The Electrochemical Mediation of Oxygen Delignification of Pulp with a Manganese
Polyol Complex.

by

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Abstract.

A redox cycle involving a manganese gluconate complex and oxygen in an aqueous alkaline media was investigated for its ability to delignify chemical pulp. Current applied at a cathode was used to reduce the higher oxidation states of the manganese complex. The reaction of the manganese (II) and (III) complex forms with oxygen is believed to produce hydrogen peroxide. Evidence presented in this study suggests a redox cycle was operating involving the manganese III and IV oxidation states of the manganese complex, oxygen and sufficient current. It is thought hydrogen peroxide produced in this redox cycle was responsible for the larger Kappa number and viscosity reductions observed in experimental runs employing the manganese gluconate complex/oxygen redox cycle, than in corresponding runs in the absence of the manganese complex/oxygen redox cycle.

For a pulp consistency of 1%, in 1 M sodium hydroxide, with oxygen purge, for 3 hours at 50 ^{O}C and atmospheric pressure, the presence of the manganese gluconate complex and sufficient current on a platinised titanium cathode reduced the pulp Kappa number from 29 --> 17 and the viscosity from 33 --> 20 cP. In the absence of the complex and current the pulp Kappa number was reduced from 29 --> 20 while the viscosity was reduced from 33 --> 29 cP.

The manganese complex/oxygen redox cycle did not significantly enhance the delignification or cellulose degradation reactions in factorial experiments at 20 ^{O}C or 90 ^{O}C. At 20 ^{O}C it is believed that increased peroxide stability prevented the delignification and cellulose degradation reactions. The formation of free radical species being necessary in peroxide delignification. At 90 ^{O}C it is believed the increased activity of the hydroxide ions and oxygen mask any effect of peroxide produced in the manganese complex/oxygen redox cycle.

The presence of a contaminant, likely copper or iron ions, in the reactor is believed to cause the larger viscosity drop in experimental runs where the contaminant was present. It is thought that the copper and iron ions increased the production of free radical species in the bleaching mixture, thus promoting cellulose degradation.

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Nomenclature.

a   : Tafel equation constant

A   : Absorbance

b   : Tafel equation constant

c   : Concentration

CINT : Confidence interval

E   : Electrode potential

E^o : Standard reduction potential

E^r : Reversible electrode potential

F   : Faraday constant

i   : Current density

i_{lim} : Limiting current density

I   : Current

    : Interaction of variables in factorial design

I_o : Intensity of incident light

I_t : Intensity of transmitted light

K   : Mass transfer coefficient

l   : Thickness of absorbing medium

M   : Main effect estimate

N   : Number of runs in the factorial design experiment

Q   : Activity quotient

r_i : Replicate runs

R   : Universal gas constant

s : Response error

t : Time
  : Transport number

T : Temperature

v : Degrees of freedom

X : Independent variables in factorial design experiments

Y : Response in factorial design experiments

z : Electron stoichiometric coefficient

ϵ : Absorption coefficient

μ : Overpotential

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Chapter 1.

Introduction.

One of the main problems facing the chemical pulp bleaching industry is the need to find an effective delignifying agent that meets the increasingly stringent environmental standards being imposed by the regulatory bodies. Oxygen delignification, while effective and environmentally friendly is expensive in comparison to chlorine based bleaching methods largely due to the cost of the high pressure equipment required. Oxygen bleaching also suffers from low selectivity when compared to chlorine based bleaching methods. The pulp treated by the more selective system has a higher cellulose content for the same reduction in lignin content.

Hydrogen peroxide is also an environmentally friendly bleaching chemical. While its use in both chemical and mechanical pulp brightening is well documented, its use in chemical pulp delignification has not been as extensively studied. However recent research employing 1 % H_2O_2 and 3 % NaOH, on oven-dry pulp, at 15 % pulp consistency and 90 $^{\circ}$C for 90 mins, indicated the ability of hydrogen peroxide to reduce the lignin content of Kraft pulp by 28 % [1].

