fenton's reagent (15). Various methods have been employed for the detection of radicals, especially the hydroxyl radical, including ESR (16), chemiluminescence (17) and UV-Vis spectroscopy techniques (18-20).

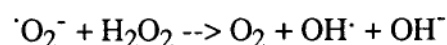
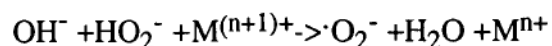
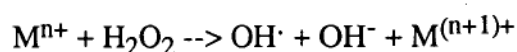
These examples indicate that the role hydroxyl radicals play in peroxide bleaching systems is not well understood. This chapter will attempt to clarify the role of radicals and also to correlate the concentrations of radicals produced with the observed bleaching response of pulps.

During peroxide bleaching the two major radical species produced are the hydroxyl radical and the superoxide anion radical,  $\text{OH}^\cdot$  and  $\cdot\text{O}_2^-$ . Of these, the hydroxyl radical is thought to be the species most likely to have any effect during bleaching (4).

The generation of hydroxyl and superoxide anion radicals can occur in two major ways (7,15). Firstly, the base induced cleavage of hydrogen peroxide (7,15,21);



or by transition metal ion catalysed decomposition of hydrogen peroxide (3,7,21);



Work using potassium superoxide (22-24) has shown no noticeable change in either lignin model compounds or kraft lignin. The conclusions are that the active radical species is the hydroxyl radical. The superoxide anion radical has, however, been shown to depolymerise cellulose (24). While this work is related to chemical pulp delignification it gives some indication that hydroxyl radicals are more reactive than other radical species present. This situation may be similar for mechanical pulps.

The use of Fenton's Reagent (hydrogen peroxide and ferrous ions) has been used as a source of hydroxyl radicals in many studies (25). It has been shown that hydroxyl radicals react to degrade carbohydrates (25). As the hydroxyl radical is a very reactive species, being the most powerful one electron oxidant in aqueous solution (3,10) with a standard reduction potential of 2.72V in acidic media and 2.32V in neutral media, the lifetime of the species is very short. This means that a radical will react with any substance near the site of generation. If transition metal ion catalysed decomposition of hydrogen peroxide is the main source of hydroxyl radicals, then the location of these

metal ions may be of particular importance. Some previous work (Chapter 3.2.2) has shown that, under the conditions employed, manganese binds to the lignin and hemicellulose portions of the pulp and only very small amounts are bound to the cellulose. This implies that, in the case of manganese at least, the radical species would be expected to only attack the lignin and hemicellulose portions of the pulp and not cause degradation of the cellulose.

Hydroxyl radicals react in the following ways:

1. Electrophilic addition to double bonds or to aromatic nuclei (3). Both of these reactions reduce conjugation and hence reduce the colour of the residual lignin.
2. Hydrogen atom abstraction from a saturated carbon atom (3).

Of these, the first reaction mode is 1-2 orders of magnitude faster than the second. At increased pH values the oxyl anion radical,  $\cdot\text{O}^-$ , the anionic form of the hydroxyl radical is formed [3], but this only has a standard reduction potential of 1.4V and reacts more slowly than the hydroxyl radical in reactions involving addition to aromatic nuclei.

Some transition metal ions are known to catalytically decompose hydrogen peroxide via a radical mechanism (3-5,7,15,26-27) producing hydroxyl radicals. The location of the decomposition process, whether in solution or on the fibre surface, may have an influence on the effectiveness of the radicals produced. If the site of radical generation is in close proximity to a chromophore or a potential chromophore, then reactions influencing the resulting brightness of the pulp are more likely. By similar reasoning it has been postulated (28) that at higher pulp consistencies, radical species play a more significant role as their site of generation is more likely to be adjacent to a fibre.

Other recent interest in the hydroxyl radical has arisen in other areas of chemistry and biochemistry. For example the interaction of hydroxyl radicals with Deoxyribonucleic acid (DNA) (29) is of great interest. Modelling of atmospheric chemistry (30) usually includes hydroxyl radicals as an important part of these systems. The self-purification of natural waters is also related to the presence of hydroxyl radicals (31-33).

#### **4.1.1 The Role of Radical Species in Peroxide Bleaching**

Hydrogen peroxide has been used as a bleaching reagent in the pulp and paper industry for over 40 years, mainly to achieve higher brightness for mechanical pulps.

Approximately 90% of the hydrogen peroxide currently supplied in Canada is used for this purpose and is becoming the dominant chemical for mechanical pulp bleaching (34). It has traditionally been thought that the active species present under alkaline bleaching conditions is the perhydroxyl anion,  $\text{HO}_2^-$  (7,35-38). Oxidative reactions involving nucleophilic attack of this species on specific chromophore types such as  $\alpha$ - $\beta$  unsaturated aldehydes,  $\alpha$ -carbonyls and *o*-quinones have been described as the major route for elimination of chromophores (1,14,39-45). Over the past decade there has been a growing awareness that other species, particularly the hydroxyl radical ( $\text{OH}^\cdot$ ) may also play an important role during peroxide bleaching processes (1,2,10,13,15,44). There are, however, contradictory reports in the literature concerning whether this radical species leads to beneficial or detrimental effects during chromophore elimination (1,2,9,10,13,15,44). It has been suggested that hydroxyl radicals contribute to alkali darkening (9), carbohydrate degradation (4), bleaching (1,3,4) and peroxide decomposition.

The superoxide anion radical, also present in alkaline hydrogen peroxide solutions, is considered to be less likely to cause significant changes in optical and physical properties. Superoxide is capable of reacting with cellulose and decreasing the degree of polymerisation to approximately that achieved with acid hydrolysis (24). It appears that the radical weakens the fibre and subsequent mechanical processing can break the

fibre, thus reducing fibre length and the strength of the pulp. Superoxide radicals do not react with lignin models vanillin, acetovanillin, guaiacol,  $\alpha$ -methyl vanillyl alcohol and catechol even after extended times (22). The radical also causes no significant changes to kraft lignin (22). This may indicate that hydroxyl radicals rather than superoxide anion radicals could also be more important in the bleaching of mechanical pulps.

The superoxide anion radical only shows a small degree of radical character as the unpaired electron appears to be in a molecular orbital between the oxygen atoms, and thus the representation ' $O_2^-$ ', over emphasises the radical character of this species. The  $pK_a$  is 4.69 (23) so will be unprotonated in typical bleaching conditions, forming the perhydroxyl radical under acidic conditions.

The hydroxyl radical has a significantly higher standard reduction potential under acidic and neutral conditions as mentioned previously (chapter 4.1), and is typically thought to be the species most likely to react with lignin and cellulose. The modes of reaction of the hydroxyl radical have been mentioned previously (chapter 4.1)

Phenolic units in lignin, represented by  $\alpha$ -methyl syringylalcohol (13), have been studied, and the major reacting species has been shown to be the hydroxyl radical. This reaction is accelerated by the presence of transition metal ions, again indicating the role that these radicals have in some aspects of peroxide bleaching. However, the reaction of conjugated carbonyl structures ( $\alpha$ - $\beta$  unsaturated aldehydes) (14), a major source of colour in mechanical pulps, has been shown to have a first-order dependence on the perhydroxyl anion, which is usually considered to be the active bleaching species. This work does, however, still suggest that the presence of transition metal ions accelerates the reaction.

Model lignin compounds with biphenyl linkages (5-5'-dehydrodivanillic acid), when

treated with hydrogen peroxide under UV irradiation, show breakage of this type of linkage (15). This same study found that  $\beta$ -O-4 linkages were also broken by direct addition of the hydroxyl radical (15). Under conditions of UV irradiation of hydrogen peroxide, hydroxyl radicals can react with simple non-phenolic lignin models. The two main reactions are  $C_{\alpha}$ - $C_{\beta}$  cleavage and the cleavage of the aryl-alkyl ether bond, forming phenoxyl radicals (10). Creosol and methylated creosols have also been studied (12) reacting with the hydroxyl radical to form a variety of products. Phenolic structures produce mainly coupling products whereas non-phenolic structures give rise to phenolic structures via demethylation and hydroxylation (12), which then can undergo the reactions typical of phenolic model compounds.

Therefore, it is clear that the hydroxyl radical is capable of reacting with lignin and the chromophoric material present to have an influence on the optical properties of mechanical pulps during peroxide bleaching.

#### **4.1.2 The Effect of Consistency**

Peroxide bleaching, as outlined in chapter 1.4.1, is generally performed at high stock consistencies as this is thought to lead to more efficient brightening of mechanical pulps (46). This increased brightness response appears to be related to the increased concentration of peroxide as the pulp to peroxide ratio is generally kept constant but the peroxide to water ratio increases. Experiments to determine the effect of consistency, therefore, need to be carried out under conditions of equal peroxide concentration. To eliminate the different pH and peroxide consumption profiles observed with different consistencies it is necessary to work under conditions where the concentration of peroxide and the pH are maintained at fixed levels throughout the bleaching experiment. Such conditions are described in chapter 5.1.2.2, and are typically used in the kinetic analysis of peroxide bleaching (28,47,48).

It has been postulated (28) from a kinetic analysis of peroxide bleaching, that as the



consistency is increased the rate of peroxide bleaching increases also. This study reports only the rate constants, and from this infers that at consistencies between 0.25 and 4.0%, increasing consistency causes an increase in bleaching rate. The rate appears to double over this consistency range. This increased brightness response is discussed in terms of movement of particularly reactive species between pulp fibres. At higher consistencies there is a greater possibility of these species being generated adjacent to a fibre, and able to transfer between fibres. Therefore, if these species have a positive effect on brightness, an increased bleaching response should be observed. In peroxide bleaching systems radical species are present and could behave in this manner.

Unfortunately, it is not possible to extend the range of consistencies studied using this method to those used industrially due to problems related to mixing, sampling and maintaining the peroxide and alkali charges.

#### **4.1.3 Radical Detection Methods**

A number of methods have been developed to measure the levels of hydroxyl radical present in aqueous systems. These include using phthalic hydrazide as a trap and detection via chemilluminescence of the species formed (17), UV determination of radicals formed by the interaction of hydroxyl radicals with thiocyanate (20) or bicarbonate ions (19) and ESR techniques. A simple spectrophotometric method based on the oxidation of *N,N*-dimethyl-4-nitrosoaniline (DMNA) has been demonstrated to be specific for hydroxyl radicals in alkaline media (18,49). The method has been applied to studies of the influence of metal ions in neutral and mild alkaline solutions of hydrogen peroxide (32,33,50-52). In this study pH conditions at levels encountered under industrial bleaching conditions have been used (pH 11), and a kinetic analysis developed to show the influence of both transition metal additives and also several stabilising reagents commonly encountered in commercial bleaching processes.

The use of DMNA for the detection of hydroxyl radicals has been used for many years (18), but has rarely been used in conjunction with peroxide bleaching, although some work has been reported (53) in which the production of radicals in peroxide bleaching liquors in the absence of pulp has been investigated. Hydroxyl radicals react quantitatively with DMNA, and this reaction reduces the observed absorption of DMNA. This decrease in absorption allows calculation of the amount of DMNA reacted.

#### **4.1.4 Problems of Detection**

While there are many proposed methods for the detection of hydroxyl radicals there are many factors to be considered in order to choose the most appropriate for the particular application. For this reason direct methods, such as ESR (53) are most suitable as no interference is encountered, but the issue of availability, limits of detection and cost need to be considered. Indirect methods can also be employed but caution must be exercised to minimise interferences.

In the case of peroxide bleach liquors the reagent chosen for the detection of hydroxyl radicals should not alter the peroxide decomposition or react with peroxide and ideally should not interrupt the radical chain processes. The first consideration is relatively simple to check and many reagents are available that met this requirement. The second issue is more complex. If a trapping reagent competes successfully for a high proportion of the radicals available then the chain processes will not proceed as they do in the absence of the reagent. This means that the presence of the radical trap alters the course of the reaction, and the results obtained do not necessarily accurately reflect the situation in the absence of the radical trap. Therefore, a reagent that traps a small percentage of the radicals will only have a slight influence on the course of the reaction and will give results that more accurately reflect the radical concentration. If the reagent does not interfere with the physical or optical properties of the pulp it can be used during bleaching experiments. If this is not possible then experiments must be

undertaken to ensure that a valid correlation exists between the bleaching response in the absence of the radical trap and the solution studies.

## **4.2 The Effect of Consistency**

In order to determine the effect of consistency conditions of constant concentration of peroxide and alkali are required. The brightness-time response of pulp at various consistencies can then be directly compared. If increasing consistencies give rise to enhanced bleaching rate then higher brightness would be expected to be observed. This increase in brightness can not be related to the concentration of the perhydroxyl anion. The concentration of metal ions would also increase with consistency and may have an effect on the concentration of peroxide decomposition products. Any effect of consistency, therefore, would appear to be related to the presence of metal ions or radical species.

### **4.2.1 Constant Conditions Bleaching**

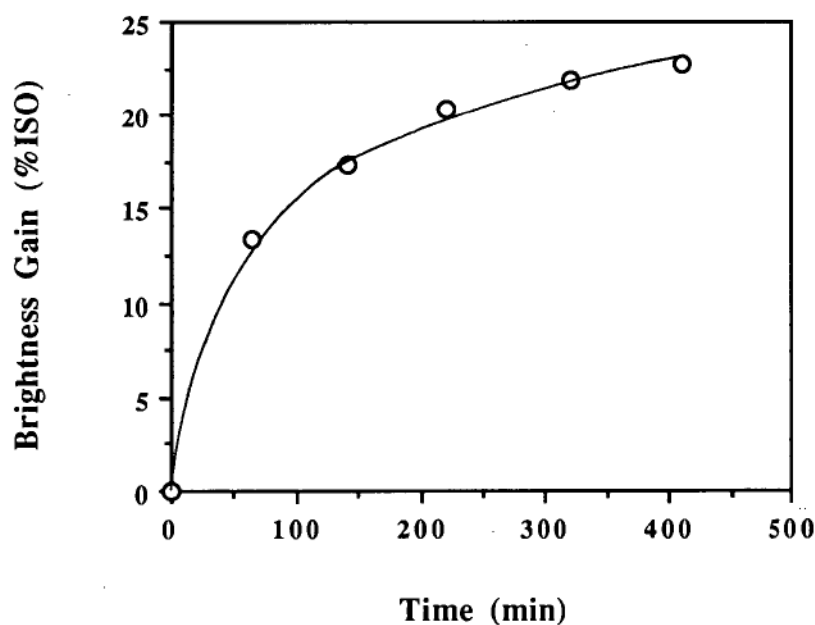
Bleaching of pulps under conditions of constant concentrations of peroxide and constant pH gives more easily interpretable information regarding the effect of consistency compared to bleaching under conditions of reducing peroxide and alkali concentration. This is because peroxide and pH profiles vary with consistency and the addition of various peroxide decomposition catalysts and stabilisers, thus meaning that results can not easily be compared. Studies related to the kinetics of peroxide bleaching are often performed under similar conditions (28,47,48). Figure 1.3 (Chapter 1) shows a typical brightening response under these conditions.

Interestingly the response shows many similarities to a pulp bleached under conventional conditions, a rapid initial stage followed by a much slower stage of bleaching (48), apparently reaching a brightness limit after long reaction times. In the case of reducing reagent concentration this can be explained in terms of loss of bleaching reagent, however, this is not the case for constant conditions bleaching,

indicating that the apparent limiting brightness reached after extended times is related to the concentration of peroxide and alkali (54,55)

#### 4.2.2 Varying Pulp Consistency

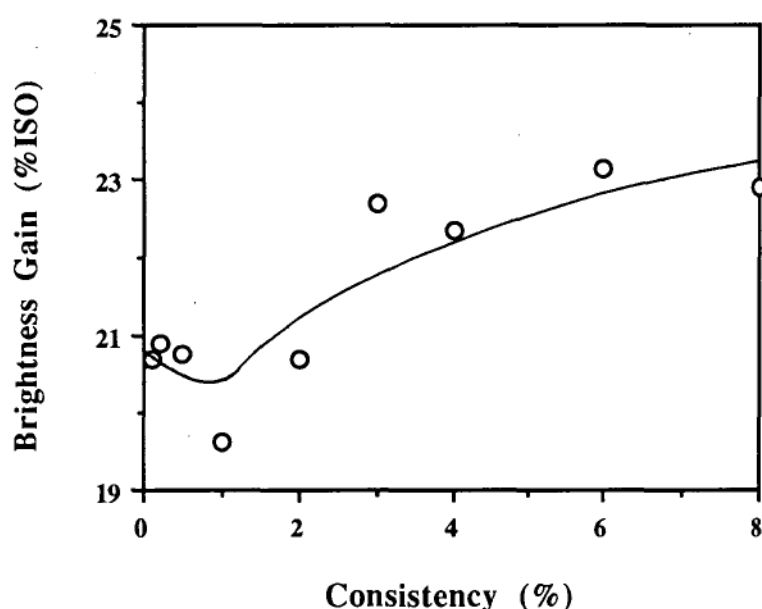
The effect of consistency can be determined by working under conditions of constant concentrations of peroxide and alkali, as described above, and varying only the consistency of the pulp. Using such conditions the pulp consistency was varied from 0.1% to 8% and the brightness time response monitored. As can be seen from figure 4.1 the increase in brightness after approximately six hours is slow, so comparisons were made at extended times of bleaching. Figure 4.2 shows the effect of varying the consistency on final pulp brightness while keeping all other conditions constant.



**Figure 4.1** Bleaching response of SGW. Conditions: 1.2g/L peroxide, pH 11.0, 50°C, 3% consistency, peroxide and alkali maintained at initial levels.

Although there is no clear trend observable it can be seen that at higher consistencies (3-8%) a brightness increase of approximately 1-2 %ISO higher is obtained indicating that the increasing consistency does improve the bleaching response of the pulp. This may be related to the presence of radicals that are produced by peroxide

decomposition. As the consistency is increased these are more likely to be generated close to a fibre and so be more likely to effect the colour of the pulp. This is in agreement with previous work (28) which related an empirical rate constant to the pulp consistency. This showed an increase in the rate of bleaching with increasing consistency.



**Figure 4.2** The effect of consistency of the final brightness of Eucalypt SGW. Conditions as in Figure 4.1. Points are the average of duplicates, maximum deviation was 0.3%ISO.

#### 4.2.3 Inert Fibre Addition

The addition of an inert fibre, that does not consume considerable amounts of peroxide or change brightness when bleached with alkaline hydrogen peroxide can also allow a study of the effect of consistency on bleaching response. If the total consistency is kept constant while the proportions of the inert and bleachable fibre are changed, this effectively alters the consistency of the bleachable fibre.

It was found that *P. Radiata* bleached kraft pulp, after being bleached for 6 hours with alkaline peroxide, consumed very little peroxide when again exposed to peroxide and,

as expected, showed very little change in brightness. The brightness of the kraft pulp after the initial peroxide treatment was 85%ISO. Bleached kraft pulp that has been previously exposed to peroxide, therefore, was considered suitable as an inert fibre. Kraft:SGW pulp ratios of 7:1, 3:1, 1:1, 1:3 and 0:1 were used giving effective consistencies of SGW of 0.5, 1.0, 2.0, 3.0 and 4.0%.

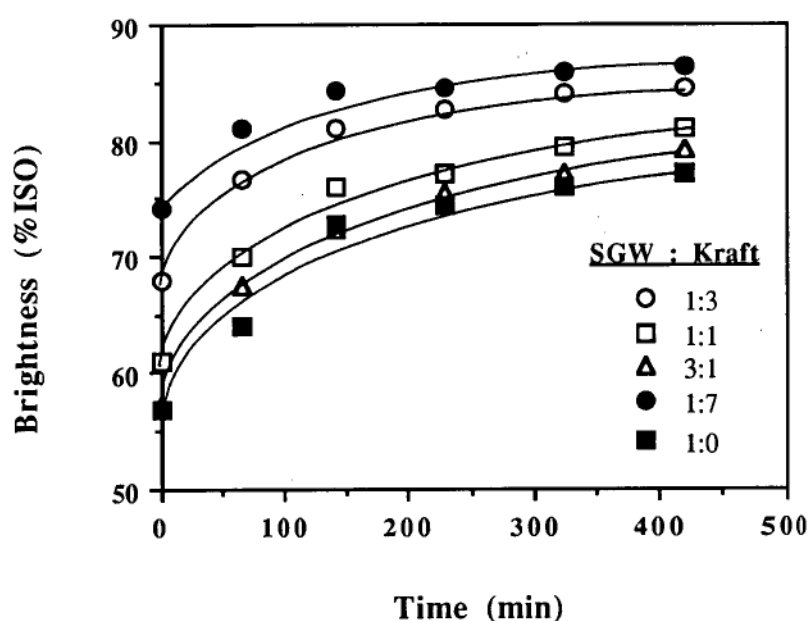
Two series of experiments were performed, both under constant concentrations of peroxide and alkali. Firstly, kraft and SGW were bleached together in the above ratios and the brightnesses of samples withdrawn at suitable intervals were measured. Secondly, samples of kraft and SGW were bleached separately at 4% consistency and handsheets were then prepared in the above ratios to give a comparative set of data. Figure 5.1 shows a diagrammatic representation of the experiment. The comparison of the two sets of results should show the effect of the addition of inert fibres, and give some information about the effect of consistency in peroxide bleaching.

If bleaching at a higher consistency is beneficial, possibly due to the effect of radical species, then we would expect to observe greater brightness in the samples bleached separately (as the bleachable fibre was effectively bleached at a higher consistency (4%)) than those bleached together, as the inert fibre reduces the consistency of the bleachable fibre.

Figure 4.3 shows the bleaching response of various ratios of SGW and bleached kraft pulp together. This graph shows that for the various kraft:SGW ratios the bleaching response is typical of peroxide bleaching with a rapid initial stage followed by a slower phase. Also, as expected, the higher kraft:SGW ratios correspond to higher initial brightness and lower brightness gain with there being a smaller percentage of bleachable fibre present.

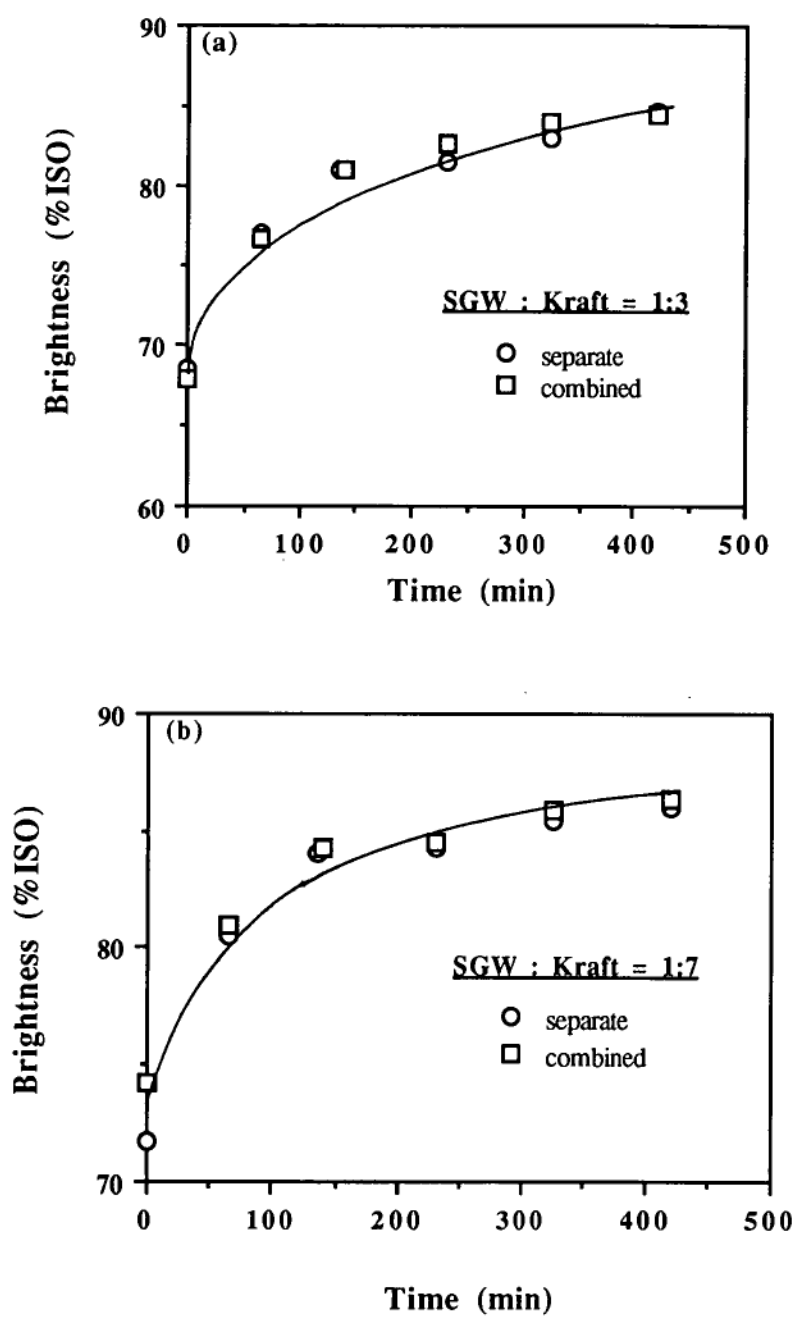
Figure 4.4 shows a comparison of the brightness of sheets formed from a fixed ratio

of kraft:SGW, but bleached by the two methods, either separately or combined. These figures show that there is no significant difference in brightness response associated with the method of bleaching. This shows that the SGW bleaching response does not appear to alter over the range of consistencies covered (0.5% - 4.0%) when the total consistency is maintained at 4% by inert fibre addition.



**Figure 4.3** Bleaching response of mixtures of SGW and kraft pulp bleached together in the given ratios to make appropriate handsheets. Conditions: 50°C, pH 11.0, 4% consistency, 3% Peroxide on o.d. pulp, constant conditions of alkali and peroxide.

From these experiments it can be concluded that the effect of varying the consistency for bleaching of SGW is small (approximately 10% of the brightness change) and there is no observable effect in the case of kraft:SGW bleaching. In the case of mixed kraft:SGW bleaching the total pulp consistency is always 4%, so, although the consistency of the bleachable fibre is altered, the transfer of radical species between fibres may not be altered significantly. Therefore meaning that the component of bleaching due to radical reactions and transfer of reactive species is always equivalent to that of 4% consistency.



**Figure 4.4** Comparison of separate and combined bleaching of SGW:kraft in a ratio of (a)1:3 and (b) 1:7. Conditions: 1.2g/L peroxide, pH 11.0, maintained throughout the experiment.



### 4.3 The Interaction of DMNA with the Hydroxyl Radical

The simplest method of hydroxyl radical trapping was found to be the use of *N,N*-dimethyl-4-nitrosoaniline (DMNA). Being highly coloured ( $\epsilon_{440} = 34200$ ) allows detection of very small quantities of hydroxyl radicals, but also has the disadvantage that it may not be used directly during bleaching experiments.

While the use of DMNA as a specific hydroxyl radical trap is well established (18,49), and it has previously been used in conjunction with hydrogen peroxide solutions (32,33,50-52), no kinetic analysis of this interaction has been performed and no studies in conjunction with peroxide bleaching have been reported.

#### 4.3.1 Previous DMNA Studies

The bleaching or oxidation of DMNA by the hydroxyl radical has been studied previously (18,49). Most of these studies have utilised either photolysis (49) or radiolysis (18,49) to generate hydroxyl radicals in aqueous solutions of DMNA. It has been concluded from these studies that the method is specific to the hydroxyl radical and that the photolysis and radiolysis induced reactions appear to be the same. The rate of the reaction is very fast, and is nearly diffusion controlled (18).

One of the limitations of this system is that some of the products of the reaction between DMNA and the hydroxyl radical have significant absorbances close to 440 nm, the absorption maxima for DMNA. As DMNA is oxidised the the maximum absorption moves to lower wavelengths. To overcome this problem decomposition of DMNA is kept to approximately 30% of the initial charge.

Most of the work performed with hydrogen peroxide solutions has been principally investigating the role of hydroxyl radicals in the self-purification of natural waters (31,32). These studies have concluded that manganese - bicarbonate catalysed decomposition of hydrogen peroxide produces a significant quantity of hydroxyl

radicals and so the mechanism of decomposition appears to be a radical chain mechanism (51), as does the osmium tetroxide catalysed decomposition of hydrogen peroxide (50).

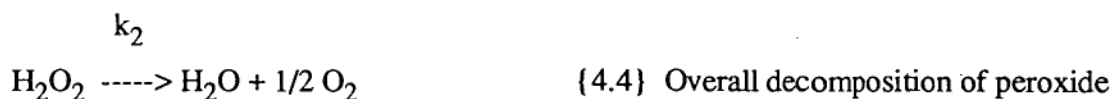
In a study of hydrogen peroxide stability at low levels of transition metal ion impurities, the spontaneous decomposition of hydrogen peroxide was found to consist of two distinct parts (31). One part depends on the formation of micro-colloidal iron complexes (31,32) and the other on the level of such transition metal ions such as copper, manganese, nickel, chromium and cobalt (31,32). Another study (32) reports that micro-colloidal iron does not cause an increase in radical production, suggesting that this decomposition does not proceed via a radical chain mechanism, but the addition of copper does increase both the decomposition of peroxide and the concentration of hydroxyl radicals. Similar studies also support the radical mechanism for copper catalysed decomposition of hydrogen peroxide (31-33) but suggest that manganese does not produce significant quantities of radical species, similar to iron.

In a study of hydrogen peroxide stability related to the use of peroxide as a bleaching reagent for mechanical pulps, Colodette (53) performed studies with DMNA. He concluded that copper does appear to decompose peroxide via a radical mechanism, while manganese and iron do not.

#### 4.3.2 Kinetic Models

Simplified kinetic expressions for oxidation of DMNA can be developed as follows:





- Where:
- M is a metal species.
  - X are species (other than DMNA) which can trap hydroxyl radicals.
  - DMNA is *N,N*-dimethyl-4-nitrosoaniline.
  - P<sub>1</sub> and P<sub>2</sub> are oxidation products.

The rate of removal of DMNA (32) is given by:

$$\frac{-d[\text{DMNA}]}{dt} = k_3[\text{DMNA}][\text{OH}'] \quad \{4.5\}$$

The steady state concentration of hydroxyl radicals is given by:

$$\frac{-d[\text{OH}']}{dt} = k_3[\text{DMNA}][\text{OH}'] - k_1[\text{H}_2\text{O}_2][\text{M}] + k_{-1}[\text{OH}'][\text{X}] = 0 \quad \{4.6\}$$

Two limiting cases can be considered:

Case 1:

Reaction with DMNA is the dominant reaction leading to the removal of radicals:

$$\text{i.e. } k_3[\text{DMNA}][\text{OH}'] \gg k_{-1}[\text{OH}'][\text{X}]$$

so that:

$$[\text{OH}'] = \frac{k_1[\text{H}_2\text{O}_2][\text{M}]}{k_3[\text{DMNA}]} \quad \{4.7\}$$

$$\text{and: } \frac{-d[\text{DMNA}]}{dt} = k_1[\text{M}][\text{H}_2\text{O}_2] \quad \{4.8\}$$

### Case 2:

Reaction with other species (X) is the dominant termination reaction for hydroxyl radicals. In our system X could be metal species (2), hydrogen peroxide (32) or another radical species (13).

Under this condition  $k_{-1}[\text{OH}^\cdot][\text{X}] \gg k_3[\text{DMNA}][\text{OH}^\cdot]$   
leading to

$$[\text{OH}^\cdot] = \frac{k_1[\text{H}_2\text{O}_2][\text{M}]}{k_{-1}[\text{X}]} \quad \{4.9\}$$

$$\text{and : } \frac{-d[\text{DMNA}]}{dt} = \frac{k_1 k_3 [\text{DMNA}][\text{H}_2\text{O}_2][\text{M}]}{k_{-1}[\text{X}]} \quad \{4.10\}$$

The derived kinetic expressions {4.8} and {4.10} indicate first-order dependence on concentrations of metal ion species and peroxide concentrations. It is well known that the nature of the metal ion species present in aqueous systems is strongly dependent on the pH of the medium (57). For studies carried out at constant pH, [M] could be regarded as constant throughout a particular experiment.

Assuming no peroxide decomposition, integrating equations {4.8} and {4.10} results in the following expressions:

### Case 1

$$[\text{DMNA}]_t = [\text{DMNA}]_0 - k_1[\text{M}][\text{H}_2\text{O}_2].t \quad \{4.11\}$$

Case 2:

$$\frac{\ln[\text{DMNA}]_t}{[\text{DMNA}]_0} = \frac{k_1 k_3 [\text{DMNA}][\text{M}][\text{H}_2\text{O}_2].t}{k_{-1}[\text{X}]} \quad \{4.12\}$$

Now, allowing for decomposition of hydrogen peroxide, which is typically first order:

$$\frac{-d[\text{H}_2\text{O}_2]}{dt} = k_2[\text{H}_2\text{O}_2] \quad \{4.13\}$$

on integrating we have:

$$[\text{H}_2\text{O}_2] = [\text{H}_2\text{O}_2]_0 e^{-k_2 t} \quad \{4.14\}$$

where  $[\text{H}_2\text{O}_2]_0$  denotes the initial concentration of hydrogen peroxide.

Substituting equation {4.14} into equation {4.11} and {4.12} we have:

Case 1:

$$[\text{DMNA}]_t = [\text{DMNA}]_0 - k_1[\text{M}][\text{H}_2\text{O}_2]_0 e^{-k_2 t}.t \quad \{4.15\}$$

Case 2:

$$\frac{\ln[\text{DMNA}]_t}{[\text{DMNA}]_0} = \frac{k_1 k_3 [\text{DMNA}][\text{M}][\text{H}_2\text{O}_2]_0 e^{-k_2 t}.t}{k_{-1}[\text{X}]} \quad \{4.16\}$$

Case 1 requires a zero-order dependence on  $[\text{DMNA}]$ , while a first order dependence is predicted in case 2. It should be easily established which model is preferable by observing whether the rate of removal of DMNA depends on the concentration of the amine initially introduced. Thereafter, the the validity of the proposed model can be

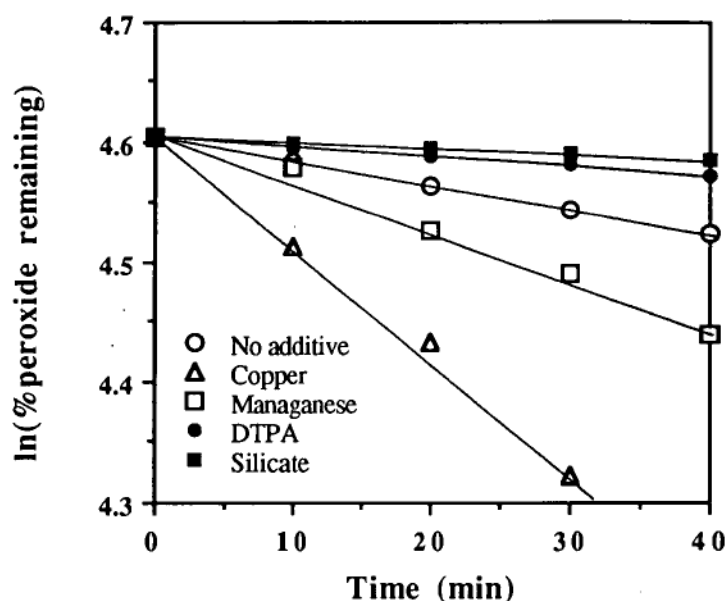
further tested by examining plots of the appropriate [DMNA] function against the time variable  $te^{-k_2t}$ .

#### 4.3.3 Model Testing

Experiments were performed to follow the rate of removal of DMNA in alkaline peroxide solutions at 50°C, under conditions of constant pH = 11.0. The concentration of DMNA was measured spectrophotometrically, while decomposition of hydrogen peroxide was measured by periodic titration of samples. The effect on kinetic phenomena of introducing transition metal ions, including iron, manganese and copper were observed, as well as the influences of adding stabilisers such as sodium silicate, magnesium nitrate and complexing agents.

The development of the kinetic models as shown in the theory section assumes that the rate of peroxide decomposition is first-order with respect to peroxide concentration. This was found to be a reasonable assumption for each of the systems investigated, with linear logarithm-time relationships as shown in Figure 4.5. Addition of transition metal ions or stabilisers to the alkaline peroxide solution changed the magnitude of the rate constant for peroxide decomposition ( $k_2$ ) as shown in Tables 4.1 and 4.2 respectively.

Experiments also showed that the rate of DMNA removal is dependent on the initial concentration of the amine, as shown in Figure 4.6. This demonstrates that the kinetic expression developed as Case 1 cannot be valid under these conditions. Analysis of kinetic phenomena was therefore based on testing the validity of equation {4.16} (Case 2).



**Figure 4.5** First-order rate plots for hydrogen peroxide decomposition in the presence of various catalysts and stabilisers. Peroxide concentration = 0.0353M, pH 11.0, 50°C, copper =  $8.02 \times 10^{-6}$ M, manganese =  $9.14 \times 10^{-6}$ M, DTPA =  $5.09 \times 10^{-5}$ M and silicate =  $4.00 \times 10^{-2}$ M

Figure 4.7 shows that, in the the absence of added transition metal ions or stabilisers, plots of  $\ln([DMNA]_t/[DMNA]_0)$  against the time function  $te^{-k_2t}$  are linear, with values of the coefficient of determination ( $R^2$ ) close to unity. This is consistent with equation {4.16}, assuming that the concentration of radical terminating species  $[X]$  can be regarded as constant for a particular system.

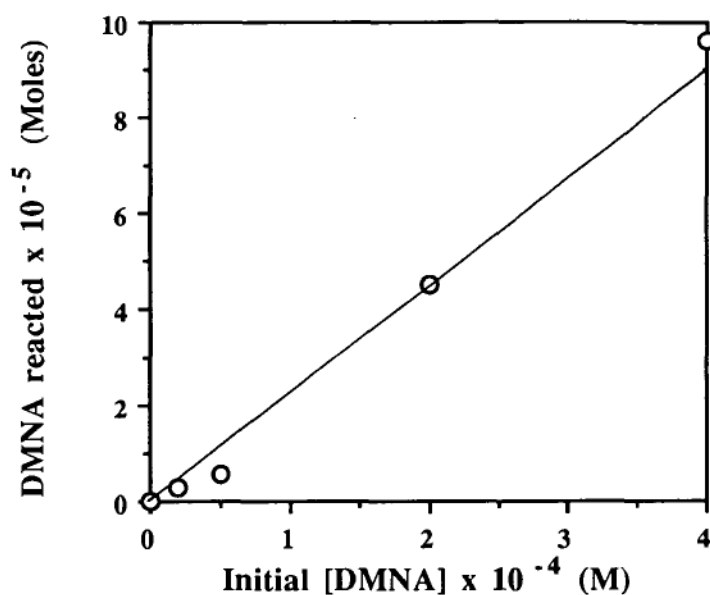
**Table 4.1** Rate constants for peroxide decomposition in the presence of added transition metal ions. Rate =  $2.00 \times 10^{-3}$  in the absence of additives.

Copper		Manganese		Iron	
[Cu] ( $\times 10^{-6}$ )	$k_2$ $\times 10^{-3}/\text{min}$	[Mn] ( $\times 10^{-6}$ )	$k_2$ $\times 10^{-3}/\text{min}$	[Fe] ( $\times 10^{-6}$ )	$k_2$ $\times 10^{-3}/\text{min}$
4.01	6.57	4.55	2.33	4.49	1.74
8.02	9.33	9.10	4.18	8.98	1.65
20.0	13.3	22.7	10.3	22.5	2.74
40.1	20.3	45.5	25.0	44.9	3.05

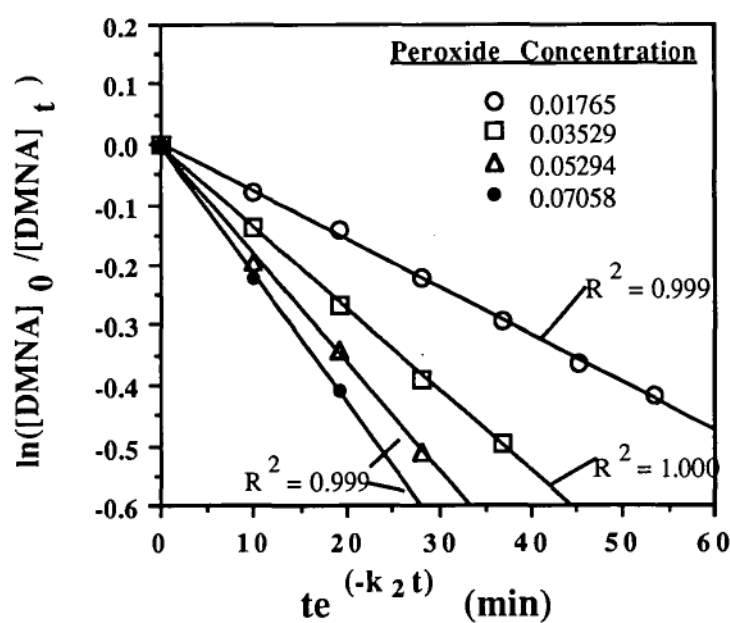
**Table 4.2** Rates constants for peroxide decomposition in the presence of added stabilisers. Rate =  $2.00 \times 10^{-3}$  in the absence of additives.

Magnesium		DTPA		Silicate	
[Mg] ( $\times 10^{-5}$ )	$k_2$ $\times 10^{-4}/\text{min}$	[DTPA] ( $\times 10^{-4}$ )	$k_2$ $\times 10^{-4}/\text{min}$	[Si] ( $\times 10^{-3}$ )	$k_2$ $\times 10^{-3}/\text{min}$
6.63	3.30	2.54	5.50	5.26	2.71
15.8	3.36	5.09	5.77	10.1	2.21
37.5	3.65	10.2	7.68	20.1	1.3
		20.4	8.32	40.0	0.45





**Figure 4.6** Relationship between the initial DMNA concentration and the quantity reacted after 20 minutes. Other conditions as in Figure 4.5



**Figure 4.7** Model fit for various levels of peroxide concentration. DMNA concentration =  $2.00 \times 10^{-5}$  M, pH 11.0, 50°C.

The slopes of the plots illustrated in Figure 4.7 can be related to the value of the rate constant for removal of DMNA defined by

$$K = \frac{k_1 k_3}{k_{-1}} \quad \{4.17\}$$

The magnitude of  $K$  gives the rate constant for the removal of DMNA in each case. This term also reflects the relative ratio of  $k_1/k_{-1}$ , and is therefore a measure of the hydroxyl radical concentration available for reaction with DMNA.

#### 4.3.4 Kinetic Phenomena under Alkaline Conditions

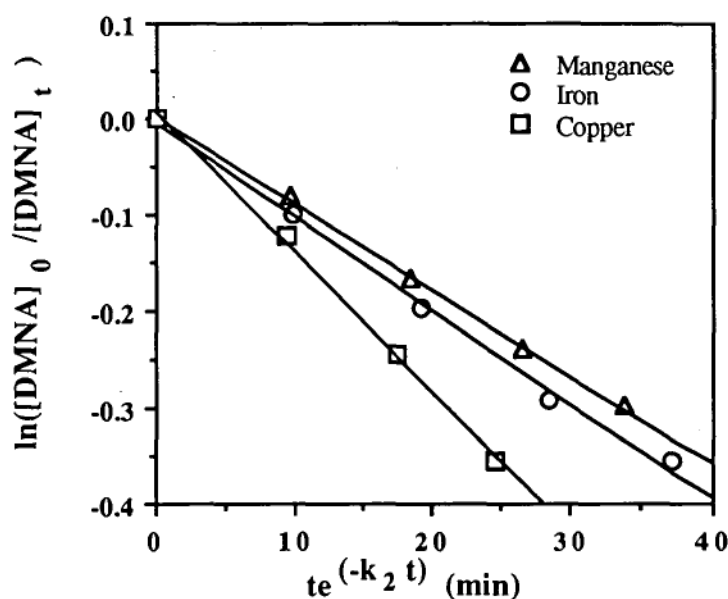
As peroxide bleaching is usually performed under alkaline conditions the effect of various peroxide decomposition catalysts and stabilisers was investigated at pH 11.0 and 50°C. The proposed model was found to be valid in the presence of all additives and the values of  $K$  and  $k_2$  are reported.

##### 4.3.4.1. The Influence of Added Transition Metal ions

The transition metals commonly reported to have most influence on hydrogen peroxide stability during industrial bleaching of mechanical pulps are manganese, iron and copper (57-60). The presence of manganese in particular is a concern under conditions normally encountered during bleaching (61). Traces of these transition metal impurities are derived either from the wood itself or are introduced during pulp processing.

The influence of addition of copper, manganese and iron on the kinetics of peroxide decomposition and DMNA oxidation was investigated at pH 11.0 and 50°C. As already described, in the presence of these catalysts first order kinetics was observed for peroxide decomposition, with calculated rate constants ( $k_2$ ) reported in Table 4.1. The validity of equation {4.16} was tested in the presence of introduced metal ions by plotting  $\ln[DMNA]_t/[DMNA]_0$  against the time function  $te^{-k_2t}$ . In all cases tested,

adequate linear relationships were obtained, as illustrated in Figure 4.8. Using the slopes of these plots, values of  $K$  were plotted as a function of metal additive concentrations as shown in Figure 4.9.

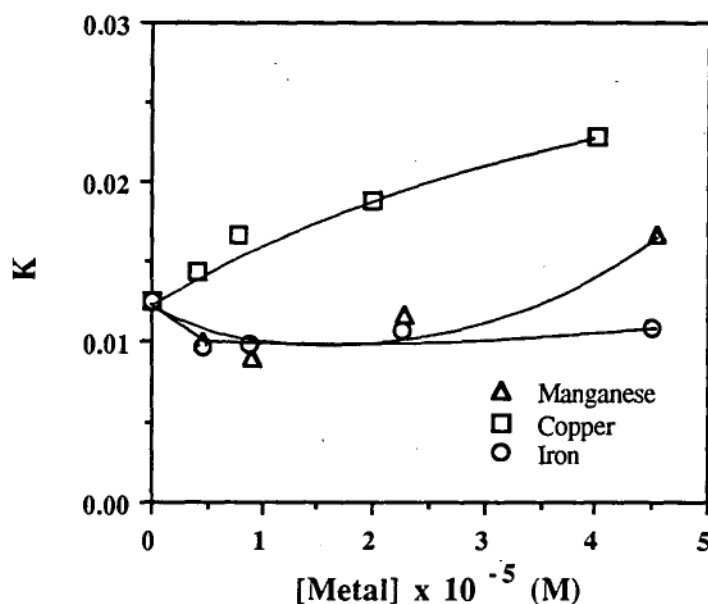


**Figure 4.8** Model fit for the addition of transition metal ion catalysts.

Conditions as in Fig. 1, DMNA concentration =  $5.00 \times 10^{-5}M$ , copper =  $4.01 \times 10^{-6}M$ , manganese =  $9.14 \times 10^{-6}M$ , iron =  $4.49 \times 10^{-6}M$

Previous studies by Ernestova and Skurlatova on the DMNA-peroxide system have been reported at  $70^\circ C$  at pH 7 (32). Their results showed that addition of iron(III) had no effect on the bleaching of DMNA (32), and concluded that micro-colloidal iron particles present do not contribute to the formation or disappearance of hydroxyl radicals. Other studies have concluded that iron does not decompose peroxide via a radical mechanism (31).

Figure 4.9 shows that the rate constant  $K$  is not significantly affected by increasing the amount of iron in the system. In fact it appears that the addition of iron causes a slight reduction in  $K$  compared to the system where no iron is introduced.

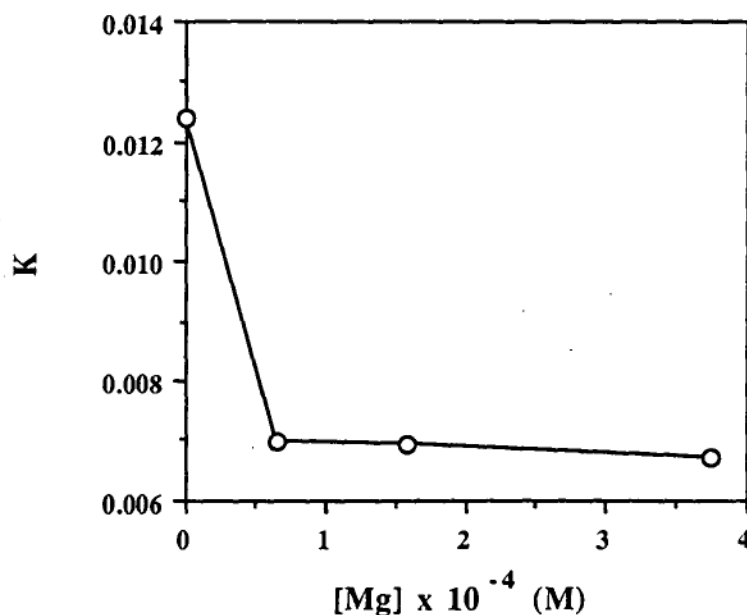


**Figure 4.9** Plots showing the variation in K for the addition of copper, iron and manganese.

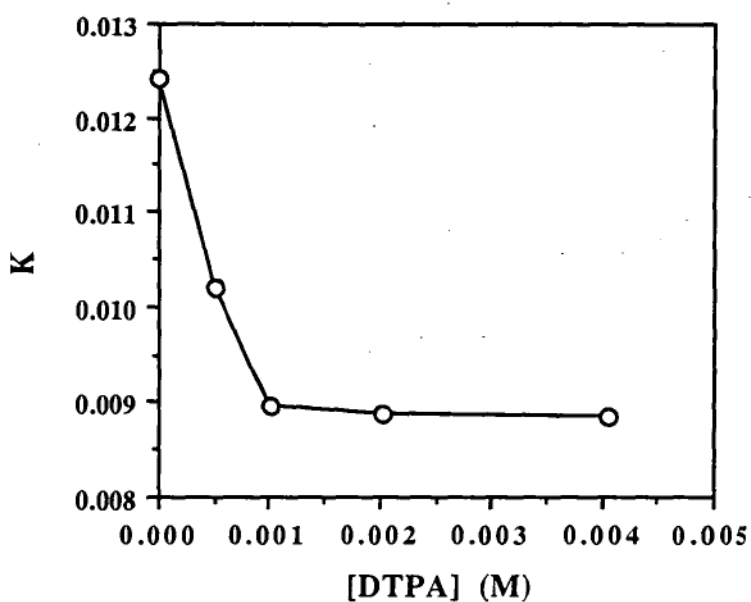
In contrast, the addition of copper to the alkaline peroxide system produces a significant increase in the values of K as illustrated in Figure 4.9. Steady state levels of hydroxyl radicals as measured by K are almost directly proportional to the levels of copper introduced. These observations are in agreement with previous studies (31-33) where addition of Cu(II) is found to produce a proportionate increase in the rate of oxidation of DMNA. These workers also reported that the effects of added Mn(II) was similar to that of iron and the addition of manganese had little influence on the formation or removal of hydroxyl radicals. Other studies have concluded that the catalytic decomposition of hydrogen peroxide in the presence of Mn(II) does proceed via a radical chain mechanism involving hydroxyl radicals (51). The results show little influence of manganese on radical concentration.

#### 4.3.4.2 The Influence of Added Stabilising Agents

Stabilising agents commonly used in the peroxide bleaching of mechanical pulps are magnesium salts (57,62,63), sodium silicate (36,57,62,63) and chelating agents such as DTPA and EDTA (35,36,57,61,63). The addition of these reagents aims to reduce the catalytic decomposition of hydrogen peroxide, and thus leave higher levels of peroxide available for pulp bleaching. Peroxide decomposition in the presence of these stabilisers follows first-order kinetics and the values of  $k_2$  are reported in Table 4.2. In all cases stabilisation of peroxide is achieved and plots of  $\ln[DMNA]_t/[DMNA]_0$  against  $t e^{-k_2 t}$  again showed adequate linear correlations. Values of  $K$  were calculated from these plots for the addition of magnesium, silicate and DTPA are shown in Figure 4.10, 4.11 and 4.12.

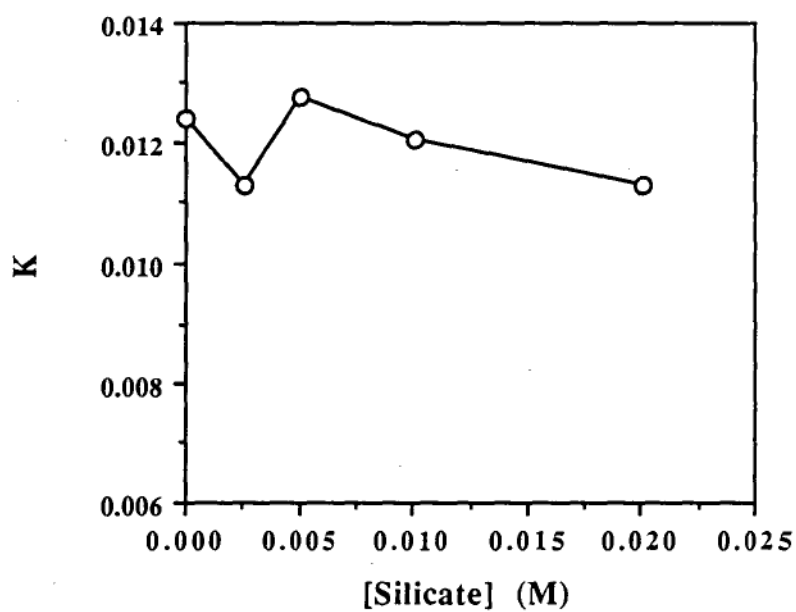


**Figure 4.10** Plots showing the variation in the rate constant  $K$  for magnesium. Conditions as in Figure 4.8.



**Figure 4.11** Plots showing the variation in the rate constant  $K$  for DTPA.

Conditions as in Figure 4.8.



**Figure 4.12** Plots showing the variation in the rate constant  $K$  for silicate.

Conditions as in Figure 4.8.

The effect of the addition of magnesium is shown in Figure 4.10. The value of  $K$  and

is decreased markedly at low levels of magnesium and further addition does not effect these values significantly. From this it would appear that the mechanism of stabilisation of alkaline peroxide solutions by magnesium involves either the interruption of free radical processes that are initiated by the residual transition metal ions present in the solution, or deactivation of the catalytically active species in some way.

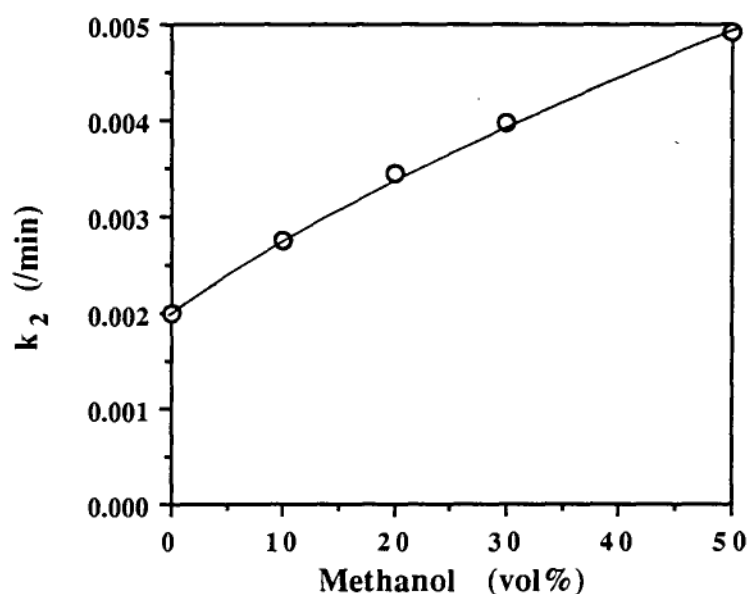
The addition of DTPA, as shown in Figure 4.11 shows a very similar trend for  $K$  as magnesium. The value is reduced to low levels compared to unstabilised peroxide solutions, and further addition of stabiliser has little or no effect. It has previously been proposed (61) that the mechanism of DTPA stabilisation of alkaline peroxide solutions is related to the ability of DTPA to bind and deactivate the residual transition metal ions in solution and thus reduce the catalytic decomposition of hydrogen peroxide. This appears to be supported by the results obtained here.

The effect of sodium silicate addition, as shown in Figure 4.12, is different from magnesium and DTPA. The value of  $K$ , which is a measure of the hydroxyl radical concentration, does not decrease on addition of silicate. This tends to indicate that the mechanism of stabilisation by silicate is different than for either magnesium or DTPA.

#### **4.3.4.3 The Influence of Added Methanol**

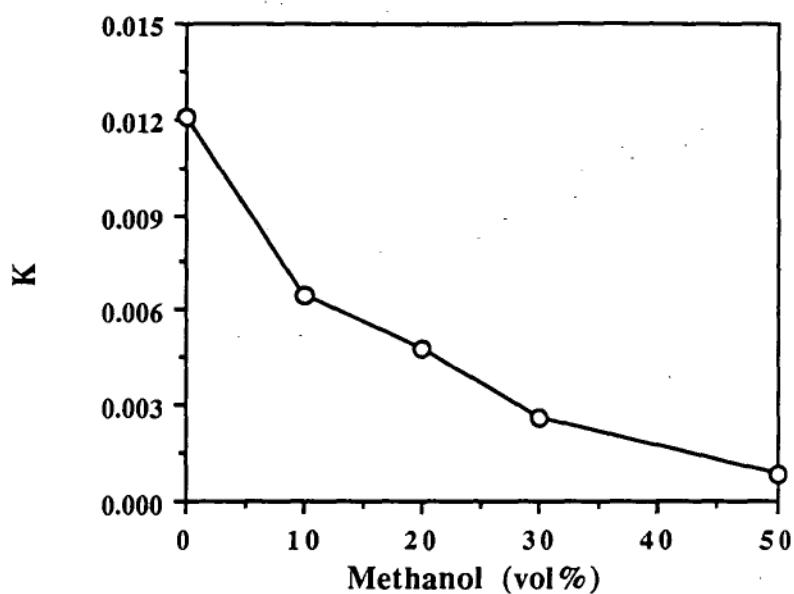
Alcohols, particularly methanol and ethanol, are known to be effective hydroxyl radical traps (33), and have been used as such in experiments similar to these. Figure 4.13 and 4.14 show the effect of varying the methanol concentration on the rate of decomposition of peroxide, the rate of decolorization of DMNA and the calculated steady state concentration of hydroxyl radicals. Figure 4.13 shows that increasing the concentration of methanol leads to an increase in the rate of decomposition of peroxide. The reason for this is not clear but could be related to the level of impurity transition metal ions in the methanol being at such a level that catalytic decomposition of peroxide

is increased. Figure 4.14 shows that increasing the proportion of methanol in solution significantly decreases the value of  $K$ , indicating that methanol successfully competes for hydroxyl radicals with DMNA. Figure 4.15 shows the effect of increasing hydrogen peroxide concentration on the values of  $K$  in 1:1 methanol:water. As expected, higher concentrations of hydrogen peroxide results in higher values of these constants.

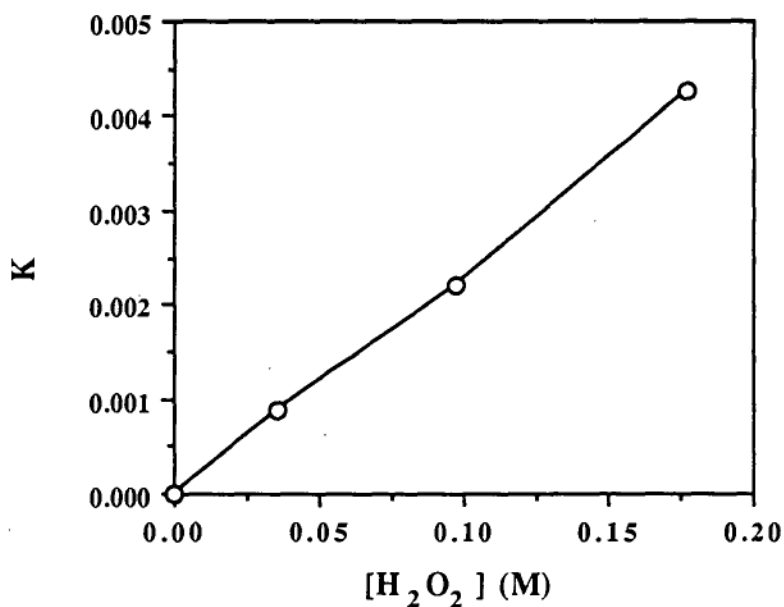


**Figure 4.13** The effect of methanol addition on peroxide decomposition rate. Conditions as in Figure 4.8.





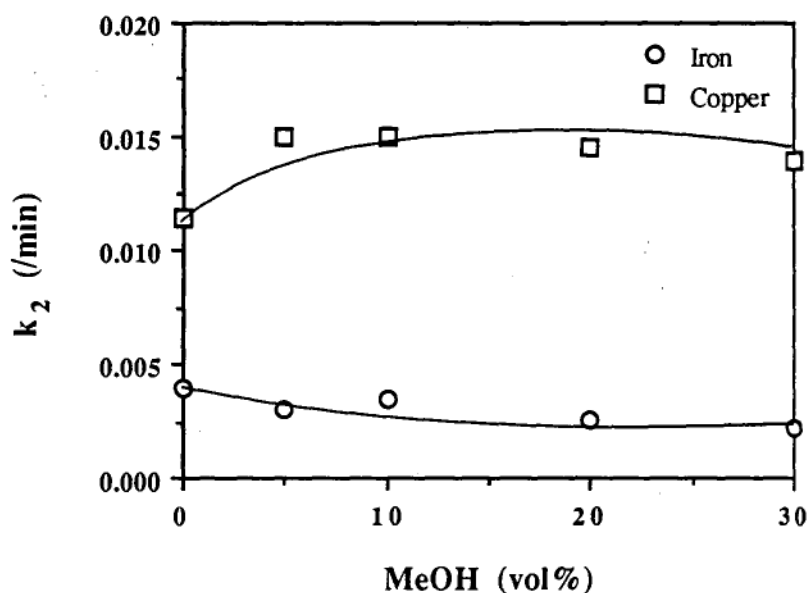
**Figure 4.14** The effect of methanol addition on K. Conditions as in Figure 4.8.



**Figure 4.15** The effect of varying peroxide concentration in 1:1 methanol:water on K. Conditions as in Figure 4.8.

Figures 4.16 and 4.17 show the effect of increasing the methanol to water ratio in the

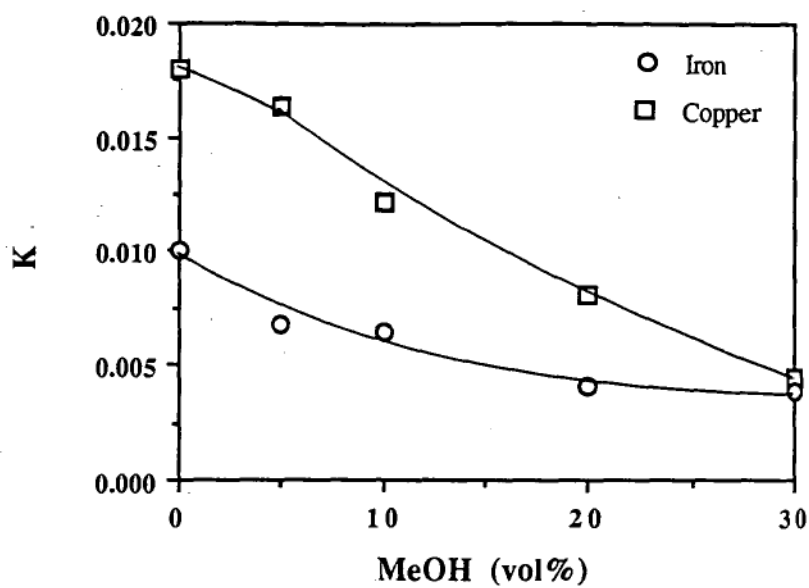
presence of added iron and copper. The effect of methanol on the rate of decomposition of peroxide, as shown in Figure 4.16, is small. Increasing the proportion of methanol in the solution markedly decreases the rate of DMNA decolorization (Figure 4.17) and, therefore, the calculated steady state concentration of hydroxyl radicals decreases markedly.



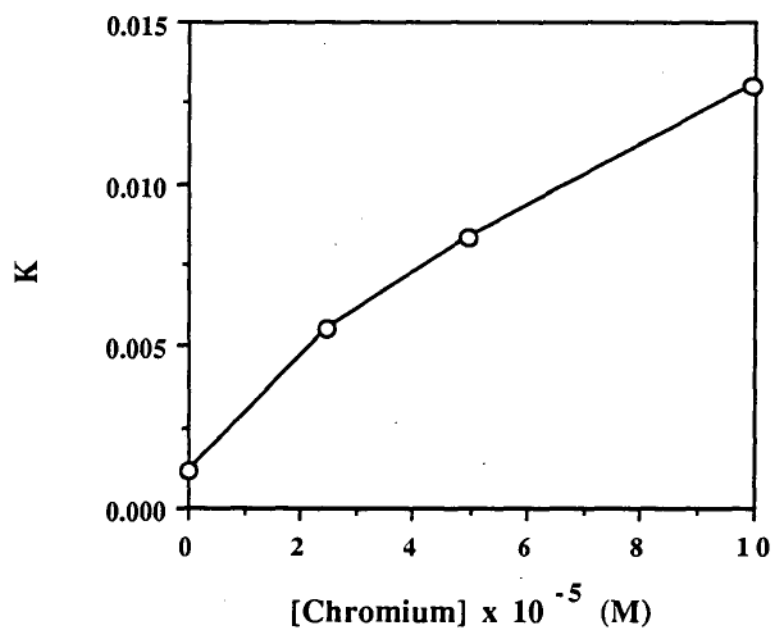
**Figure 4.16** The effect of methanol addition on  $k_2$ , in the presence of added copper ( $1.003 \times 10^{-5} \text{M}$ ) and iron ( $1.113 \times 10^{-5} \text{M}$ ). Conditions as in Figure 4.8.

#### 4.3.5 Kinetic Phenomena under Acidic Conditions

Some transition metals exhibit maximum catalytic activity towards peroxide decomposition under acidic conditions (64). Under such conditions the rate of decomposition of peroxide is usually low without added catalysts. Table 4.3 shows the first-order rate constant for decomposition of hydrogen peroxide in the presence of added chromium. Again the model (equation {4.16}) gives adequate linear correlations. Figure 4.18 shows that the rate of removal of DMNA and, therefore, the steady state concentration of hydroxyl radicals increases with the addition of chromium.



**Figure 4.17** The effect of methanol addition on K in the presence of added copper and iron. Conditions as in Figure 4.16.



**Figure 4.18** Plots showing the variation in K for the addition of chromium. Conditions: pH = 5.8, [DMNA] =  $5 \times 10^{-5}$  M.

**Table 4.3.** Rates of peroxide decomposition in the presence of added chromium.

[Cr] ( $\times 10^{-5}$ )	$k_2$ $\times 10^{-4}/\text{min}$
0.00	4.206
2.49	6.000
4.97	9.866
9.95	16.03

The addition of methanol to acidic solution of hydrogen peroxide containing chromium results in marked decreases in  $K$  at much lower levels of methanol than required in the case of alkaline solutions, as shown in Figure 4.19a. The rate of decomposition of peroxide is greatly reduced in the presence of methanol, compared to the significant increases noted in alkaline solution. The addition of magnesium under acidic conditions to this system has a similar effect on  $K$  at low levels of addition as shown in Figure 4.19b. However, at higher levels of addition the value of  $K$  approaches that of the unstabilised system.

Previous investigations (64) have shown that under acidic pH conditions addition of chromium to peroxide bleaching liquors can improve the subsequent response of mechanical pulps under conventional alkaline bleaching conditions. These studies showed that although no brightness gain was observed under acidic bleaching conditions, the chromophores present are rendered more susceptible to bleaching in an alkaline peroxide medium. This implies that hydroxyl radicals may have a positive effect on bleaching provided pulp is exposed to radicals under acidic pH.

#### 4.4 Studies of Hydroxyl Radical Concentration

Attempts were made to directly measure hydroxyl radical concentrations in peroxide bleach liquors, in order to verify the results obtained using the oxidation of DMNA. It

was not possible with ESR spectroscopy, presumably due to the very low concentration of hydroxyl radicals in these solutions. Therefore it was necessary to confirm the validity of the method by comparison with similar reported methods.

Results obtained here are in agreement with those of Reitberger *et al.* who used a method based on chemiluminescence of solutions after addition of phthalic hydrazide (17) to follow generation of hydroxyl radicals during peroxide bleaching. They reported that copper was particularly efficient in formation of hydroxyl radicals from alkaline hydrogen peroxide, while silicate, DTPA and magnesium sulfate reduced their concentration (4).

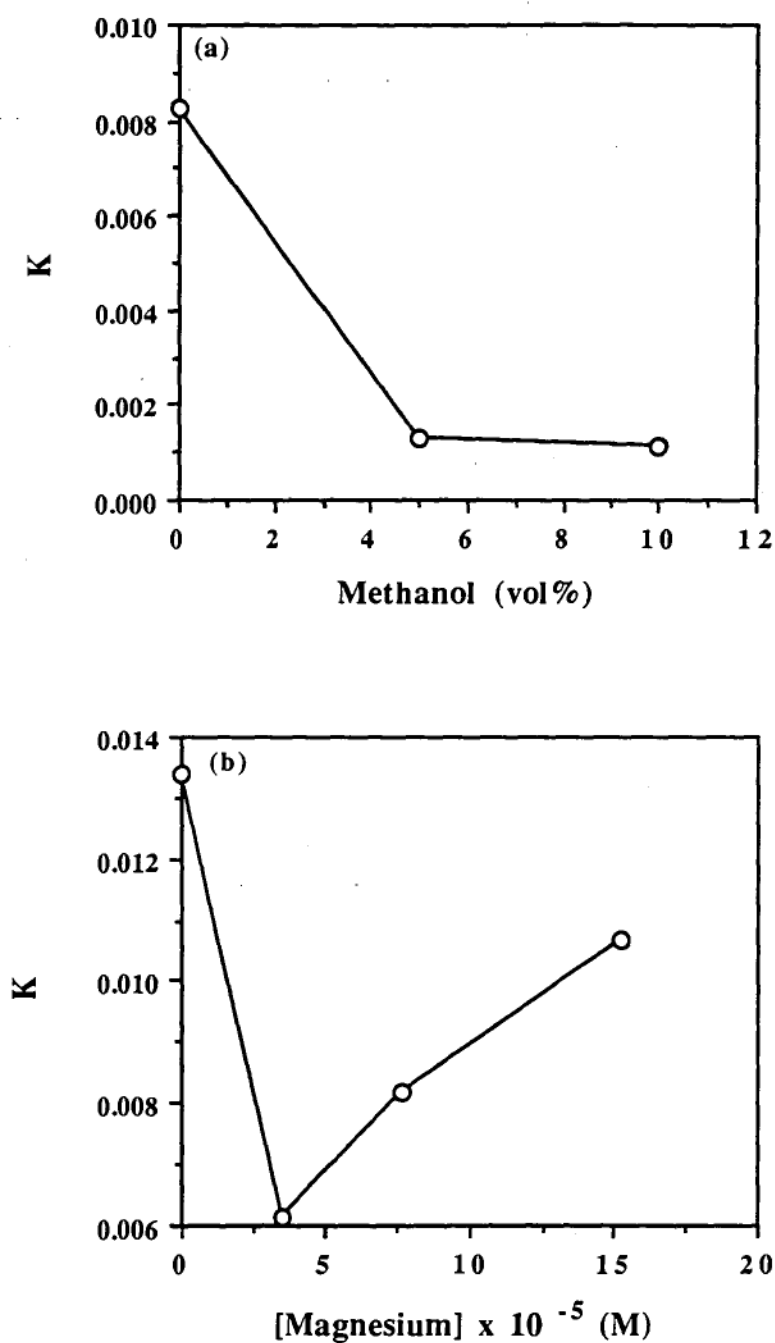
Colodette (53) measured hydroxyl radical concentrations by observing the hydroxylation of benzene, forming phenol and biphenyl, as well as the oxidation of DMNA. His study concluded that both methods gave similar results, thus supporting the method used in this study. He found that copper significantly increased the level of hydroxyl radicals while iron and manganese, at very low levels, actually decreased the radical concentration.

Previous studies using DMNA, although not using the kinetic analysis developed here have reached similar conclusions to this study. Copper appears to produce hydroxyl radicals in its catalytic decomposition of hydrogen peroxide (31,32), iron does not decompose peroxide via a radical mechanism (32) and the mechanism of manganese catalysed decomposition depends on the metal ion concentration (32,51).

Studies of the interaction of DMNA with the hydroxyl radical have shown that DMNA is a specific trapping agent for this radical species (18,49).

Therefore, it appears that results obtained from the oxidation of DMNA are in agreement with other reported studies relating to hydroxyl radical concentration, and

although direct evidence of the correctness could not be obtained there would seem to be strong supporting evidence for the results obtained.



**Figure 4.19** Plots showing the variation in  $K$  for the addition of (a) chromium and methanol and (b) chromium and magnesium. Conditions:  $\text{pH} = 5.8$ ,  $[\text{DMNA}] = 5 \times 10^{-5} \text{ M}$ .

#### 4.5 Bleaching Studies with Radical Traps

In theory it is possible to examine the influence of hydroxyl radical concentration during alkaline peroxide bleaching by following DMNA oxidation in the presence of pulp. Brightness gain could then be correlated with the radical concentration profile for each system. However, this approach has the drawback that DMNA, being highly coloured, may directly affect the brightness of the pulp by adsorption onto the fibres. Figure 4.20 shows the effect of DMNA concentration on brightness gain during alkaline peroxide bleaching and also in the absence of peroxide under alkaline conditions. Clearly, DMNA itself can influence the optical properties of the pulp. It is therefore preferable to draw correlations between the calculated radical concentrations from our solution studies with the results of peroxide bleaching experiments in the absence of DMNA. However, it is first necessary to determine whether the presence of the pulp affects the oxidation of DMNA under our experimental conditions, as reflected by the calculated parameters. Table 4.4 shows that the calculated values for  $K$  are similar in the presence and absence of pulp. In order to achieve this samples of pulp were withdrawn and filtered prior to determining the DMNA concentration. Values of  $k_2$  are increased in the presence of pulp in the case of magnesium addition and with no additive present, due to the consumption of peroxide by bleaching processes. It therefore appears reasonable to correlate values of  $K$  from solution studies (in the absence of pulp) with the observed bleaching response of the pulp in the absence of DMNA.

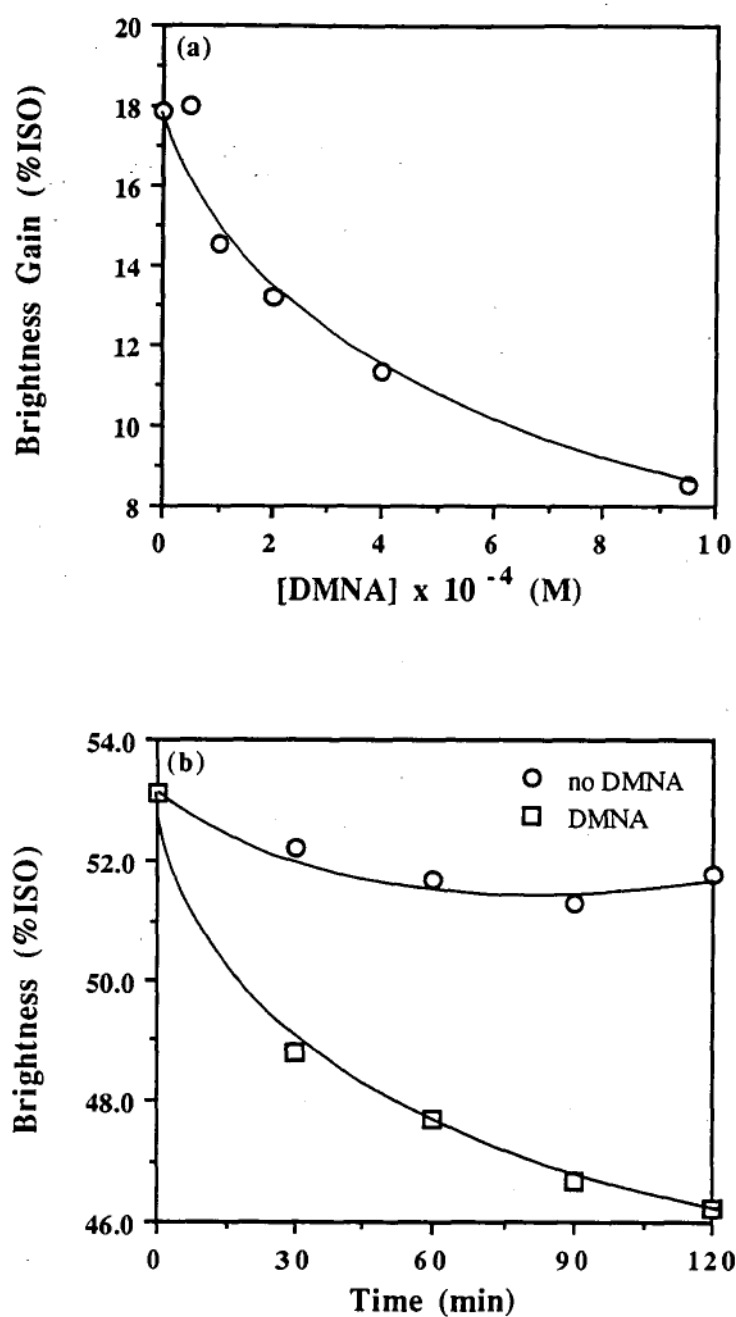
**Table 4.4** Values of rate constants for hydrogen peroxide decomposition and DMNA removal in the presence and absence of pulp. Conditions: 50°C, 1% consistency, pH 11.0, 0.0353M peroxide.

Additive		$k_2$ ( $\times 10^{-3}$ /min)	K ( $\times 10^{-2}$ )
none	solution	2.00	1.24
copper	solution	13.3	1.89
magnesium	solution	0.36	0.67
none	pulp	3.10	1.27
copper	pulp	9.17	1.71
magnesium	pulp	1.29	1.28

#### 4.5.1 Alkaline Conditions

Figure 4.21a shows results obtained for the addition of various amounts of magnesium nitrate to peroxide bleaching of pulp. The final brightness of the pulp is not significantly effected by the presence of magnesium or the implied reduced concentration of hydroxyl radicals. A slight reduction in peroxide consumption was achieved with the introduction of magnesium, but the brightness gains in the presence and absence of magnesium are similar. Bleaching studies in the presence of varying quantities of methanol, illustrated in Figure 4.21b, also show that pulp brightness is not significantly effected by the presence of a radical trap, thus supporting the results obtained with magnesium.





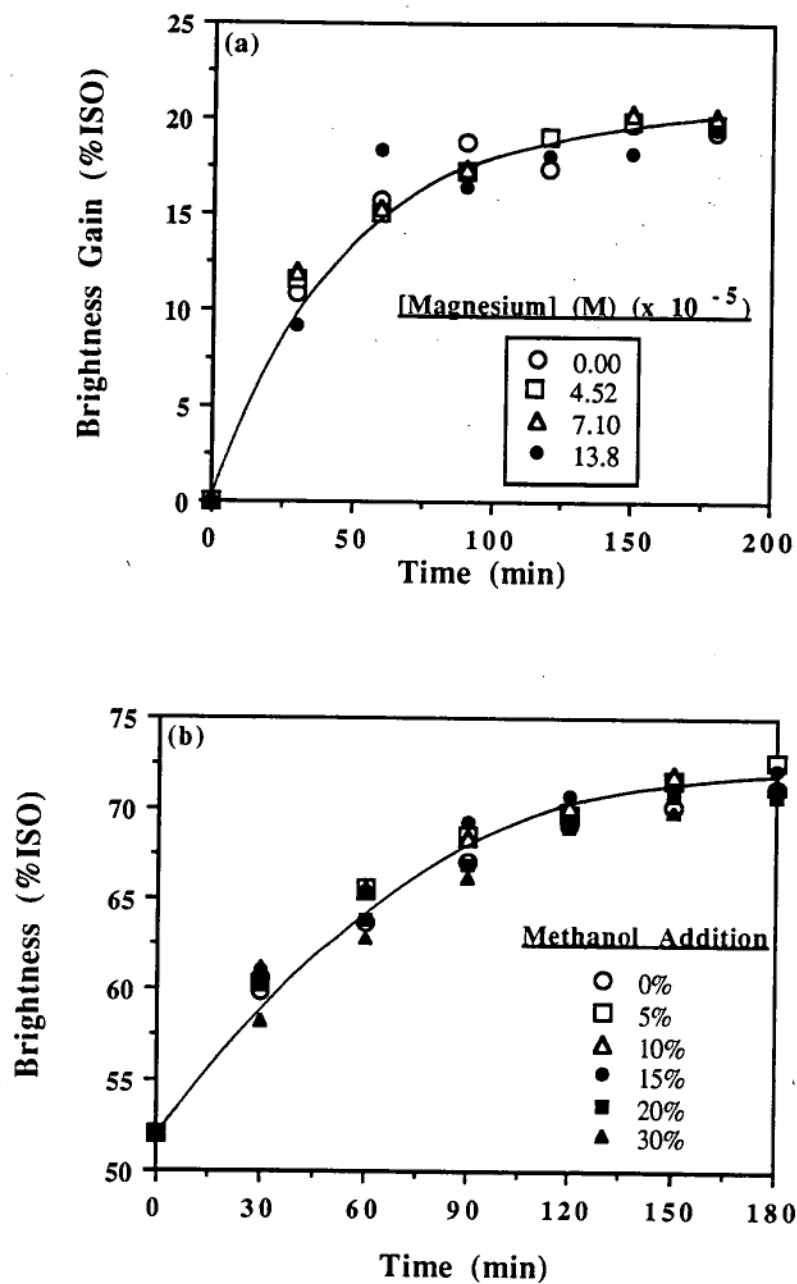
**Figure 4.20** The effect of DMNA concentration on (a) the bleaching response of pulp and (b) alkali darkening. Conditions: pH 11.0, 50C, 1% consistency, (a) 12% peroxide on o.d. pulp, (b) [DMNA]  $2 \times 10^{-4}$ M.

Figure 4.22 shows negative effects of additions of iron, copper and manganese on brightness gain during peroxide bleaching experiments. However, it is difficult to

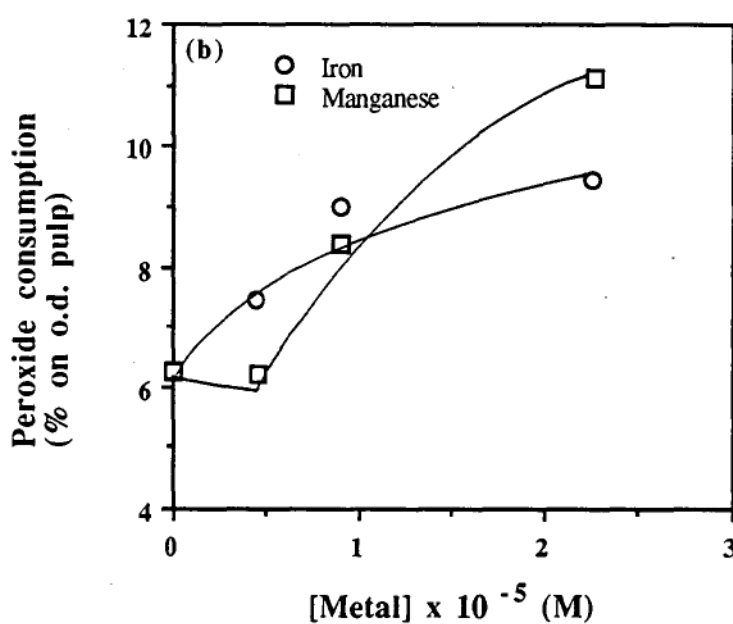
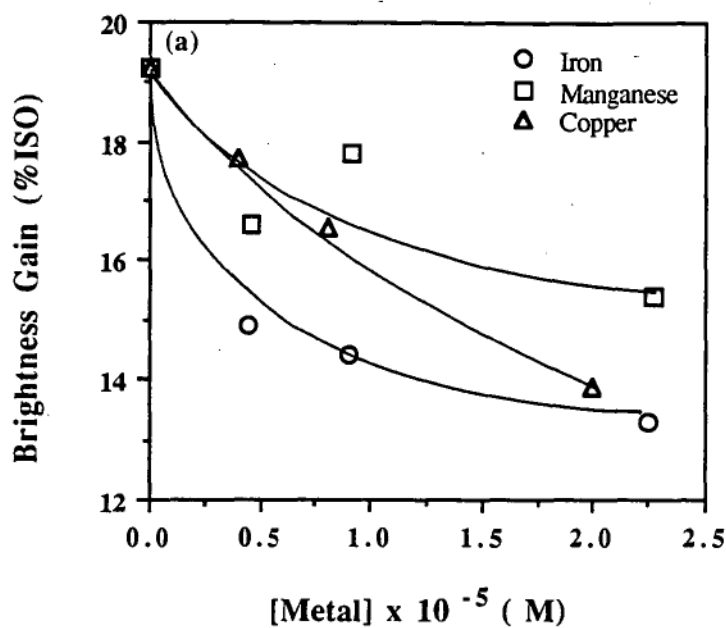
isolate the influences of radical concentration in these experiments, as the concentration profile for total peroxide is also strongly dependent on the introduction of these additives. For this reason experiments were performed under conditions where both the pH and peroxide concentration were maintained at constant levels (48,49). Table 4.5 shows that for the introduction of either transition metal ions or stabilisers under constant conditions there is no significant difference in brightness gain, even though the solution studies indicate that significantly different concentrations of hydroxyl radicals would be available.

The addition of DTPA under these conditions gives an unusual result. With all other additives approximately the same brightness is achieved after three hours bleaching, independent of the calculated radical concentration. The hydroxyl radical concentration for the addition of DTPA is lower than for no addition but not lower than magnesium addition, so this difference in brightness response does not appear to be caused by the variation in hydroxyl radical concentration. As has been reported previously (chapter 3.2), chelating agents, including DTPA, appears to have an unusual effect with this pulp and this result adds further weight to the conclusions of that chapter.

These results are in agreement with those of Reitberger *et al.* who used a method based on chemiluminescence of solutions after addition of phthalic hydrazide (17) to follow generation of hydroxyl radicals during peroxide bleaching. They reported similar results with copper, silicate, DTPA and magnesium sulfate (2). Their method also showed that at low pulp consistencies (2.5%) there were no positive effects due to enhanced formation of hydroxyl radicals during alkaline peroxide bleaching of a mechanical pulp.



**Figure 4.21** The brightness response of *E. regnans* SGW in the presence of (a) magnesium and (b) methanol. pH 11.0, 12% peroxide on oven dry. pulp, 1% stock consistency, 50°C.



**Figure 4.22** The change in a) final brightness and b) peroxide consumption for bleaching in the presence of added transition metal ions. Conditions: 1% pulp consistency, 50°C, pH 11.0, 12% peroxide on o.d. pulp, duration of bleach: 180 minutes.  $[\text{Cu}] = 1.00 \times 10^{-5}$ ,  $[\text{Mn}] = 1.14 \times 10^{-5}$ ,  $[\text{Fe}] = 1.12 \times 10^{-5} \text{ M}$ .

**Table 4.5** Bleaching response of *E. regnans* pulp under conditions of constant concentration of peroxide (12% on oven dry pulp) and alkali (pH 11.0). Other conditions as in Figure 4.21a.

Additive	Concentration M (x 10 <sup>-5</sup> )	Brightness Gain (%ISO)		Kk <sub>2</sub> (/min x 10 <sup>-5</sup> )
		60 minutes	180 minutes	
None		11.9	18.4	2.41
Copper	1.00	10.6	17.6	15.0
Manganese	1.14	12.7	17.5	3.56
Iron	1.12	12.1	18.3	1.98
Magnesium	7.98	10.6	17.2	0.23
Silicate	2000	11.5	18.1	1.60
DTPA	50.8	9.7	15.3	0.52

However, other investigations have concluded that peroxide decomposition products can have either positive or negative effects on brightness gain. Sjogren *et al.* (4) have reported positive effects of hydroxyl radicals produced by irradiation with  $\gamma$  rays during peroxide bleaching of a mechanical pulp. Kutney and Evans (9) observed brightness reversion when a bleached pulp was exposed to alkaline peroxide in the presence of catalysts including iron, manganese and copper, and attributed the effects to peroxide decomposition products.

The apparent inconsistencies in these observations regarding the influence of the hydroxyl radical during alkaline peroxide bleaching of mechanical pulps may lie in the experimental conditions used, for example pulp consistency. From analysis of the kinetics of chromophore removal during peroxide bleaching, Moldenius and Sjorgen (28) postulated that the effects of short lived species become much more apparent as

the pulp consistency is increased, as these active intermediates could more easily migrate between fibres. Reitberger (2) also found that at increased pulp consistency positive effects of hydroxyl radicals become apparent.