At present peroxide delignification is unlikely to rival oxygen delignification due to the high chemical cost of the oxidant as indicated in Table 1.

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Oxidant	Price $/kg
O_2	0.11
H_2O_2	1.43

Table 1. Chemical Cost of Oxidants [2].

However, peroxide delignification has the advantage of the use of lower temperature when compared to conventional oxygen bleaching [1]. Also peroxide delignification has not been as extensively studied as oxygen delignification and thus there is the potential of improving its effectiveness and selectivity.

If the cost of hydrogen peroxide could be decreased, the use of peroxide in chemical pulp delignification would become more attractive. The objective of the following study is to examine the effectiveness and selectivity of delignification of chemical pulp by hydrogen peroxide generated through a cathodically mediated redox cycle involving oxygen and a manganese complex in an alkaline environment. The in-situ generation of the relatively expensive oxidant hydrogen peroxide from the cheaper oxidant oxygen, via the redox cycle, may make peroxide delignification more attractive (competitive).

Chapter 2.

Background and Literature Review.

2.1 Structure and Chemical Composition of Wood Fiber and Unbleached Pulp.

2.1.1 Chemical Components in Wood Fiber and Pulp

Wood fiber consists of three principle chemical components. They are cellulose, hemicellulose and lignin. These three materials are all polymeric in structure.

Cellulose.

Cellulose, a polysaccharide, is a high molecular weight stereo regular linear polymer. Cellulose is the chief structural element and major constituent of the cell walls of trees [3]. The fibre bundles it forms impart a high tensile strength to wood. Cellulose is a homogeneous polysaccharide composed of beta-D-glucopyranose units linked by (1-->4)-glycosidic bonds. The structure is as shown below in Figure 1 [4].
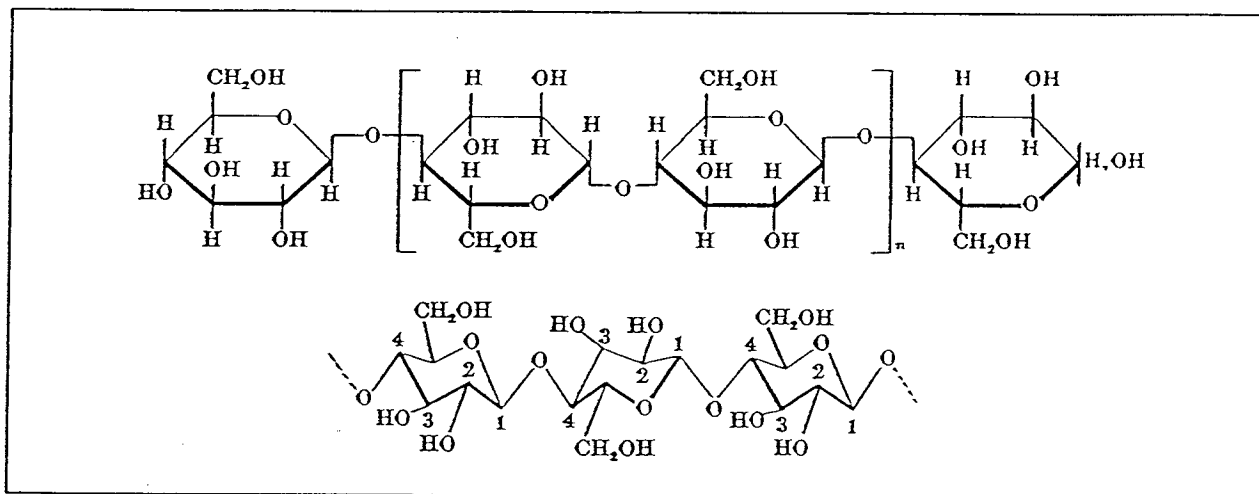
Figure 1. Structure of Cellulose.

Hemicellulose.

Hemicellulose functions as a supporting material in wood fibre. Hemicellulose is a short chain polymer composed of various different sugar monomers. It is relatively easily hydrolysed by acids to these monomeric components when compared to cellulose.

Lignin.

In chemical pulping and bleaching processes, lignin is the unwanted component of wood in the final product. It is an important mechanical reinforcement agent for the entire tree. The structure of lignin is extremely complex and not fully understood. Lignin is an amorphous substance that is partly aromatic in nature. It contains methoxy, aliphatic and phenolic groups

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in a three dimensional polymer linked by C-O-C and C-C bonds. It is responsible for the coloured impurities in pulp [3]. The structure of lignin is indicated in Figure 2 [4].
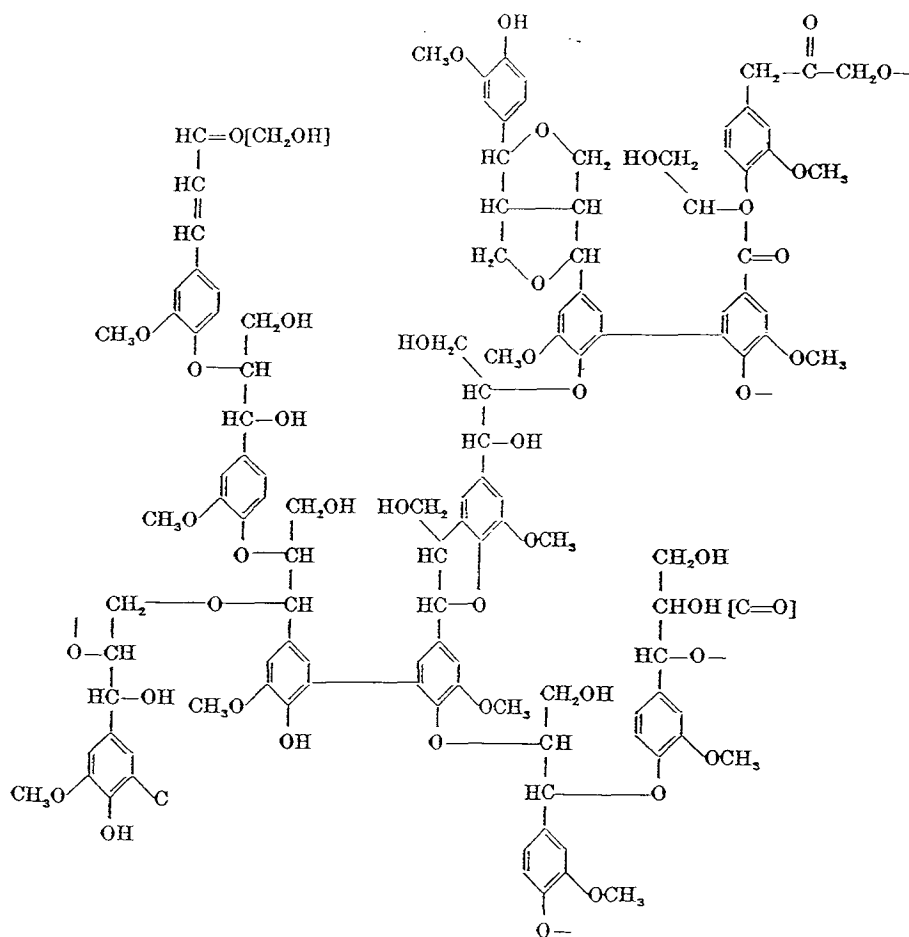
Figure 2. Structure of Lignin.

<u>2.1.2 Structure and Chemical Composition of Wood Fiber [3,5].</u>

Wood is of plant origin and therefore variability in structure is common. Differences in structure can be between species, between trees within a species and between wood from different locations within one tree.

The most characteristic differences are between softwoods and hardwoods. Hardwoods typically contain less lignin and more cellulose as indicated in Table 2.