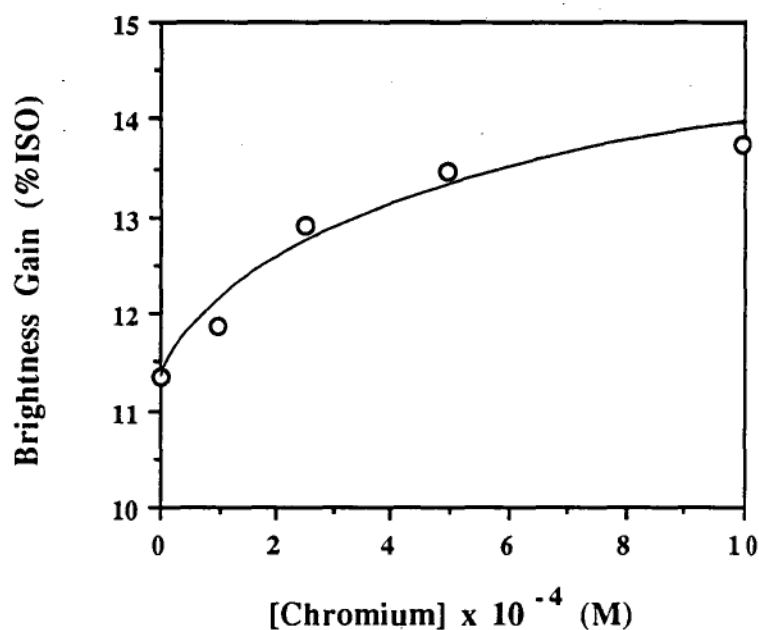
#### **4.5.2 Two-stage acid-alkali Bleaching**

Previous investigations (Chapter 2.3) have shown that under acidic pH conditions addition of chromium to peroxide bleaching liquors can improve the subsequent response of mechanical pulps under conventional alkaline bleaching conditions. These studies showed that although no brightness gain was observed under acidic bleaching conditions, the chromophores present are rendered more susceptible to bleaching in an alkaline peroxide medium. This implies that hydroxyl radicals may have a positive effect on bleaching, provided the pulp is exposed to radicals under acidic conditions.

Figure 4.23 shows the bleaching response after the two-stage acid/alkali process in the presence of added chromium in the first stage. This can be compared to Figure 4.18 showing the calculated hydroxyl radical concentrations. By increasing the hydroxyl radical concentration in the acidic stage of a two-stage process, the final brightness of the pulp can be increased. This process has been explained previously in terms of a dual mechanism of peroxide bleaching (Chapter 2.3), with bleaching being related to both the presence of the perhydroxyl anion and the hydroxyl radical, and these results support such a mechanism.

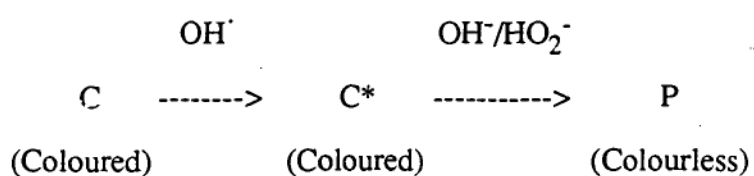
In the presence of stabilisers to reduce the hydroxyl radical concentration (Figure 4.19), a decrease in brightness may be anticipated. Figure 4.24 show that for the addition of methanol or magnesium, a decrease in brightness is indeed observed after the alkaline stage. Clearly, as the radical concentration is reduced the brightness gain also decreases, indicating that the presence of hydroxyl radicals can result in an increased brightness response. This cannot be associated with a change in radical concentration in the alkaline stage as has previously been

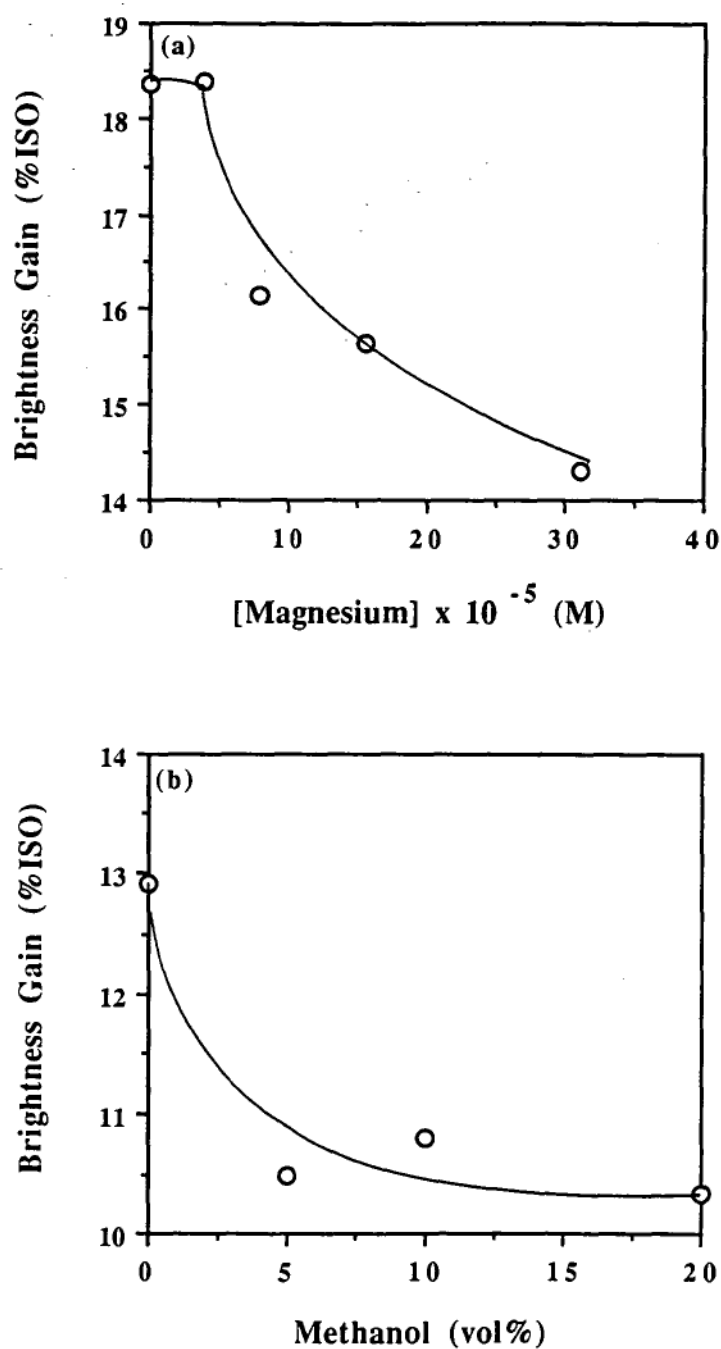
shown (Table 4.5, Figure 4.21)



**Figure 4.23** The effect of chromium addition on the brightness response during a two-stage bleaching process. Conditions: 1% pulp consistency, 50°C, 12% peroxide on o.d. pulp, acidic stage: 15 minutes, pH 5.8; alkaline stage 120 minutes, pH 11.0.

Bleaching under acidic conditions in the presence of the hydroxyl radical enhances the final brightness of the pulp after the alkaline stage. However, no change in brightness is observed after the acidic stage as reported previously (Chapter 2.3). This indicates that changes occur within the lignin structure that do not cause a change in colour of the pulp, but increases the susceptibility of the chromophores to elimination in the subsequent alkaline stage, as outlined below.





**Figure 4.24** The effect of (a) chromium and methanol and (b) chromium and magnesium addition on the brightness response during a two-stage bleaching process. Conditions: as in figure 2.23.

The reason for the hydroxyl radical not having an influence under alkaline conditions may be related to the oxidation potential of this species. Under alkaline conditions the



oxidation potential of the hydroxyl radical is significantly lower than under neutral or acidic conditions (3), thus lowering the reactivity. Furthermore, the  $pK_a$  of the hydroxyl radical is 11.6 (1,3), producing the oxyl radical,  $O^-$ , which has a significantly lower oxidation potential than the hydroxyl radical, and is therefore less likely to be a major bleaching species.

Under acidic conditions, the oxidation potential of the hydroxyl radical is increased compared to alkaline conditions (3) and, therefore, the effect of hydroxyl radicals under acidic conditions may be more easily observed. Several two-stage peroxide bleaching processes have been reported, as outlined in Chapter 2.1.1, under acidic conditions followed by alkaline conditions, and the effects appear to be related to the action of the hydroxyl radical.

#### 4.6 Conclusions

Work using constant concentrations of peroxide and alkali also shows some evidence for the importance of radicals in peroxide bleaching. Increasing the consistency leads to some improvement in the bleaching response of the pulp, and this can be related to the higher radical mobility and activity at higher consistencies. This effect however, appears to be small (1-2%ISO) and indicates that under alkaline conditions the principal bleaching species appears to be the perhydroxyl anion with radical species only making a small contribution to the overall bleaching.

Kinetic analysis of the interaction between DMNA and the hydroxyl radical has shown that the dominant termination reaction does not involve DMNA. The kinetic analysis, however, gives information regarding the steady state concentration of hydroxyl radicals in solution.

The decomposition of hydrogen peroxide under alkaline conditions proceeds, at least partly, via a radical mechanism. Under acidic conditions hydroxyl radicals are also

produced when hydrogen peroxide decomposes. The presence of various transition metal ion peroxide decomposition catalysts under both acidic and alkaline conditions can alter the radical concentration.

Copper has been shown to greatly increase the hydroxyl radical concentration when used to catalytically decompose hydrogen peroxide under alkaline conditions, but the addition of iron and manganese has little effect on the radical concentration. This indicates that copper catalysed decomposition of hydrogen peroxide proceeds via a radical chain mechanism, but iron and manganese decompose peroxide via a non-radical mechanism. Stabilisers such as DTPA and magnesium salts cause a significant decrease in hydroxyl radical concentration at low levels of addition, and could be acting by binding active metal ions such as copper. Silicate has little effect on radical concentrations. Methanol, a known radical scavenger, can also significantly reduce the observed hydroxyl radical concentration, presumably by providing an alternate termination reaction for these radicals.

Chromium, under acidic conditions, also appears to decompose peroxide via a radical mechanism. The addition of magnesium and methanol to such a system shows similar trends to those observed under alkaline conditions, significantly reducing the hydroxyl radical concentration.

Having shown that a valid comparison can be made between hydroxyl radical concentration in the presence and absence of pulp, a correlation between bleaching response and radical concentration can be performed. Under alkaline conditions there appears to be no influence on bleaching response with varying radical concentration. However, when two-stage, acid-alkali peroxide bleaching sequences are employed, a correlation exists between the final pulp brightness after the alkaline stage and the radical concentration in the acid (first) stage. This appears to be related to the action of the hydroxyl radical under acidic conditions, as postulated earlier (chapter 2), when the

reduction potential of the hydroxyl radical is maximised.

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# CHAPTER 5

## EXPERIMENTAL

## CHAPTER FIVE

### Experimental

#### 5.1 General Procedures

The following procedures were used throughout this work unless otherwise stated, either in section 5.2, or in the section relevant to the results.

##### 5.1.1. Chemicals used

The following chemicals were used throughout the work presented in this thesis. Hydrogen peroxide (30%), aluminium nitrate (97%) and sulfuric acid (98%) were obtained from Ajax chemicals. Metal nitrates of iron, copper, manganese, chromium and magnesium, all 99% purity or higher, and semiconductor purity potassium hydroxide (99.99%) were obtained from Aldrich chemicals. Semiconductor purity potassium hydroxide was used as the source of alkali in all bleaching studies and solution work to reduce the level of added transition metal ions (1). Sulfuric acid was used as the source of acid when required. Diethylenetriamine-pentaacetic acid (DTPA) (97%), ethylenediaminetetraacetic acid (EDTA) (99%) and sodium silicate solution (30%  $\text{SiO}_2$ , 16%  $\text{NaOH}$ ), and N,N-dimethyl-4-nitrosoaniline (DMNA) (97%) were obtained from Aldrich chemicals.

Potassium iodide (Laboratory grade), sodium thiosulfate (Aldrich, 99%), dilute sulfuric acid, saturated ammonium molybdate and 1% starch solution were used for iodometric determination of hydrogen peroxide (2).

All bleaching experiments, and work in the absence of pulp was performed in Milli-Q deionised water (1), to reduce the level of added transition metal ions in solution.

### 5.1.2 Bleaching Procedures

All experiments were performed in polyethylene reaction vessels suspended in a constant temperature water bath maintained at 50°C. The reaction vessels were periodically washed with warm, dilute sulfuric acid to prevent the accumulation of metal ions. The reaction vessels were washed with multiple portions of deionised water before all experiments.

Pulp suspensions were prepared by adding appropriate amounts of pulp to Milli-Q water, and pre-heating the slurry to 50°C prior to addition of bleaching chemicals and other additives. The order of addition was always additive(s), hydrogen peroxide and then acid or alkali to achieve the required pH.

Samples were withdrawn at intervals to allow sheet formation for brightness determination and calculation of peroxide consumption.

Peroxide determination was performed by titration of a known sample volume of the filtered bleach liquor which was acidified with dilute sulfuric acid, and an excess of potassium iodide added. Saturated ammonium molybdate solution was added to catalyse the formation of iodine. The resulting solution was titrated against sodium thiosulfate to a starch endpoint (2).

Brightness sheets were formed by filtering a sample of the pulp suspension on a Whatman number 1 filter paper. For 1% consistency bleaching, the sheet was then washed twice with 50 mL portions of deionised water. For higher consistencies, the filtered pulp was resuspended in 100 mL of deionised water, filtered and then washed with two 50 mL portions of deionised water. The same mass of pulp was used in all cases. The sheets were then dried prior to brightness determination. Brightnesses (%ISO) were determined on either a Zeiss Elrepho (Chapter 2 and 3), using a 457 nm filter or a Datacolor Elrepho 2000 (Chapter 4). The brightness of unbleached pulp was

regularly monitored to allow calculation of brightness gains.

#### **5.1.2.1 Reducing Peroxide Concentration**

Typically industrial peroxide brightening of pulps is performed by applying an initial charge of chemicals to the pulp slurry and allowing the bleaching reagents to be consumed until the required brightness is obtained (3). In this work much bleaching was performed in this manner. An initial charge of peroxide was applied and the pH of the bleach liquor adjusted to the required level. For two stage acid/alkali bleaching sequences the pH was adjusted to the level required for the first stage, either 5.8, 6.0 or 7.0. Alkaline peroxide bleaching was usually performed at pH 11.0, unless otherwise stated.

In some cases, where indicated in the text, the pH of the solution during bleaching was maintained at a constant level, generally pH 11.0. This was to allow easier comparisons with solution studies, in which the pH was maintained at a fixed level, and to allow comparisons between bleaching systems that have different pH profiles during the course of the bleaching, for example, experiments with different consistencies. In solution studies the pH tends to increase with peroxide consumption, due to hydrogen peroxide being a weak acid, whilst during bleaching the pH tends to fall due to consumption of alkali in the bleaching reaction, therefore maintaining the pH at the required level makes comparisons possible.

#### **5.1.2.2 Constant Peroxide Concentration**

Using this method both the pH and the concentration of peroxide were maintained at fixed levels for the duration of the bleach (4). This was achieved by monitoring these values and adding either alkali or peroxide as deviations from the starting conditions are observed. Generally chemical addition every ten to fifteen minutes keeps peroxide charge within 5-10% and pH within 0.1 units of the set values.

Samples were withdrawn at intervals and peroxide levels determined. From this the amount of peroxide required to reestablish the set conditions was calculated and subsequently added. Overall peroxide consumption was not monitored in these experiments. The pH was also monitored and alkali added as required.

#### 5.1.2.3 Alkali Darkening

Alkali darkening experiments were performed at 50°C in polyethylene reaction vessels. To a pulp slurry at the appropriate consistency was added sufficient alkali to reach the required pH. Brightness sheets were prepared at various times in accordance with previous procedures.

#### 5.1.3 Pulps

*Eucalyptus regnans* stoneground wood (SGW) was prepared on a small scale grindstone at ANM, Boyer mill. Blocks of *E. regnans* wood were soaked in deionised water for three days prior to grinding. The wood was ground at 80°C, in the presence of dilute sodium hydroxide (3% on o.d wood). The pulp produced was filtered to increase the consistency from 1.5% to approximately 20%. The pulp, in approximately 60g batches, was then washed with two portions of deionised water (~500 mL total) prior to storage at 4°C until use. SGW pulps were kept for a maximum period of three months during which time the brightness of the unbleached pulp was monitored to ensure no significant deterioration of the pulp occurred during storage. The brightness of the unbleached pulp was in the range 52-55 %ISO. Generally bleaching results are presented as brightness gains to reduce differences caused by slight changes in the unbleached pulp brightness.

Bleached *P. radiata* kraft pulp was obtained from Tasman Pulp and Paper, New Zealand. Before use in any experiments, the pulp was bleached with alkaline peroxide (50°C, 4% consistency, 3% peroxide on o.d. pulp, pH 11.0, peroxide and alkali concentrations were maintained at these levels throughout the experiment) for six hours

to remove any chromophoric material that could be removed with hydrogen peroxide and to limit any brightness change in subsequent experiments. The brightness of the pulp only changed very slightly with this peroxide treatment.

The *Pinus radiata* thermomechanical pulp was provided by Australian Newsprint Mills from TMP unit 2 at their Boyer mill. The pulp was stored at 8% consistency and 4°C until used. The brightness of the unbleached pulp was 58-60 %ISO.

Cellulose (3.2.2) was obtained by disintegrating Whatman number 42 filter papers. These filter papers consist of highly purified cotton cellulose.

#### 5.1.4 Atomic Absorption Spectrophotometry

The following method was used to analyse pulp samples for manganese, iron and copper. Samples of bleach liquor were also analysed on some occasions.

An oven dry sample of accurately known mass, generally about 5.0 g, was placed in a conical flask, to which 50 mL of concentrated nitric acid (70%) and 5 mL of concentrated sulfuric acid (98%) was added. The sulfuric acid was present to prevent the solution boiling to dryness, which is potentially dangerous after the addition of perchloric acid. This solution was gently heated, with occasional stirring, until no pulp was visible. This takes between five and fifteen minutes depending on the pulp type. At this stage 5 mL of concentrated perchloric acid (70%) was added, along with boiling chips, and the solution was boiled until a clear or straw coloured solution was obtained. The final solution, after cooling, was carefully diluted to 100 mL in a volumetric flask.

Solution of manganese, iron and copper were prepared by standard methods and used for calibrating the spectrophotometer prior to sample analysis.

Samples were analysed for manganese, copper and iron on a Varian spectrAA-10

spectrophotometer with an acetylene-air flame. Aluminium analysis was performed on a Varian AA1475 spectrophotometer using an acetylene - nitrous oxide flame. Results are generally reported as ppm metal on o.d pulp.

Milli-Q water was used in the preparation of all samples and a blank digestion, in the absence of pulp, was analysed to determine if the leaching of metal ions from the glass flask or boiling chips was significant.

Typical values of metal ion contents of pulps are reported in Table 5.1.

**Table 5.1** Metal ion content of pulps used in this work.

Wood type	Metal ion (ppm)			
	Iron	Manganese	Copper	Aluminium
<i>Eucalypt</i> SGW	32	8	72	12.8
Chelated <i>Eucalypt</i> SGW	32	1	32	11.4

#### 5.1.5 Chelation of Pulps

In some cases pulps were pretreated with either EDTA or DTPA prior to bleaching. The required amount of pulp, generally 5 or 10 g o.d., was added to to Milli-Q water to give a pulp slurry of 2% consistency, and maintained at 20°C. To this slurry either 0.2% or 0.5% (on o.d. pulp) of the chelating agent was added and the mixture stirred. The pulp was stirred occasionally during the chelation treatment. After the appropriate time, usually 15 or 30 minutes, the slurry was filtered to approximately 20% consistency and washed with two 200 mL portions of deionised water. Atomic absorption results show that metal ion concentrations, particularly copper and

manganese, are reduced with this treatment.

Bleaching pulps in the presence of chelating agents, without pre-treatment, was also undertaken in some experiments.

#### **5.1.6 Solution Chemistry**

Peroxide decomposition experiments were performed in polyethylene reaction vessels that were maintained at either 20°C or 50°C in a constant temperature water bath.

Before experiments the vessels were washed with warm, dilute sulfuric acid and then with multiple portions of deionised water to prevent accumulation of metal ions.

To an appropriate volume of preheated Milli-Q water were added, any additives to be used, hydrogen peroxide and acid or alkali to obtain the required pH. The order of addition of chemicals was kept constant to minimise any effect such as species formation that may influence results (5). An initial sample was analysed for peroxide concentration and periodically throughout the experiment the peroxide concentration was determined to allow calculation of decomposition rates. Generally the decomposition was first order with respect to hydrogen peroxide concentration, and first order rate constants were obtained from plots of  $\ln(\text{concentration})$  against time. All first order rate constants are reported in units of  $(\text{min}^{-1})$ .

#### **5.1.7 UV-Visible Spectroscopy**

All spectra were recorded on a Varian DMS-100 spectrophotometer. 1 cm quartz cells were used in all cases, with Milli-Q water as the reference and the baseline was corrected in all spectra. When rates of decomposition of DMNA were being observed, samples were taken every 10 minutes. The residual rate of DMNA reaction was subtracted before further calculations were performed. This residual rate of reaction was very low compared to the other rates in the presence of peroxide. The difference in absorbance was used to calculate the change in concentration of DMNA. Plots of



$\ln([DMNA]_t/[DMNA]_0)$  against the appropriate time function were plotted, and the slope calculated. The slope gives the value of the rate constant  $K$ , as outlined in Chapter 4.3.2.

### 5.1.8 ESR Spectroscopy

Attempts to detect hydroxyl radicals in alkaline hydrogen peroxide solutions were performed using a Joel JES-FE3X ESR Spectrometer using X-band microwave radiation. Solutions were analysed both in liquid and frozen states with no detection being possible by either method.

## 5.2 Specific Procedures

In certain aspects of this work different procedures were used either in addition to, or instead of those mentioned in the previous section (5.1)

### 5.2.1 Chapter 3

The determination of the absorbance of manganese to various pulps (3.2) was carried out as follows. To a 2.0g sample of pulp at 1% consistency and 20°C a calculated amount of manganese was added and the pH adjusted to the required level. The pulp was then allowed to stand, with occasional stirring for given time. At the completion of this time the pulp was filtered and washed with two 100mL portions of deionised water prior to drying at 105°C. The digestion and atomic absorption spectrophotometry then followed the procedures outlined previously (5.1.4).

The bleaching of pre-bleached pulps (5.3) was performed as follows. The given pulp was bleached for 4 hours at 50°C with an initial peroxide charge of 3% on o.d. pulp, 4% consistency and pH 11.0. At the completion of this stage the pulp was filtered, washed and stored at 4°C until required. The pulps were then exposed to alkali or alkaline peroxide in the presence or absence of added transition metal ions.

### 5.3 References

1. J. Abbot and D.G. Brown, *Int. J. Chem. Kinet.*, **22**(9), 963-974 (1990).
2. F. Kraft, *Pulp and Paper Manufacture*, R.G. McDonald (ed.), 2nd Ed., Vol. 1, McGraw-Hill, New York, 724 (1967).
3. W.G. Strunk, Peroxide Bleaching, in *Pulp and Paper Manufacture*, R.A Leask (ed.), 3rd Ed., Vol. 2, Joint Textbook Committee of the Paper Industry, 238-251 (1987).
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## CHAPTER 6

## CONCLUSIONS

## CHAPTER SIX

### Conclusions

The role of radical species, particularly the hydroxyl radical, and transition metal ions in peroxide bleaching processes has been investigated. While the addition of transition metal ions to bleach liquors causes increased decomposition of peroxide, no negative effects could be related to the presence of the decomposition products. Indeed, under certain circumstances the presence of transition metal ions appears to have a positive effect on bleaching response. The hydroxyl radical, produced via the catalytic decomposition of hydrogen peroxide by some transition metal ions, appears to have a significant positive influence on peroxide bleaching processes under certain conditions.

An analysis of previously reported kinetic expressions describing peroxide bleaching indicates the possibility of two distinct mechanisms of bleaching associated with the perhydroxyl anion and the hydroxyl radical. By performing experiments that separate the effect of the hydroxyl radical from the combined effect of radical species and the perhydroxyl anion it has been shown that the predictions of the kinetic analysis are essentially correct. Enhanced brightness response can be achieved by exposing pulp to both these species in a two-stage bleaching sequence. Whilst there are economic problems with the implementation of such processes in terms of capital expenditure, a further understanding of the mechanism of peroxide bleaching of mechanical pulps has been achieved.

From the kinetics of the oxidation of *N,N*-dimethyl-4-nitrosoaniline (DMNA), variations in the calculated hydroxyl radical concentration can be achieved by the addition of various peroxide decomposition catalysts and stabilisers. During bleaching experiments these differing levels of hydroxyl radical concentration appear to have no effect on the brightness response at low pulp consistency. However, at increased pulp

consistency there does appear to be some benefit to bleaching response, presumably related to the presence of reactive radical species. The hydroxyl radical being the most reactive of these species, is most likely to react with the pulp. Under acidic conditions, as part of a two-stage, acid-alkali sequence, there appears to be some benefit in exposing pulp to hydroxyl radicals. An increased final pulp brightness can be correlated to the calculated hydroxyl radical concentration.

There appears to be no evidence for darkening of pulps caused by decomposition products of hydrogen peroxide.

Therefore, from these studies it can be concluded that hydroxyl radicals can contribute significantly to hydrogen peroxide bleaching particularly when acidic or neutral conditions are employed or high pulp consistency is employed, as is typically the case for industrial bleaching of mechanical pulps with hydrogen peroxide. It would appear that the perhydroxyl is the major bleaching species, particularly under alkaline conditions. The initial kinetic analysis appears correct in that both anion and radical processes appear to operate in peroxide bleaching with radical bleaching being most significant under acidic conditions.

It appears, therefore, that the presence of transition metal ions during peroxide bleaching may not be totally undesirable as previously thought. If the catalytic decomposition of transition metals can be modified so as to reduce the overall consumption of bleaching reagent while still producing significant quantities of hydroxyl radicals, new processes employing novel conditions may be developed.

# APPENDIX 1

## PUBLICATIONS

## Appendix 1

### Publications

1. Peroxide Bleaching Reactions under Alkaline and Acidic Conditions.

G.C. Hobbs and J. Abbot, J. Wood Chem. Technol., **11**(2), 225-246 (1991).

2. Two-Stage Peroxide Bleaching of Eucalypt SGW with Chromium Catalysts.

G.C. Hobbs and J. Abbot, J. Wood Chem. Technol., **11**(3), 329-348 (1991).

3. The Role of Radical Species in Peroxide Bleaching Processes.

G.C. Hobbs and J. Abbot, Proceedings of the 1992 Appita Conference and also Appita, **45**(5), 344-348 (1992).

4. The Influence of Metal ions on Two-Stage Peroxide Bleaching of Radiata Pine TMP.

J. Abbot and G.C. Hobbs, J. Pulp Paper Sci., **18**(2), J67-70 (1992).

5. Peroxide Bleaching under Alkaline and Acidic conditions: The role of Transition Metal Ions.

G.C. Hobbs and J. Abbot, Proceedings of the 6th International Symposium on Wood and Pulping Chemistry, Melbourne, Australia, **1**, 579-586 (1991).

6. Two-Stage Peroxide Bleaching of Eucalypt SGW with Aluminium and Metal ion Catalysts.

G.C. Hobbs, J. Abbot, J. Pulp Paper Sci., Submitted (1992).

7. The Influence of Magnesium and Manganese on Alkaline Peroxide Bleaching of Pinus Radiata TMP.

J. Abbot, D.G. Brown, G.C. Hobbs, I.J. Jewell, P.J. Wright, Proceedings of the 1991 Appita Conference, **1**, 223-230 (1991) and also Appita, **45(2)**, 109-112 (1992).

8. The Role of Radical Species in Peroxide Bleaching Processes.

G.C. Hobbs and J. Abbot, J. Wood Chem. Technol., Submitted (1992).



**Peroxide Bleaching Reactions under Alkaline and Acidic Conditions.**

G.C. Hobbs and J. Abbot, *J. Wood Chem. Technol.*, **11(2)**, 225-246 (1991).

## PEROXIDE BLEACHING REACTIONS UNDER ALKALINE AND ACIDIC CONDITIONS

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### ABSTRACT

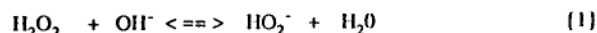
An examination of previously reported kinetic expressions describing peroxide bleaching of wood pulp under alkaline conditions reveals that the overall process can be considered as a combination of two parallel reaction routes. The first route corresponds to a reaction involving direct participation of the perhydroxyl anion in chromophore elimination. This mechanism can be identified with the classical explanation for peroxide bleaching. The second route can be associated with reactions in which chromophores are eliminated through the action of free radical intermediate species. New experimental evidence is presented to show that processes catalysed by transition metal ions can lead to enhancement of bleaching. A two stage peroxide bleaching sequence, initially under acidic conditions in the presence of chromium, followed by alkaline conditions produces an acceleration in bleaching rate, without significant additional consumption of peroxide.

### INTRODUCTION

Alkaline hydrogen peroxide is used extensively for bleaching of mechanical pulps (1-6). Although the relative proportion of mechanical pulp bleached with peroxide (approximately 8%) is significantly smaller than that bleached with hydrosulfite (7), this proportion is expected to increase. Hydrogen peroxide is also used under alkaline conditions during production of fully bleached chemical pulps (8). A peroxide stage is often used as the final stage after a conventional multistage

bleaching sequence (8) when several extra points of brightness are required. With increasing environmental concerns, there has also been recent interest in the possibility of replacing chlorinated reagents with hydrogen peroxide during production of bleached chemical pulps (9,10).

For many years the action of alkaline hydrogen peroxide as a bleaching agent has been explained through the action of the perhydroxyl anion  $\text{HO}_2^-$  (1,2,5), which can be produced according to the equation:



It was believed that this anion was the principal active species involved in the elimination of chromophores in lignin structures (1,2,5). This explanation is consistent with the observation that bleaching activity is generally enhanced by increasing the pH, up to approximately pH 11 (1). Decreased bleaching efficiency at higher pH levels can be explained on the basis of reactions leading to increased peroxide decomposition, particularly those involving the catalytic effects of transition metal ions (11-13). It is also believed that at high pH levels competing reactions producing new chromophores become important (1), giving rise to the "alkali darkening" effect (13).

During the past decade the bleaching action of peroxide has been an active area for research, with many workers concluding that these systems are much more complex than once thought. In particular, it is now believed that various radical species including  $\text{OH}^\cdot$  and  $\text{O}_2^\cdot$  can participate in chromophore elimination (14-17). Furthermore, there has been consideration of possibilities for bleaching processes over a much wider range of pH conditions than used in conventional peroxide bleaching, including neutral and acidic conditions (19-21). In the present work we have examined parallel pathways for peroxide bleaching using a range of pH conditions. We have also undertaken further experimental work aimed at providing additional evidence for this dual mechanism, and discussed our results in the context of the literature pertaining to active species in peroxide bleaching.

There have been two basic approaches to formulating models to simulate the kinetics of alkaline peroxide bleaching (6,22-26). One approach is to relate brightness increase to variables such as initial pH and peroxide charge, temperature, stock concentration etc. (6,26). This type of formulation may be useful in predicting final brightness of a pulp using a given set of conditions, particularly under mill

conditions. The other type of kinetic formulation can be closely associated with the approaches of standard chemical kinetics. In this case, too, kinetic expressions must also be regarded initially as empirical expressions. However, these expressions should reflect the net result of many concurrent elementary processes which occur during bleaching. By analysis of such expressions, particularly if they are formulated directly in terms of the concentrations of the active species, a better understanding of mechanisms involved should be achieved. We have therefore also attempted to further analyse kinetic expressions reported in the literature (22-25) to show how these can be reconciled with our observations concerning bleaching mechanisms.

### EXPERIMENTAL

Hydrogen peroxide (30%) and sulfuric acid (98%) were obtained from Ajax Chemicals. Chromium(III) nitrate (99%), DTPA (97%) and potassium hydroxide (99.99%) of semiconductor purity were supplied by Aldrich Chemicals. Semiconductor grade potassium hydroxide was used as the source of alkali in these studies as this introduces very low levels of transition metal impurities (27,28).

All bleaching studies were performed in polyethylene reaction vessels maintained at 50°C in a constant temperature water bath. Blocks of *Eucalyptus Regnans* wood were soaked in Milli-Q water for three days prior to grinding. The wood was ground in the presence of dilute aqueous sodium hydroxide, using a small scale grindstone at Australian Newsprint Mills, Boyer, Tasmania. The pulp was filtered to increase the consistency from 1.5% to approximately 20% and stored at 4°C until used.

Bleaching experiments were performed by adding sufficient *E. Regnans* pulp to a solution prepared by adding the required amount of hydrogen peroxide, chromium nitrate and acid or alkali (for pH control) as required to give a total volume of 500 mL with addition of Milli-Q water (26-27). All experiments were carried out at 1% pulp consistency and the solutions were stirred (29) throughout the bleaching runs. For bleaching under acidic conditions the pH was adjusted to 6.0 with either potassium hydroxide or sulfuric acid. After the prescribed time, sufficient potassium hydroxide was added to give a pH of 11.0 for the alkaline bleaching phase. The acidic treatment was performed for 30 minutes and followed by an alkaline phase for 30 - 120 minutes.

Chelated pulps were prepared by treating the pulp with 0.2% DTPA (on o.d. pulp) at 2% consistency for 15 minutes, then filtering and washing the pulp thoroughly.

Iodometric determinations of hydrogen peroxide were performed before the pulp was added, and to the initial filtrate, at the completion of the bleaching run. After addition of acidified potassium iodide and a few drops of ammonium molybdate solution, the liberated iodine was titrated against sodium thiosulfate solution (30). The initial concentration of hydrogen peroxide was 0.10M.

The brightness (%ISO) of the handsheets prepared were then measured using a Zeiss Elrepho with a 457nm filter. Blanks were regularly prepared to monitor any changes in the original pulp with storage time and to allow brightness gains to be calculated.

## RESULTS AND DISCUSSION

### Kinetic Models

Kinetic phenomena during peroxide bleaching of wood have been much less extensively reported than for many other important reactions, particularly alkaline pulping processes (31-33). Several recent studies (22-25) have considered kinetic behaviour during alkaline peroxide bleaching of mechanical pulps. Kinetic expressions obtained under conditions of constant concentrations of peroxide and alkali, usually obtained at low consistency, are most appropriate to a consideration of reaction mechanisms. Under such conditions the rate of removal of chromophores has been described by the expression:

$$\frac{-d[C_k]}{dt} = k [H_2O_2]_{tot}^a [OH^-]^b [C_k]^c \quad (2)$$

where  $[C_k]$  = concentration of chromophores  
 $[H_2O_2]_{tot}$  = total concentration of peroxide  
 $[OH^-]$  = hydroxide ion concentration

It has been reported (22-25) that the orders of the reaction had the following values: a (1.0), b (0.3 - 0.5) and c (4 - 5). Specific values were found to depend on the particular pulp studied. Although this expression has been derived for conditions of low consistency and constant concentrations of reactants, it has also been applied to typical bleaching situations found for mill conditions (4,34).

Many of the difficulties with interpretation of this type of kinetic expression are identical to those encountered when considering expressions describing alkaline pulping processes (31-33). These include the heterogeneous nature of the reaction, uncertainties in the importance of diffusion processes and questions regarding the validity of defining species within the lignin macromolecules on a molar concentration basis (33). However, accepting these possible limitations, it is possible to proceed with an analysis of this kinetic expression.

The high apparent order of reaction with respect to chromophore concentration would be expected to occur for a set of chromophores with a wide variation in susceptibility to peroxide bleaching. High apparent orders with respect to lignin during pulping and bleaching processes have been discussed previously (32,33). This effect is similar to that found for other heterogeneous systems involving complex components, as often encountered for processes of industrial importance. For example, during cracking of hydrocarbons, while simple reaction orders are found for single components (35) high reaction orders are calculated applying a kinetic model to complex mixtures (gas-oils) containing a wide diversity of chemical structures with different reactivity (36).

The dependence on the rate of chromophore elimination in equation (2) is expressed in terms of the total peroxide concentration, which remains constant during the reaction and is given by

$$[H_2O_2]_{tot} = [H_2O_2] + [HO_2^-] \quad (3)$$

where  $[H_2O_2]$  and  $[HO_2^-]$  are the concentrations of undissociated hydrogen peroxide and perhydroxyl anion respectively. As these species probably differ significantly in their activity in bleaching processes, and many studies have suggested that the presence of the anion has the dominant influence, we have rearranged equation (2), taking values of a, b and c as 1.0, 0.5 and 5.0 respectively, and using the relationships (22):

$$\frac{[\text{H}^+][\text{HO}_2^-]}{[\text{H}_2\text{O}_2]} = K_a = 10^{-11} \quad [4]$$

$$[\text{H}^+][\text{OH}^-] = K_w = 10^{-14} \quad [5]$$

to give the following kinetic expression:

$$\frac{-d[\text{C}_k]}{dt} = k ([\text{OH}^-]^{0.5} + 10^{-3}/[\text{OH}^-]^{0.5}) [\text{HO}_2^-] [\text{C}_k]^5 \quad [6]$$

Equation [6] shows that the rate of chromophore elimination is directly proportional to the concentration of perhydroxyl anions. The dependence of the rate on alkalinity of the solution is a more complex function, however, consisting of the sum of two terms. The first term increases with alkalinity while the second decreases with increasing pH of the medium. Fig 1a shows the behaviour of the two components of this expression as the pH is changed.

This formulation can be interpreted by assuming chromophore elimination can arise through two parallel pathways following different mechanisms and hence

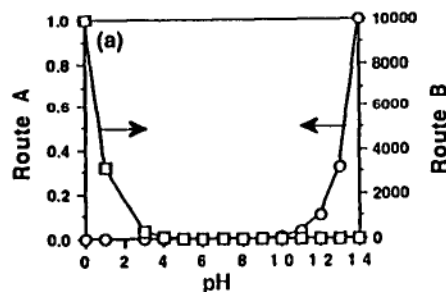


FIGURE 1a. Plots of the two pH dependent terms of the rate expression  $([\text{OH}^-]^{0.5} + 10^{-3}/[\text{OH}^-]^{0.5})$  against pH. Rates have been calculated based on the appropriate concentration of hydroxide ion.

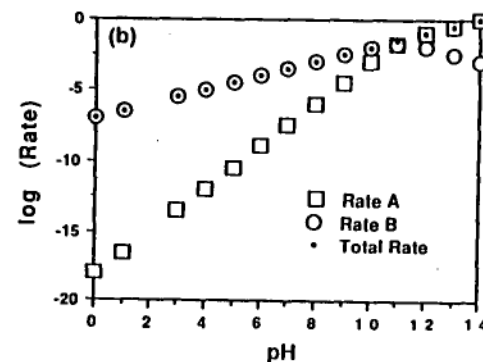


FIGURE 1b. Logarithmic plot of the two components of the rate expression  $([\text{OH}^-]^{0.5} + 10^{-3}/[\text{OH}^-]^{0.5}) [\text{HO}_2^-]$  and the total rate as the pH is varied. Rates have been calculated based on the appropriate concentration of hydroxide ion and using  $pK_a = 10^{-11}$  for  $\text{H}_2\text{O}_2$ .

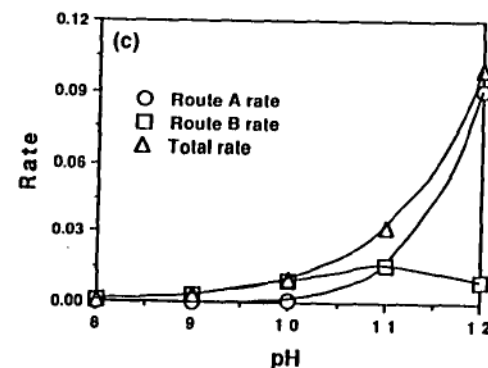


FIGURE 1c. Plots of the two components of the rate expression as in Figure 1b, and the sum of the two rates in the pH range 8-12. Rates have been calculated based on the appropriate concentration of hydroxide ion and using  $pK_a = 10^{-11}$  for  $\text{H}_2\text{O}_2$ .

leading to distinct kinetic behaviour. Route A is favoured by the presence of  $\text{OH}^-$  and  $\text{HO}_2^-$ , while route B is favoured by the presence of  $\text{HO}_2^-$  and  $\text{H}^+$ . Fig 1b shows the variation in the in the two components of the expression  $([\text{OH}^-]^{0.5} + 10^{-3}/[\text{OH}^-]^{0.5})[\text{HO}_2^-]$  as the pH is varied. A small magnitude is associated with both components under neutral and acidic conditions. Under alkaline conditions the rate for route A increases with pH, while a maximum rate is observed for route B at approximately pH 11. It is apparent that, according to this analysis, both routes are of importance in the pH range 8 - 12 normally encountered in conventional peroxide bleaching (Fig 1c), with route A dominant at  $\text{pH} > 11$  and route B dominant at  $\text{pH} < 11$ . At pH 11.0 which would be a typical initial pH value in peroxide bleaching the relative contribution from the two routes would be very similar.

#### Mechanisms and Active Species

##### Route A

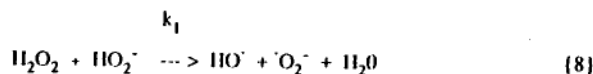
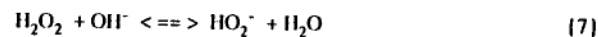
The classical explanation for the action of alkaline hydrogen peroxide is given in terms of the perhydroxyl anion as the active species (1,8). This anion is thought to act as a nucleophile, preferentially attacking centres of low electron density in the lignin structure (14). These reactions would include addition of the perhydroxyl anion to a double bond in a conjugated structure derived from a quinone methide intermediate at the  $\text{C}_2$  position of the side chain, at unsubstituted positions in the ring (14) or at the carbonyl group (15). Addition to carbonyl groups in the alpha position of the side chain has also been suggested (9). Most mechanisms presented to illustrate these types of process involve a series of sequential steps, some of which may depend on the presence of hydroxide ions, either during formation of a quinone methide structure (9), or during breakdown of a perhydroxyl intermediate (15).

It would appear reasonable to identify this type of mechanism with route A in our kinetic model, where the rate of chromophore elimination depends on  $[\text{OH}^-]^{0.5}$ ,  $[\text{HO}_2^-]$  and  $[\text{C}_k]^{0.5}$ . The appearance of three concentration terms in the rate expression and the non-integer order of the hydroxide ion is consistent with the proposal of a sequential mechanism, in which the perhydroxyl anion and the hydroxide ion interact with the chromophore in different steps of the overall mechanism.

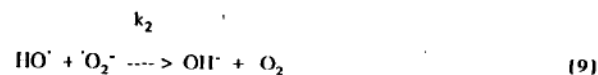
It is apparent that the predicted bleaching rate via route A would increase continuously with pH, so that the total rate of bleaching would not exhibit a maximum value. Most bleaching studies have been reported under conditions where the peroxide concentration falls as the reaction progresses, and in most cases (1) a maximum bleaching rate is found in the range pH 11-12. This could be attributed to an increased rate of peroxide decomposition at high pH levels (5). However, a maximum in bleaching rate is also observed at approximately pH 11 when the peroxide charge is maintained at a constant level throughout (23). This has been explained by the alkali darkening effect, which has been attributed to competing alkali induced creation of new chromophores at high pH levels.

##### Route B

It has been known for many years that decomposition of aqueous hydrogen peroxide to produce molecular oxygen can occur through free radical intermediates (21), particularly when the process is catalysed by the presence of transition metal ions (21). Those processes have traditionally been regarded as detrimental to peroxide bleaching efficiency, leading to loss of the bleaching agent. Consequently, additives such as sodium silicate, DTPA and magnesium salts are routinely incorporated into bleaching systems to retard decomposition (1,11). During the past decade, however, there has been an increasing awareness that free radicals derived from peroxide decomposition may, in fact, play an important role in the bleaching reactions of wood pulp (14-17,37,38). In the absence of metal ion catalytic species, hydroxyl and superoxide radicals can be produced as follows (39):



Taking equations (7) and (8) as the principal route to generation of free radicals, and including a termination step (40):



we have a simple overall mechanism for decomposition of hydrogen peroxide to produce molecular oxygen. The final step in which two free radicals combine is very fast (40) compared to the overall rate of reaction (41). Assuming that equilibrium has been established according to equation (7) and  $k_2 \gg k_1$  the steady state concentration of free radicals (42) established will depend on the pH of the solution. The kinetic behaviour of this system can be modelled by computer methods (31) using a dynamic simulation program to give a profile of the variation in steady state total free radical concentration with pH as shown in Fig 2a. It is apparent that this profile has a maximum at approximately pH 11, and is similar to that describing the magnitude of route B in Fig 1b. These distributions can also be compared with Fig 2b, which shows the reported (17) variation in rate constant with pH for oxidation of alpha-methyl syringyl alcohol with hydrogen peroxide at 30°C. The rate of alkaline peroxide oxidation for this lignin model compound also exhibits a maximum at approximately pH 11, and the mechanism for this process has been discussed in terms of free radical intermediates derived from hydrogen peroxide (17).