Component	Hardwood %	Softwood %
Cellulose	40-50	40-45
Lignin	20-25	25-35
Hemicellulose	25-35	25-30

Table 2. Chemical Composition of Wood [3].

Fibres from softwood and hardwood also differ. Generally fibres from softwoods are hollow, 3-6 mm in length, with a diameter 25-60 um and a wall thickness of around 2-7 um. Hardwood fibres however tend to be smaller, the fibres are 0.8-1.9 mm in length and 10-40 um in diameter.

A typical fibre wall contains four main layers. The primary wall is a thin outer layer surrounding the fibre. The secondary wall consists of 3 layers, the outer (S_1), middle (S_2) and inner (S_3) layers. The secondary wall layers (S_1,S_2,S_3) are built up by lamellae formed by

almost parallel microfibrils (cellulose bundles) between which the lignin and hemicellulose are located.

2.1.3 Chemical Composition of Unbleached Pulp [3,5,6].

Before the bleaching stage the wood chips undergo pulping, the purpose of pulping is the selective removal of the chemical fibre bonded lignin with a minimum dissolution of the hemicellulose and cellulose. Pulping converts the wood chips into separate fibres via reaction of chemicals in the pulping liquor (in the case of Kraft pulping NaOH and Na_2S) with the lignin. Unfortunately the chemicals employed in pulping also degrade the cellulose and hemicellulose components. Kraft pulping is normally stopped at 4-5 wt% lignin for softwood pulps as indicated in Table 3. Continuing the pulping further results in excessive cellulose degradation. The lignin remaining after pulping is highly coloured and is difficult to remove. It is located mainly in the secondary wall.

Component	Softwood %
Cellulose	72
Lignin	4
Hemicellulose	24

Table 3. Chemical Composition of Unbleached Pulp [6].

2.2 Objectives in Chemical Pulp Bleaching.

The main objective of chemical pulp bleaching is to make the pulp whiter and brighter. The pulp can be considered to be made up of lignin and cellulosic components [7]. The main coloured constituents in the pulp are due to the lignin. It is therefore desirable to remove the lignin from the pulp. The cellulosic component of the pulp is important with respect to the strength properties of the final bleached product [5]. Chemical pulp bleaching can be considered as the process of removing the lignin from the pulp while minimising the degradation of the cellulosic component of the pulp [8].

Bleaching agents react with pulp in two major ways, 1) reaction with lignin and other non-cellulosic materials (desirable), or 2) reacting to degrade the cellulosic component of the pulp (undesirable) [7]. Since lignin can be oxidised it can be removed through oxidation and solution in alkali [4] the conditions being manipulated to minimise the cellulose degradation.

A standard pulp industry method (T230) involving determination of the solution viscosity [9] is the most commonly used method for measuring the average degree of polymerisation of cellulose. This method is based upon the relationship of solution viscosity to the length of the solute molecules [3]. Therefore the pulp viscosity, as measured by the standard method, can be related to the strength properties of the pulp [5].

The lignin content of pulp is commonly measured in terms of the Kappa number (T236) of the pulp [5,9]. The relationship between the lignin content and Kappa number of pulp is very good for bleachable pulps.

For Kraft pulp,

$$\text{Lignin \%} = 0.147 \times \text{Kappa number} \qquad (1)$$

Conventional oxygen bleaching reduces the Kappa number of pulp from around 30 to 15 and reduces the viscosity from around 40 to 25 cP.