Consequently, it is proposed that the generation of free radical species which can interact with chromophores in the lignin structure give rise to route B in the kinetic model. A number of studies have concluded that it is the hydroxyl radical rather than the superoxide radical that is active in reactions with lignin (21,43-45). The hydroxyl radical is a strong oxidant (38) and is thought to add to aromatic rings in the lignin structure as an electrophile (14).

In the presence of transition metal ions which can catalyse peroxide decomposition we might expect the steady state concentrations of free radical species would be increased, and this has indeed been observed (42). Furthermore, it has been found that the position of the maximum rate occurs at a pH which depends on the metal present under both homogeneous (11) and heterogeneous (46,47) conditions. The metal ions most commonly present in wood pulp which are also active towards peroxide decomposition are manganese, copper and iron. These ions have been found to produce maxima in the pH range 9-12 (42) as illustrated for manganese in Fig 3a. This range includes the pH at which maximum brightness is usually observed for peroxide bleaching (15). Other metal ions, not normally present in pulp in high concentrations, can exhibit maxima under neutral or acidic conditions as for example with cobalt and chromium (11). Fig 3b shows that for chromium the maximum initial activity occurs at pH 5.8. This observation is useful,

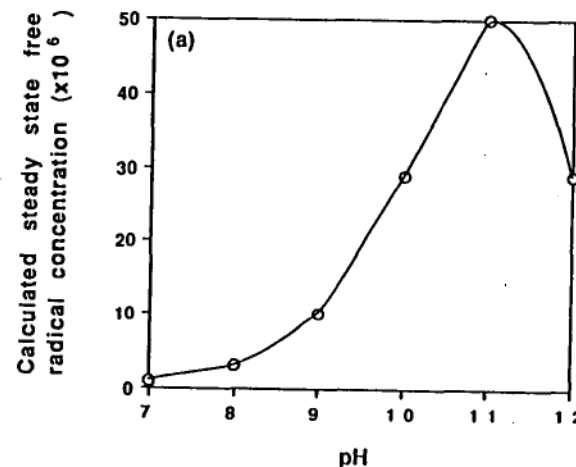


FIGURE 2a. Plot of the variation of steady state free radical concentration with pH. Values calculated using TUTSIM dynamic simulation program (31) with  $k_1 = 10^{-3} \text{ s}^{-1}$  and  $k_2 = 10^6 \text{ s}^{-1}$ .

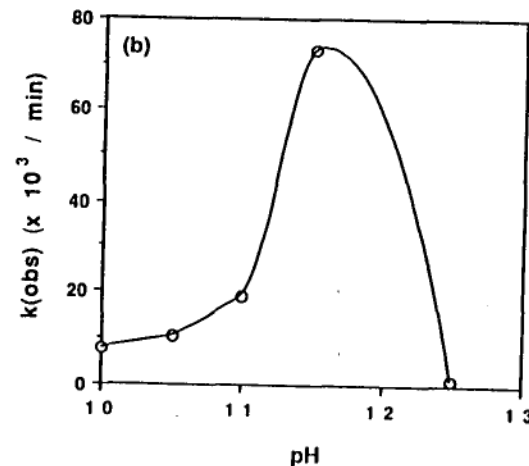


FIGURE 2b. Plot of the variation in the rate constant for the oxidation of alpha-methyl syringyl alcohol by hydrogen peroxide as a function of pH (17).

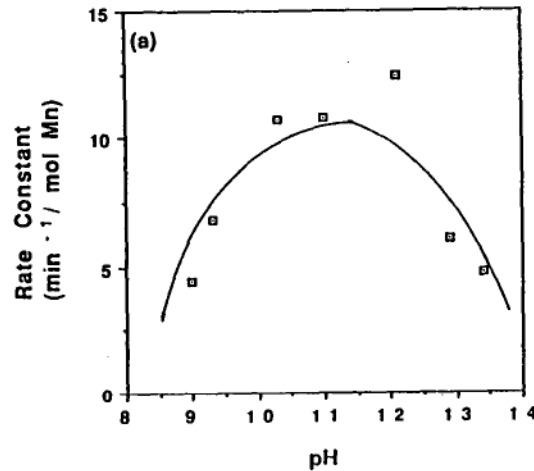


FIGURE 3a. Plot of the variation in the rate of decomposition of hydrogen peroxide in the presence of manganese against pH at 20°C. Initial concentration of hydrogen peroxide 0.10M; initial concentration of manganese nitrate  $4.4 \times 10^{-6}$ M.

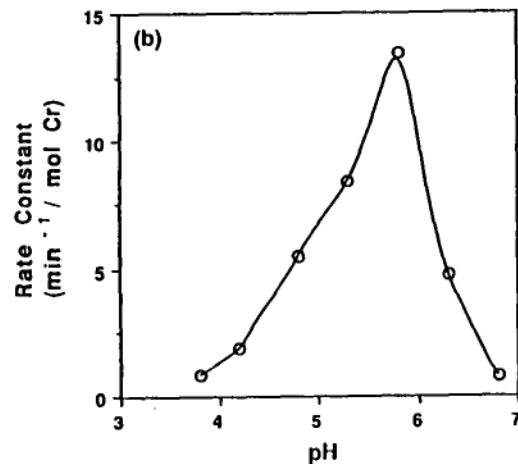


FIGURE 3b. Plot of the variation in the rate of decomposition of hydrogen peroxide in the presence of chromium against pH at 20°C. Initial concentration of hydrogen peroxide 0.10M; initial concentration of chromium nitrate  $2.5 \times 10^{-4}$ M.

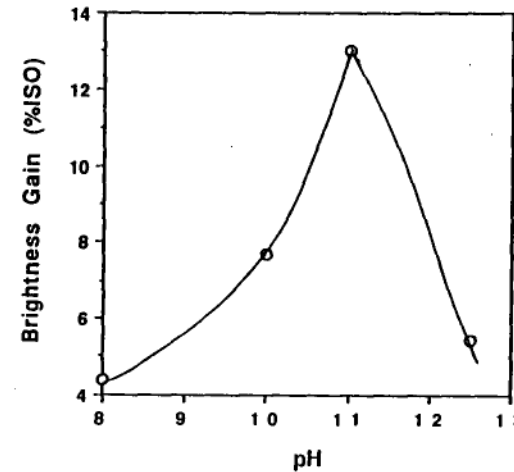


FIGURE 4. Plot of brightness gain against pH for samples of *E. Regnans* bleached for 120 minutes at 1% consistency, 50°C, with 30% peroxide (w/w on o.d. pulp). Initial brightness of pulp : 53.2 (%ISO).

as it may enable us to expose pulp samples to high concentrations of radical species under conditions where the perhydroxyl ion concentration is low, and the contribution from route A should be very small.

Several recent studies have discussed the possibility of catalytic effects due to the presence of transition metal ions leading to increased rates of delignification with alkaline hydrogen peroxide (12,17). Other investigations have shown that acidic peroxide treatment of pulp can have beneficial effects (48-53), and there are indications that these may be promoted by the presence of metal ions acting as catalysts (50). These observations, coupled with our interpretations of kinetic phenomena led us to undertake further bleaching studies under both acidic and alkaline conditions, and the results of these observations are described below.



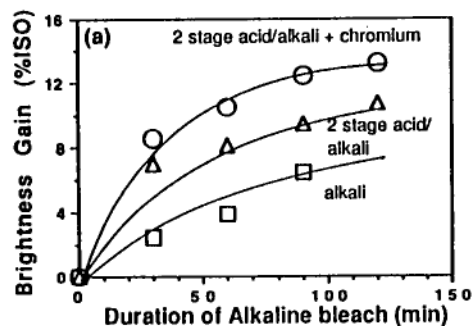


FIGURE 5a. Comparison of one and two stage bleaching processes showing the brightness gain for *E. Regnans* bleached at 1% consistency, 50°C, with 30% peroxide (w/w on o.d. pulp) under various conditions; Initial brightness of pulp : 56.0 (%ISO).

E) 30 minute acid bleach with  $2.5 \times 10^{-4}$  mol/L chromium nitrate followed by an alkaline bleach at pH 11.0.

C) 30 minute acid bleach with no added chromium followed by an alkaline bleach at pH 11.0.

G) alkaline bleach at pH 11.0 (no acidic treatment).

#### Bleaching Studies with *Eucalyptus Regnans*

Experimental studies were undertaken with *Eucalyptus Regnans* groundwood. Bleaching was carried out at 50°C at constant pH levels using 1% consistency and 30% hydrogen peroxide (on o.d. pulp). Under these conditions the peroxide concentration did not decrease to low residual levels during the bleaching runs, but it was possible to measure the amount of peroxide consumed. Fig 4 shows the influence of pH on the brightness of the pulp after bleaching for a period of 2 hours in a single stage alkaline process. For single stage bleaching at pH 6.0 there was no significant increases in brightness of the pulp, even after 10 hours.

Fig 5a shows the increase in brightness of the groundwood pulp under alkaline conditions (initial pH 11.0) over a period of 2 hours for three different bleaching processes. The brightness increase for a standard one stage alkaline

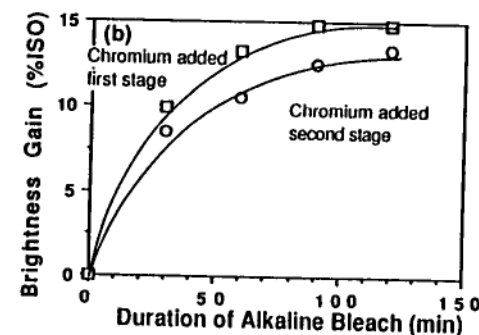


FIGURE 5b. The influence of addition of chromium during the first and second stages (conditions as Figure 5a). Initial brightness of pulp : 55.6 (%ISO).

G) 30 minute acid bleach with  $2.5 \times 10^{-4}$  mol/L chromium nitrate followed by an alkaline bleach at pH 11.0.

E) 30 minute acid bleach with no added chromium followed by an alkaline bleach with  $2.5 \times 10^{-4}$  mol/L chromium nitrate at pH 11.0.

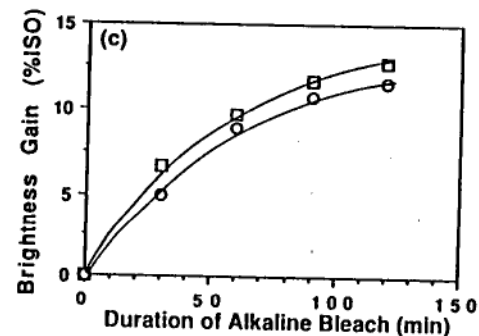


FIGURE 5c. The influence of pulp chelation on two stage acid/alkali bleaching sequence in the presence of chromium (conditions as Figure 5a). Initial brightness of pulp : 55.6 (%ISO).

G) 30 minute acid bleach with  $2.5 \times 10^{-4}$  mol/L chromium nitrate followed by an alkaline bleach at pH 11.0.

E) 30 minute acid bleach with no added chromium followed by an alkaline bleach at pH 11.0.

bleaching process gives the lowest brightness improvement at any particular time. The figure also shows the effect on brightness increase for two-stage processes with prior acid treatment of the pulp at pH 6.0, both with and without addition of a catalytic amount of chromium nitrate (1.0% on o.d. pulp). For these two stage bleaching experiments the duration of the acid treatment was 30 minutes in each case, after which the pH of the solution was adjusted to 11.0 by addition of potassium hydroxide. Fig 5a shows that the rate of brightness enhancement is increased by an acid treatment prior to alkaline peroxide bleaching at pH 11.0. The addition of chromium to the system at pH 6.0 increases the effect of the first stage acid treatment. Our results can be compared to a previously reported study in which a two stage peroxide bleaching sequence was used for brightening an oxygen bleached hardwood kraft pulp (50). In that study compounds of tin, vanadium or titanium were introduced during the first stage under acidic conditions at pH 4-6, followed by an alkaline bleaching stage. Another study (51) has described an improved bleaching response with a two stage acid/alkali peroxide treatment without addition of a catalyst.

Figure 5b shows that the chromium is active in the first stage of the two stage bleaching sequence. When chromium is added to the alkaline stage of a two stage bleaching sequence significantly less brightness gain is achieved. Comparing these curves with figure 5a, it is apparent that when chromium is present only in the alkaline stage, the response is approximately the same as when no chromium is added, thus further supporting the view that the chromium is having an effect during the first stage of the bleaching sequence.

Figure 5c shows the influence of chelating and washing the pulp prior to a two stage acid/alkali bleaching sequence in the presence of chromium. Table 1 shows that this procedure has a significant effect on reducing the levels of transition metal ions in the pulp. The results in figure 5c show that there is a reduced brightness enhancement when metal ions are removed from the pulp, and it appears that the effects of chromium and the other transition metal ions in the pulp are additive. We have also shown that the removal of transition metal ions from *Pinus Radiata* TMP by chelation and washing reduces the effectiveness of two stage acid/alkali peroxide bleaching (52).

It would appear that the acidic peroxide treatment results in changes in the lignin structure promoted by the species formed by the catalytic decomposition of hydrogen peroxide (18,54). This can happen even when no catalyst is introduced

TABLE 1. Metal ion content of Pulps used in this work.

Wood type	Metal ion (ppm) <sup>1</sup>		
	Iron	Manganese	Copper
<i>Eucalypt</i> SGW	32	8	72
Chelated <i>Eucalypt</i> SGW	32	1	32

1) Concentration determined by atomic absorption after digestion of pulp.

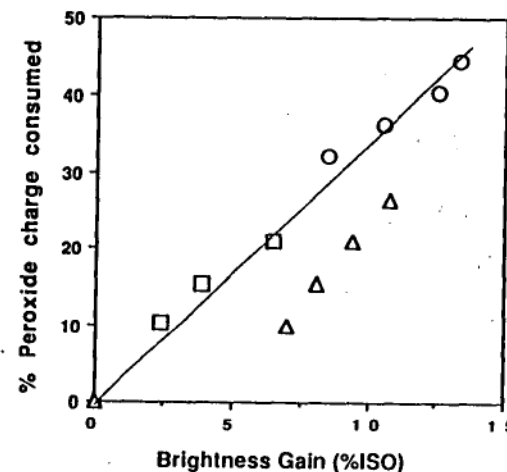


FIGURE 6. Plot of the peroxide consumption against brightness gain for pulps bleached at 1% consistency, 50°C and 30% peroxide (on o.d. pulp) under various conditions:

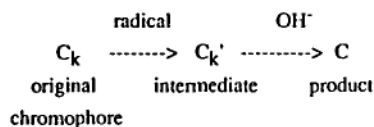
E) 30 minute acid bleach with  $2.5 \times 10^{-4}$  mol/L chromium nitrate followed by an alkaline bleach at pH 11.0.

G) alkaline bleach at pH 11.0 (no acidic treatment).

C) 30 minute acid bleach with no added chromium followed by an alkaline bleach at pH 11.0.

(55), as metal ions from the wood itself may be active. A number of studies have indeed shown that lignin structures are reactive under acidic conditions (14,20,48,49), most likely through processes involving free radicals (14), although little enhancement in brightness may be achieved (19) as expected from our kinetic analysis. We can regard the initial product of reaction between a radical species and a lignin chromophore as an intermediate, the formation of which does not in itself improve pulp brightness. The rate of formation of the intermediate will depend primarily on the concentration of free radical species as shown in Fig 2b.

In order to observe an increase in brightness a second step is required in the overall mechanism to eliminate the chromophore, which depends directly or indirectly on the presence of the hydroxide ion :



Under acidic conditions where  $[\text{OH}^-]$  is low the intermediate is formed, and its production is enhanced by the presence of catalysts which promote radical formation. Under alkaline conditions, this intermediate species may again be produced, but it rapidly reacts in the presence of hydroxide ions leading to elimination of the chromophore.

Fig 6 shows the consumption of hydrogen peroxide plotted against the increase in pulp brightness for pulps bleached by a one stage alkaline process (initial pH 11.0) and the two stage acid/alkali process both in the presence and absence of chromium. Comparing the single stage alkaline bleach and the two stage bleach in the presence of chromium, it is apparent that the brightness gain achieved in each case is approximately proportional to the amount of peroxide consumed. It is also clear that use of a two stage process without added chromium can increase the efficiency of bleaching under the conditions employed in this study.

### CONCLUSION

This study has provided further evidence for a dual mechanism for chromophore elimination during peroxide bleaching. Analysis of a previously

reported kinetic expression leads to the conclusion that the two parallel routes for bleaching correspond to: [1] a reaction which depends upon the direct participation of the perhydroxyl anion; [2] a reaction in which free radical species participate in chromophore elimination. Our analysis shows that both routes are important at pH levels normally encountered in conventional bleaching of wood pulp with hydrogen peroxide. Although the rate of chromophore elimination is very slow under acidic conditions, reactions occur which render the chromophores present more susceptible to subsequent reaction under alkaline conditions. Formation of these reactive intermediates is promoted by the formation of free radical species produced through catalytic decomposition of peroxide by transition metals such as chromium.

### ACKNOWLEDGEMENT

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Two-Stage Peroxide Bleaching of Eucalypt SGW with Chromium Catalysts.

G.C. Hobbs and J. Abbot, J. Wood Chem. Technol., **11(3)**, 329-348 (1991).

## TWO-STAGE PEROXIDE BLEACHING OF EUCALYPT-SGW WITH CHROMIUM CATALYSTS

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### ABSTRACT

The addition of chromium nitrate to a two-stage hydrogen peroxide bleach of *Eucalypt* SGW can enhance the brightness of the pulp. It is proposed that radicals produced in the catalytic decomposition of hydrogen peroxide by chromium under acidic conditions participate in reactions which render the chromophores more susceptible to bleaching in the alkaline stage. This two-stage process, under optimised conditions, consumes no more peroxide than a traditional single stage alkaline bleach and allows the pulp to be bleached to a given brightness in a shorter time. Enhanced bleaching response was also observed for a two-stage acid/alkali peroxide bleaching sequence without the addition of chromium, and we have attributed this effect to catalytic effects of transition metal ions which occur naturally in the pulp.

### INTRODUCTION

Catalytic processes have been developed and utilised to a much less significant extent in the pulp and paper industry than in many other important chemical process industries. The reason for this may lie partly in the greater difficulty encountered in

catalyst recovery and recycling in heterogeneous systems with liquid and solid components compared to vapour/solid systems. The soda-anthraquinone pulping process<sup>1-4</sup> represents an important exception, where a catalytic process received widespread interest and has been subsequently developed through to a commercial scale. There are many reports in the literature concerning catalytic effects during bleaching of pulp, particularly with regard to the effect of transition metal ions<sup>5-10</sup>. In most cases, however, the reported catalytic influences during bleaching are considered to have a detrimental effect on overall efficiency.

For example, colloidal sulfur is thought to promote the catalytic decomposition of sodium dithionite during bleaching of mechanical pulp under acidic conditions<sup>11</sup> producing thiosulfate ions which are a major source of corrosion in paper machines<sup>11-14</sup>. Certain transition metal ions including copper and iron are found to have negative influences during both oxygen delignification<sup>5,6</sup> and bleaching with hydrogen peroxide<sup>7-10</sup> under alkaline conditions. During oxygen delignification the presence of catalytic amounts of transition metals can cause both reduction in delignification rate and loss of pulp viscosity<sup>5,6</sup>. Catalytic decomposition of hydrogen peroxide by transition metal ions is well established<sup>15,16</sup>, and can lead to loss of bleaching efficiency unless reagents such as DTPA, magnesium or sodium silicate are introduced<sup>17,18</sup>.

There are fewer reports of beneficial effects resulting from the presence of catalytic species during bleaching<sup>19-24</sup>. Introduction of manganese has been shown to accelerate delignification and reduce carbohydrate degradation in studies of oxygen delignification<sup>5,20</sup>. Transition metal species have also been shown to be effective in catalyzing oxygen delignification of residual lignin in chemical pulps<sup>21,22</sup>. Recent studies have also shown that transition metal catalysts can promote peroxide bleaching efficiency during two-stage processes, initially using acidic conditions followed by a conventional alkaline peroxide step<sup>21-24</sup>. In this study we have investigated the use of chromium catalysts in this type of bleaching sequence for a stone ground eucalypt pulp.

## EXPERIMENTAL

### Materials

Hydrogen peroxide (30%) and sulfuric acid (98%) were obtained from Ajax chemicals. Chromium nitrate (99%), magnesium nitrate (99.999%), sodium silicate

(30%) and potassium hydroxide (99.99%) of semiconductor purity were supplied by Aldrich chemicals. Semiconductor grade potassium hydroxide was used as the source of alkali as this introduces very low levels of transition metal ion impurities<sup>16,18</sup>.

### Procedures

Blocks of *Eucalyptus Regnans* wood were soaked for three days in Milli-Q water and then ground at 80°C in the presence of dilute sodium hydroxide on a small scale grindstone at ANM, Boyer. The pulp was washed with distilled water and filtered to increase the consistency from 1.5% to 20%. The pulp was then stored at 4°C until used.

Bleaching studies were carried out in polyethylene reaction vessels maintained at 50°C in a constant temperature water bath. Bleaching experiments were performed by adding the required amounts of pulp, hydrogen peroxide, chromium nitrate and acid or alkali to give a total volume of 500 mL with addition of Milli-Q water<sup>16,18</sup>. In some bleaching experiments the required amounts of sodium silicate and magnesium nitrate were added to the bleaching solution. All experiments were performed at 1% pulp consistency and the solutions were stirred<sup>25</sup> throughout the bleaching runs. The initial charge of hydrogen peroxide was 6% on o.d. pulp. For bleaching under acidic conditions the pH was adjusted to the appropriate level (generally 5.8) with either potassium hydroxide or sulfuric acid. After the prescribed time sufficient potassium hydroxide was added to adjust the pH to the level required for the second stage (generally 11.0).

Chelated pulps were prepared by treating the pulp with 0.5% EDTA (on o.d. pulp) at 2% consistency for 15 minutes then filtering and washing the pulp thoroughly before use<sup>26</sup>. Metal ions present in the original pulp and after chelation were determined by atomic absorption spectroscopy. 5.00g o.d. pulp was digested in 50 mL concentrated nitric acid and 5 mL sulfuric acid until no pulp was visible, 5 mL concentrated perchloric acid was then added and the solution heated until a clear solution was obtained. The results are given in Table 1.

Iodometric determinations of hydrogen peroxide were performed before the pulp was added, and to the initial filtrate at the completion of the bleaching run. After addition of acidified potassium iodide and a few drops of ammonium molybdate solution the liberated iodine was titrated against sodium thiosulfate solution<sup>27</sup>.



TABLE I. Metal ion content of Pulps used in this work.

Wood type	Metal ion (ppm)*		
	Iron	Manganese	Copper
<i>Eucalypt</i> SGW	32	8	72
Chelated <i>Eucalypt</i> SGW	32	1	32

\* Concentration determined by atomic absorption after digestion of pulp.

Hydrogen peroxide levels were also determined at the completion of the acidic treatment and sufficient peroxide was added to restore the level to 6% on o.d. pulp at the start of the alkaline stage.

The brightness (%ISO) of the bleached pulps were measured on a Zeiss Elrepho using a 457nm filter. Handsheets were also regularly prepared to monitor any changes in the original pulp with storage time and to allow brightness gains to be calculated. The brightness of the unbleached pulp was in the range 53-55 %ISO.

## RESULTS AND DISCUSSION

### Transition Metal Ion Catalysts

Transition metal ions are known to catalytically decompose hydrogen peroxide<sup>28,29</sup>. This catalytic decomposition is generally considered detrimental during bleaching processes due to increased consumption of peroxide and much work has been carried out to reduce the effect of the catalytically active species<sup>28-30</sup>. Traditionally the perhydroxyl anion,  $\text{HO}_2^-$ , is thought of as the active bleaching species<sup>31-33</sup>.

Transition metal catalysed decomposition of hydrogen peroxide is thought to proceed

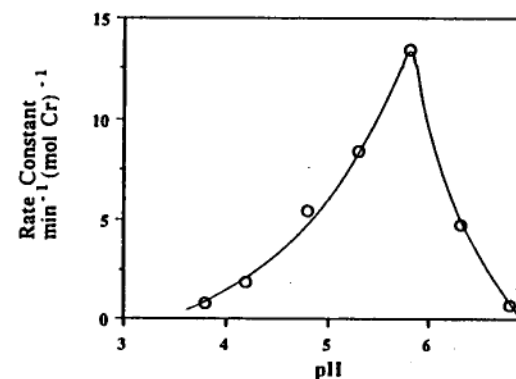


FIGURE 1. Variation in the first order rate constant with pH for decomposition of hydrogen peroxide in the presence of chromium at 20°C. Initial concentration of hydrogen peroxide 0.10M; concentration of chromium  $2.5 \times 10^{-4}\text{M}$ .

via free radical chain reactions, producing intermediate species such as  $\text{OH}^\cdot$  and  $\text{O}_2^\cdot$ , and there has been recent interest in the possible role of these active species in chromophore elimination<sup>34,35</sup>. Chromium is unusual in that the maximum decomposition rate for hydrogen peroxide in the presence of this transition metal occurs under slightly acidic conditions (at pH 5.8) as shown in Fig. 1, while the rate of decomposition is negligible at pH > 8.0. In contrast, transition metal ions including manganese, copper and iron, which are often present in pulp samples, have maximum activity under alkaline conditions<sup>36,37</sup>. This observation for the behaviour of chromium may allow the pulp to be exposed to radicals produced by the catalytic decomposition of hydrogen peroxide in a pH range where traditional bleaching is ineffective, which enables us to study effects which occur under both acidic and alkaline conditions separately.

Fig. 2 shows the effect of a two-stage peroxide treatment with chromium nitrate (0.13% Cr on o.d. pulp) initially introduced. In the first stage, the pH was maintained at 5.8, with an initial charge of 6% peroxide (on o.d. pulp). After 30 minutes the concentration of hydrogen peroxide was restored to its initial level before adding alkali to raise the pH to 11.0 in the second stage of the bleaching sequence. Curve (a) shows

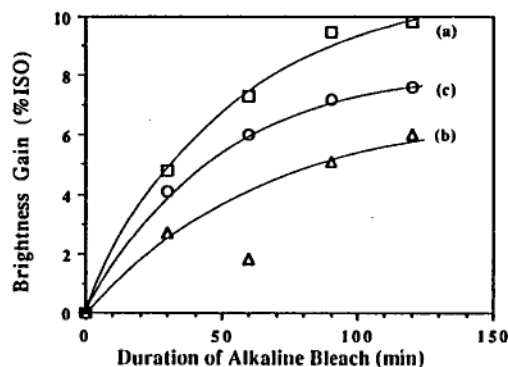


FIGURE 2. Brightness gain plotted against time of alkaline bleach (pH 11.0). (a) acidic treatment (pH 5.8) for 30 minutes with 0.13% chromium (on o.d. pulp) ( $2.5 \times 10^{-4}M$ ); (b) no acidic treatment; (c) acidic treatment (pH 5.8) for 30 minutes with no added chromium.

the increase in brightness with time during the second stage of the bleaching process, at a constant pH under alkaline conditions. This can be compared with curve (b), which corresponds to bleaching under the same conditions, but without pre-treating the pulp with acidic peroxide or introducing chromium. It is apparent that chromophore elimination occurs more rapidly for the pulp which has been subjected to the two-stage bleaching sequence. It is important to point out that no brightness gain could be detected for these pulps after only the first (acidic) stage. It would appear that even though chromophores are not eliminated by acidic peroxide treatment in the presence of chromium, the chromophores present are rendered more susceptible to subsequent removal by alkaline peroxide bleaching. Previous work<sup>24,38,39</sup> has shown that a two-stage hydrogen peroxide bleaching sequence involving an acidic stage followed by alkaline treatment can give an enhanced brightness over a conventional one stage alkaline bleach. Curve (c) in Fig. 2 shows the effect of an acidic treatment followed by an alkaline treatment without initial introduction of chromium. It is apparent that the bleaching response for this pulp under alkaline conditions is intermediate between the case where no acidic pre-treatment is applied, and that in which chromium is introduced

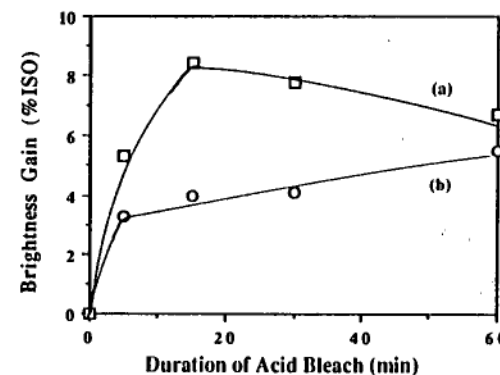


FIGURE 3. Effect of removing metal ions from the pulp prior to bleaching: (a) unchelated pulp; (b) chelated pulp. Acid stage: pH 5.8; alkaline stage: pH 11.0, 120 minutes.

with acidic peroxide. These effects can be explained on the basis of other metal ions which occur naturally in the wood, or have been introduced during pulp production. Manganese, iron and copper are found to be typically present in mechanical pulps<sup>7,26</sup>, as shown in Table I for our SGW eucalypt pulp. We believe that the presence of these transition metal ions can induce effects on the chromophores in the presence of acidic peroxide similar to those produced in the presence of chromium. The total effect seen (curve (a)) in Fig. 2 can therefore be attributed to the combined effects of chromium and the other metal ions in the pulp.

Evidence for the effect of the residual metal ions can be obtained by bleaching experiments with chelated pulps. Table I shows that chelation with DTPA removes most of the manganese initially present in the pulp, and also produces a significant reduction in copper content. The amount of iron present, however, is little influenced by the chelation procedure, and these results are consistent with previous reports<sup>26</sup>. Fig. 3 shows that the brightness gain for two-stage acid/alkali bleaching in the presence of chromium is significantly reduced using the chelated pulp compared to an unchelated pulp. It can be concluded that the presence of manganese and copper, and possibly other metal ions initially present in the pulp, contribute to the observed effects on brightness enhancement for the two-stage bleaching sequence.

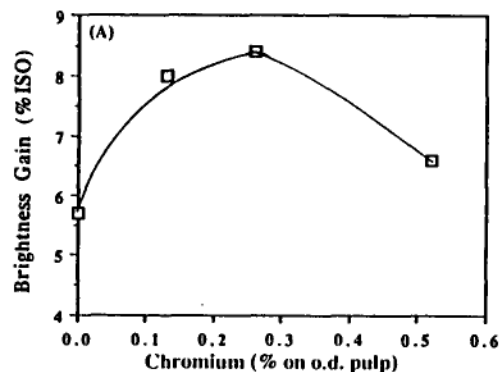


FIGURE 4A. The effect of varying the dose of chromium catalyst on the brightness gain. Acid stage: 15 minutes, pH 5.8; Alkaline stage: pH 11.0.

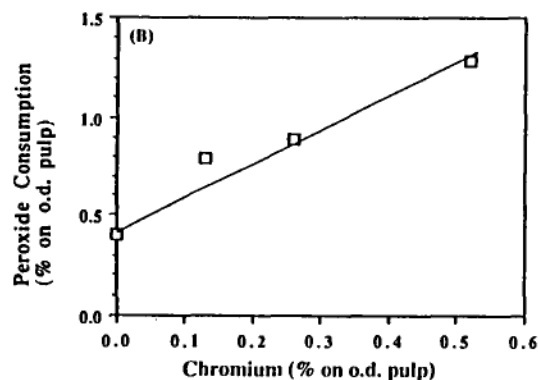


FIGURE 4B. Effect of varying the amount of chromium on the peroxide consumption after the first (acidic) stage. Acid stage: pH 5.8, 15 minutes.

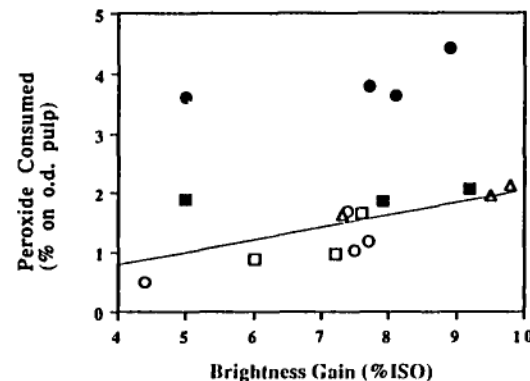


FIGURE 5. Plot showing the correlation between peroxide consumed and the brightness gain. Acid stage: 30 minutes, pH 5.8; alkaline stage: 30 - 120 minutes, pH 11.0. □; 0% Cr added, △; 0.13% Cr added, ■; 0.26% Cr added, ●; 0.52% Cr added, ○; single stage alkaline bleach only, no added Cr.

#### Optimization of Conditions and Peroxide Consumption

Fig. 4A shows the effect of varying the amount of chromium introduced prior to the two-stage acid/alkali peroxide bleaching sequence. It is clear that there is an optimum range for addition of chromium to achieve maximum brightness gain of the eucalypt pulp. This effect may be attributed to the additional reduction in peroxide concentration under acidic conditions as the chromium concentration is increased (Fig. 4B). At the highest level of chromium addition shown, about 25% of the initial peroxide charge was consumed at the end of the first stage. The presence of high levels of chromium also leads to excess total consumption of peroxide to reach a given level of brightness after the alkaline bleaching stage. Fig. 5 shows that addition of chromium beyond the optimum range results in increased total consumption of peroxide without a proportional increase in pulp brightness. At lower chromium levels, peroxide consumption is approximately proportional to brightness gain for both the two-stage acid/alkali bleaching sequence and single-stage alkali treatment.

With the conditions used in this study (1% consistency, 6% hydrogen peroxide on o.d. pulp, 50°C, no stabilisers) our experiments showed that a maximum brightness

TABLE 2. Time to Reach a Brightness Gain of 8 Points.

wt% Cr (on o.d. pulp)	Time (min)			Peroxide* Consumed (% on pulp)	Brightness Gain/ Weight Peroxide (ISO/%)	Bleaching Efficiency* (ISO/%/hour)
	acid	alkali	total			
0	-	170	170	2.08	3.83	1.35
0	30	120	150	1.74	4.59	1.84
0.13	15	120	135	1.58	5.03	2.24
0.26	30	60	90	1.86	4.30	2.87
0.52	30	60	90	3.64	2.19	1.46

Bleaching experiment at 50°C, 1% consistency. Acid stage: pH 5.8, initial peroxide charge 6.0% on o.d. pulp. Alkaline stage: pH 11.0, initial peroxide charge 6.0% on o.d. pulp. Initial brightness of eucalypt pulp 54.0.

\* Efficiency = Brightness Gain / % peroxide consumed (on o.d. pulp) / time (hours)

\* It should be noted that, due to the restoration of the peroxide charge to its initial level after the first stage of the two stage bleaching process, the peroxide charge is higher than 6.0% in some cases.

gain of approximately 10 %ISO can be achieved for this eucalypt pulp. The more rapidly this level is reached, and the smaller the amount of peroxide consumed, the more efficient will be the process. Table 2 shows that the two-stage acid/alkali treatment enables a target brightness increase of 8 units to be reached in less time compared to a single stage alkali process while consuming a similar amount of peroxide.

Fig. 6A shows the effect on brightness gain resulting from varying the pH of the first stage of the two-stage bleaching sequence. Both in the presence and absence of chromium a minimum response is observed in the pH range 4-5, whereas at pH 7 the response is similar both with and without chromium. The lower curve (b) can be attributed to the effects of metal ions in the original pulp (e.g. manganese and copper). Fig. 6B shows the effect of chromium alone, obtained by taking the difference between

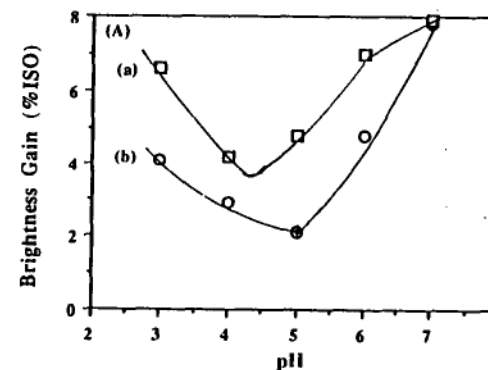


FIGURE 6A. The effect of varying the pH of the acidic stage for (a) 0.26% chromium (on o.d. pulp) added; (b) no added chromium. Acid treatment: 30 minutes; alkaline stage: pH 11.0, 120 minutes.

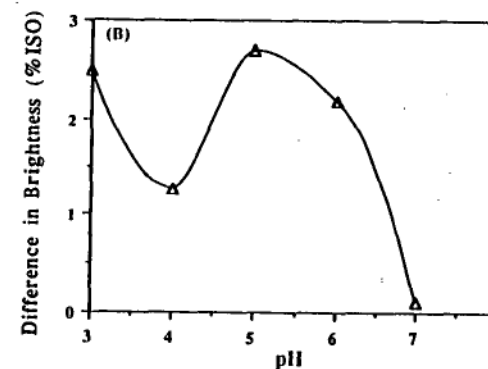


FIGURE 6B. Difference in the brightness gain after the alkaline stage (pH 11.0, 120 minutes) for the pulps bleached in Fig. 6A.

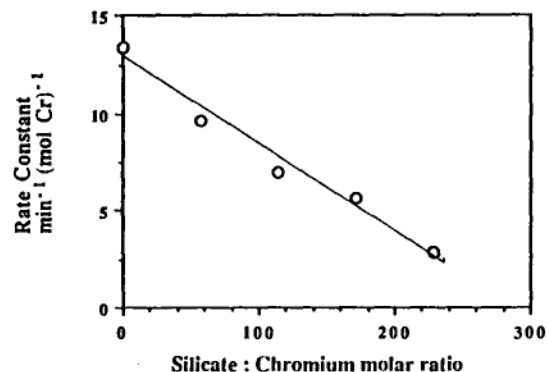


FIGURE 7. The effect of varying the chromium : silicate molar ratio on the rate of decomposition of hydrogen peroxide. Initial hydrogen peroxide concentration 0.10M, 20°C, chromium concentration of chromium  $2.5 \times 10^{-4}\text{M}$ .

the two curves in Fig. 6A. Fig. 6B shows a maximum in the pH range 5-6, and this may be compared with Fig. 1, which also shows a maximum in this range for peroxide decomposition catalyzed by chromium. This apparent correlation between catalyzing peroxide decomposition under acidic conditions and inducing brightness gain in the subsequent alkaline step may be significant. The result may show that it is the products from catalytic decomposition of hydrogen peroxide (i.e free radicals) which are active under acidic conditions in causing changes in the susceptibility of chromophores to subsequent alkaline peroxide treatment, where there are much higher concentrations of the perhydroxyl anion<sup>40</sup>.

There has been recent interest in the idea that free radical species, particularly the hydroxyl radical ( $\text{HO}^\cdot$ ), may indeed play an important role in peroxide bleaching, under conventional alkaline bleaching conditions as well as under acidic conditions<sup>41,42</sup>. Model compound studies with alpha-methyl syringyl alcohol, a model lignin compound, shows a maximum rate of oxidation by hydrogen peroxide at pH 11, and the mechanism for this process has been discussed in terms of free radical intermediates derived from hydrogen peroxide<sup>43</sup>. The idea that free radicals as well as the

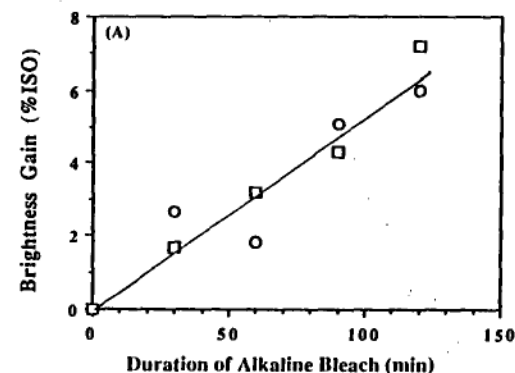


FIGURE 8A. Plot of the brightness gain against time for an alkaline bleach ( pH 11.0) with (O) no added silicate; (□) 18% silicate (on o.d. pulp) added.

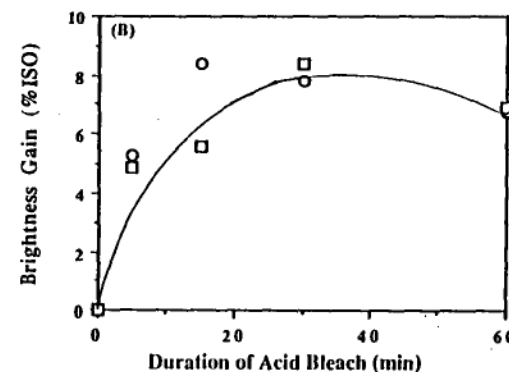


FIGURE 8B. Plot of the brightness gain against time for a two-stage bleach (Acid stage: pH 5.8; alkaline stage: pH 11.0, 120 minutes) with (O) 0.26% chromium (on o.d. pulp); (□) 0.26% chromium (on o.d. pulp) and 18% (on o.d. pulp) silicate. (Si:Cr molar ratio 114:1)

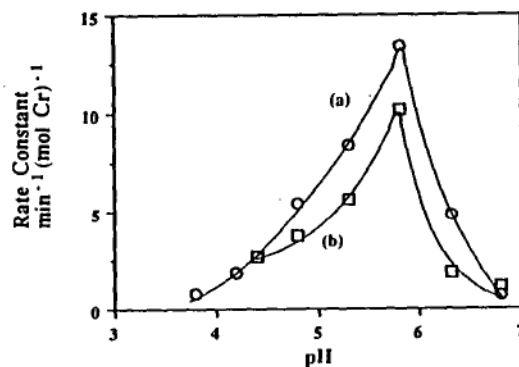


FIGURE 9. Variation in the rate of decomposition of hydrogen peroxide against pH at 20°C (a) in the presence of  $2.5 \times 10^{-4}\text{M}$  chromium; (b) in the presence of  $2.5 \times 10^{-4}\text{M}$  chromium and  $5.0 \times 10^{-3}\text{M}$  magnesium. Initial concentration of hydrogen peroxide 0.10M.

perhydroxyl anion may be active in brightness development during peroxide bleaching suggests that there may be more than one mechanism for chromophore elimination. A recent analysis of kinetic phenomena during peroxide at various pH levels was based on the assumption of two distinct mechanisms of chromophore removal, one dependent on the perhydroxyl anion concentration and the other depending on participation of free radicals<sup>24</sup>. The results of the present study also provide support for the concept of a dual mechanism for chromophore elimination.

#### Effect of Magnesium and Silicate

Both magnesium salts and sodium silicate are commonly used as stabilisers for peroxide bleaching liquors<sup>28,29,44-46</sup>. The effect of these stabilisers has been investigated in the two-stage process currently being studied. Silicate reduces the rate of hydrogen peroxide decomposition in the presence of chromium at pH 5.8 as shown in Fig. 7. Silicate is thought to retard transition metal ion catalysed decomposition of hydrogen peroxide by acting as a free radical trap<sup>47</sup>. Other studies have also concluded

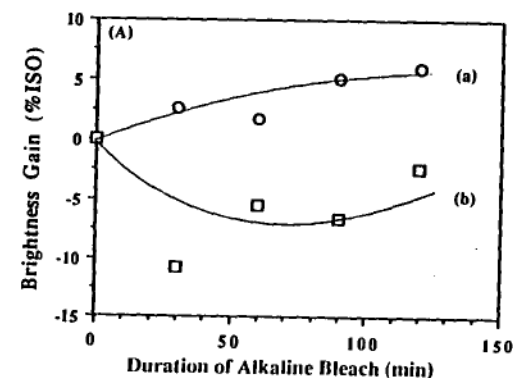


FIGURE 10A. Plot of brightness gain against time for an alkaline bleach (pH 11.0) with (a) no added magnesium; (b) 2.44 % magnesium (on o.d. pulp) added.

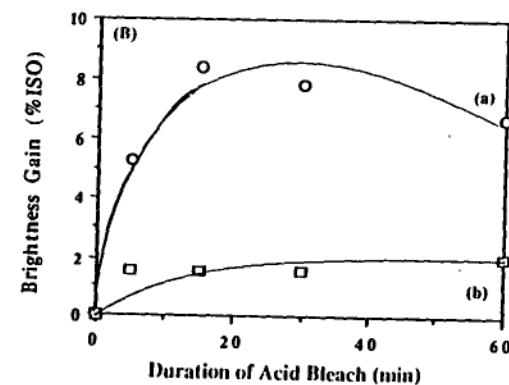


FIGURE 10B. Plot of the brightness gain against time for a two-stage bleach (Acid stage: pH 5.8.; alkaline stage: pH 11.0, 120 minutes) with (a) 0.26% chromium (on o.d. pulp); (b) 0.26% chromium and 2.44% magnesium (on o.d. pulp). (Mg:Cr molar ratio 20:1)

that sodium silicate is effective in stabilising peroxide under alkaline bleaching conditions through buffering action<sup>32</sup> and through deactivation of metal ions<sup>28</sup>. Fig. 8A shows that similar brightness gains were observed in a single stage alkaline bleach in the presence or absence of silicate, although the amount of peroxide consumed was reduced in the presence of silicate. Similar brightness gains were also observed in a two-stage process in the presence of silicate and chromium, as shown in Fig. 8B, again with slightly lower peroxide consumption.

Magnesium also inhibits the rate of chromium catalysed decomposition of hydrogen peroxide as shown in Fig. 9. In a single stage alkali bleach, magnesium, as shown in Fig. 10A, has the effect of reducing the brightness of the pulp. This is an interesting result in view of the common practice of including magnesium salts as a stabilising agent during commercial bleaching of mechanical pulps with hydrogen peroxide. The effectiveness of magnesium as a stabiliser under alkaline conditions appears to be related to the nature of the other metal ions present in the pulp. It has been shown<sup>15</sup> that addition of magnesium to solutions containing manganese ions causes a significant increase in catalytic activity towards peroxide decomposition. In contrast, addition of magnesium to solutions containing iron produces a stabilising effect<sup>16</sup>, and this has been attributed to formation of an iron-magnesium complex<sup>16</sup>. The observed loss in pulp brightness observed here on addition of magnesium cannot be explained simply on the basis of peroxide stability. However, it is likely that the nature of catalytic species present is modified by the addition of magnesium which may in turn modify the types and concentrations of decomposition products formed. Fig. 10B shows that in a two-stage process a much lower brightness is also obtained in the presence of magnesium, the lower brightness probably being caused by the presence of the magnesium in the alkali stage.

### CONCLUSION

The presence of transition metal ions during a two-stage hydrogen peroxide bleach of *Eucalypt* SGW has been found to enhance the brightness of the pulp. The total effect produced appears to be derived from the influence of chelatable ions naturally present in the pulp and also introduced chromium species. The influence of these metal species during acidic peroxide treatment renders the chromophores present in the pulp more easily removed during subsequent bleaching under alkaline conditions.

This effect may be related to generation of active radical species through catalytic decomposition of hydrogen peroxide at low pH. Using such a process, optimised for dosage of catalyst and time of acidic treatment, brightness gains can be achieved in less time while consuming no additional peroxide.

This study has shown that there is potential scope for development of beneficial catalytic processes for the enhancement of peroxide bleaching. Such processes may utilise the presence of metal ions naturally present in the wood pulp, or species which may be introduced prior to peroxide treatment. The development of such processes would appear to depend on recent concepts of peroxide bleaching in which species other than the perhydroxyl anion are implicated in chromophore removal. This may in turn revise the traditional view that the presence of transition metal ions in wood pulp should be associated with adverse effects in bleaching sequences.

### ACKNOWLEDGEMENT

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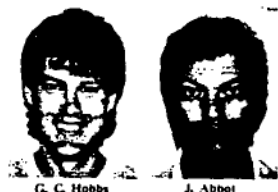
The Role of Radical Species in Peroxide Bleaching Processes.

G.C. Hobbs and J. Abbot, Proceedings of the 1992 Appita Conference and also  
Appita, **45(5)**, 344-348 (1992).

# The role of radical species in peroxide bleaching processes

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J. Abbot

The role of radical species, and particularly the hydroxyl radical has been the topic of much debate recently(1-6). Traditionally the perhydroxyl anion,  $\text{HO}_2^-$ , has been considered the active bleaching species in alkaline peroxide bleaching of mechanical pulps(1,7), but recent work(1-6) suggests that hydroxyl radicals can play a major role in bleaching. However it is not clear whether radical species have a positive or negative effect.

Some transition metal ions are known to catalytically decompose hydrogen peroxide via a radical mechanism(3-5,7-10) producing hydroxyl radicals. The location of the decomposition process, whether in solution or on the fibre surface, may have an influence on the effectiveness of the radicals produced. If the site of radical generation is in close proximity to a chromophore or a potential chromophore, then reactions influencing the resulting brightness of the pulp are more likely. By this reasoning it has been postulated(11) that at higher pulp concentrations, radical species play a more significant role as their site of generation is more likely to be adjacent to a fibre.

Hydroxyl radicals have also been linked with the phenomenon of photoyellowing of pulp(12) as well as alkali darkening of pulps in the presence of transition metal ions and hydrogen peroxide(13). Lignin model compound studies(14-18) have revealed that the hydroxyl radical is capable of reacting with chromophoric structures typically present in pulp.

Various methods have been employed for the detection of radicals, especially the hydroxyl radical, including electron spin resonance (ESR)(19), chemiluminescence(20) and UV-visible spectroscopy(21-23).

These examples indicate that the role hydroxyl radicals play in peroxide bleaching systems is not well understood. This paper will make some attempts to clarify the role of radicals and also to correlate the concentrations of radicals produced with the bleaching response of pulps.

## SUMMARY

The role of radical species, particularly the hydroxyl radical, in peroxide bleaching systems has been investigated for bleaching of Eucalyptus regnans stone groundwood.

Under conditions of constant concentration of peroxide and alkali, increasing the pulp concentration showed a small positive effect on brightness gain after extended bleaching times. Bleaching of a mixture of bleachable stone groundwood and inert fibres showed no increased brightness response when increasing the proportion of bleachable fibre, or effectively increasing the concentration of the bleachable fibre.

Studies using *N,N*-Dimethyl-4-nitroso aniline as a radical trap have shown that the trapping of hydroxyl radicals reduces the final brightness of pulps by 1 to 5% ISO, and that the final brightness of the pulps can be related to the initial rate of radical formation. The addition of transition metal ions usually present in pulps (manganese, iron and copper), to peroxide bleaching liquors increases the peroxide decomposition but does not significantly increase the rate of radical generation, whereas the presence of peroxide stabilizers decreases the peroxide consumption and the rate of radical generation.

## EXPERIMENTAL

### Materials

Hydrogen peroxide (30%) was obtained from Ajax Chemicals. Potassium hydroxide (99.99%) of semiconductor purity, copper nitrate, manganese nitrate, iron nitrate and chromium nitrate (all 99.9%), EDTA (99%), DTPA (98%), sodium silicate (30%) and *N,N*-Dimethyl-4-nitroso aniline (DMNA) (97%) were obtained from Aldrich Chemicals.

### Procedures

Eucalypt stone groundwood (SGW) was produced on a small scale grindstone at Australian Newsprint Mills Boyer mill. The wood was ground in the presence of dilute sodium hydroxide (3% on o.d. wood). After grinding the pulp was filtered and washed prior to storage at 4°C and 20% concentration until used.

Bleaching experiments were performed by preheating appropriate amounts of pulp, Milli-Q water\*(24) and other additives to 50°C prior to addition of alkali and peroxide. Samples were withdrawn at intervals to allow the calculation of peroxide consumption and for handsheet formation. Two methods of bleaching were used. Firstly an initial charge of peroxide and alkali was applied and allowed to decrease with time. Secondly pulps were bleached under constant conditions of peroxide and alkali concentration. This was achieved by applying initial chemical charges and maintaining these concentrations by addition of appropriate amounts of chemical when deviation from initial conditions was observed, generally every 10 to 15 minutes. For these experiments the usual conditions were 1.2 g/L peroxide and pH 11.0.

For bleaching mixtures of SGW and kraft pulp, appropriate amounts of samples were added to sufficient water to give the required pulp concentration and ratio. Bleached radiata pine kraft pulp was bleached with peroxide for six hours prior to use in further experiments under the conditions stated above for work with constant conditions of peroxide and alkali concentration.

Studies with *N,N*-Dimethyl-4-nitrosoaniline (DMNA),  $\lambda_{\text{max}} = 440 \text{ nm}$   $\epsilon = 34200$ , were performed using  $5 \cdot 10^{-3} \text{ M}$  solutions diluted from  $1 \cdot 10^{-1} \text{ M}$  solution which was stored away from strong light and discarded after two weeks(21). Bleaching was performed as previously mentioned except DMNA was added just prior to the peroxide and alkali. Solution studies were performed at 50°C and pH 11.0 initially.

\* Type 1 (> 18 Mohm). The reference gives an analysis of the water. The water is passed through a carbon cartridge, two ion exchange cartridges and a further carbon filter. The resistance is measured to ensure quality.

Brightness (%ISO) was measured using a Daticolor Elrepho 2000. The brightness of the unbleached pulp was 51.0% and samples were regularly prepared to monitor any changes in the pulp with storage.

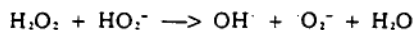
## RESULTS AND DISCUSSION

### Literature review

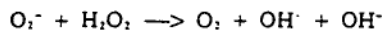
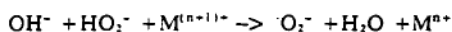
Recently much discussion has appeared in the literature regarding the role of radical species in both bleaching and photobleaching of pulp. The focus of this paper is on the role radicals play in peroxide bleaching processes.

During peroxide bleaching the two major radical species produced are the hydroxyl radical and the superoxide anion radical,  $\text{OH}^\cdot$  and  $\text{O}_2^{\cdot-}$ . Of these, the hydroxyl radical is thought to be the species most likely to have any effect during bleaching(4).

The generation of hydroxyl radicals can occur in two major ways(7,10). Firstly the base induced cleavage of hydrogen peroxide(7,10,25)—



or by transition metal ion catalysed decomposition of hydrogen peroxide(3,7,10)—



Work using potassium superoxide(26-28) has shown no noticeable change in either lignin model compounds or kraft lignin. The conclusions are that the active radical species is the hydroxyl radical. The superoxide anion radical has, however, been shown to react to depolymerize cellulose(28).

Model compound studies have shown that the hydroxyl radical can react with certain types of lignin groupings(14-18). In many of these cases the radicals are produced by photolysis of hydrogen peroxide solutions.

Phenolic units in lignin, represented by  $\alpha$ -methyl syringylalcohol(1,8), have been studied, and the major reacting species has been shown to be hydroxyl radicals. This reaction is accelerated by the presence of transition metal ions, again indicating the role that these radicals have in some aspects of peroxide bleaching.

However, the reaction of conjugated carbonyl structures(17), a major source of colour in mechanical pulps, has been shown to have a first order dependence on the perhydroxyl anion, which is usually considered to be the active bleaching species. This work does, however, still suggest that the presence of transition metal ions accelerates the reaction.

The use of Fenton's Reagent (hydrogen peroxide and ferrous ions) has been used as a source of hydroxyl radicals in many studies(29). It has been shown that hydroxyl radicals react to degrade carbohydrates(29). As the hydroxyl radical is a very reactive species, being the most powerful one electron oxidant in aqueous solution(3,14) with a standard reduction potential of 2.72 V in acidic media and 2.32 V in neutral media the life time of the species is very short. This means that a radical will react with any substance near the site of generation. If transition metal ion catalysed decomposition of hydrogen peroxide is the main source of hydroxyl radicals, then the location of these metal ions may be of particular importance. Some previous work(30) has shown that, under the conditions employed, manganese is bound almost exclusively to the lignin portion of the pulp and only very small amounts are bound to the cellulose. This implies that, in the case of manganese at least, the radical species would be expected to attack only the lignin portion of the pulp and not cause degradation of the cellulose.

Hydroxyl radicals react in these ways—

- Electrophilic addition to double bonds or to aromatic nuclei(3). Both of these reactions reduce conjugation and hence reduce the colour of the residual lignin.
- Hydrogen atom abstraction from a saturated carbon atom(3).

Of these the first reaction mode is 1 to 2 orders of magnitude faster than the second. At increased pH values the oxyl anion radical  $\text{O}_2^{\cdot-}$ , the anionic form of the hydroxyl radical, is formed(3) but this only has a standard reduction potential of 1.4 V and reacts more slowly than the hydroxyl radical.

### Effect of pulp concentration

Bleaching of eucalypt SGW under constant conditions of peroxide and alkali gives more easily interpretable information regarding the effect of pulp concentration than bleaching under conditions of reducing peroxide and alkali concentration. This is because peroxide consumption and pH vary with pulp concentration, thus meaning that results cannot be easily compared. Figure 1 shows a typical brightening response under these conditions.

Interestingly the response shows many similarities to a pulp bleached under conventional conditions, a rapid initial stage followed by a much slower stage of bleaching(31), apparently reaching a brightness limit after long reaction times. In the case of reducing reagent concentration this can be explained in terms of loss of bleaching reagent, however, this is not the case for bleaching under constant conditions, indicating that the apparent limiting brightness reached after extended times is related to the concentration of peroxide and alkali(32). Figure 2 shows the effect of varying the pulp concentration while keeping all other conditions constant.

Although there is no clear trend observable it can be seen that at higher concentrations (3 to 8%) a brightness increase approximately 1 to 2% ISO higher is obtained indicating that the increasing concentration does improve the bleaching response of the pulp. This may be related to the presence

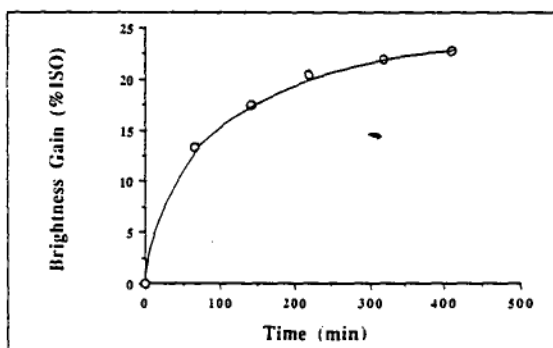


Fig. 1 — Bleaching response of SGW. Conditions: peroxide 1.2 g/L, pH 11.0, temp. 50°C, p.c. 3%, peroxide and alkali maintained at initial levels.

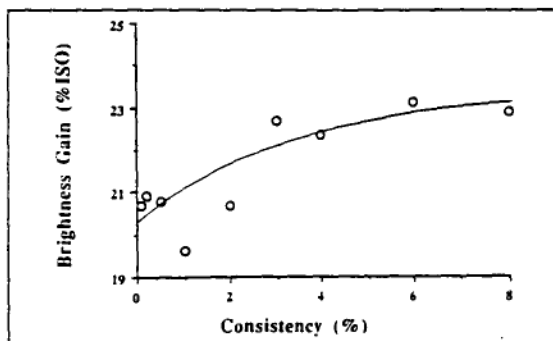


Fig. 2 — Effect of pulp concentration on final brightness of eucalypt SGW. Conditions as in Figure 1.

of radicals produced by peroxide decomposition. As the pulp concentration increased these are more likely to be generated close to a fibre and so be more likely to affect the colour of the pulp. This is in agreement with previous work(11) which related an empirical rate constant to the pulp concentration. This showed an increase in the rate of bleaching with increasing concentration.

The addition of an inert fibre, that does not consume considerable amounts of peroxide or change brightness when bleached with alkaline hydrogen peroxide can allow a study of the effect of pulp concentration on bleaching response. If the total concentration is kept constant but the proportions of the inert and bleachable fibre are changed, this effectively alters the concentration of the bleachable fibre.

It was found that radiata pine kraft pulp, after being bleached for six hours with alkaline peroxide, consumed very little peroxide when again exposed to peroxide and, as expected, showed very little change in brightness. The brightness of the kraft pulp after the initial peroxide treatment was 85% ISO. Bleached kraft pulp that has been previously exposed to peroxide, therefore, was considered suitable as an inert fibre. Kraft:SGW pulp ratios of 7:1, 3:1, 1:1 and 1:3 were used giving effective concentrations of SGW of 0.5, 1.0, 2.0 and 3.0%.

Two series of experiments were performed. Firstly kraft and SGW were bleached together in the above ratios and the brightness of samples withdrawn at suitable intervals was measured. Secondly samples of kraft and SGW were bleached separately and handsheets were then prepared in the above ratios to give a comparative set of data. The comparison of the two sets of results should show the effect of the addition of inert fibres, and give some information about the effect of pulp concentration in peroxide bleaching.

If bleaching at a higher concentration is beneficial, possibly due to the effect of radical species, then we would expect to observe higher brightness in the samples bleached separately (as this was effectively bleached at a higher concentration) than those bleached together, as the inert fibre reduces the concentration of the bleachable fibre.

Figure 3 shows the bleaching response of various ratios of SGW and bleached kraft pulp when bleached together.

This graph shows that for the various kraft:SGW ratios the bleaching response is typical of peroxide bleaching with a rapid initial stage followed by a slower phase. Also, as expected, the higher kraft:SGW ratios correspond to smaller initial brightness and lower brightness gain with the smaller percentage of bleachable fibre present.

Figures 4a and 4b show a comparison of the brightness of sheets formed from a fixed ratio of kraft:SGW, but bleached by the two methods, either separately or combined.

These figures show that there is no significant difference in brightness response associated with the method of bleaching. This shows that the SGW bleaching response does

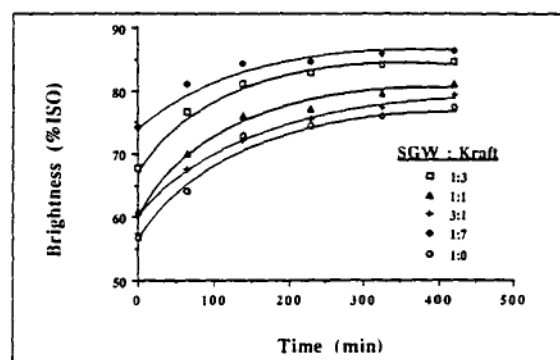


Fig. 3 — Bleaching response of SGW and kraft bleached together in the given ratios to make appropriate handsheets. Conditions: temp. 50°C, pH 11.0, p.c. 4%, 3% peroxide on o.d. pulp, alkali constant.

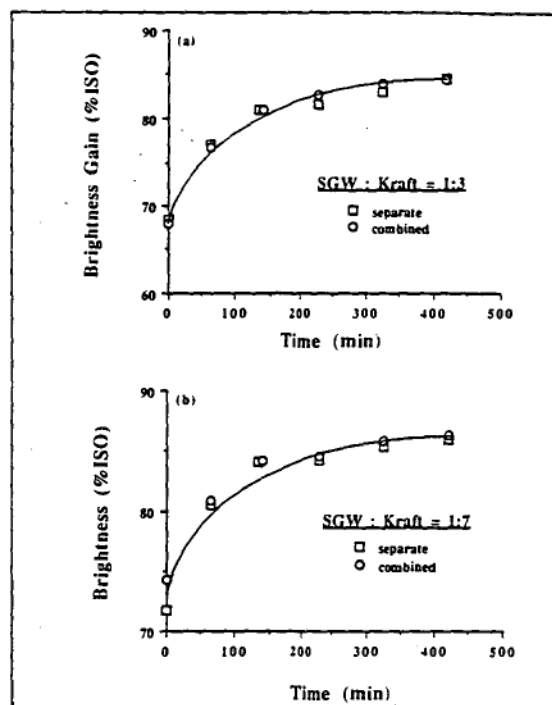


Fig. 4 — Comparison of separate and combined bleaching of SGW:kraft in ratios of 1:3 and 1:7. Conditions: peroxide 1.2 g/L, pH 11.0, maintained throughout the experiment.

not appear to alter over the range of concentrations covered (0.5 to 4.0%).

From these experiments it can be concluded that the effect of varying the pulp concentration for bleaching SGW is small (approximately 10% of the brightness change) and there is no observable effect in the case of kraft:SGW bleaching. In the case of mixed kraft:SGW bleaching the total pulp concentration is always 4%, so, although the concentration of the bleachable fibre is altered, the transfer of radical species between fibres may not be altered significantly.

#### Radical detection

The use of DMNA for the detection of hydroxyl radicals has been used for many years(21), but has rarely been used in conjunction with peroxide bleaching, although some work has been reported(19) in which the production of radicals in peroxide bleaching liquors in the absence of pulp has been investigated. Hydroxyl radicals react quantitatively with DMNA; this reaction reduces the observed absorption of DMNA. This decrease in absorption allows calculation of

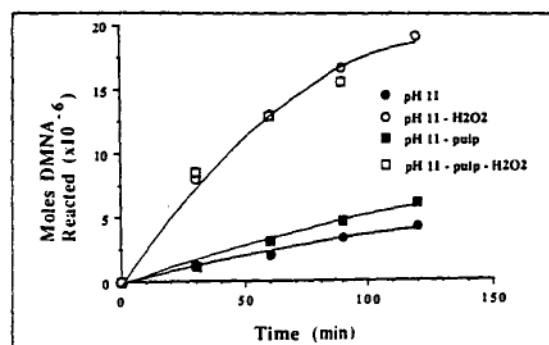


Fig. 5 — Amounts of DMNA reacted in the presence of various additives initially at temp. 50°C and pH 11.0.

the amount of DMNA reacted. Figure 5 shows the amounts of DMNA reacted under various conditions.

As can be seen from Figure 5, some DMNA reacts in the absence of peroxide so this must be considered in all other cases. The presence of peroxide greatly increases the amount of DMNA reacted, indicating the presence of hydroxyl radicals, but the brightness of the pulp is not affected in the presence of DMNA alone. Table 1 shows the amount of DMNA reacted in solutions of peroxide in the presence of various additives. In all cases the amount of DMNA that decolorizes in the absence of peroxide in 60 minutes has been subtracted.

From Table 1 several significant points are noticeable. Firstly, the addition of stabilizing agents reduces the quantity of hydroxyl radicals produced and, except in the case of silicate, reduced the consumption of peroxide. For EDTA, DTPA and magnesium there is little change in the ratio of DMNA and peroxide reacted, indicating that the mechanism of peroxide decomposition may not be significantly altered by the addition of these stabilizers.

Secondly, the addition of iron, copper and manganese greatly increases the amount of peroxide consumed, but only in the case of copper is more DMNA reacted than in the case of peroxide alone. The ratio of DMNA to peroxide consumed in these cases indicates that a far smaller proportion of peroxide decomposition is via mechanisms involving radicals. This result for copper is different from previously reported work(19) and requires further investigation.

The addition of chromium nitrate to acidic peroxide shows that a free radical mechanism involving the production of hydroxyl radicals is a more important route leading to peroxide decomposition. The ratio of DMNA to peroxide consumed is far greater than the blank at this pH. The decomposition of peroxide at lower pH generates far fewer radicals than at higher pH, probably due to the base induced mechanism being far less significant. This result is significant in terms of previous work utilizing acid/alkaline two stage peroxide bleaching sequences with the addition of chromium(33-34). It now appears that the interaction of hydroxyl radicals with chromophoric structures in the first (acidic) stage causes changes in the chromophores which render them more susceptible to removal in the subsequent alkaline stage, thus giving the pulp a higher brightness compared to a single stage alkaline peroxide bleach.

In the presence of pulp DMNA can also be used to detect hydroxyl radicals. This allows a determination of the quantity of radicals and also the effect their removal has on the brightness of the pulp by performing parallel experiments in the presence and absence of DMNA. In all cases the peroxide consumption was similar, indicating that the presence of DMNA does not affect the stability of the peroxide, and the brightness of unbleached or bleached pulp was not affected by soaking in DMNA for 30 minutes. As can be seen from Figure 6 in the absence of DMNA a higher brightness is achieved.

Here it is evident that the presence of DMNA, and hence the removal of hydroxyl radicals reduces the brightness of the pulp. Therefore, it appears that the presence of hydroxyl

radicals enhances the brightness response of the pulp. This has been observed in all cases. Table 2 shows the quantity of DMNA reacted when bleaching under various conditions.

This table shows that the loss in brightness due to the removal of hydroxyl radicals is between 1 to 5% ISO (c.6 to 30% of total brightness gain). Similar differences in brightness are recorded after 120 minutes, indicating that the radicals may be involved in initiating reactions that cause colour changes in the pulp. The bleaching response of the pulps, as can be seen in Figure 6, shows little difference after 30 minutes. In some cases this can be associated with the complete removal of DMNA, allowing radical processes to again be significant (eg 4% p.c., Fe addition), but similar observations are made when DMNA is still present. It can also be seen that increasing the pulp concentration greatly increases the production of hydroxyl radicals. It has previously been postulated(11) that the ability of hydroxyl radicals to transfer between fibres is beneficial to bleaching efficiency but it appears that more radicals are produced, so any improvement in bleaching with higher pulp concentration could be related to the increased production of hydroxyl radicals. This increased production of hydroxyl radicals could be related to a greater number of potential sites for production of radicals and an increased concentration of transition metal ions.

The addition of chromium again shows a significant increase in radical production when compared to the blank.

The addition of manganese, iron and copper also shows some interesting trends as presented in Table 3.

This table shows that an increased initial hydroxyl radical production appears to be correlated to an increased final

Table 2  
DMNA reacted under various conditions\*

Additive	pH	Moles DMNA reacted $10^4$	$\Delta$ Brightness % ISO
DTPA	11	4.17	3.80
	11	3.78	0.77
2% pulp conc	11	8.75	2.75
4% pulp conc	11	11.7	4.05
Mn	11	4.82	4.40
Fe	11	8.46	0.69
Cu	11	2.95	1.20
	5.8	1.15	2.88
Cr	5.8	4.53	3.01

\* Conditions:  $5.10^{-3}$  M DMNA, 30 minutes reaction time, Mn, Fe, Cu:  $9.1 \cdot 10^{-3}$  M, Cr  $2.51 \cdot 10^{-3}$  M, DTPA 0.5% on o.d. pulp prior to bleaching. Pulp concentration 1% except where indicated.

Table 3  
Comparison of brightness and radical production\*

Additive	Moles DMNA reacted $10^4$ 30 min	Brightness gain % ISO 120 min
DTPA	4.17	15.07
Mn	3.78	11.49
Fe	8.46	15.78
Cu	2.95	14.58
Cr	4.53	16.56

\* Conditions as in Table 2. Brightness in the absence of DMNA after 120 minutes.

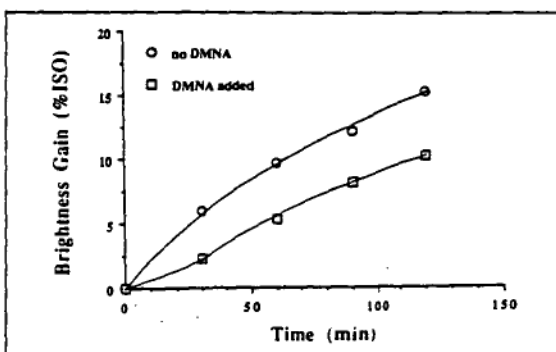


Fig. 6 — Comparison of brightness of pulp bleached in the presence and absence of DMNA. Conditions: temp. 50°C, initial pH 11.0, p.c. 1%, peroxide 12% on o.d. pulp.

Table 1  
Peroxide and DMNA reacted in the presence of various additives

	pH	H <sub>2</sub> O <sub>2</sub> Moles reacted $\times 10^3$	DMNA Moles reacted $\times 10^3$	Molar ratio DMNA/H <sub>2</sub> O <sub>2</sub> $\times 10^3$
Mn	11	0.67	8.14	12.2
Cu	11	7.34	3.41	0.47
Fe	11	16.1	9.05	0.56
Si	11	8.00	5.07	0.63
Mg	11	0.91	2.75	3.02
EDTA	11	0.47	3.89	8.27
DTPA	11	0.47	4.37	9.30
	5.8	0.39	4.06	10.41
Cr	5.8	0.42	0.99	2.34
	5.8	0.71	13.3	18.73

Conditions: 60 minutes 50°C,  $3.53 \cdot 10^{-3}$  M peroxide, Mn, Fe:  $1.79 \cdot 10^{-3}$  M, Cu:  $3.58 \cdot 10^{-3}$  M, sodium silicate: 0.6 g/L, EDTA, DTPA: 0.20 g/L, Mg:  $1.95 \cdot 10^{-3}$  M, Cr:  $3.03 \cdot 10^{-3}$  M.

brightness, again indicating that radicals have an important role in peroxide bleaching systems. Chelation of the pulp has the effect of reducing the radical production and also reducing the final brightness of the pulp. However, as can be seen in Table 2, the difference in brightness between chelated pulp bleached in the presence and absence of DMNA is very small, indicating that few radicals are involved in bleaching pulps pre-treated with a chelating agent, under the conditions employed here. The presence of certain transition metal ions can enhance the bleaching response of the pulps.

### CONCLUSION

This work has shown that hydroxyl radicals play an important role in peroxide bleaching systems. Preliminary studies with DMNA have shown that under typical bleaching conditions more hydroxyl radicals are produced at higher pulp concentrations. A correlation between the initial rate of radical formation and the final brightness of the pulp appears to indicate the positive role these radicals play in bleaching. It appears that hydroxyl radicals are involved in bleaching reactions and need to be considered, along with the perhydroxyl anion, as a major bleaching species.

Work using constant concentrations of peroxide and alkali also shows some evidence for the importance of radicals in peroxide bleaching. Increasing the pulp concentration leads to some improvement in the bleaching response of the pulp; this can be related to the higher radical concentrations under these conditions.

Further work is required in this area to firstly determine the reactions of hydroxyl radicals and secondly to determine the optimum balance between radical induced bleaching and bleaching by the perhydroxyl radical.

### ACKNOWLEDGEMENT

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**The Influence of Metal ions on Two-Stage Peroxide Bleaching of Radiata Pine TMP.**

J. Abbot and G.C. Hobbs, *J. Pulp Paper Sci.*, **18(2)**, J67-70 (1992).

# The Influence of Metal Ions on Two-Stage Peroxide Bleaching of Radiata Pine TMP

J. ABBOT and G.C. HOBBS

*The influence of metal ions during a two-stage peroxide bleaching process has been studied with Radiata pine TMP. Brightness development of the pulp carried out under alkaline conditions could be enhanced by the presence of certain metal ions during the initial stage under neutral conditions. Removal of metal ions naturally present in the pulp reduced brightness gain for the two-stage process, while addition of chromium nitrate had the opposite effect. The results of this study show that, under certain conditions, the presence of transition metal ions can have beneficial effects during peroxide bleaching of pulp, and this may be related to the generation of free radical species under low pH conditions.*

## INTRODUCTION

The presence of transition metal ions is generally considered to produce detrimental effects during bleaching of wood pulp with hydrogen peroxide [1-4]. Under alkaline conditions, metal ions can catalyze decomposition of peroxide [1-4], leading to loss of the bleaching reagent. These effects can be reduced by addition of complexing agents such as diethylenetriaminepentaacetic acid

(DTPA), sodium silicate or magnesium salts [5-6]. A number of recent studies have reported that it is possible to bleach pulp in a two-stage process with hydrogen peroxide [7-8], using acidic peroxide in the first stage followed by a conventional alkaline stage. In the present study we have examined further this type of two-stage peroxide bleaching sequence, using neutral conditions in the initial step, followed by alkaline bleaching at pH 11 to evaluate the possible role of particular metal ions in the process.

## EXPERIMENTAL

Hydrogen peroxide (30%) was obtained from Ajax Chemicals. Chromium nitrate (99%), cobalt nitrate (97.5%), nickel nitrate (97.0%), sodium silicate (30%), DTPA (97%) and sodium hydroxide of semiconductor purity (99.99%) were supplied by Aldrich Chemicals.

The *Pinus radiata* thermomechanical pulp was provided by Australian Newsprint Mills from TMP unit 2 at their Boyer Mill. The pulp was stored at 18% consistency at 4°C until used.

Bleaching studies were carried out using polyethylene reaction vessels maintained at 50°C in a constant temperature water bath. The pulp suspensions were stirred [9] during the course of the bleaching reactions. The bleaching experiments were performed by mixing the required amounts of pulp, hydrogen peroxide, so-

dium hydroxide (and catalyst where appropriate) with the required volume of Milli-Q deionized water to give the desired consistency. The pulp and dilution water were heated to reaction temperature before addition of reagents. Sodium silicate and DTPA were also added where indicated.

The pre-chelated pulps were prepared by treating the TMP with 0.5% DTPA at 2% consistency for 30 min, filtering and then thoroughly washing the pulp with Milli-Q deionized water. The concentrations of transition metal ions present in the original pulp and after pre-chelation were determined by atomic absorption after digestion with nitric acid and are given in Table I. Metal ion concentrations present in the Milli-Q deionized water and the hydrogen peroxide have been reported previously [10].

Pulp samples were withdrawn at intervals to determine the brightness of the pulp and consumption of hydrogen peroxide. Residual peroxide concentrations were determined on filtrates by iodometric titration with standard sodium thiosulphate [11], after acidification and addition of potassium iodide and a few drops of saturated ammonium molybdate solution.

All pulp samples were thoroughly washed with deionized water before making handsheets. The brightness (% ISO) of bleached pulp handsheets was measured with a Zeiss Elrepho using a 457 nm



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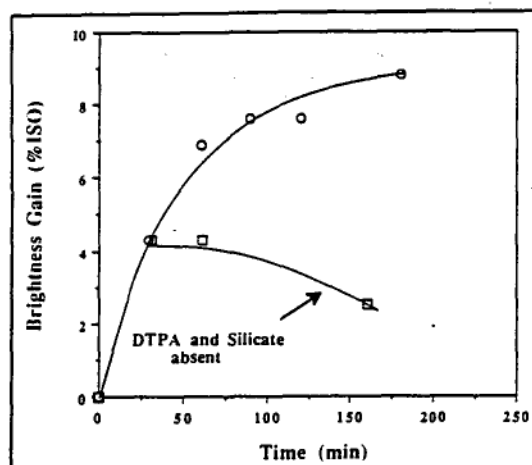


Fig. 1. The influence of DTPA and sodium silicate on brightness gain. Bleaching at 50°C, constant pH 11.0, 4% consistency, 6% initial peroxide charge (on o.d. pulp); ○: 0.25% DTPA, 10% sodium silicate (on o.d. pulp); □: no addition of DTPA or silicate.

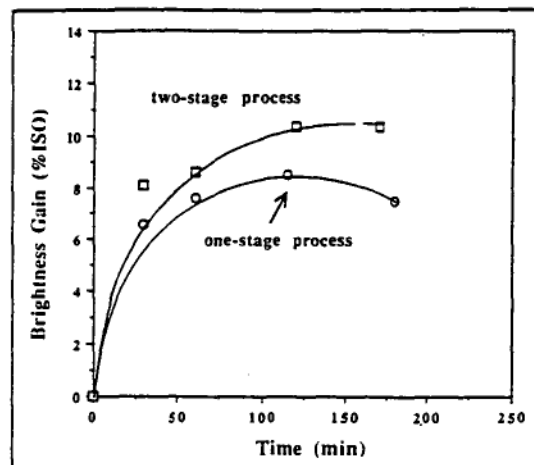


Fig. 2. Effect on brightness gain of pre-treating pulp at pH 7.0 for 30 min with hydrogen peroxide (initial charge 3% on o.d. pulp), followed by alkaline conditions at pH 11.0 with 0.25% DTPA and 10% sodium silicate (on o.d. pulp). Bleaching at 50°C and 4% consistency with initial 3% peroxide charge during alkaline stage. □: two-stage process; ○: one-stage process.

filter. The measured brightness of the unbleached pulp was 58.5, and this was not found to vary over a 30 day period during storage.

## RESULTS AND DISCUSSION

Samples of a thermomechanical pulp produced from *Pinus radiata* were bleached with alkaline hydrogen peroxide at a constant pH of 11.0. Bleaching was carried out in the presence of the complexing reagent DTPA (0.25% on o.d. pulp) and sodium silicate (10% on o.d. pulp). In the absence of these reagents, peroxide decomposition occurred rapidly resulting in significantly lower brightness gains as shown in Fig. 1. This accelerated decomposition can be attributed to catalytic effects of transition metals present in the pulp [1-4]. Manganese, copper and iron are often present in wood pulp, originating from both the wood itself and also processing equipment, and these metals are generally considered to be the main cause of peroxide decomposition. Table I shows the levels of these metals present in the TMP, and the results are comparable to other reported analyses [12].

The active species during bleaching with hydrogen peroxide is generally thought to be the perhydroxyl anion

$\text{HO}_2^-$  [13,14]. The concentration of this species is very low under neutral and acidic conditions [15], and consequently peroxide bleaching is usually carried out under alkaline conditions (above pH 9). There has, however, been some recent interest in the possibility of two-stage processes in which the pulp is initially treated with peroxide at an acidic pH, followed by a second stage under normal alkaline conditions (7.8), as such processes can lead to enhanced brightness development and lower peroxide consumption [16].

Figure 2 shows a comparison between brightness gain for a standard one-stage alkaline peroxide bleach at pH 11.0 with that for a two-stage process using neutral conditions (pH 7.0) for 30 min, followed by alkaline conditions. The time indicated corresponds to the duration of the alkaline treatment in both cases. For the two-stage process, the peroxide concentration was restored to the initial level after 30 min, after which DTPA (0.25% on o.d. pulp) and sodium silicate (10% on o.d. pulp) were added and the pH adjusted to 11.0. Although no increase in brightness was observed at the end of the neutral stage of the two-stage process, it is apparent that the resulting pulp is more susceptible to brightness gain

in the alkaline stage, compared to the pulp exposed to only alkaline peroxide. Although the concentration of  $\text{HO}_2^-$  is very low under neutral conditions, reactions must nevertheless occur which render the chromophores present more susceptible to removal during alkaline bleaching.

Figure 3 shows that the effectiveness of the two-stage process is reduced by prior application of a chelating agent (DTPA) to the TMP followed by thoroughly washing the pulp with deionized water. This treatment significantly reduces the concentration of metal ions in the pulp, as shown in Table I. It can be concluded that effective peroxide treatment under neutral conditions depends on the presence of metal ions in the pulp. Enhancement of brightness gain using the two-stage process with the pre-chelated pulp can be restored by addition of certain transition metal ions to the pulp at the start of the neutral stage. For example, the effect of adding between  $1.25 \times 10^{-2}$  and  $5.0 \times 10^{-2}$  mol chromium nitrate (0.033% - 0.13% Cr on o.d. pulp) is illustrated in Fig. 4. We have also found [8,16] that addition of chromium during a two-stage acid/alkali peroxide bleaching process for a hardwood species (*E. regnans*) is beneficial. For the TMP this effect is dependent, however, on the nature of the metal introduced. Figure 5 shows that, while addition of chromium to the pre-chelated pulp improves brightness gain in the two-stage process, the introduction of nickel nitrate ( $2.5 \times 10^{-2}$  mol) has very little observable influence. In contrast, addition of cobalt nitrate ( $2.5 \times 10^{-2}$  mol) actually causes a decrease in pulp brightness. The lack of brightness development in the latter case can be at-

TABLE I  
METAL ION CONTENT OF PULPS USED IN THIS WORK

Wood type	Metal ion (ppm) <sup>1</sup>		
	Iron	Manganese	Copper
<i>P. radiata</i> TMP	16	64	5
Chelated <i>P. radiata</i>	16	8	0.5

1. Concentration determined by atomic absorption after digestion of pulp.

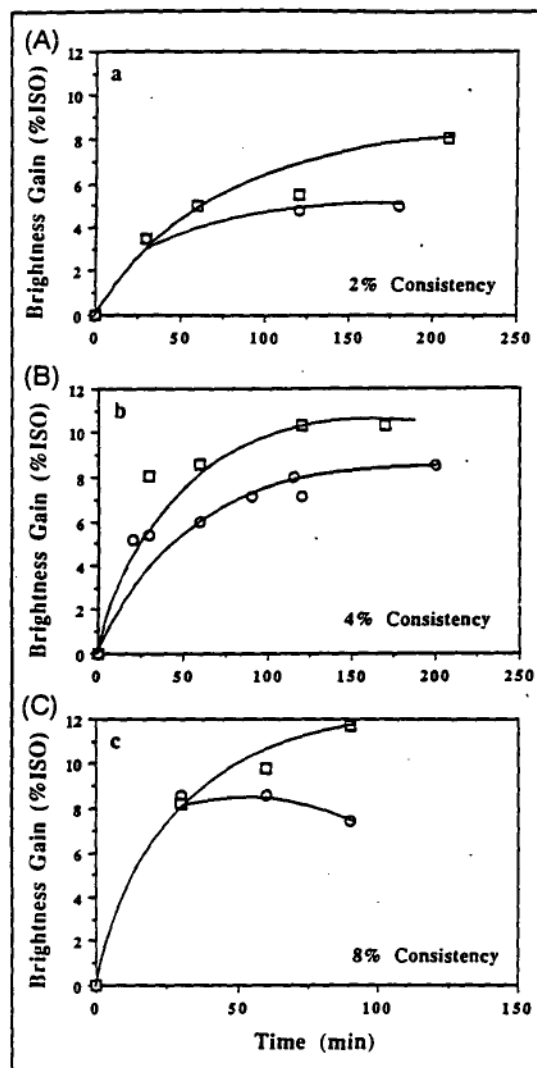


Fig. 3. The effect of removal of metal ions by pre-chelation on two-stage bleaching processes at a) 2%, b) 4% and c) 8% consistency. Other conditions as in Fig. 3.  $\square$ : no pulp pre-treatment;  $\circ$ : pulps pre-treated with 0.5% DTPA for 30 min then washed with deionized water.

tributed to the rapid decomposition of hydrogen peroxide in the presence of cobalt at high pH, whereas chromium is active as a catalyst only at lower pH [1].

Figure 6 shows results for the total consumption of hydrogen peroxide plotted as a function of brightness gain corresponding to experiments at 4% consistency. This shows that the two-stage process in the presence of chromium nitrate consumed less peroxide than that required for the corresponding brightness gain using a single-stage alkaline bleach. For two-stage processes without addition of chromium, peroxide consumption was increased for both the pre-chelated pulp and the untreated pulp. These results in-

dicate that the efficiency of the two-stage process must depend on the nature of catalytic species present.

The effects of metal ions in pulp described here may also explain brightness gains reported for two-stage processes using acidic peroxide in the initial stage with no specific introduction of catalytic agents [17]. The mechanism of these processes may be linked to the concept of the participation of free radical species in peroxide bleaching reactions [18]. There has been recent interest in the idea that free radicals, particularly the hydroxyl radical  $\text{OH}^\bullet$  may be active in chromophore elimination, as well as the perhydroxyl anion  $\text{HO}_2^-$ . It is possible

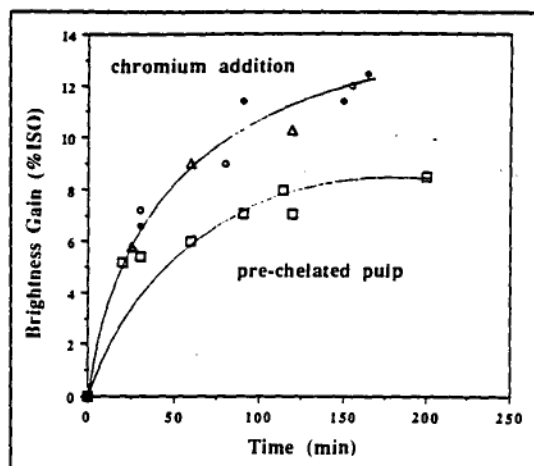


Fig. 4. The effect on brightness gain of addition of chromium nitrate to a pre-chelated pulp for a two-stage process. Pulp consistency 4%, with other conditions as in Fig. 3.  $\square$ : no chromium addition; Chromium addition —  $\triangle$ :  $1.25 \times 10^{-2}$  mol;  $\diamond$ :  $2.50 \times 10^{-2}$  mol;  $\circ$ :  $5.0 \times 10^{-2}$  mol.

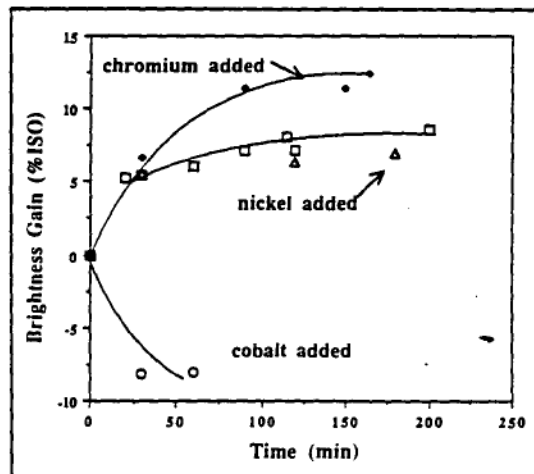


Fig. 5. Effects on brightness gain of addition of metal ions to a pre-chelated pulp for a two-stage process. Pulp at 4% consistency, other conditions as in Fig. 3. Metals introduced as nitrates ( $2.5 \times 10^{-2}$  mol)  $\diamond$ : Cr;  $\circ$ : Co;  $\triangle$ : Ni;  $\square$ : no metal added.

that the role of the transition metal ions under neutral or acidic conditions is to promote formation of active radicals which subsequently interact with chromophores present, causing these functional groups to be more easily removed during the alkaline stage.