2.3 Oxygen and Hydrogen Peroxide Delignification.

2.3.1 Basic chemical reactions.

In aqueous solution hydrogen peroxide is weakly acidic. Under alkaline conditions it forms the perhydroxyl ion by Reaction 1 and decomposes to oxygen and water by Reaction 2 [10].

$$H_2O_2 + H_2O <--> H_3O^+ + HO_2^- \qquad \text{Rxn 1}$$

$$H_2O_2 --> H_2O + \tfrac{1}{2} O_2 \qquad \text{Rxn 2}$$
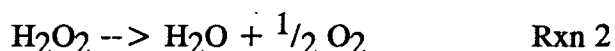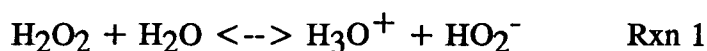
Oxygen on the other hand is a diradical which reacts with unsaturated compounds, metal ions and free radicals [8]. In alkaline solutions oxygen reacts with phenolate anions to produce superoxide radicals via Reaction 3 [8].

$$O_2 + e^- \text{ (from substrate)} --> \cdot O_2^- \qquad \text{Rxn 3}$$
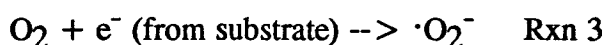
Reaction 3 is endothermic and requires activation of the substrate and/or higher temperatures to proceed at a reasonable rate. For this reason oxygen bleaching is usually carried out in an alkaline environment (pH > 10) and at a temperature > 80 $^\circ$C [11].

The free radical reactions of oxygen and hydrogen peroxide in bleaching environments are intertwined and many of the same free radical species are produced from both.

In the case of oxygen the superoxide radical can lead to the formation of hydrogen peroxide (Reaction 4) [11].

$$2 \cdot O_2^- + H_2O \rightarrow O_2 + OH^- + HO_2^- \qquad Rxn\ 4$$

In practice this reaction is not favoured and the production of hydrogen peroxide is generally catalysed by protons (Reaction 5) or metal ions (Reactions 6 and 7) [11].

$$\cdot O_2^- + \cdot O_2^- + 2H^+ \rightarrow H_2O_2 + O_2 \qquad Rxn\ 5$$

$$M^{n+} + \cdot O_2^- \longleftrightarrow M(:O_2 \cdot)^{(n-1)+} \qquad Rxn\ 6$$

$$H_2O + \cdot O_2^- + M(:O_2 \cdot)^{(n-1)+} \rightarrow O_2 + M^{n+} + OH^- + HO_2^- \quad Rxn\ 7$$
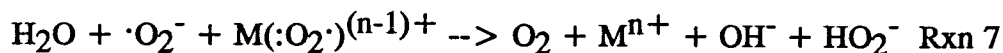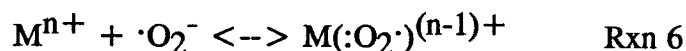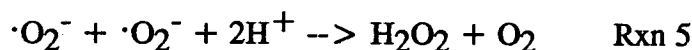
It has been recognised that hydroxyl radicals play an important role in both oxygen and hydrogen peroxide bleaching of pulp [8,11,12]. These radicals can arise through metal catalysed decomposition of hydrogen peroxide (Reaction 8).

$$M^{n+} + H_2O_2 \rightarrow M^{n+1} + OH^- + OH \cdot \qquad Rxn\ 8$$
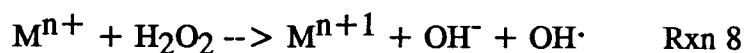
To be catalytic in its action the metal ion (M^{n+1}) must return to its M^{n+} form. In oxygen bleaching this is may be achieved through the action of the superoxide radical (Reaction 9) [11].

$$\cdot O_2^- + M^{n+1} \longrightarrow M^{n+} + O_2 \qquad \text{Rxn 9}$$
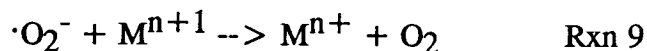
The net reaction being

$$\cdot O_2^- + H_2O_2 \longrightarrow O_2 + OH^- + OH\cdot \qquad \text{Rxn 10}$$
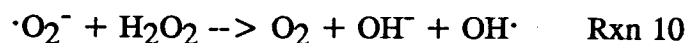
Reaction 10 is often called the superoxide driven Fenton reaction (M = Fe). According to this mechanism the formation of the hydroxyl radicals requires the presence of both the superoxide radicals and hydrogen peroxide.

2.3.2 Oxygen Delignification.

During oxygen delignification in alkaline systems reactions of oxygen with lignin initiate the delignification process through the formation of phenoxy free radicals and superoxide anions (Reaction 11) [12].

$$RC_6H_4O^- + O_2 \longrightarrow RC_6H_4O\cdot + \cdot O_2^- \qquad \text{Rxn 11}$$

Degradation of carbohydrates occurs through the direct reaction of oxygen as well as through the reactions of hydroxyl radicals produced from the hydrogen peroxide formed [8]. In the bleaching environment hydroxyl radicals can oxidise both the lignin and carbohydrate components of the pulp [11]. The reaction with cellulose yielding carbonyl structures opening the way for alkaline degradation of cellulose through beta-elimination (peeling) [11]. Gustavsson and Swan [13] suggested the carbohydrate damage during oxygen delignification to

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be due to the formation of hydrogen peroxide and other peroxides and their reactions with the metal ions present.

2.3.3 Metal Ions in Oxygen Delignification.

Lindeburg and Walding [14] reported that pretreatment of Kraft pulp with nitrogen dioxide/oxygen under acidic conditions allowed for extended delignification in the following oxygen bleaching stage without undue loss of pulp viscosity. The major portion of this result seems to be due to the removal of the metal ions (particularly iron, copper and manganese) via both nitrogen dioxide and acid treatment. This suggests that metal ions may not be necessary for oxygen delignification and that their presence is probably harmful to the cellulose in pulp. The observed protection effect against cellulose degradation by magnesium ions [13] during oxygen delignification supports the view that the reaction of metal ions with peroxides to produce free radicals (reaction 8) is harmful during oxygen delignification. The protection effect of magnesium ions is attributed to their ability to form complexes capable of stabilising peroxides or through the adsorption of transition metal ions on an insoluble magnesium compound preventing their free radical generating reactions with peroxides [15].

In contrast Landucci [16] reported that the ions of manganese, copper and iron are of great importance in oxygen delignification and that their effective removal (via a chelating agent, EDTA) caused the delignification rate to fall dramatically. In Landucci's study the role of the three metal ions varied. Manganese appeared to preferentially catalyse the oxidation of lignin, copper appeared to catalyse the oxidation of both the lignin and carbohydrate, and iron appeared to preferentially promote carbohydrate oxidation.

Obviously further work is required to clarify the role of metal ions in pulp delignification.

2.3.4 Hydrogen Peroxide Delignification.

When applied under relatively mild conditions hydrogen peroxide is a very effective brightening agent used for bleaching mechanical pulps without significant yield loss. Under more severe conditions hydrogen peroxide may be used for the delignification of chemical pulps [17]. The lignin preserving bleaching effect of hydrogen peroxide in mechanical pulp bleaching is attributed to the oxidative action of the perhydroxyl ion (HO_2^-) [17].

As shown in Reaction 8 hydrogen peroxide is susceptible to catalytic decomposition by certain metal ions [10,17,18] and its stability tends to decrease with increasing alkalinity and increasing temperature. For this reason the bleaching of mechanical pulps is usually carried out at pH 10-12 and temperature 35 - 50 ^{O}C [15]. Also the hydrogen peroxide used in mechanical pulp bleaching must be buffered and stabilised before application. The most common buffer is sodium silicate which can also act as a stabiliser. Magnesium ion is usually added to prevent the decomposition of hydrogen peroxide. Some of the silicate reacts with the magnesium ion to form a colloidal precipitate which is believed to protect against decomposition through the adsorption and thus deactivation of trace metal catalysts responsible for the generation of free radicals from hydrogen peroxide. While the use of these additives in mechanical pulp bleaching is required their benefit in chemical pulp delignification is not so clear.