## CONCLUSIONS

The present study shows that there are influences of metal ions during bleaching with hydrogen peroxide which can enhance the development of pulp brightness. The active metal ions may be those naturally present in the original wood, those introduced in processing or ions artificially introduced, as illustrated

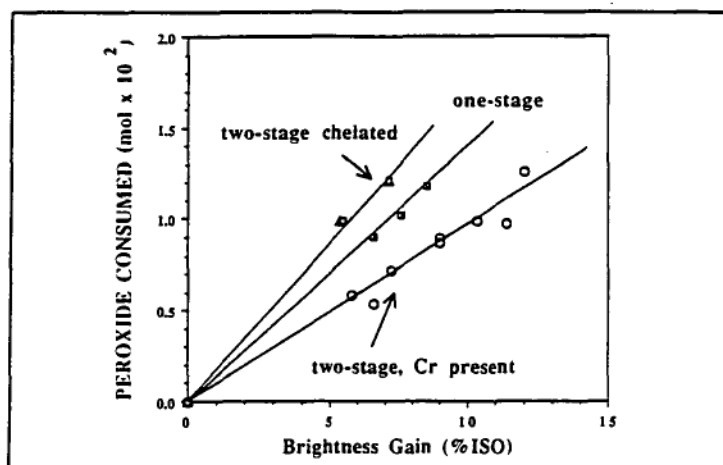


Fig 6. Plots of total consumption of hydrogen peroxide against brightness gain for one- and two-stage bleaching processes. Bleaching at 50°C, 4% consistency, constant pH 11.0.

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**ABSTRACT:** The influence of metal ions during a two-stage peroxide bleaching process has been studied with Radiata pine TMP. Brightness development of the pulp carried out under alkaline conditions could be enhanced by the presence of certain metal ions during the initial stage under neutral conditions. Removal of metal ions naturally present in the pulp reduced brightness gain for the two-stage process, while addition of chromium nitrate had the opposite effect. The results of this study show that, under certain conditions, the presence of transition metal ions can have beneficial effects during peroxide bleaching of pulp, and this may be related to the generation of free radical species under low pH conditions.

**RÉSUMÉ:** Nous avons étudié l'influence des ions métalliques sur la PTM de pin Radiata au cours du procédé de blanchiment au peroxyde à double stade. L'élaboration du degré de blancheur de la pâte réalisée dans des conditions alcalines pourrait être améliorée par la présence de certains ions métalliques au niveau du premier stade de blanchiment dans des conditions neutres. L'élimination des ions métalliques naturellement présents dans la pâte réduit l'accroissement du degré de blancheur dans le cas du procédé à deux stades, pendant que l'addition de nitrate de chrome a l'effet contraire. Les résultats de notre étude montrent que, dans certaines conditions, la présence d'ions métalliques de transition peut avoir des effets favorables au cours du procédé de blanchiment de la pâte. Ce phénomène peut être relié à la production de variétés radicalaires libres dans des conditions à faible pH.

**KEYWORDS:** PINUS RADIATA, THERMOMECHANICAL PULPS, CATIONS, TRANSITION METALS, HYDROGEN PEROXIDE, BLEACHING, REAGENTS, REACTION MECHANISMS, PARAMETERS, CHELATION.

here for the case of chromium. The results reported here for a two-stage peroxide bleaching process with chromium using neutral followed by alkaline conditions indicate that there is scope for designing catalysts which will promote brightness development without increasing peroxide consumption. It may also be possible to develop processes for commercial pulp bleaching which utilize potential effects of ions naturally present, rather than regard the presence of these trace elements as universally undesirable.

#### ACKNOWLEDGEMENTS

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Peroxide Bleaching under Alkaline and Acidic conditions: The role of Transition Metal  
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**PEROXIDE BLEACHING UNDER ACIDIC AND ALKALINE CONDITIONS: THE ROLE OF TRANSITION METAL IONS.**

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**ABSTRACT**

The effect of metal ions, particularly manganese, during alkaline peroxide bleaching of a *Eucalypt*-SGW has been investigated. Contrary to traditional views, the removal of metal ions from the pulp prior to bleaching using chelating agents, has been shown to negatively effect the brightness gain under the conditions used in this study. For pulps not treated with a chelating agent, bleaching at low consistency exhibits an induction period during which little brightening is observed. These observations can be linked to the amount of manganese present, both in the pulp and also in solution. The adsorbance of manganese from solution and its location within the pulp has been studied in order to understand these results. The observed brightness losses and induction periods can be removed by use of higher consistencies, manganese addition or using a two-stage, acid-alkali bleaching sequence.

**INTRODUCTION**

The presence of transition metal ions, particularly iron, manganese and copper, has generally been considered undesirable during peroxide bleaching of mechanical pulps [1-5] as they are thought to reduce the effective charge of bleaching chemical. The decomposition products of transition metal ion catalysed decomposition of hydrogen peroxide, including radical species such as  $\text{OH}^\cdot$  and  $\text{O}_2^\cdot$  are traditionally thought to play no positive role in bleaching [5-9] or even darken the pulp [3,9]. Much effort is usually expended on either trying to remove these metal ions prior to bleaching by using complexing agents such as DTPA or DTPA [5,6,8-12], or rendering the metal ions inactive by addition of stabilizers such as sodium silicate or magnesium salts [8,10-11,13].

During the past decade interest has been shown in the use of hydrogen peroxide under

conditions not previously employed. Usually peroxide bleaching is performed in a single alkaline stage at pH 9-11 to maximize the concentration of the perhydroxyl anion,  $\text{HO}_2^-$  [2,8-10,14-15]. However some recent studies have shown that two stage bleaching processes with the pulp initially under acidic or neutral conditions, followed by a conventional alkaline stage can give greater final brightness enhancement. It has also been demonstrated that the addition of various transition metal ions can, in fact, enhance the brightness development during these two-stage processes [16-20]. This work presents further results which show the importance of metal ions in peroxide bleaching for both conventional single stage alkaline processes and two stage acid/alkali peroxide bleaching sequences.

**EXPERIMENTAL**

Hydrogen peroxide (30%) and sulfuric acid (98%) were obtained from Ajax chemicals. EDTA (99.5%), DTPA (97%), chromium nitrate (99%), manganese nitrate (99.9%) and potassium hydroxide (99.99%) of semiconductor purity were supplied by Aldrich chemicals. Semiconductor grade potassium hydroxide was used as the source of alkali as this introduces very low levels of transition metal ion impurities [21-22].

Blocks of *Eucalyptus Regnans* wood were soaked for three days in Milli-Q water and then ground at 80°C in the presence of dilute sodium hydroxide on a small scale grindstone at Australian Newsprint Mills, Boyer. The pulp was washed with distilled water and filtered to increase the consistency from 1.5% to 20%. The pulp was then stored at 4°C until used. This pulp will be referred to as normal or untreated pulp throughout this paper.

Bleaching studies were carried out in polyethylene reaction vessels maintained at 50°C in a constant temperature water bath. Bleaching experiments were performed by adding the required amounts of pulp, hydrogen peroxide, manganese nitrate and acid or alkali to give a total volume of 500mL with addition of Milli-Q water [21-22]. Experiments were performed at 1%, 2% and 4% pulp consistency. The initial charge of hydrogen peroxide was 6% (1% consistency), 3% (2% consistency) or 1.5% (4% consistency) on o.d. pulp. For bleaching under acidic conditions the pH was adjusted to the appropriate level (6.0) with sulfuric acid. After the prescribed time sufficient potassium hydroxide was added to adjust the pH to the

level required for the second stage (11.0).

Chelated pulps were prepared by treating the pulp with 0.2% EDTA or DTPA (on o.d. pulp) at 2% consistency for 15 minutes then filtering and washing the pulp thoroughly [9,23]. Metal ions present in the original pulp and after chelation were determined by atomic absorption spectroscopy. The pulp (5.00g o.d.) was digested in 50 mL concentrated nitric acid and 5 mL sulfuric acid until no pulp was visible. Concentrated perchloric acid (5 mL) was then added and the solution heated until a clear solution was obtained. The results of metal ion analysis are given in Table 1.

TABLE 1. Metal ion content of pulps used in this work.

Wood type	Metal ion (ppm)*		
	Iron	Manganese	Copper
Eucalypt SGW	32	8	72
Chelated and washed Eucalypt SGW	32	1	32

\* Concentration determined by atomic absorption after digestion of pulp.

Iodometric determinations of hydrogen peroxide were performed at the commencement and completion of each bleaching sequence. Residual hydrogen peroxide levels were also determined at the completion of the acidic treatment. After addition of acidified potassium iodide and a few drops of ammonium molybdate solution, the liberated iodine was titrated against standard sodium thiosulfate solution [24].

Manganese adsorption experiments were performed by adding an appropriate amount of manganese nitrate to 1.0 g of pulp in 200 mL of Milli-Q water and allowing the suspension to stand at 20°C for 16 hours. After this time the pulp was filtered and washed twice with 100 mL of water. The cellulose used in these experiments was obtained from filter paper that had been stirred as an aqueous solution for several hours to allow separation of the fibres.

The brightness (ISO) of the bleached pulps were measured on a Zeiss Elrepho using a 457nm filter. Handsheets were also regularly prepared to monitor any changes in the original pulp

with storage time and to allow brightness gains to be calculated. The brightness of the unbleached pulp was in the range 53-55 ISO.

## RESULTS AND DISCUSSION

### Single Stage Bleaching under Alkaline Conditions.

Figure 1a shows the increase in brightness with time for the Eucalypt pulp at 4% consistency during alkaline bleaching at 50°C. The type of response observed is typical of many reported bleaching experiments using alkaline hydrogen peroxide, with the rate of brightness gain declining continuously as time progresses. For experiments at lower consistency, however, Figure 1a also shows an interesting effect during the initial stages of bleaching. At both 1% and 2% consistency, the initial rate of brightness gain is very low, and the typical bleaching profile is observed only after an extended bleaching period. This type of "induction effect" can also be observed for pulps which were chelated with EDTA and washed prior to alkaline peroxide bleaching, as shown in Figure 1b. This shows that at very low consistency, an induction effect is also observed, in which the brightness of the pulp actually decreases below the initial level of the unbleached pulp.

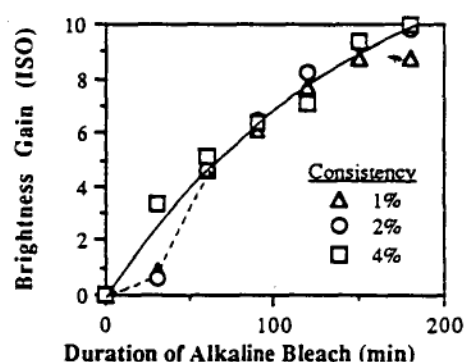


FIGURE 1a: Brightness response of untreated pulps to alkaline peroxide bleaching at 1%, 2% and 4% consistency, pH 11.0.

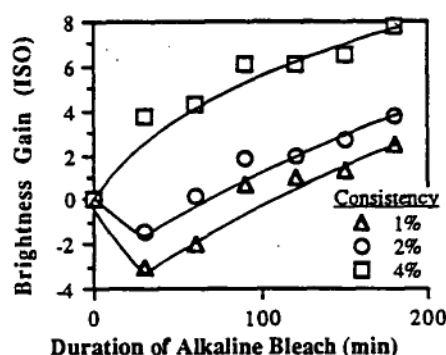


FIGURE 1b: Brightness response of chelated pulps to alkaline peroxide bleaching at 1%, 2% and 4% consistency, pH 11.0.

This evidence indicates that removing metal ions from a pulp can, under certain conditions, adversely effect the bleaching of the pulp during single stage alkaline peroxide treatment. If the metal ion concentration is reduced to very low levels the brightness response of the pulp can actually be retarded. From the analysis of the metal ions in the pulp (Table 1) it would appear that removal of manganese or copper is probably responsible for this effect as iron levels do not change significantly with chelation and washing.

Figures 2a and 2b show the influences of adding various levels of manganese to a pulp which has been chelated with DTPA and then washed. In each case, the pulp was allowed to remain in contact with a solution containing manganese nitrate at the appropriate concentration for 20 minutes at pH 7 prior to bleaching at 1% consistency. The concentration of manganese reported indicates the amount of manganese added, which does not include the residual level in the pulp after chelation (1 ppm). It is clear that as the total amount of manganese is increased, the response to brightness gain in alkaline peroxide is enhanced, and the effect of the induction process is reduced. However, addition of manganese in excess of the levels normally encountered in the pulp does not continue to give increased brightness. From this we can deduce that an optimum amount of transition metal ions needs to be present to give the most effective bleaching. Figure 2b shows that this corresponds to approximately 8 ppm manganese for bleaching at 1% consistency. If insufficient metal ions are present then an

induction period is observed, while if excess metal ions are present peroxide decomposition leads to loss of active bleaching species.

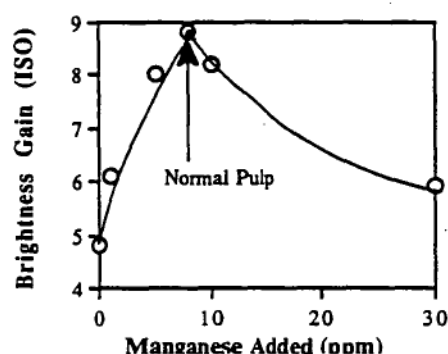


Figure 2a: Brightness response of pulps to a single stage alkaline bleach, pH 11.0, 1% consistency.

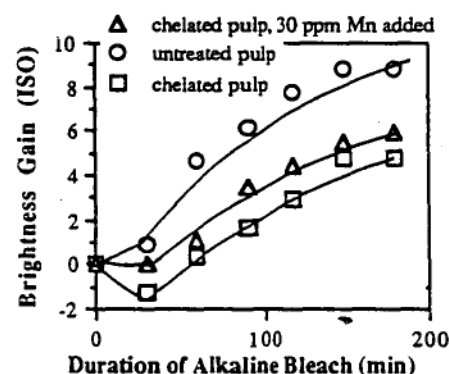


FIGURE 2b: Brightness gain plotted against amount of manganese added. Chelated pulp, pH 11.0, 1% consistency, 180 minutes.

Figure 3 shows the effect of treating pulps with alkali (pH 11.0) in the absence of peroxide at 1%, 2% and 4% consistency. For both chelated and untreated pulps alkaline treatment produces a darkening of the pulp. For the chelated pulps much greater brightness losses are observed than for untreated pulps. This indicates that metal ions in some way prevent the reactions that give rise to alkali darkening from occurring. This again indicates that the presence of metal ions may be useful in peroxide bleaching in reducing darkening of pulps. This is in accordance with other results [25] which indicate that some metal ions can indeed inhibit darkening reactions. Iron, manganese and copper, however, are reported to

accelerate darkening [25]. Other metal ions which are present in the normal pulp could be responsible for this reduced darkening observed for normal pulps compared to chelated pulps. The darkening reactions appear to be near completion after 30 minutes at 50°C, which is similar to results previously reported [25]. It is not clear from this data whether the metal ions protect potential chromophore sites in the lignin or act in some other way. It should also be noted that the situation in the absence of peroxide may be different to that in the presence of peroxide. If the pH in a bleach is too high, or the peroxide residual at the end of a bleach is too low darkening reactions may still occur.

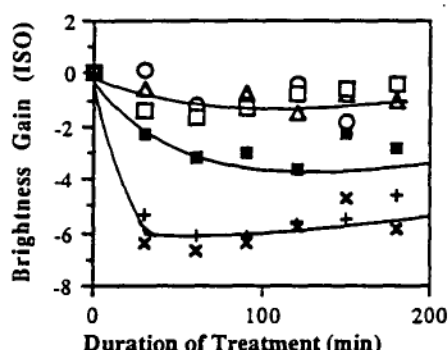


Figure 3: Brightness response of various pulps to treatment with alkali in the absence of peroxide, pH 11.0. Normal pulps at various consistencies: Δ, 1%; ○, 2%; □, 4%. Chelated pulps: +, 1%; x, 2%; ⊞, 4%.

#### Location of Manganese During Bleaching Processes.

The manganese ions present in mechanical pulps are generally considered to originate in the wood itself, rather than from processing equipment, as in the case of iron [26]. Having shown that under certain conditions the presence of manganese can have beneficial effects during conventional single stage alkaline peroxide bleaching, it is useful to consider the location of the manganese within the pulp and during the bleaching process, as this may influence the observed effects of the presence of transition metal ions. The uptake of manganese ions from solution by various pulps after allowing the system to equilibrate for 16 hours at 20°C is shown in Figures 4a and 4b. These figures show that manganese does not bind to any significant degree to pure

cellulose at either pH 7 or 9. In contrast, levels of up to 5000 ppm of manganese were observed for the unbleached SGW, thus indicating that the manganese is probably bound to the lignin portion of the pulps, as has been previously reported [26]. Under neutral conditions, using a limiting uptake of 3000 ppm for unbleached pulp and 5000 ppm for bleached pulp, each manganese ion could be associated with approximately 3% of the C<sub>9</sub> lignin units for the unbleached pulp and 5% for the bleached pulp. At pH 9 for both bleached and unbleached pulps manganese is associated with approximately 5% of lignin units. These results indicate that the manganese ions are bound at specific sites in the lignin structure. However, the ratios of manganese to lignin C<sub>9</sub> units do not appear to correlate with the amount of any simple functional group such as carbonyl or phenolic hydroxyl, as the measured ratios are too low [27]. However, the manganese may be linked with some specific combination of groups within the lignin such as an adjacent carbonyl and free phenolic hydroxyl group in some particular stereochemical configuration.

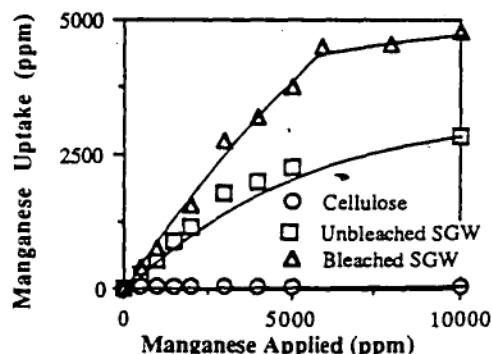


FIGURE 4a: The uptake of manganese by various pulps as a function of manganese concentration in solution. 0.5% consistency, room temperature, pH 7.0.

If the presence of manganese in pulp can give rise to beneficial effects during peroxide bleaching, then it would be reasonable to suggest that the manganese bound to chromophores would be the most effective. Once the chromophore has been eliminated the manganese could either remain attached to the lignin or be released into solution. Figure 5a shows that during bleaching of the SGW pulp, manganese is released into the solution, with more manganese released from the untreated pulp compared to the chelated pulps.



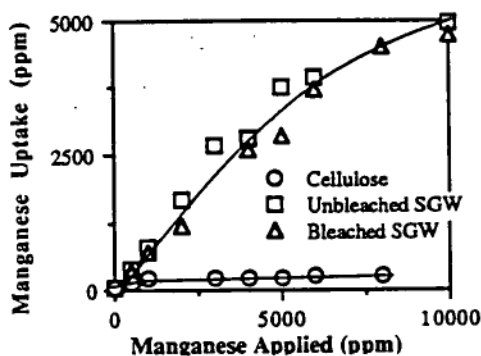


FIGURE 4b: The uptake of manganese by various pulps as a function of manganese concentration in solution. 0.5% consistency, room temperature, pH 9.0.

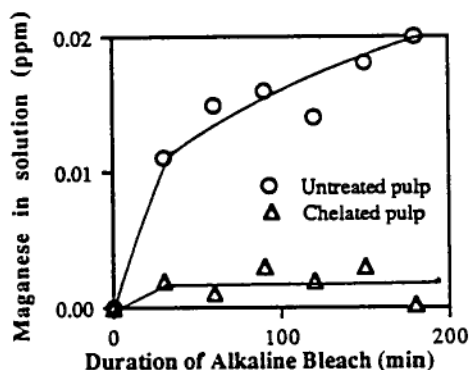


FIGURE 5a: The variation of manganese concentration in solution with time during bleaching of pulps. 1% consistency, pH 11.0, 50°C.

In the presence of alkali alone, the levels of manganese in solution vary as shown in Figure 5b. It appears that the manganese is initially released from the sites to which it is bound. However with time, the levels decrease due to precipitation of manganese as insoluble oxides and hydroxides. This maximum, at approximately 30 minutes, also corresponds to the time over which alkali darkening reaction occur (see Figure 3).

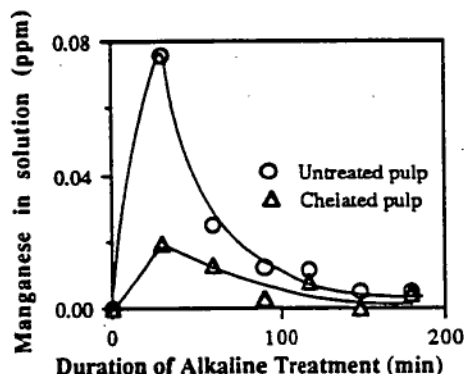


FIGURE 5b: Variation of manganese concentration in solution with time during treatment of pulps with alkali in the absence of peroxide, 1% consistency, pH 11.0.

During bleaching approximately 25% of the total manganese is released from the untreated pulp. This may indicate that the sites of attachment may be being destroyed during the bleaching process. During alkaline treatment approximately 100% of the manganese is released.

#### Two Stage Bleaching Processes

Two stage bleaching sequences using acidic and alkaline conditions have been reported previously [16-20]. In many of these processes [16,18-19] the addition of transition metal ions to the first stage of the sequence is an important part of the process. In the other studies [17,20] it would appear that the metal ions occurring naturally in the pulp are sufficient to give the enhanced brightness. We have suggested [18-19] that the presence of transition metal ions, whether naturally occurring or artificially introduced, is important in the first stage of these two stage processes, and may be associated with the production of free radical species. Although we did not observe any increase in brightness after acidic peroxide treatments of *Eucalypt* SGW pulps [18] we have suggested that free radical species generated through decomposition of hydrogen peroxide in the presence of certain transition metal ions may render the chromophores present in the pulp more susceptible to subsequent alkaline peroxide bleaching [18].

Figure 6a shows the brightness response of pulps (chelated with DTPA and washed) comparing a conventional single stage alkaline peroxide treatment with a two stage, acid-alkali

treatment, both at 1% consistency. At any time the brightness of the pulp bleached using the two stage process is greater than that using only a single stage bleach. It can also be seen that the initial brightness loss observed in the single stage process is not present in the two stage process, although there is still an induction period. The total peroxide consumption after three hours for the single stage bleach (0.29% on o.d. pulp) and the two stage process (0.33% on o.d. pulp) are comparable. However, the brightness gain for the two stage process (6.5) is greater than that for the single stage bleach (4.8), indicating an increased efficiency for the two stage process.

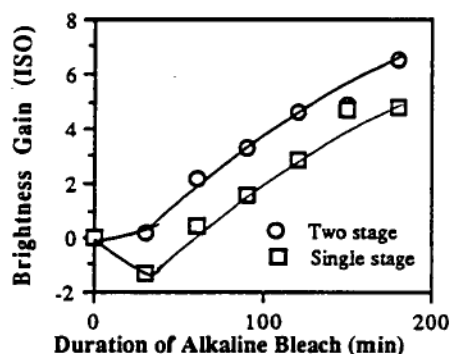


FIGURE 6a: Brightness response of a chelated pulp to single stage and two stage bleaching. Two stage: Acidic stage: pH 6.0, 15 minutes; Alkaline stage: pH 11.0. Single stage: pH 11.0.

Figure 6b shows the effect of adding various levels of manganese to a pulp which has been chelated with DTPA and washed prior to a two stage bleaching sequence. The pulp was allowed to stand in contact with the manganese solution for 20 minutes before commencement of the bleach. The amount of manganese reported corresponds to that added to the pulp and does not include that already present (1ppm). It is clear that increasing the total amount of manganese present enhances the brightness response of the pulp. However, as shown in Figures 6c and 6d, it is clear that this enhanced brightness is achieved by consuming considerably more hydrogen peroxide.

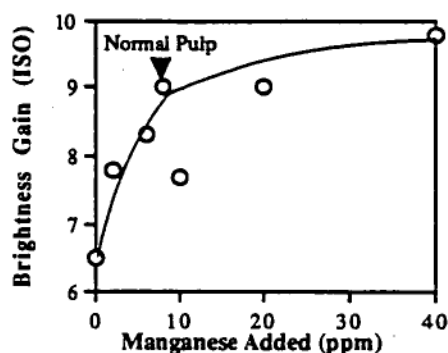


FIGURE 6b: Final brightness of chelated pulps after a two stage bleaching sequence with manganese addition. Acidic stage: pH 6.0, 15 minutes; Alkaline stage: pH 11.0, 180 minutes.

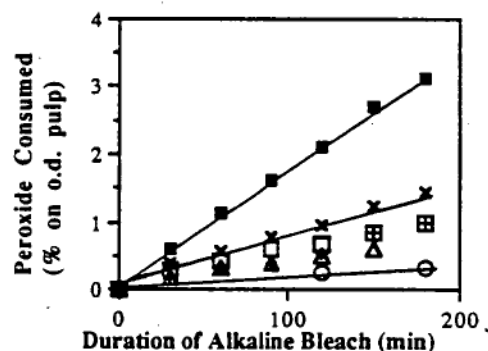


FIGURE 6c: Variation in peroxide consumption with manganese addition during a two stage bleaching sequence. Conditions as in Figure 6b. O, chelated pulp; □, normal pulp; Manganese added: Δ, 2 ppm; +, 10 ppm; x, 20 ppm; ■, 40 ppm.

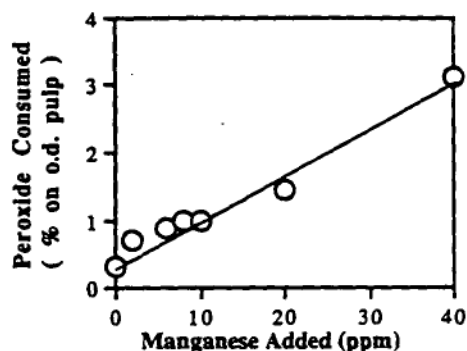


Figure 6d: Peroxide consumption against the amount of manganese added. Conditions the same as in figure 6b.

Figure 7a shows the brightness response of both chelated and untreated pulps to a two stage, acid-alkali bleaching sequence at 1% consistency. Clearly the presence of additional metal ions in normal pulp gives an increased brightness and also removes the induction period.

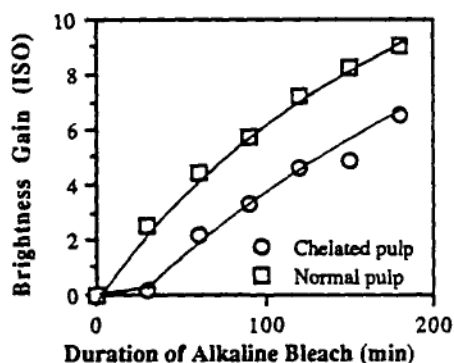


FIGURE 7a: Brightness response of normal and chelated pulps to a two stage bleaching sequence. Conditions as in Figure 6b.

Chromium ions are known to catalytically accelerate decomposition of hydrogen peroxide in the pH range 4 to 7. The addition of chromium [18], to a two stage bleaching sequence can be used to give brighter pulps. Figure 7b shows that the brightness response of pulp to a two stage process in the presence of chromium (curve a) can give a significantly higher brightness than a single stage alkaline bleach (curve b). For a two stage process without added chromium (curve c) an intermediate brightness gain is achieved. This

clearly shows that the metal ions naturally present in the pulp, or addition of chromium ions can cause increased brightness in these two stage processes. In each of these cases the peroxide consumption per unit of brightness gain is approximately equal [18].

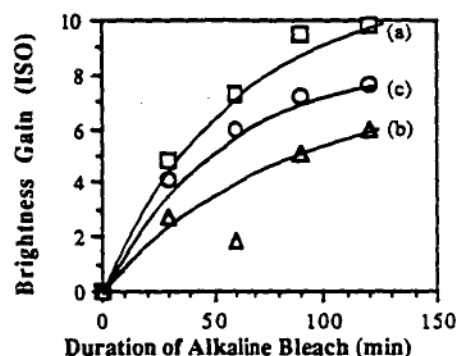


FIGURE 7b: Brightness gain plotted against time of alkaline bleach (pH 11.0) (a) acidic treatment: pH 5.8, 30 minutes, 0.13% chromium (on o.d. pulp); (b) no acidic treatment; (c) acidic treatment: pH 5.8, 30 minutes, no added chromium.

## CONCLUSION

Removal of metal ions prior to bleaching with hydrogen peroxide can have a negative effect on the brightness of the pulp under certain conditions. This effect, however, is reversible with the addition of metal ions to the pulp prior to bleaching. By increasing the consistency of the pulp, which effectively increases the concentration of metal ions in solution, the effect can also be removed. Alternatively use of a two stage bleaching sequence using an acidic peroxide treatment, followed by a traditional alkaline bleach stage can nullify the effects of metal ion removal.

This study has shown that contrary to the traditional viewpoint in the pulp and paper industry, transition metal ions can have a positive role in peroxide bleaching of pulps under certain conditions. It is possible that these effects can be observed only under conditions not normally used in bleaching (e.g. low consistency, very low metal ion content). However, the influences of these processes may still be valid under normal bleaching conditions, and may be important to the overall understanding of the mechanisms involved.

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Two-Stage Peroxide Bleaching of Eucalypt SGW with Aluminium and Metal ion  
Catalysts.

G.C. Hobbs, J. Abbot, J. Pulp Paper Sci., Submitted (1992).

## TWO-STAGE PEROXIDE BLEACHING OF EUCALYPT-SGW WITH ALUMINIUM AND METAL ION CATALYSTS.

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### ABSTRACT

The addition of aluminium nitrate to a two-stage, acid/alkali, hydrogen peroxide bleach of *Eucalypt* SGW can enhance the brightness gain of the pulp over a range of consistencies. It is proposed that the presence of aluminium ions modifies the catalytic behaviour of the transition metal ions present in the pulp, especially manganese, reducing peroxide consumption whilst increasing the brightness of the pulp. The two-stage process, under optimised conditions at low consistency, consumes considerably less peroxide while achieving a greater brightness increase than a conventional single stage alkaline peroxide bleach.

### INTRODUCTION

Traditionally transition metal ions, particularly iron, manganese and copper, are thought to have a detrimental influence during peroxide bleaching as they catalytically decompose hydrogen peroxide (1,2), effectively reducing the charge of bleaching agent (3-6). However, recent work (7-10) has shown that under certain conditions transition metal ions can be beneficial to peroxide bleaching. This idea, together with bleaching under conditions not normally employed, such as the use of acidic and neutral pH as part of a two-stage bleaching sequence, can give rise to efficient peroxide bleaching processes (7). For example, the addition of chromium nitrate (which catalytically decomposes hydrogen peroxide under slightly acidic conditions) to a two-stage acid/alkali bleaching sequence has been shown (7,11) to give greater brightness enhancement than a conventional single stage process. Metal ions naturally occurring in

wood (3) or released from processing equipment (12) can also give rise to enhanced brightness using a two-stage bleach. The aim of this work is to investigate possibilities for modifying the catalytically active species present to reduce the peroxide consumption while still achieving the enhanced brightness levels attained for two-stage bleaching sequences.

### EXPERIMENTAL

#### Materials

Hydrogen peroxide (30%), aluminium nitrate (98%) and sulfuric acid (98%) were obtained from Ajax chemicals. Manganese nitrate (99.9%), iron(III) nitrate (99.9%), copper nitrate (99.9%) and potassium hydroxide (99.99%) of semiconductor purity were supplied by Aldrich chemicals. Semiconductor grade potassium hydroxide was used as the alkali source, as this introduces very low levels of transition metal ion impurities (1,2).

#### Procedures

Blocks of *Eucalyptus Regnans* wood were soaked for three days in Milli-Q water and then ground at 80°C in the presence of dilute sodium hydroxide on a small scale grindstone at Australian Newsprint Mills, Boyer. The pulp was washed with distilled water and filtered to increase the consistency from 1.5% to 20%, then stored at 4°C until used.

Bleaching studies were carried out in polyethylene reaction vessels maintained at 50°C in a constant temperature water bath. Duplicate experiments were performed in all cases. Bleaching experiments were performed by pre-heating the required amounts of pulp and Milli-Q water (1,2) prior to addition of solutions of aluminium nitrate and, where indicated, transition metal ion nitrates, hydrogen peroxide and finally acid or alkali to give a total volume of 500ml. The resulting suspension was mechanically stirred to ensure even distribution of chemicals. Experiments were performed at 1%, 4% and 8% pulp consistency. The initial charges of hydrogen peroxide were 6% (1% consistency), 1.5% (4% consistency) and 0.75% (8% consistency) on o.d. pulp. For bleaching under acidic conditions the pH was adjusted to the appropriate level (generally 6.0) with sulfuric acid. After the prescribed time sufficient potassium hydroxide was added to adjust the pH to the level required for the second stage (generally 11.0).

Chelated pulps were prepared by treating the pulp with 0.2% DTPA (on o.d.

pulp) at 2% consistency for 15 minutes then filtering and washing the pulp thoroughly (12). Metal ions present in the original pulp and after chelation were determined by atomic absorption spectroscopy. The pulp (5.00g o.d) was digested in 50 mL concentrated nitric acid and 5 mL sulfuric acid until no solid was visible, 5 mL concentrated perchloric acid was then added and the solution heated until a clear solution was obtained. The resulting solution was diluted to 100 mL prior to analysis.

Iodometric determinations of hydrogen peroxide were performed on the initial pulp suspension, and to the filtrate at the completion of the bleaching run. Hydrogen peroxide levels were also determined at the completion of the acidic treatment. After addition of acidified potassium iodide and a few drops of ammonium molybdate solution the liberated iodine was titrated against sodium thiosulfate solution (13).

The brightness (%ISO) of the bleached pulps was measured on a Zeiss Elrepho using a 457nm filter. Handsheets were also regularly prepared to monitor any changes in the original pulp with storage and to measure brightness gains. Unbleached pulp brightness was in the range 53-55 %ISO.

## RESULTS AND DISCUSSION

### The Role of Aluminium in Peroxide Bleaching.

Generally the presence of aluminium is considered undesirable in conventional alkaline peroxide bleaching of mechanical pulps, as it results in lower final pulp brightness (14,15). This is illustrated for a *Eucalypt* stoneground wood (SGW) pulp, in Figure 1a for a conventional single stage alkaline peroxide bleach. However, Figure 1a also shows that when a two-stage, acid-alkali peroxide bleaching sequence is employed the addition of aluminium to the bleaching liquor can enhance pulp brightness beyond that achieved in a single stage process by approximately 2-3 %ISO, concurrently reducing peroxide consumption. Figure 1b shows that although there is a reduction in peroxide consumption with increasing aluminium addition, this does not result in a higher brightness gain for a single stage bleach. The dose of aluminium added is also critical in achieving maximum brightness gain in the two-stage process, although increasing the dose of aluminium above that required for maximum brightness enhancement still leads to stabilization of the bleach liquor. Most of the peroxide consumption occurs during the first (acid) stage of the bleaching sequence as shown in Table 1. However, as shown in Figure 2, the brightness gain achieved during this stage is negligible, as previously reported for other two-stage processes of this type (7,11).

Figure 3a shows that the duration of the first stage of the acid/alkali bleaching

sequence is important in achieving maximum brightness gain, with the optimum time being 15 minutes under the conditions used here if peroxide consumption is also considered. Longer times appear to result only in increased peroxide consumption during the acid stage, leaving less peroxide available for bleaching in the alkaline stage, as shown in figure 3b. Figure 4 shows that the pH of the first stage of the bleaching sequence does not significantly change the final pulp brightness after the alkaline stage. Therefore, neutral conditions would be most economical as this will eliminate the need to add acid to the initial liquor and subsequently reduce the amount of alkali required to reach sufficiently alkaline conditions during the second stage.

At 1% stock consistency the addition of small quantities of aluminium to a two-stage acid/alkali peroxide bleaching sequence can enhance the brightness gain with a simultaneous decrease in the amount of peroxide consumed. Figures 5a and 6a show that enhanced brightness response can also be achieved at 4% and 8% stock consistency at aluminium levels of 25-100 ppm (on pulp). However, the reduced peroxide consumption observed at 1% stock consistency is not observed at higher consistencies, as shown in figures 5b and 6b.

### The Interaction of Aluminium with Transition metal ions.

Table 2 shows the metal ion content of the pulp before and after chelation and washing. In particular, this shows that the levels of manganese and copper are changed significantly by chelation, whereas the iron and aluminium content remains at similar levels. This is in agreement with other studies (16) which have shown similar results. If the presence of transition metal ions in the pulp is important in producing the enhanced brightness observed in the present studies, removal of the metal ions by chelation and washing prior to bleaching may vary brightness response. Figure 7 shows the effect on brightness gain of removing metal ions from the pulp prior to bleaching using the two-stage acid/alkali process in the presence of aluminium. Clearly the brightness response of the chelated pulp is greatly reduced compared to that of the untreated pulp, indicating that the presence of transition metal ions is indeed important in this process.

As chelated pulps produce a lower brightness response, it may be possible to determine which transition metal ions are involved in promoting brightness development during the two-stage process. For a fixed addition of aluminium to the chelated pulp, the brightness gain was reduced with increasing doses of copper as shown in Figure 8a. The peroxide consumption does not change significantly with copper addition in the presence of aluminium, even though copper is known to catalytically decompose hydrogen peroxide under typical alkaline bleaching conditions

(3). Figure 8b shows the effect of addition of iron. This shows that the peroxide consumption increases with addition of the metal ion and that the brightness of the pulp initially decreases. However at higher levels of iron addition the brightness gain increases, possibly indicating a role in bleaching for the products of catalytic decomposition of hydrogen peroxide (17).

The addition of manganese in the presence of a constant amount of aluminium exhibits a different effect compared to the addition of either iron or copper. Figure 8c shows that the addition of less than 10 ppm manganese in the presence of 40 ppm aluminium enhances the brightness gain during the two-stage acid/alkali process. The optimum level of manganese addition was found to be 2 ppm, corresponding to an Al:Mn molar ratio of 35. This can be compared with a molar ratio of 16 corresponding to maximum brightness gain in Figure 1a. It is not clear at this stage whether these ratios reflect the chemical composition of particularly active catalytic species formed through interactions between aluminium and manganese. Mixed binuclear species formed through oxy or hydroxy bridges between transition metal ions and other centres capable of undergoing hydrolysis have been postulated, as for example in Mg-O-Fe structures implicated in the stabilization of iron catalysts by magnesium in the presence of alkaline peroxide (6,18). Both magnesium (1) and aluminium (19) are known to undergo hydrolysis to produce dimers and higher polymers, even in acidic and neutral solution. Studies in the absence of pulp (1) have shown that the addition of aluminium ions to alkaline solutions containing manganese shows a reduction of peroxide decomposition for molar ratios of Al:Mn in the range 100:1 to 200:1. It has been proposed that complex species linking metal ion centres through oxy and hydroxy bridges may explain this type of effect. For example Gilbert et al (6) suggest that this type of species could account for the stabilizing influence of magnesium salts when added to alkaline peroxide solutions containing iron. This concept has been further extended to include other transition metals in the presence of silicate, magnesium and zinc. Further studies will be required to identify and characterize active catalytic species formed through interaction of manganese and aluminium.

It has previously been reported (7-8,10) that the addition of transition metal ions such as chromium, titanium and vanadium during two-stage peroxide bleaching processes can enhance the brightness development of mechanical pulps. It has also been shown (9,11) that the metal ions occurring naturally in the pulp can give rise to enhanced brightness gains for a two-stage acid/alkali peroxide bleaching sequence. This has been demonstrated by observing the effects of removing the naturally occurring metal ions by chelation and washing prior to two-stage peroxide bleaching (7,8). When aluminium is added to the pulp changes occur in the nature of the catalytic species present under acidic or neutral conditions. Reactions occurring in acidic or neutral

peroxide in the presence of these catalysts render the chromophores present in the pulp more susceptible to elimination in the subsequent alkaline stage. It has been suggested that generation of free radical species in the presence of these catalysts may play a significant role in these types of processes (7-11).

### CONCLUSION

This study has shown that transition metal ions present in mechanical pulps can play a useful role in peroxide bleaching. At low consistency (1%) the addition of aluminium nitrate to a two-stage, acid-alkali peroxide bleaching sequence can enhance the brightness gain of the pulp, and reduce the amount of peroxide consumed compared to a conventional single-stage alkaline processes. A similar enhancement of brightness response is also observed at 4% and 8% consistency. These effects may be due to an interaction between the manganese present in the pulp and added aluminium. The properties of transition metal ion catalysts naturally present in the pulp appear to be modified by the addition of aluminium so that enhanced brightness gain is achieved.

This study provides further evidence that transition metal ions can indeed play an important role in peroxide bleaching, and are not universally undesirable as traditionally thought. Our work demonstrates the potential for utilizing the catalytic properties of naturally occurring transition metal ions in the pulp, and shows that these positive effects can be promoted through addition of trace amounts of catalytically inactive elements such as aluminium. The use of these types of catalytic systems are more likely to be given commercial consideration than other previously reported systems which rely on the addition of transition metals such as chromium or titanium.

### ACKNOWLEDGMENT

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TABLE I. Comparison of peroxide consumption in acid and alkaline stages of a two-stage bleaching sequence.

Aluminium dose (ppm on o.d. pulp)	Peroxide consumed (% on o.d. pulp)		Total
	Acid stage	Alkaline stage	
0	0.51	1.65	2.16
50	0.41	0.08	0.49
100	0.24	0.15	0.39
250	0.33	0.15	0.48
500	0.43	0.15	0.58

Conditions: 1% consistency, 50°C, Initial charge peroxide 6.0% on pulp. Acid stage: 30 minutes, initial pH 6.0. Alkaline stage: 120 minutes, initial pH 11.0.

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**TABLE 2** Metal ion content of pulps used in this work.

Wood type	Metal ion (ppm)*			
	Iron	Manganese	Copper	Aluminium
<i>Eucalypt</i> SGW	32	8	72	12.8
Chelated <i>Eucalypt</i> SGW	32	1	32	11.4

\* Concentration determined by atomic absorption after digestion of pulp.

## LIST OF FIGURES

- Figure 1a. Brightness response of pulp to both a single stage and two-stage bleach with varying levels of aluminium. 1% consistency; Acidic stage: pH 6.0, 30 minutes; Alkaline stage: pH 11.0, 120 minutes.
- Figure 1b. Variation in peroxide consumption during a single stage and two stage bleaching sequence in the presence of various levels of aluminium. Conditions as in Figure 1a
- Figure 2. Brightness response of pulp to an acidic peroxide treatment in the presence of various levels of aluminium. 1% consistency, pH 6.0, 60 minutes.
- Figure 3a. The effect of varying the time of the acidic treatment on the brightness gain of the pulp during a two-stage peroxide bleaching sequence. 1% consistency; 50 ppm added aluminium, Acidic stage: pH 6.0; Alkaline stage: pH 11.0, 120 minutes.
- Figure 3b. The effect of time on peroxide consumption in the acid (pH 6.0) stage in the presence of 50 ppm added aluminium, 1% consistency, 50°C.
- Figure 4. The effect of varying the pH of the first stage of a two-stage treatment. 1% consistency; First stage: 30 minutes; Second stage: pH 11.0, 120 minutes.
- Figure 5a. Brightness response of pulp to two-stage bleach with various levels of aluminium. 4% consistency, 1.5% peroxide charge; Acidic stage: pH 6.0, 15 minutes; Alkaline stage: pH 11.0, 150 minutes.
- Figure 5b. Peroxide consumption of pulp during a two-stage bleach with various levels of aluminium. Conditions as in Figure 7a.

Figure 6a. Brightness response of pulp to two-stage bleach with various levels of aluminium. 8% consistency, 0.75% peroxide charge; Acidic stage: pH 6.0, 15 minutes; Alkaline stage: pH 11.0, 120 minutes.

Figure 6b. Peroxide consumption of pulp during a two-stage bleach with various levels of aluminium. Conditions as in Figure 7a.

Figure 7. Plot showing the different brightness response of normal and chelated pulps to a two-stage bleach. 1% consistency; Acidic stage: pH 6.0, 30 minutes; Alkaline stage: pH 11.0, 120 minutes.

Figure 8. Correlation between the brightness gain and the peroxide consumption for chelated pulp treated with various levels of transition metal ion. 1% consistency, 40 ppm aluminium; Acidic stage: pH 6.0, 15 minutes; Alkaline stage: pH 11.0, 180 minutes (a) Fe, (b) Cu, (c) Mn.

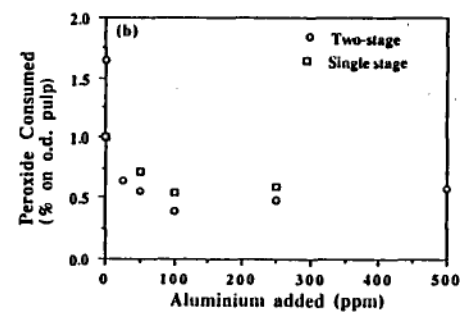
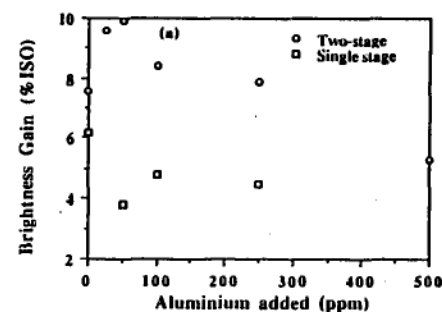


Figure 1

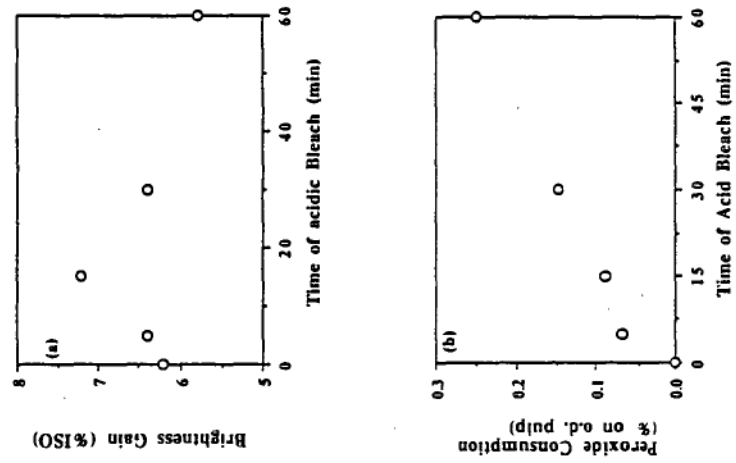


Figure 3

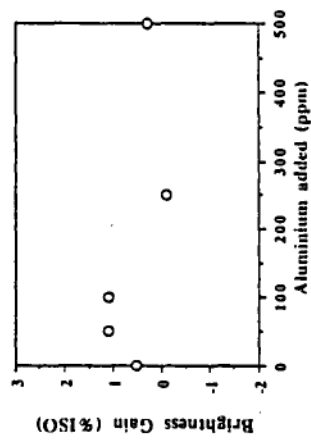


Figure 2

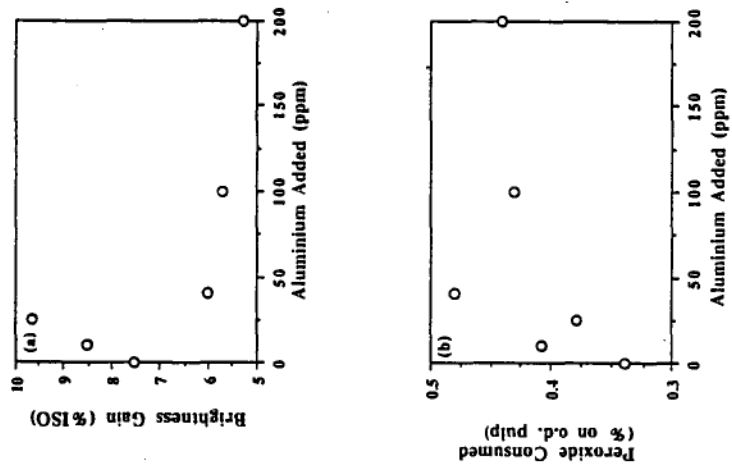


Figure 5

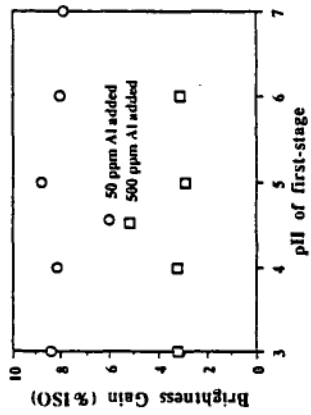


Figure 4

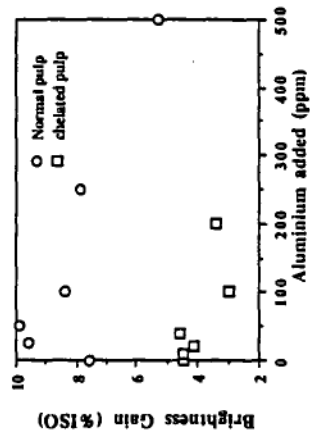


Figure 7

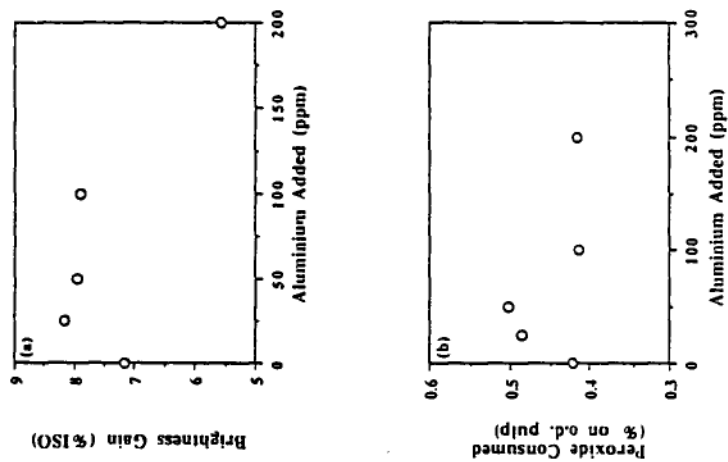


Figure 6

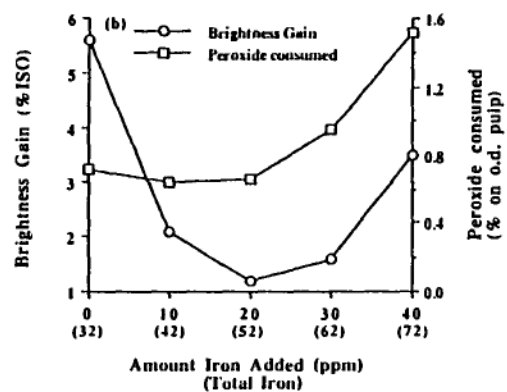
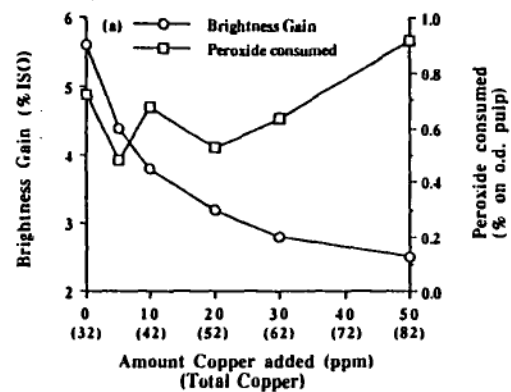
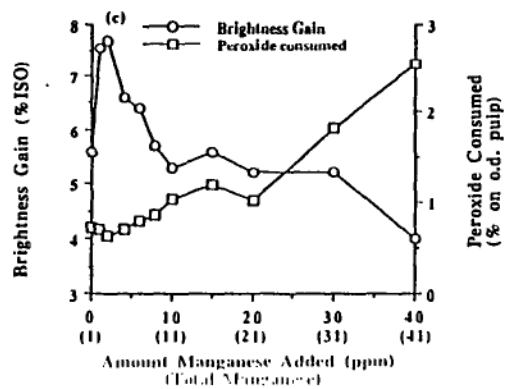


Figure 8



The Influence of Magnesium and Manganese on Alkaline Peroxide Bleaching of Pinus  
Radiata TMP.

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**THE INFLUENCE OF MANGANESE AND  
MAGNESIUM ON ALKALINE PEROXIDE  
BLEACHING OF *PINUS RADIATA* TMP**

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**ABSTRACT**

The presence of manganese in mechanical pulps can produce a significant contribution to decomposition of hydrogen peroxide under bleaching conditions. Removal of manganese by chelation and washing or the addition of magnesium salts reduces peroxide decomposition. Studies on the effect of magnesium addition to alkaline solutions containing manganese in the absence of pulp do not provide a good model to simulate the behaviour of the system under bleaching conditions, as increased decomposition is observed. Introduction of a lignin model compound, such as vanillin, however, leads to peroxide stabilization in the presence of magnesium and provides a more appropriate system to study. The influence of the presence of manganese in pulp on brightness gain can be explained solely on the basis of additional peroxide consumption. The effect of magnesium, however, cannot be attributed solely to additional stabilization of peroxide, and these results are discussed in the context of kinetic models for peroxide bleaching.

**INTRODUCTION**

It is well known that the presence of certain transition metal ions in mechanical pulps can have a detrimental influence during bleaching with alkaline hydrogen peroxide (1-7). This has been attributed to increased decomposition of the bleaching reagent (1,4). Iron, copper and manganese are thought to play a major role in this particular problem, because these metals are present in the wood itself and can also accumulate from sources including process equipment (5). Several inorganic species are known to have stabilizing influences during peroxide bleaching, with sodium silicate and magnesium salts used commonly during industrial processing (8). This study focuses on the action of manganese as a major cause of

decomposition under alkaline conditions, and also the role of magnesium, which can contribute to stabilization.

**EXPERIMENTAL**

Hydrogen peroxide (30%) was obtained from Ajax Chemicals. Magnesium nitrate (99.0%), vanillin (99%), manganese nitrate (99.99%), DTPA (97%) and sodium hydroxide of semiconductor purity (99.99%) were supplied by Aldrich Chemicals. The *Pinus radiata* thermo-mechanical pulp was provided by Australian Newsprint Mills, Boyer Mill, from TMP unit 2. The pulp was stored at 8% consistency at 4°C until used.

Bleaching studies were carried out using polyethylene or Teflon reaction vessels maintained at 50°C or 95°C in a constant temperature water bath. Pulp suspensions were stirred during the course of the bleaching reactions. The bleaching experiments were performed by mixing the required amounts of pulp, hydrogen peroxide, sodium hydroxide (and metal salts where appropriate) with the required volume of Milli-Q deionised water to give the desired consistency. The pulp and dilution water were heated to reaction temperature before addition of reagents. The chelated pulps were prepared by treating the TMP with 0.5% DTPA at 2% consistency for 30 minutes, filtering and then thoroughly washing the pulp with Milli-Q deionised water. The concentrations of transition metal ions present in the original pulp and after chelation were determined by atomic absorption after digestion with nitric acid.

Pulp samples were withdrawn at intervals to determine the brightness of the pulp and consumption of hydrogen peroxide. Residual peroxide concentrations were determined on filtrates by iodometric titration with standard sodium thiosulfate, after acidification and addition of potassium iodide and a few drops of saturated ammonium molybdate solution (9). All pulp samples were thoroughly washed with deionised water. The brightnesses (%ISO) of bleached pulp handsheets were measured with a Zeiss Elrepho using a 457nm filter. The measured brightness of the unbleached pulp was 58.0, and this was not found to vary over a 30 day period during storage.

Peroxide decomposition experiments in the absence of pulp were carried out in polyethylene vessels at either 50°C or 20°C. The volume of solutions was 500mL. UV/visible absorbance measurements were made using a Varian DMS 100 spectrophotometer.

## RESULTS AND DISCUSSION

### Bleaching of *Pinus Radiata* TMP in the presence of Manganese and Magnesium

Table 1 shows the concentrations of manganese, iron and copper present in the pulp, as determined by atomic absorption. Chelation of the pulp with DTPA, followed by washing with deionised water is effective in reducing the concentrations of these transition metal ions (Table 1). It is apparent that, while the concentration of manganese is highest in the original pulp, it is also most easily removed by complexation and washing (5,10).

Table 1 Concentrations of transition metal ions (ppm) in *Pinus radiata* TMP

TMP	Mn	Fe	Cu
Normal	32.1	6.0	4.2
Chelated	2.29	2.45	1.3

Figure 1 shows the increase in brightness with time for alkaline peroxide bleaching, initial peroxide charge 6% on o.d. pulp, of *P. radiata* TMP at 4% consistency and 50°C. As expected, the chelated pulp is more easily bleached than the normal pulp. This can be associated with reduced loss of the peroxide during the initial period of bleaching due to catalytic decomposition induced by the presence of transition metals.

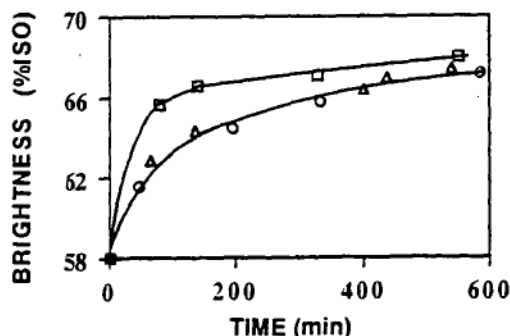


Figure 1. Brightness gain for (a) normal pulp ○ ; (b) chelated and washed pulp □ ; (c) chelated and washed pulp with manganese addition (30ppm on pulp) Δ.

Figure 2 shows a comparison between peroxide decomposition for the normal and chelated pulps throughout the bleaching experiments. In all cases there is a rapid initial decline in peroxide concentration, with very little peroxide decomposition occurring after 1 hour. The difference in the levels of peroxide residuals reflects the extent of peroxide decomposition in side reactions caused by the presence of chelatable transition metals (approximately 30% of the initial charge).

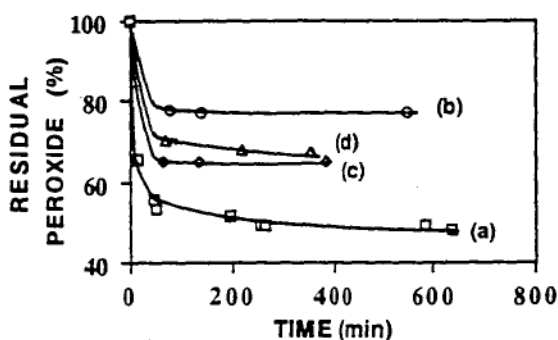


Figure 2 Changes in total peroxide concentration with time (a) normal; (b) chelated and washed pulp; (c) chelated and washed pulp with manganese added; (d) normal pulp with 2.5% magnesium nitrate (on o.d. pulp).

It can be demonstrated that manganese contributes significantly to this excess peroxide consumption (3,11). Figure 1 shows the effect on bleaching of restoring the concentration of manganese to the same level as that present in the original pulp. The pulp was allowed to stand in contact with a solution of manganese nitrate for 1 hour prior to bleaching. It is apparent that the bleaching response is reduced to a level somewhat above that for the original pulp. There is additional peroxide consumption compared to the chelated and washed pulp as shown in Figure 2, leading to a lower residual level of peroxide. The observed decomposition of peroxide is not as great as for the original pulp, however, showing that there is some contribution to catalytic decomposition from other chelatable metals in the pulp such as copper and iron.

Stabilization of hydrogen peroxide by use of complexing agents such as DTPA is widely used to improve efficiency during the bleaching of mechanical pulps (2,6,7). Other reagents known to produce stabilizing effects and improved

bleaching response include sodium silicate (8,12) and magnesium salts (8,12). The function of these additives is not yet clearly defined and remains the subject of debate (13-19). Figure 3 shows that addition of magnesium nitrate to the TMP improves brightness gain, and there is a corresponding stabilization of hydrogen peroxide as shown in Fig 2. As manganese has been shown to contribute significantly to peroxide decomposition, it is reasonable to assume that magnesium can produce a retarding influence on the catalytic activity of the manganese associated with the pulp, and this is now discussed.

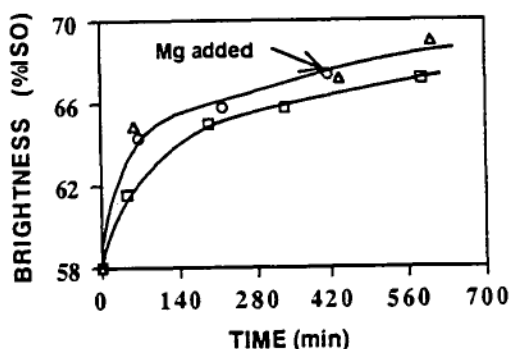


Figure 3. Brightness gain for (a) normal pulp  $\square$ ; (b) normal pulp with addition of magnesium nitrate:  $\circ$  2.5% on o.d. pulp;  $\Delta$  5.0% on o.d. pulp. Bleaching conditions as in Figure 1.

#### Hydrogen Peroxide Decomposition by Manganese

Catalytic decomposition of alkaline hydrogen peroxide has been shown to follow first order kinetics with respect to total peroxide concentration for introduction of both manganese salts (20-22) and manganese dioxide (23-26). Linear relationships between the calculated first order rate constants (figures 4 and 5) show that these processes are also first order with respect to manganese. Catalytic activity towards peroxide decomposition is also found to depend on pH (20,23,27) exhibiting a maximum at pH 11 for both systems as shown (Figure 6). This shows that addition of manganese nitrate to the alkaline medium produces a catalyst with approximately twice the activity compared to addition of manganese dioxide. However, it has previously been reported that the activity of manganese dioxide depends also on the particular crystalline modification used (23).

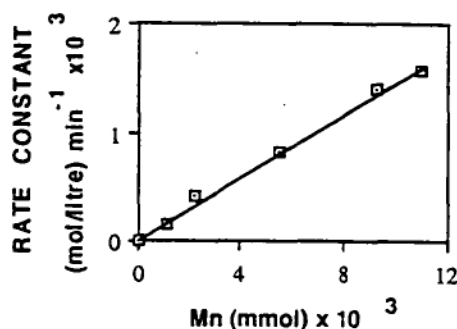


Figure 4. Dependence of first order rate constants for peroxide decomposition on manganese nitrate addition.

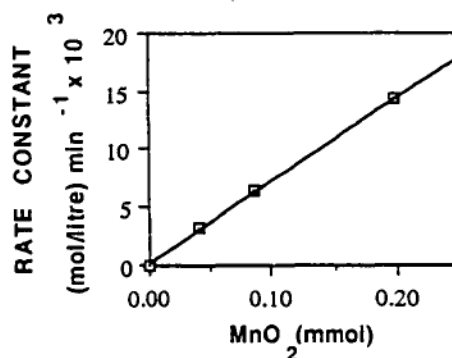


Figure 5. Dependence of first order rate constants for peroxide decomposition on manganese dioxide addition.

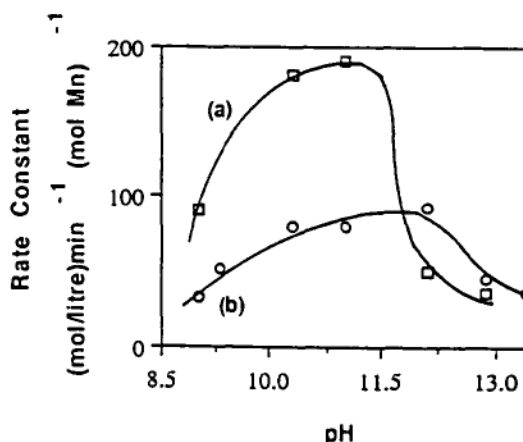


Figure 6. Effect of pH on the rate constant for peroxide decomposition at 20°C. (a) manganese nitrate added (b) manganese dioxide added.

Although manganese dioxide and soluble manganese salts appear similar in their behaviour as catalytic agents in peroxide decomposition, the two systems are not equivalent. Filtration of reaction mixtures containing manganese dioxide was found to remove the active catalyst, which is in agreement with previous observations that catalytic decomposition by manganese dioxide is a heterogeneous process (24). Filtration of alkaline solutions to which manganese nitrate has been added is found to remove most of the manganese (15), and the filtrate has little residual activity towards peroxide decomposition. Filtration of these alkaline systems after addition of hydrogen peroxide, however, shows that the manganese is present in a soluble form during the catalytic decomposition processes, and is reprecipitated as a brown solid when all the hydrogen peroxide has been consumed. It is well known that most transition metal ions are hydrolysed in aqueous media to give dimeric and polymeric structures in which the metal centres are linked by oxy and hydroxyl bridges (28-31). It is likely that manganese is present in these types of structure on addition of a soluble manganese salt to an alkaline solution (28), but not in a rigid lattice as found for manganese dioxide. Further evidence for this can be found by an examination of the manganese-magnesium systems.

#### Peroxide Decomposition by Manganese and Magnesium

The introduction of a combination of soluble magnesium and manganese salts has previously been reported to accelerate the catalytic decomposition of alkaline hydrogen peroxide (32,33). Figure 7 shows the effect of Mg/Mn molar ratio on the initial rate constant for peroxide decomposition at pH 11. These effects have been explained by suggesting that a manganese-peroxide complex decomposes on the surface of precipitated magnesium hydroxide (32). It has also been proposed that a complex is formed in which manganese and magnesium centres are linked through oxygen bridges (20) and this complex species is more active as a catalyst towards peroxide decomposition. Evidence for formation of a new species is provided by following the effect of the Mg/Mn molar ratio on absorbance (20) as shown in Figure 8. Further evidence is provided by e.s.r. studies (32), which have shown that when manganese and magnesium are coprecipitated from solution, the manganese centres are not coupled

since the distinctive set of six signals is clearly observed.

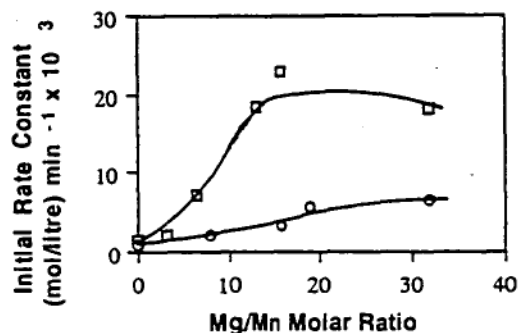


Figure 7. Effect of Mg/Mn molar ratio on initial rate constant for peroxide decomposition. Initial pH 11.0, initial amount of Mn introduced: □  $1.10 \times 10^{-5}$  mol; ○  $5.50 \times 10^{-6}$  mol.

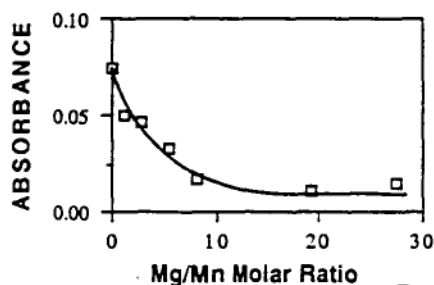


Figure 8. Effect of Mg/Mn molar ratio on absorbance at 350nm of solutions containing manganese nitrate and magnesium nitrate at 20°C. pH 10.3.

In contrast, addition of magnesium ions to a system initially containing manganese dioxide is found to have little influence on the decomposition of alkaline hydrogen peroxide, as shown in Figure 9. This implies that the linking of Mg and Mn centres through oxygen does not occur, as the manganese dioxide lattice does not break down to permit formation of Mn-O-Mg structures, except perhaps as a surface layer.

It is apparent from the above discussion that an examination of alkaline manganese-magnesium systems in isolation does not simulate the phenomena observed when magnesium is added

during peroxide bleaching of TMP containing high levels of manganese, as the stabilization of peroxide decomposition was not observed in either case. It is therefore appropriate to examine somewhat more complex systems where possible interactions with components of the pulp are also considered.

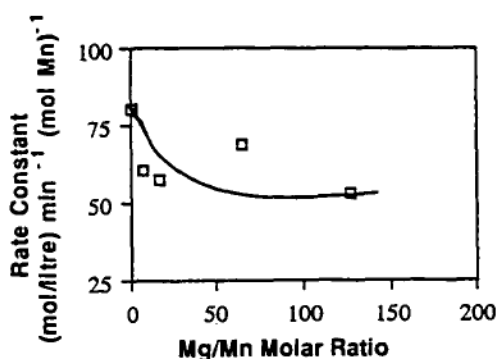


Figure 9. Effect of Mg/Mn molar ratio on initial rate constant for peroxide decomposition with initial introduction of manganese dioxide at 20° C. pH 10.3.

#### Binding of Manganese to Pulp and Pulp Components

The origin of manganese present in mechanical pulps can be attributed to the natural occurrence of the element in wood, where it is generally thought to be loosely complexed with components of the pulp (33). Over 90% of the manganese present in our TMP was removed by complexation with DTPA followed by washing as shown in Table 1. Figure 10 shows the uptake of manganese by the chelated pulp from solutions at pH 7 and 20°C containing dissolved manganese nitrate. The pulps were allowed to stand in contact with the solutions for 16 hours before filtration and analysis. The relationship in Figure 10 where a limiting concentration is approached suggests that manganese is bound at specific sites in the pulp, and there is a limiting value corresponding to 900 ppm. Figure 10 also shows the uptake of manganese for cellulose suspensions prepared from filter paper. It is clear that there is little affinity for binding between cellulose and manganese under neutral conditions at 20°C. It would seem probable that the large uptake of manganese by the TMP is associated with binding to lignin rather than carbohydrate components. If this is the case, the limiting level of adsorption shown in Figure 10 would correspond

to approximately one manganese for every 100 C<sub>9</sub> lignin units in the TMP. This calculation assumes that all groups present within the lignin macromolecule are accessible to the metal ions. Reported analyses of common (34) functional groups present in softwood lignins suggest that this amount does not correspond to any single type of functional group such as carbonyl or free phenolic hydroxyl. For example Adler and Marton (35) have estimated that a coniferaldehyde group associated with a free phenolic hydroxyl is present to the extent of approximately 1 in 100 phenyl propane units in spruce lignin. It is however possible that this corresponds to some specific combination of groups, perhaps located in some particular stereochemical arrangement within the lignin structure. The compound vanillin was therefore used in subsequent studies on peroxide decomposition to serve as a potential model binding site in the lignin structure.

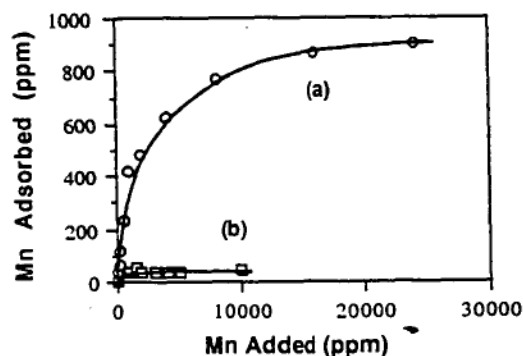


Figure 10. The uptake of manganese from solutions containing dissolved manganese nitrate at pH 7, and 20°C. (a) chelated and washed TMP, O ; (b) cellulose, □.

#### Peroxide Decomposition in the Presence of Pulp Components

Figure 11a shows the extent of peroxide decomposition with time in the presence of manganese concentration equivalent to that found in 20g of TMP (at 30 ppm). Addition of magnesium (equivalent to 2.5% on o.d. pulp) produces an acceleration in peroxide decomposition as might be expected from the previous discussion. Introduction of cellulose had no significant effect on peroxide decomposition as shown in Figure 11b, as might be expected from our observations regarding the affinity of cellulose for manganese. Addition

of magnesium to the manganese/peroxide system is seen to produce a small stabilizing effect as shown in Figure 11b.

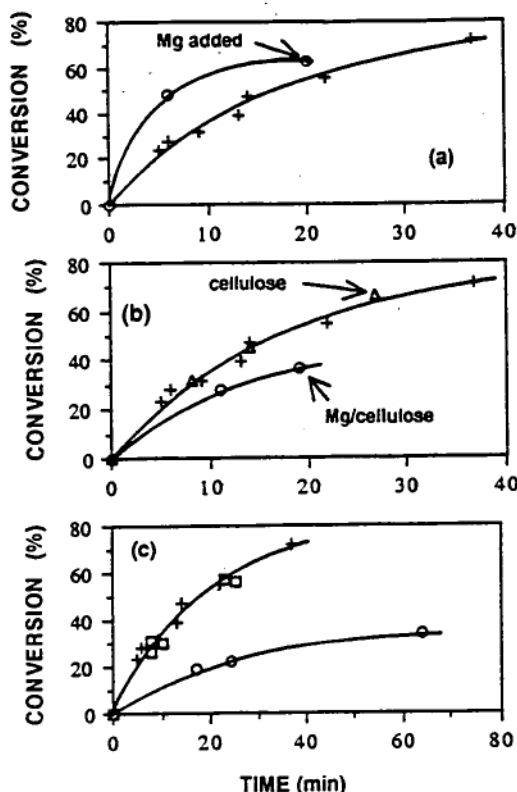


Figure 11. Decomposition of hydrogen peroxide by manganese nitrate,  $1.2 \times 10^{-5}$  mol, at  $20^\circ\text{C}$ , initial pH 11.0 (+). (a) Influence of magnesium nitrate addition O, Mg/Mn molar ratio 160. (b) influence of cellulose  $\Delta$  (10.0g) and cellulose/magnesium O (Mg/Mn = 160). (c) influence of vanillin  $\square$  and vanillin/Mg O ; vanillin/Mn molar ratio = 55.

Addition of vanillin to alkaline solutions containing manganese also produces little observable effect on peroxide decomposition as shown in Figure 11c. Introduction of magnesium to this system, however, can produce a significant stabilizing influence (Figure 11c). The extent of stabilization depends on the amount of magnesium present, and shows a maximum corresponding to a magnesium/manganese ratio of 580. This is also shown in Figure 12 where peroxide decomposition after 15 minutes is plotted as a function of the amount of magnesium introduced. Also plotted in this

figure is the peroxide consumed during bleaching of TMP with magnesium added. It can be seen that there is also a maximum stabilization corresponding to this molar ratio of magnesium/manganese.

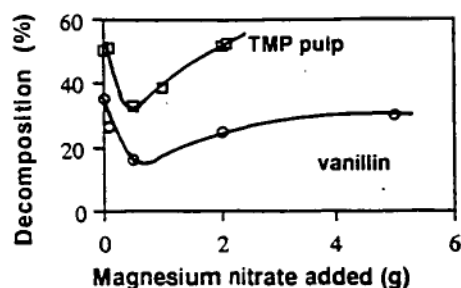


Figure 12. The influence of magnesium addition on decomposition of hydrogen peroxide in the presence of manganese nitrate (a) vanillin (b) TMP.

#### Kinetic Models for Bleaching with Peroxide

The development of kinetic models for peroxide bleaching of mechanical pulps has received much less attention than other processes of importance to the pulp and paper industry which occur under alkaline conditions, such as soda-additive pulping (36-38). We have recently developed several models to describe kinetic phenomena during alkaline peroxide bleaching of mechanical pulps based on various assumptions concerning the types of chromophores present. At present, the most successful model appears to be based on the assumption of a rapid equilibrium reaction process between chromophores (C) and colourless species which can be identified with leucochromophores ( $C_L$ ), coupled with a slower irreversible process to give a colourless product  $C_p$ . This model is illustrated in figure 13a. Figure 13b shows that peroxide bleaching of TMP at pH 10.0 can be fitted successfully with this model. The overall rate of removal of chromophores depends on the concentration of the  $\text{HO}_2^-$  anion, and is also inhibited by hydroxide ions. Strictly speaking, the model has been developed in terms of chromophore concentrations which are assumed to be directly proportional to the light absorption coefficient ( $k$ ). However, very similar trends are observed in the behaviour of both  $k$  and brightness (Figure 14), so the model can be used to describe the brightness response of the pulp in a qualitative manner.

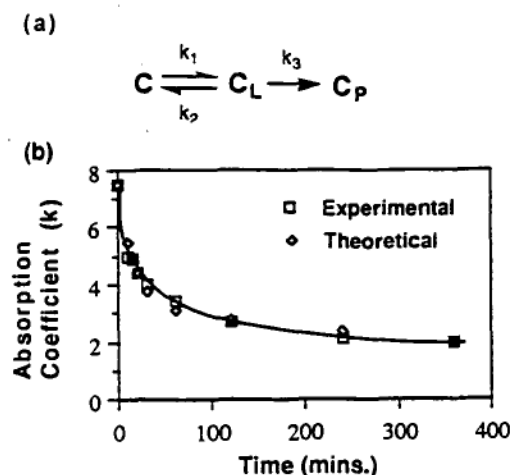


Figure 13. (a) The equilibrium model for alkaline peroxide bleaching. (b) Theoretical and experimental results for bleaching of TMP with constant reagent concentrations at 50°C. pH 10.0, hydrogen peroxide concentration 4.1 g/L.

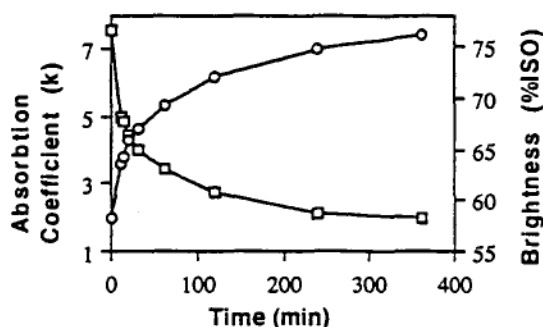


Figure 14. Variation in the absorption coefficient (k) □ and brightness ○ for peroxide bleaching of TMP pulp. Bleaching conditions as in Figure 13b.

The model has been described in detail for bleaching of Eucalypt SGW pulp using constant conditions of pH and peroxide concentration during the bleaching reactions (39). Experimental results reported by other workers for peroxide bleaching of softwood mechanical pulps have also been analysed using this model. The fitting obtained is generally superior to that using a previous model which assumes a kinetic expression of the form

$$\frac{dC_k}{dt} = k [\text{OH}^-]^a [\text{H}_2\text{O}_2]^b C_k^c$$

where a, b, and c represent orders of reaction with respect to hydroxide ion, total peroxide concentration and chromophore concentration respectively (41,42).

The equilibrium model has been found to be superior to other proposed models as this kinetic formulation can account for the maximum in bleaching rate at pH 11-12 often reported during peroxide bleaching (6,43). This model also provides an explanation for the limits to brightness gain under given experimental conditions and the reversibility in brightness observed during alkali darkening (44,45).

Figure 15 shows a plot of maximum brightness gain observed during bleaching at 95°C with constant initial alkali charge (1.0% on pulp) as a function of average peroxide concentration (40). The limit to pulp brightness increases with the average peroxide concentration. Addition of manganese produces increased peroxide consumption, and lowering of the brightness, but results still lie on the same curve. This indicates that the influence of manganese can be explained by a decrease in the available peroxide. Addition of magnesium causes an increase in the stabilization of peroxide. However the plotted position of brightness against peroxide concentration lies above the curve. This indicates the action of magnesium is not likely due to the increased stabilization of peroxide.

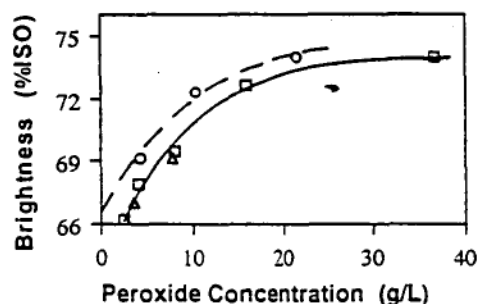


Figure 15. Effects of manganese and magnesium on limiting brightness for bleaching of TMP at 95°C at constant initial alkali addition (2.5% NaOH on o.d. pulp). Normal □, magnesium nitrate added ○ (2.5% on o.d. pulp), manganese addition Δ (corresponds to 50ppm on pulp).

#### CONCLUSION

The presence of manganese in TMP can be associated with increased decomposition of hydrogen peroxide through catalytic reactions. This excess peroxide decomposition reduces the concentration of peroxide and the brightness

gain achieved. The adverse effects of manganese can be reduced by its removal through chelation and washing, or by addition of magnesium ions. Studies of the effects of magnesium and manganese combinations in the absence of pulp, do not reveal this stabilizing influence. This appears to be a consequence of the binding of manganese at specific locations within the pulp, particularly at sites associated with lignin, which modify the observed catalytic behaviour. A more appropriate system appears to be provided by studies of manganese and magnesium in combination with a lignin model such as vanillin, which enables the stabilizing influence to be manifested.

#### ACKNOWLEDGEMENT

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**The Role of Radical Species in Peroxide Bleaching Processes.**

G.C. Hobbs and J. Abbot, J. Wood Chem. Technol., Submitted (1992).

## The role of the Hydroxyl Radical in Peroxide Bleaching Processes

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### ABSTRACT

The kinetics of *N,N*-dimethyl-4-nitrosoaniline (DMNA) oxidation in alkaline and acidic hydrogen peroxide have been studied at 50°C. Based on the premise that DMNA is a specific acceptor for the hydroxyl radical during the oxidation process, the effects of transition metal ions and stabilizing agents on steady state concentrations of the radical species have been determined. Using these kinetic formulations, it has been inferred that the hydroxyl radical has little influence on alkaline peroxide bleaching of mechanical wood pulp at low consistency. However, using a two-stage acid/alkali peroxide bleaching process a correlation exists between the calculated relative hydroxyl radical concentration in the acidic stage and the final pulp brightness after the alkaline stage.

### INTRODUCTION

Hydrogen peroxide has been used as a bleaching reagent in the pulp and paper industry for over 40 years, mainly to achieve higher brightness of mechanical pulps. Approximately 90% of the hydrogen peroxide currently supplied in Canada is used for

this purpose and is becoming the dominant chemical for mechanical pulp bleaching (1). It has traditionally been thought that the active species present under alkaline bleaching conditions is the perhydroxyl anion,  $\text{HO}_2^-$  (2-6). Oxidative reactions involving nucleophilic attack of this species on specific chromophore types such as  $\alpha$ - $\beta$  unsaturated aldehydes,  $\alpha$ -carbonyls and quinones have been described as the major route for elimination of chromophores (7-15). Over the past decade there has been a growing awareness that other species, particularly the hydroxyl radical ( $\text{OH}^\cdot$ ) may also play an important role during peroxide bleaching processes (12,14,16-19). There are, however, contradictory reports in the literature concerning whether this radical species leads to beneficial or detrimental effects during chromophore elimination (12,14,16-20).

The use of hydrogen peroxide is also expected to increase very significantly over the next decade as a bleaching agent for chemical pulps (21-24). Traditionally, high brightness chemical pulps (e.g. Kraft pulps) have been obtained using reagents such as chlorine and chlorine dioxide to remove residual lignin and achieve the high brightness levels required for market pulp. Increasingly, however, environmental concerns are applying pressure on industry to move toward chlorine-free processes using agents such as oxygen, ozone and hydrogen peroxide. The reactions occurring in these processes are as yet ill-defined, but their understanding is of enormous potential economic importance. Under conditions where selective lignin removal is required, as in bleaching of chemical pulps, it is possible that processes involving the hydroxyl radical play a very significant role (21). However, it is also known that attack on the carbohydrate component of the pulp by this radical species can also lead to depolymerisation (25), resulting in unacceptably low mechanical strength properties. The controlled activity of this radical species as a selective reagent could therefore be crucial in moving to chlorine-free bleaching.

Recently (26) a kinetic analysis of peroxide bleaching has also shown the possibility of a dual mechanism. Of these two mechanisms one can be associated with the perhydroxyl anion while the second can be related to the presence of radical species. Several two-stage acid/alkali peroxide bleaching processes (26-31) have been developed to test this kinetic analysis and also investigate alternate peroxide bleaching sequences.

Recent interest in the hydroxyl radical has arisen in other areas of chemistry and biochemistry, as for example, the interaction of hydroxyl radicals with DNA (32). Modelling of atmospheric chemistry (33) usually includes hydroxyl radicals as an important part of these systems. The self-purification of natural waters is also related to the presence of hydroxyl radicals (34-36).

A number of methods have been developed to measure hydroxyl radical concentrations in aqueous systems. These include using phthalic hydrazide as a trap and

detection via chemiluminescence of the species formed (37), UV determination of radicals formed by the interaction of hydroxyl radicals with thiocyanate (38) or bicarbonate ions (39) and ESR techniques. A simple spectrophotometric method based on the oxidation of *N,N*-dimethyl-4-nitrosoaniline (DMNA) has been demonstrated to be specific for hydroxyl radicals in alkaline media (40-41). The method has been applied to studies of the influence of metal ions in neutral and mild alkaline solutions of hydrogen peroxide (35-36,42-44). In this study we have used pH conditions typical of industrial bleaching (pH 11), as well as mild acidic conditions, and developed a kinetic analysis to show the influence of both transition metal additives and stabilizing reagents commonly encountered in commercial bleaching processes.

Using this analysis we have attempted to elucidate the effect of hydroxyl radicals in single stage alkaline peroxide bleaching and two-stage acid/alkali peroxide bleaching processes by a correlation of the calculated relative steady state hydroxyl radical concentration with the final brightness response of the pulp.

## EXPERIMENTAL

Hydrogen peroxide (30%) was obtained from Ajax Chemicals. Nitrates of copper, iron, magnesium, manganese and chromium (all 99%), diethylenetriaminepentaacetic acid (DTPA) (97%), *N,N*-dimethyl-4-nitrosoaniline (DMNA) (97%), potassium hydroxide of semiconductor purity (99.99%) and sodium silicate solution (30%) were obtained from Aldrich Chemicals. Methanol was distilled before use.

All experiments were performed in polyethylene reaction vessels immersed in a constant temperature water bath maintained at 50°C throughout the experiment. Milli-Q water (45) was used to minimize the level of introduced transition metal ions. The pH was maintained at either 5.8 or 11.0 throughout all experiments by addition of either potassium hydroxide or dilute sulfuric acid.

UV-Visible spectra were recorded on a Varian DMS 100 spectrophotometer. DMNA concentrations were determined from the absorbance at 440nm. Experiments were ceased when approximately 30% of the initial DMNA charge was consumed due to the influence of reaction products which have significant absorptions close to 440nm. In the absence of peroxide, DMNA solutions at pH 11.0 decolorize slowly. This has been taken in to consideration in all cases. Peroxide residuals were determined by iodometric titration of samples. The samples were added to sulfuric acid, excess potassium iodide and ammonium molybdate. The liberated iodine was then titrated with sodium thiosulfate

to a starch endpoint.

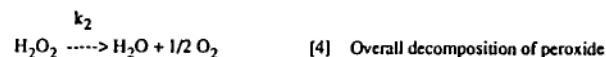
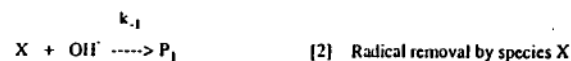
Bleaching experiments were performed in polyethylene reaction vessels maintained at 50°C in a constant temperature water bath. All bleaching was under conditions of constant pH 11.0 to allow comparison with solution studies. In two-stage bleaching processes the pH of the first stage was maintained at 5.8. The pulp used was *E. regnans* SGW, prepared on a small scale grindstone at Australian Newsprint Mills Boyer mill. The pulp, after filtration and washing, was stored at 20% consistency and 4°C until used. Experiments were performed at 1% pulp consistency with a peroxide charge of 12% on oven dried pulp. Samples were taken at 30 minute intervals for determination of peroxide residuals and brightnesses (%ISO). For bleaching under constant conditions of alkali and peroxide concentration, additions of chemicals were made when deviation from the initial conditions were observed. This was achieved by regular determination (10-15 minute intervals) of the peroxide concentration and continuous pH measurement.

The brightness of the unbleached pulp was regularly monitored to allow calculation of brightness gains and to determine if any changes occurred with storage. The brightness of the unbleached pulp was 53-55 %ISO. Pulp brightnesses were measured using a Elrepho 2000 (as %ISO) after making standard handsheets.

## THEORY

Previous studies have shown that DMNA reacts specifically with the hydroxyl radical in the presence of hydrogen peroxide (40-41).

Simplified kinetic expressions for oxidation of DMNA can be developed as follows:



- where:
- M is a metal species.
  - X are species (other than DMNA) which can trap hydroxyl radicals.
  - DMNA is *N,N*-dimethyl-4-nitrosoaniline.
  - P<sub>1</sub> and P<sub>2</sub> are oxidation products.
  - k<sub>1</sub>, k<sub>-1</sub>, k<sub>2</sub> and k<sub>3</sub> are the respective rate constants

The rate of removal of DMNA (35) is given by:

$$\frac{-d[\text{DMNA}]}{dt} = k_3[\text{DMNA}][\text{OH}^\cdot] \quad [5]$$

The steady state concentration of hydroxyl radicals is given by:

$$\frac{-d[\text{OH}^\cdot]}{dt} = k_3[\text{DMNA}][\text{OH}^\cdot] - k_1[\text{H}_2\text{O}_2][\text{M}] + k_{-1}[\text{OH}^\cdot][\text{X}] = 0 \quad [6]$$

Two limiting cases can be considered:

**Case 1:**

Reaction with DMNA is the dominant reaction leading to the removal of radicals:

i.e.  $k_3[\text{DMNA}][\text{OH}^\cdot] \gg k_{-1}[\text{OH}^\cdot][\text{X}]$   
so that:

$$[\text{OH}^\cdot] = \frac{k_1[\text{H}_2\text{O}_2][\text{M}]}{k_3[\text{DMNA}]} \quad [7]$$

$$\text{and: } \frac{-d[\text{DMNA}]}{dt} = k_1[\text{M}][\text{H}_2\text{O}_2] \quad [8]$$

**Case 2:**

Reaction with other species (X) is the dominant termination reaction for hydroxyl radicals. In our system X could be metal species (19), hydrogen peroxide (35) or another radical species (17).

Under this condition  $k_{-1}[\text{OH}^\cdot][\text{X}] \gg k_3[\text{DMNA}][\text{OH}^\cdot]$   
leading to

$$[\text{OH}^\cdot] = \frac{k_1[\text{H}_2\text{O}_2][\text{M}]}{k_{-1}[\text{X}]} \quad [9]$$

$$\text{and: } \frac{-d[\text{DMNA}]}{dt} = \frac{k_1 k_3 [\text{DMNA}][\text{H}_2\text{O}_2][\text{M}]}{k_{-1}[\text{X}]} \quad [10]$$

The derived kinetic expressions [8] and [10] indicate first-order dependence on concentrations of metal ion species and peroxide concentrations. It is well known that the nature of the metal ion species present in aqueous systems is strongly dependent on the pH of the medium (46). For studies carried out at constant pH, [M] could be regarded as constant throughout a particular experiment. Maintaining the peroxide concentration at a constant level throughout an experiment is difficult, particularly in the presence of significant concentrations of catalytic species where the rate of decomposition is appreciable. Instead, it is preferable to take account of the continuous decline in peroxide concentration with time in the kinetic expression, by assuming first-order decomposition:

$$\frac{-d[\text{H}_2\text{O}_2]}{dt} = k_2[\text{H}_2\text{O}_2] \quad [11]$$

on integrating we have:

$$[\text{H}_2\text{O}_2] = [\text{H}_2\text{O}_2]_0 e^{-k_2 t} \quad [12]$$

where  $[\text{H}_2\text{O}_2]_0$  denotes the initial concentration of hydrogen peroxide.  
Substituting equation [12] into equation [8] and [10] we have:

$$\frac{-d[\text{DMNA}]}{dt} = k_1[\text{M}][\text{H}_2\text{O}_2]_0 e^{-k_2 t} \quad [13]$$

$$\text{and } \frac{-d[\text{DMNA}]}{dt} = \frac{k_1 k_3 [\text{DMNA}][\text{H}_2\text{O}_2]_0 e^{-k_2 t} [\text{M}]}{k_{-1}[\text{X}]} \quad [14]$$

On integrating, the kinetic expressions are:

Case 1:

$$[DMNA]_t = [DMNA]_0 - \frac{k_1[M][H_2O_2]_0 e^{-k_2 t}}{k_2} \quad [15]$$

Case 2:

$$\frac{\ln[DMNA]_t}{[DMNA]_0} = \frac{k_1 k_3 [DMNA]_0 [M] [H_2O_2]_0 e^{-k_2 t}}{k_1 k_2 [X]} \quad [16]$$

Case 1 requires a zero-order dependence on [DMNA], while a first-order dependence is predicted in case 2. It should be easily established which model is preferable by observing whether the rate of removal of DMNA depends on the initial amine concentration. Thereafter, the validity of the proposed model can be further tested by examining plots of the appropriate [DMNA] function against the time variable  $te^{-k_2 t}$ .

## RESULTS AND DISCUSSION

### KINETIC PHENOMENA UNDER ALKALINE CONDITIONS

Experiments were performed to follow the rate of removal of DMNA in alkaline peroxide solutions at 50°C, under conditions of constant pH = 11.0. The concentration of DMNA was measured spectrophotometrically, while decomposition of hydrogen peroxide was measured by periodic titration of samples. The effect on kinetic phenomena of introducing transition metal ions, including iron, manganese and copper were observed, as well as the influences of adding stabilizers such as sodium silicate, magnesium nitrate and DTPA.

The development of the kinetic models as shown in the theory section assumes that the rate of peroxide decomposition is first-order with respect to peroxide concentration. This was found to be a reasonable assumption for each of the systems investigated, with linear logarithm-time relationships as shown in Fig. 1. Addition of transition metal ions or stabilizers to the alkaline peroxide solution changed the magnitude of the rate constant for peroxide decomposition ( $k_2$ ) as shown in Table 1.

TABLE 1. Rate constants for peroxide decomposition in the presence of added transition metal ions and stabilisers at 50°C.

Additive	Concentration ( $\times 10^{-5}$ M)	$k_2$ ( $\times 10^{-3}$ /min)
None	-	2.00
Copper	0.40	6.56
Manganese	0.91	4.18
Iron	0.90	1.65
Magnesium	6.63	0.33
DTPA	25.4	0.55
Silicate	2000	1.33

Experiments also showed that the rate of DMNA removal is dependent on the initial amine concentration, as shown in Fig. 2. This demonstrates that the kinetic expression developed as Case 1 cannot be valid under these conditions. Analysis of kinetic phenomena was therefore based on testing the validity of equation [16] (Case 2).

Fig. 3 shows that, in the absence of added transition metal ions or stabilizers, plots of  $\ln[DMNA]_t/[DMNA]_0$  against the time function  $te^{-k_2 t}$  are linear, with values of the correlation coefficient ( $R^2$ ) close to unity. This is consistent with equation [16], assuming that the concentration of radical terminating species [X] can be regarded as constant for a particular system.

The slopes of the plots illustrated in Fig. 3 can be related to the value of the rate constant for removal of DMNA defined by

$$K = \frac{k_1 k_3}{k_1 k_2} \quad (17)$$

### The Influence of Added Transition Metal Ions

The transition metals commonly reported to have most influence on hydrogen peroxide stability during industrial bleaching of mechanical pulps are manganese, iron and copper (46-49). The presence of manganese in particular is a concern under conditions normally encountered during bleaching (50). Traces of these transition metal impurities are derived either from the wood itself, or are introduced during pulp

processing (47).

The influence of copper, manganese and iron addition on the kinetics of peroxide decomposition and DMNA oxidation was investigated at pH 11.0 and 50°C. The validity of equation (16) was tested in the presence of introduced metal ions by plotting  $\ln[DMNA]_t/[DMNA]_0$  against the time function  $te^{-k_2t}$ . In all cases tested, adequate linear relationships were obtained, as illustrated in Fig. 4. Using the slopes of these plots, values of  $K$  and  $Kk_2$  were plotted as a function of metal additive concentrations as shown in Fig. 5. The magnitude of  $K$  gives the rate constant for the removal of DMNA in each case. This term also reflects the relative ratio of  $k_1/k_{-1}$  to  $k_2$ , and is therefore a measure of the hydroxyl radical concentration available for reaction with DMNA per mole of peroxide consumed. The term  $Kk_2$  is directly proportional to the steady state concentration of radicals (equation (9)).

Previous studies by Ernestova and Skurlatova on the DMNA-peroxide system have been reported at 70°C at pH 7 (35). Their results showed that addition of iron(III) had no effect on DMNA oxidation (35), and concluded that micro-colloidal iron particles present do not contribute to the formation or disappearance of hydroxyl radicals. Other studies have concluded that iron does not decompose peroxide via a radical mechanism (34). Fig. 5a shows that  $K$  is not significantly affected by increasing the amount of iron in the system. In fact, it appears that the addition of iron causes a slight reduction in  $K$  compared to the system where no iron is introduced. A similar trend is observed for the values of  $Kk_2$ , as shown in Fig. 5b, showing that iron species present at pH 11.0 have little influence on the level of hydroxyl radicals available.

In contrast, the addition of copper to the alkaline peroxide system produces a significant increase in the values of both  $K$  and  $Kk_2$ , as illustrated in Figs. 5a and 5b. Hydroxyl radical concentrations as measured by  $Kk_2$  are almost directly proportional to the levels of copper introduced. Our observations are in agreement with previous studies (34-36) where addition of Cu(II) was found to produce a proportionate increase in the rate of oxidation of DMNA. These workers also reported that the effects of added Mn(II) were similar to those of iron, with manganese addition producing little influence on the formation or removal of hydroxyl radicals. Other studies have concluded that the catalytic decomposition of hydrogen peroxide in the presence of Mn(II) does proceed via a chain mechanism involving hydroxyl radicals (43). Our results at low levels of manganese addition show little influence of manganese on hydroxyl radical concentration. However, at higher levels of manganese addition, the metal additive produces a significant increase in the availability of hydroxyl radicals as reflected in the values of  $Kk_2$  shown in Fig. 5b, with the value of this factor approaching that observed for copper.

## The Influence of Added Stabilizing Agents

Stabilizing agents commonly used in the peroxide bleaching of mechanical pulps are magnesium salts (46,51-52), sodium silicate (3,46,51-52) and chelating agents such as DTPA and EDTA (2,3,46,50,52). The addition of these reagents aims to reduce the catalytic decomposition of hydrogen peroxide, leaving higher levels of peroxide available for pulp bleaching. Peroxide decomposition in the presence of these stabilizers follows first-order kinetics and the values of  $k_2$  are reported in Table 1. In all cases stabilization of peroxide is achieved and plots of  $\ln[DMNA]_t/[DMNA]_0$  against  $te^{-k_2t}$  again showed adequate linear correlations. Calculated values of  $K$  and  $Kk_2$  from these plots for the addition of magnesium, DTPA and silicate are shown in Fig. 6.

The effect of the of magnesium addition is shown in Fig. 6a. The value of both  $K$  and  $Kk_2$  are decreased markedly at low levels of magnesium and further addition does not affect these values significantly. The mechanism of stabilization of alkaline peroxide solutions by magnesium involves either the interruption of free radical processes that are initiated by the residual transition metal ions present in the solution (46), or deactivation of the catalytically active species in some way (46).

The addition of DTPA, as shown in Fig. 6b shows very similar trends for both  $K$  and  $Kk_2$  as magnesium. Both values are reduced to low levels compared to unstabilized peroxide solutions at low stabilizer addition, and further addition of stabilizer has little or no effect. It has previously been proposed (50) that the mechanism of DTPA stabilization of alkaline peroxide solutions is related to the ability of DTPA to bind and deactivate the residual transition metal ions in solution, thus reducing the catalytic decomposition.

The effect of sodium silicate addition, as shown in Fig. 6c, differs from that of magnesium and DTPA. The value of  $K$ , which is a measure of the hydroxyl radical concentration available for reaction with DMNA per mole of peroxide consumed, does not decrease on addition of silicate. However, the addition of silicate does reduce the value of  $Kk_2$  significantly as a result of the reduction in the rate of peroxide decomposition.

## The Influence of Methanol

Alcohols, particularly methanol and ethanol, are known to be effective hydroxyl radical traps (36). Figs. 7a and b show the effect of methanol concentration on peroxide decomposition, decolorization of DMNA and the calculated steady state concentration of hydroxyl radicals. Fig. 7a shows that increasing the concentration of methanol leads to

an increase in the rate of peroxide decomposition. The reason for this is not clear, but could relate to transition metal ion impurities introduced with methanol. Fig. 7b shows that increasing the proportion of methanol in solution significantly decreases the values of  $K$  and  $Kk_2$ . Fig. 7c shows the effect of increasing hydrogen peroxide concentration on the values of  $K$  and  $Kk_2$  in 1:1 methanol:water. As expected, higher concentrations of hydrogen peroxide results in higher values of these constants.

Figs. 8a,b and c show the effect of increasing the methanol to water ratio in the presence of added iron and copper. The effect of methanol on the rate of peroxide decomposition, as shown in Fig. 8a, is small. Increasing the proportion of methanol in the solution markedly decreases the rate of DMNA decolorization (Fig 8b) and the calculated concentration of hydroxyl radicals (Fig 8c) also decrease significantly.

#### The variation of radical concentrations

Equation 9 shows that the concentration of hydroxyl radicals available for reaction will depend on the ratio  $k_1/k_2$ , which is proportional to the factor  $Kk_2$ , and in turn depends on the presence of stabilisers or transition metal ions. The hydroxyl radical concentration at any time also depends on the peroxide concentration, according to equation 9. Figure 9 shows plots of  $Kk_2[H_2O_2]$  against time for alkaline systems containing various levels of added transition metal ions and stabilisers. Copper and manganese greatly enhance the concentration of hydroxyl radicals, even though they concurrently accelerate the decline in peroxide concentration. Magnesium and silicate both reduce the steady state concentration of hydroxyl radicals compared to the unstabilized system.

#### BLEACHING STUDIES UNDER ALKALINE CONDITIONS

In theory it is possible to examine the influence of hydroxyl radical concentration during alkaline peroxide bleaching by following DMNA oxidation in the presence of pulp. Brightness gain could then be correlated with the radical concentration profile for each system. However, this approach has the drawback that DMNA, being highly coloured, may directly affect the brightness of the pulp by adsorption onto the fibres. Fig 10 shows the effect of DMNA concentration on brightness gain during alkaline peroxide bleaching and also in the absence of peroxide under alkaline conditions. Clearly, DMNA itself can influence the optical properties of the pulp.

It is therefore preferable to draw correlations between the calculated radical concentrations from our solution studies with the results of peroxide bleaching

experiments in the absence of DMNA. However, it is first necessary to determine whether the presence of the pulp affects the oxidation of DMNA under our experimental conditions, as reflected by the calculated parameters. Table 2 shows that the calculated values for  $K$  and  $Kk_2$  are very similar in the presence and absence of pulp. Values of  $k_2$  are increased in the presence of pulp in the case of magnesium addition and with no additive present, due to the consumption of peroxide by bleaching processes. Table 3 also shows that the values of  $Kk_2$ , which reflect availability of hydroxyl radicals, give similar trends with additives introduced, both in the presence and absence of pulp. It therefore appears reasonable for us to correlate values of  $Kk_2$  from our solution studies (in the absence of pulp) with the observed bleaching response of the pulp in the absence of DMNA.

**TABLE 2** Values of rate constants in the presence and absence of pulp. Conditions: 50°C, 1% consistency, pH 11.0, 0.0353M peroxide.

Additive		$k_2$ ( $\times 10^{-3}/\text{min}$ )	$K$ ( $\times 10^{-2}$ )	$Kk_2$ ( $\times 10^{-5}/\text{min}$ )
none	solution	2.00	1.24	2.48
copper	solution	13.3	1.89	25.2
magnesium	solution	0.36	0.67	0.24
none	pulp	3.10	1.27	3.81
copper	pulp	9.17	1.71	15.6
magnesium	pulp	1.29	1.28	1.65

Figure 11a shows results obtained for the addition of various amounts of magnesium nitrate to peroxide bleaching of pulp. The final brightness of the pulp is not significantly affected by the presence of magnesium or the implied reduced concentration of hydroxyl radicals. A slight reduction in peroxide consumption was achieved with the introduction of magnesium, but the brightness gains in the presence and absence of magnesium are similar. Bleaching studies in the presence of varying quantities of methanol, illustrated in Fig. 11b, also show that pulp brightness is not significantly affected by the presence of a radical trap, thus supporting the results obtained with

magnesium.

Figure 12 shows negative effects of additions of iron, copper and manganese on brightness gain during peroxide bleaching experiments. However, it is difficult to isolate the influences of radical concentration in these experiments, as the concentration profile for total peroxide is also strongly dependent on the introduction of these additives. For this reason experiments were performed under conditions where both the pH and peroxide concentration were maintained at constant levels (53). Table 3 shows that for the introduction of either transition metal ions or stabilisers under constant conditions there is no significant difference in brightness gain, even though the solution studies indicate that significantly different concentrations of hydroxyl radicals would be available.

**TABLE 3.** Bleaching response of *E. regnans* pulp under conditions of constant concentration of peroxide (12% on oven dry pulp) and alkali (pH 11.0). Other conditions as in Fig. 10a.

Additive	Concentration ( $\times 10^{-5}$ M)	Brightness Gain (%ISO)		$Kk_2$ ( $\times 10^{-5}$ /min)
		60 minutes	180 minutes	
None		11.9	18.4	2.41
Copper	1.00	10.6	17.6	15.0
Manganese	1.14	12.7	17.5	3.56
Iron	1.12	12.1	18.3	1.98
Magnesium	7.98	10.6	17.2	0.23
Silicate	2000	11.5	18.1	1.60

Our results are in agreement with those of Reitberger et al. who used a method based on chemiluminescence of solutions after addition of phthalic hydrazide (37) to follow generation of hydroxyl radicals during peroxide bleaching. They reported that copper was particularly efficient in formation of hydroxyl radicals from alkaline hydrogen peroxide, while silicate, DTPA and magnesium sulfate reduced their concentration (54). Their method also showed that at low pulp consistencies (2.5%) there were no positive effects due to enhanced formation of hydroxyl radicals during alkaline peroxide bleaching of a mechanical pulp.

However, other investigations have concluded that peroxide decomposition

products can have either positive or negative effects on brightness gain. Sjorgen et al (55) have reported positive effects of hydroxyl radicals produced by irradiation with  $\gamma$  rays during peroxide bleaching of a mechanical pulp. Kutney and Evans (20) observed brightness reversion when a bleached pulp was exposed to alkaline peroxide in the presence of catalysts including iron, manganese and copper, and attributed the effects to peroxide decomposition products.

The apparent inconsistencies in these observations regarding the influence of the hydroxyl radical during alkaline peroxide bleaching of mechanical pulps may lie in the experimental conditions used, for example pulp consistency. From analysis of the kinetics of chromophore removal during peroxide bleaching, Moldenius and Sjorgen (56) postulated that the effects of short lived species become much more apparent as the pulp consistency is increased, as these active intermediates could more easily migrate between fibres. Reitberger (54) also found that at increased pulp consistency positive effects of hydroxyl radicals become apparent.

#### KINETIC PHENOMENA UNDER ACIDIC CONDITIONS

Some transition metals exhibit maximum catalytic activity towards peroxide decomposition under acidic conditions (26,27), although the rate of decomposition of peroxide is usually low without added catalysts at low pH. Table 4 shows first-order rate constants for decomposition of hydrogen peroxide in the presence of added chromium. Again the model (equation [16]) gives adequate linear correlations and peroxide decomposition follows first-order kinetics. Fig. 13a shows that the rate of removal of DMNA and the steady state concentration of hydroxyl radicals both increase with the addition of chromium.

**TABLE 4.** Rate constant for peroxide decomposition in the presence of added chromium at 50°C.

[Cr] ( $\times 10^{-5}$ M)	$k_2$ ( $\times 10^{-4}$ /min)
0.00	4.20
2.49	6.00
4.97	9.86
9.95	16.0



The addition of methanol to acidic solutions of hydrogen peroxide containing chromium results in marked decreases in K and  $Kk_2$  at much lower levels of methanol than required for alkaline solutions (Fig. 7b), as shown in Fig. 13b. The peroxide decomposition rate is greatly reduced in the presence of methanol, compared to the small changes noted in alkaline solution. The addition of magnesium under acidic conditions has a similar effect on  $Kk_2$  as shown in figure 13c.

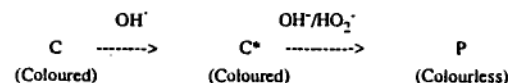
### BLEACHING STUDIES UNDER ACIDIC CONDITIONS

Previous investigations (26-28) have shown that under acidic pH conditions addition of chromium to peroxide bleaching liquors can improve the subsequent response of mechanical pulps under conventional alkaline bleaching conditions. These studies showed that although no brightness gain was observed under acidic bleaching conditions, the chromophores present are rendered more susceptible to bleaching in an alkaline peroxide medium. This implies that hydroxyl radicals may have a positive effect on bleaching, provided the pulp is exposed to radicals under acidic conditions.

Figure 14a shows the bleaching response after the two-stage acid/alkali process in the presence of added chromium in the first stage. This can be compared to figure 13a showing the calculated hydroxyl radical concentrations. By increasing the hydroxyl radical concentration in the acidic stage of a two-stage process, the final brightness of the pulp can be increased. This process has (26-27) been explained previously in terms of a dual mechanism of peroxide bleaching, with bleaching being related to both the presence of the perhydroxyl anion and the hydroxyl radical, and these results support such a mechanism.

In the presence of stabilisers to reduce the hydroxyl radical concentration (Figure 13 b,c), a decrease in brightness may be anticipated. Figures 14b and 14c show that for the addition of methanol or magnesium, a decrease in brightness is indeed observed after the alkaline stage. Clearly, as the radical concentration is reduced the brightness gain also decreases, indicating that the presence of hydroxyl radicals can result in an increased brightness response. This cannot be associated with a change in radical concentration in the alkaline stage as has previously been shown (Table 4, Figs. 11a and 11b)

Bleaching under acidic conditions in the presence of the hydroxyl radical enhances the final brightness of the pulp after the alkaline stage. However, no change in brightness is observed after the acidic stage (26-28). This indicates that changes occur within the lignin structure that do not cause a change in colour of the pulp, but increases the susceptibility of the chromophores to elimination in the subsequent alkaline stage, as outlined below.



The reason for the hydroxyl radical not having an influence under alkaline conditions may be related to the oxidation potential of this species. Under alkaline conditions the oxidation potential of the hydroxyl radical is significantly lower than under neutral or acidic conditions (16), thus lowering the reactivity. Furthermore, the  $pK_a$  of the hydroxyl radical is 11.4 (16), producing the oxyl radical,  $\text{O}^\bullet$ , which has a significantly lower oxidation potential than the hydroxyl radical, and is therefore less likely to be a major bleaching species.

Under acidic conditions, the oxidation potential of the hydroxyl radical is increased compared to alkaline conditions (16) and, therefore, the effect of hydroxyl radicals under acidic conditions may be more easily observed. Several two-stage peroxide bleaching processes have been reported (26-31) under acidic conditions followed by alkaline conditions, and the effects have been attributed to the action of the hydroxyl radical.

### CONCLUSION

Concentrations of hydroxyl radicals available for reaction in alkaline or acidic solutions of hydrogen peroxide can be calculated from an analysis of DMNA oxidation kinetics. Similar parameters relating to radical concentration are obtained both in the presence and absence of pulp. These parameters can be correlated with bleaching response in the absence of DMNA. The present studies show that a wide range of concentration levels of hydroxyl radical are available depending on whether metal ions or stabilisers are present during bleaching. However, the final pulp brightness at low consistency under alkaline conditions is not significantly affected by reactions involving the hydroxyl radical. For two-stage bleaching processes, where the pulp is first subjected to acidic conditions, the availability of hydroxyl radicals at low pH can significantly influence the final pulp brightness achieved after subsequent alkaline bleaching.

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## LIST OF FIGURES

**FIGURE 1.** First-order rate plots for hydrogen peroxide decomposition in the presence of various catalysts and stabilizers. Peroxide concentration = 0.0353M, pH 11.0, 50°C, copper =  $8.02 \times 10^{-6}$ M, manganese =  $9.14 \times 10^{-6}$ M, DTPA =  $5.09 \times 10^{-5}$ M and silicate =  $4.00 \times 10^{-2}$ M

**FIGURE 2.** Relationship between the initial DMNA concentration and the quantity reacted after 20 minutes.

**FIGURE 3.** Model fit for various levels of peroxide concentration. DMNA concentration =  $2.00 \times 10^{-5}$ M.

**FIGURE 4.** Model fit for the addition of transition metal ion catalysts. Conditions as in Fig. 1, DMNA concentration =  $5.00 \times 10^{-5}$ M, copper =  $4.01 \times 10^{-6}$ M, manganese =  $9.14 \times 10^{-6}$ M, iron =  $4.49 \times 10^{-6}$ M

**FIGURE 5.** Plots showing the variation in rate constants for the addition of copper, iron and manganese: (a) K, (b)  $Kk_2$ .

**FIGURE 6.** Plots showing the variation in rate constants K and  $Kk_2$  for (a) magnesium, (b) DTPA and (c) silicate. Conditions as in Fig. 4.

**FIGURE 7.** The effect of methanol addition on (a) peroxide decomposition rate, (b) K and  $Kk_2$ . (c) The effect of varying peroxide concentration in 1:1 methanol:water. Conditions as in Fig. 4.

**FIGURE 8.** The effect of methanol addition on (a)  $k_2$ , (b) K and (c)  $Kk_2$  in the presence of added copper ( $1.003 \times 10^{-5}$ M) and iron ( $1.113 \times 10^{-5}$ M). Conditions as in Fig. 4.

**FIGURE 9.** The variation of calculated relative radical concentration in the presence of (a) added copper ( $2.00 \times 10^{-5}$ M), iron ( $2.22 \times 10^{-5}$ M) and manganese ( $2.27 \times 10^{-5}$ M); and (b) magnesium ( $3.75 \times 10^{-4}$ M) and silicate (0.02 M)

**FIGURE 10.** The effect of DMNA concentration on (a) the bleaching response of pulp and (b) alkali darkening. Conditions: pH 11.0, 50°C, 1% consistency, (a) 12% peroxide on o.d. pulp, (b) [DMNA]  $2 \times 10^{-4}$ M.

**FIGURE 11.** The brightness response of *E. regnans* SGW in the presence of (a) magnesium and (b) methanol. pH 11.0, 12% peroxide on oven dry. pulp, 1% stock consistency, 50°C.

**FIGURE 12.** The change in a) final brightness and b) peroxide consumption for bleaching in the presence of added transition metal ions. Conditions: 1% pulp consistency, 50°C, pH 11.0, 12% peroxide on o.d. pulp, duration of bleach: 180 minutes.

FIGURE 13. Plots showing the variation in  $K$  and  $Kk_2$  for the addition of (a) chromium, (b) chromium and methanol and (c) chromium and magnesium. Conditions: pH = 5.8, [DMNA] =  $5 \times 10^{-5}$ M.

FIGURE 14. The effect of (a)chromium, (b) chromium and methanol and (c) chromium and magnesium addition on the brightness response during a two-stage bleaching process. Conditions: 1% pulp consistency, 50°C, 12% peroxide on o.d. pulp, acidic stage: 15 minutes, pH 5.8; alkaline stage 120 minutes, pH 11.0.

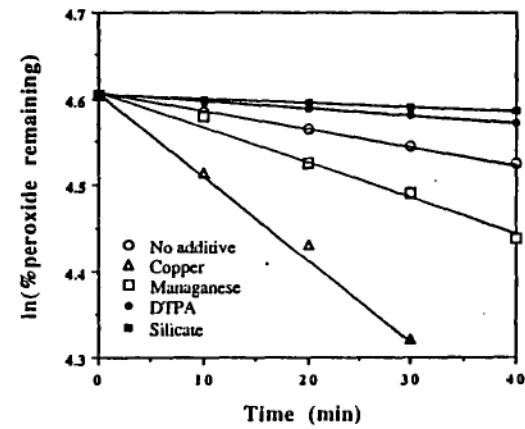


Figure 1

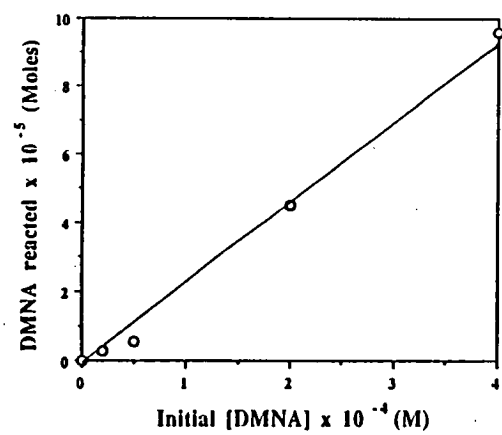


Figure 2

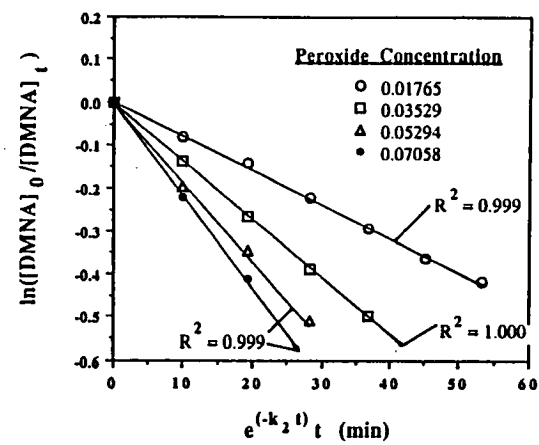


Figure 3

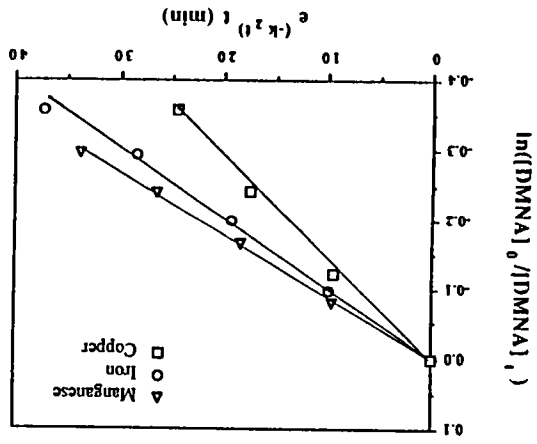


Figure 4

$Kk_2 \times 10^{-4}$  (/min)

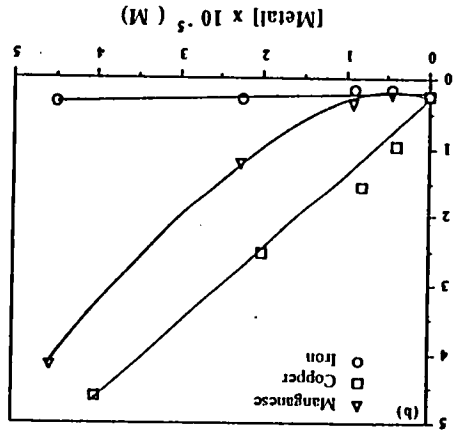
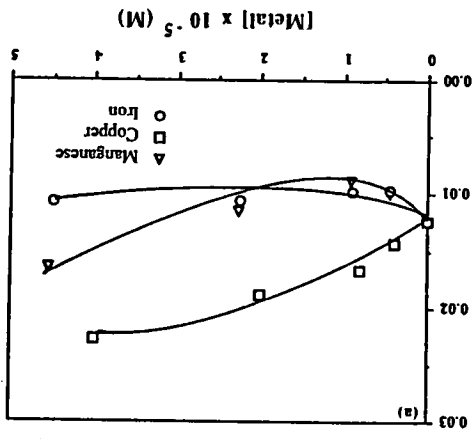
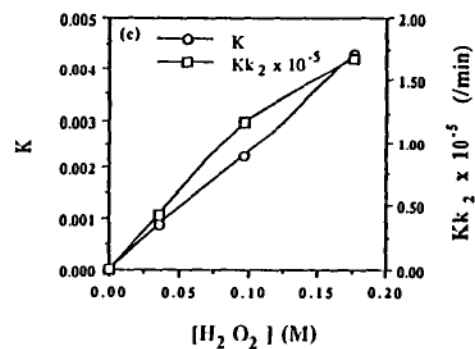
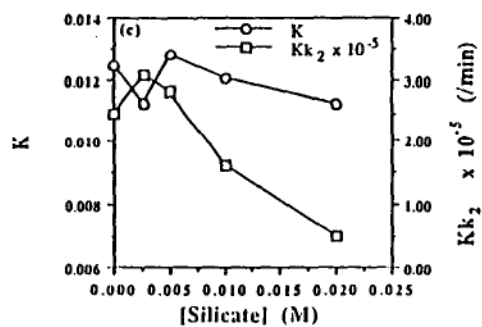
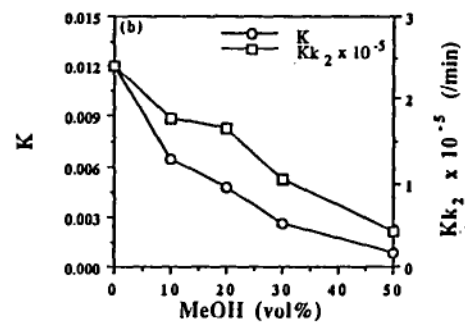
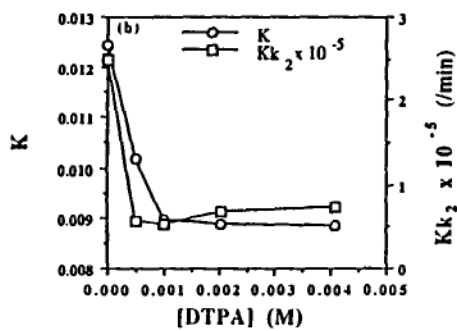
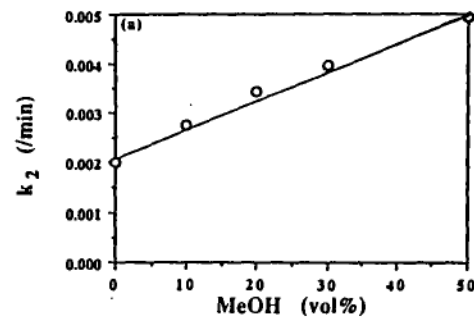
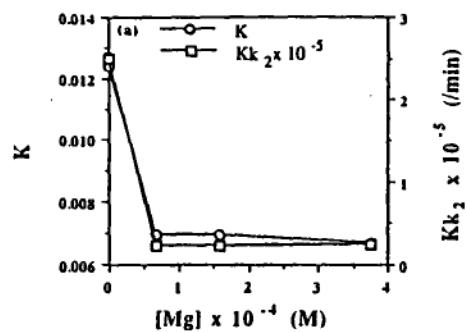


Figure 5

$K$





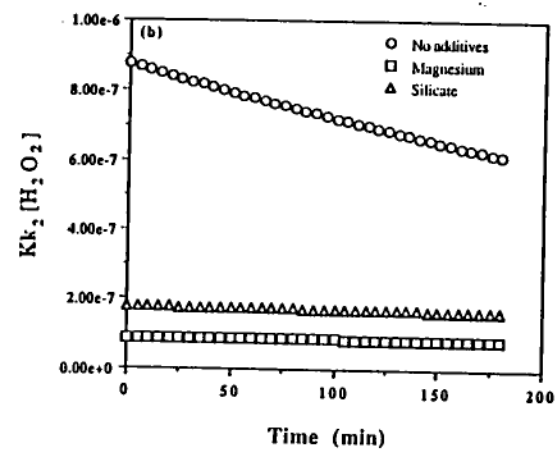
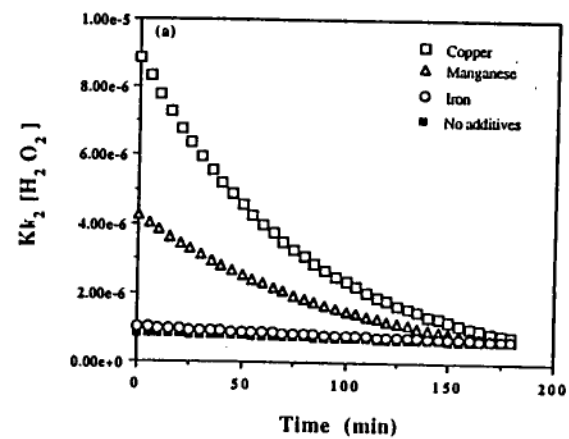
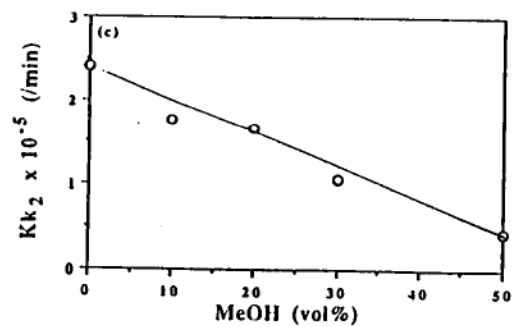
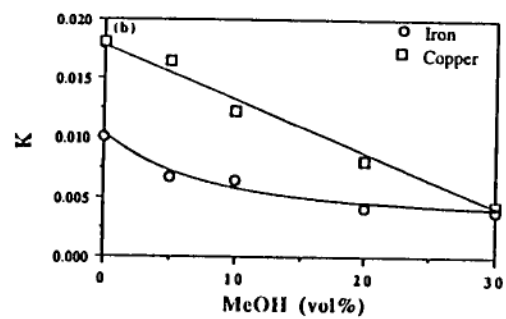
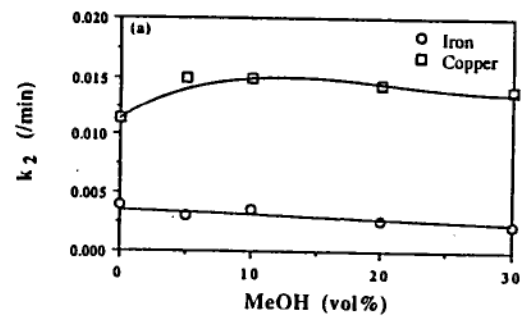


Figure 9



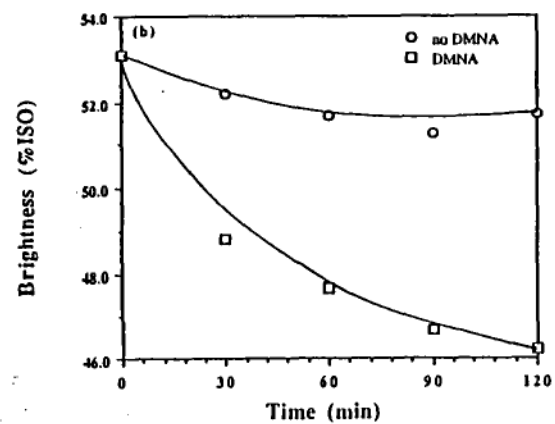
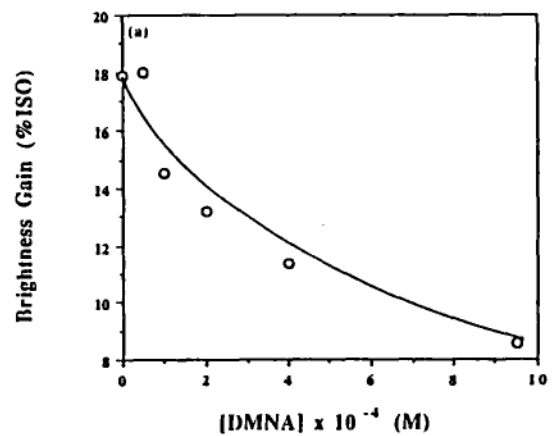


Figure 10

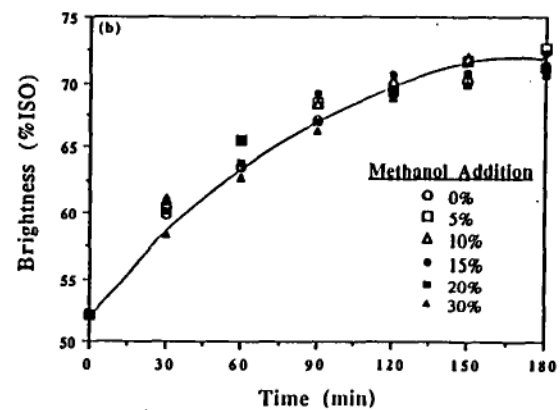
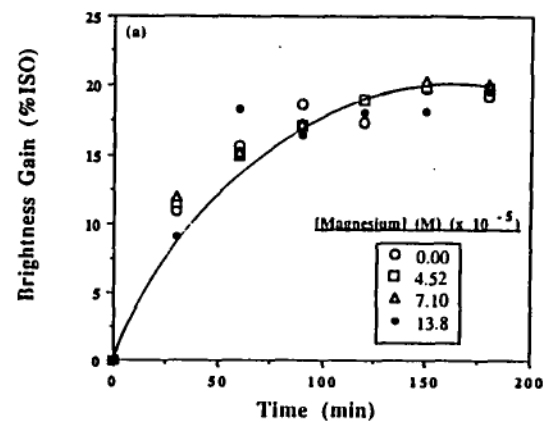


Figure 11

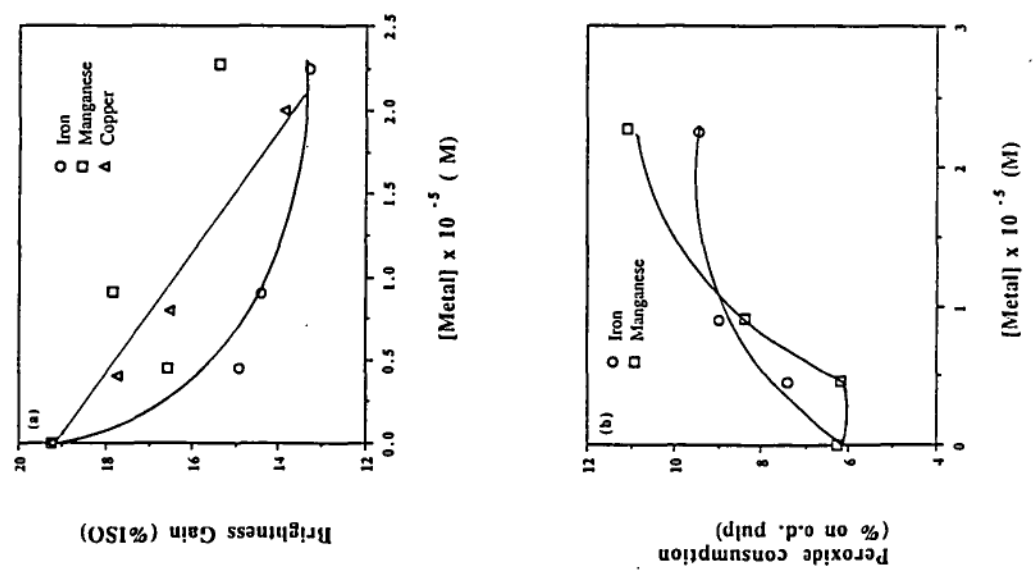
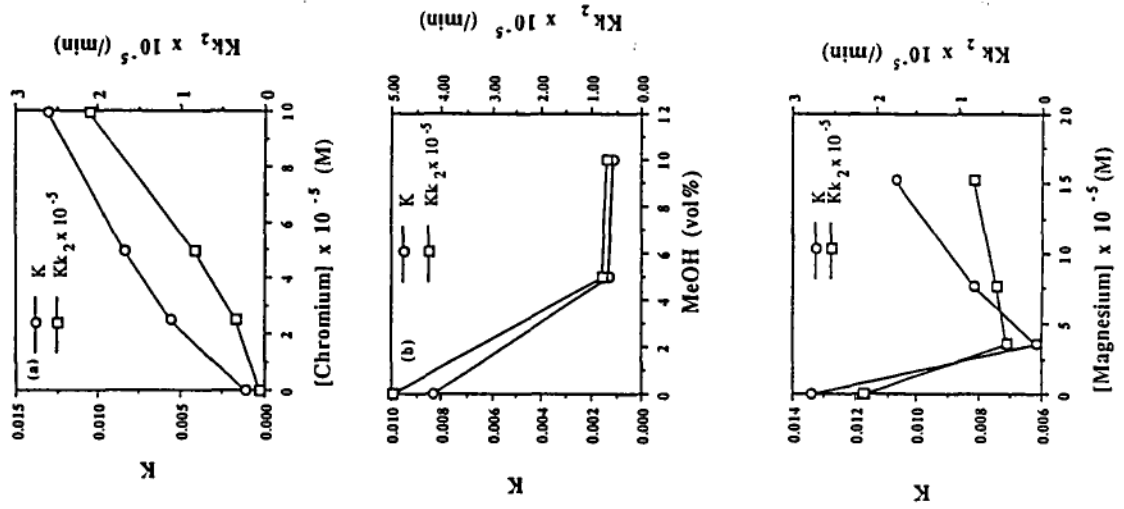


Figure 12

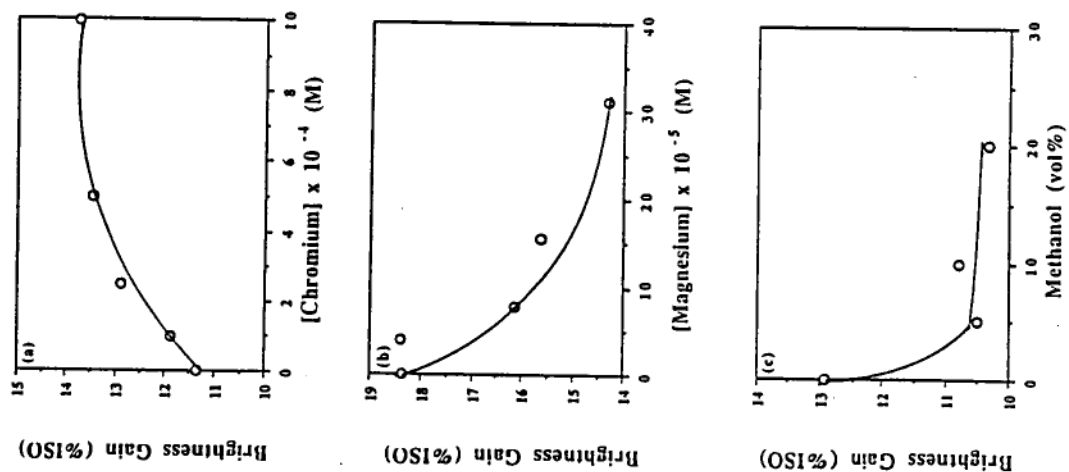


Figure 14