Chemical pulp delignification is carried out at pH 10-12 and temperature 80-90 ^{O}C, in the absence of peroxide stabilising agents. Under these conditions, two types of reaction of

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hydrogen peroxide with lignin seem to predominate [19]. 1) Nucleophilic attack of the hydroperoxide anion (HO_2^-) on the carbonyl group of the side chain, leading to lignin depolymerisation, and 2) The oxidation of the phenols to quinones which seems to be brought about by free radical reactions followed by ring opening and further oxidation to carboxyl groups. The hydroxyl radicals formed in the reaction of hydrogen peroxide with metal ions would also react with carbohydrates causing their degradation.

2.3.5 Metal Ions in Hydrogen Peroxide Delignification.

Decomposition of hydrogen peroxide into free radical species is important with respect to delignification [10]. Metal ions which catalyse that decomposition are likely to be of importance.

In their work on the oxidation of a model lignin compound with hydrogen peroxide Smith and McDonough [20] found that the addition of iron, copper or manganese salts catalyzed peroxide decomposition. The addition of copper, manganese and iron ions also increased the rate of oxidation of the model lignin compound by hydrogen peroxide. The catalytic activity of the metal, with respect to the lignin model oxidation, decreasing from copper to manganese to iron. Landucci [21] found the same ranking for the above metal ions with respect to their ability to catalyse phenoxy radical formation. Smith and McDonough concluded that peroxide decomposition to free radical species was important with respect to peroxide delignification and that metal ions played an important role in that decomposition.

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A further study by McDonough and Kirk et. al. [18] on Kraft pulp delignification with hydrogen peroxide indicated that the delignification rate of the pulp increases with increasing hydrogen peroxide decomposition, paralleling the model compound work. The hydrogen peroxide decomposition was altered through the manipulation of the metal ion concentrations in the pulp. The metal ions of importance were shown to be copper, manganese and iron. In their study metal ion removal was achieved through the use of chelating agents such as DTPA (di-ethylene triamine pentaacetic acid) in prewashing the pulp. It was found however that the addition of manganese or copper had a negligible effect on delignification and that the addition of iron actually retarded delignification. Also the addition of peroxide stabilisers which virtually stopped peroxide decomposition slowed, but did not stop, delignification. This indicated the delignification ability of uncatalysed peroxide.

The metal ions of manganese and iron both retarded cellulose degradation while copper had little effect. The protective effect of manganese may have been due to the adsorption of transition metal ions on the surface of precipitated manganese oxides [18].

2.4 Manganese Gluconate Complexes.

Research related to biological oxygen transfer systems investigated polyhydroxy ligands capable of stabilising the higher oxidation states of manganese. It revealed the ability of the gluconate ion to effectively stabilise the +2, +3 and +4 oxidation states of manganese and form soluble complexes in alkaline media [23-25]. The gluconate ion is obtained through the addition of D-glucono-lactone to sodium hydroxide solutions [24].

$$
\begin{array}{c}
\text{H} \\
\text{H H H O H} \\
/ \ / \ / \ / \ / \\
\text{HO-C-C-C-C-C-COO}^- \\
/ \ / \ / \ / \ / \\
\text{H O O H O} \\
\text{H H} \qquad \text{H}
\end{array}
\qquad \text{Gluconate ion } (GH_4^-)
$$

[26]
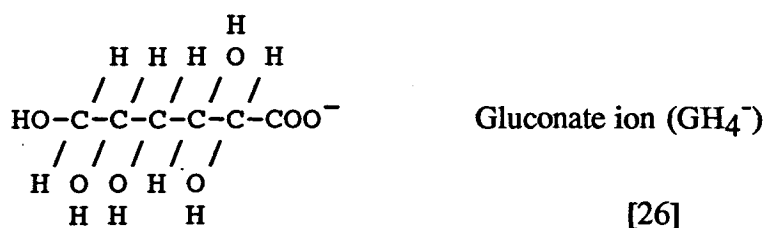
Figure 3. Gluconate Ion.

It was found that molecular oxygen was capable of oxidising the manganese(II) complex (colourless) producing the manganese(III) complex (orange-brown) and hydrogen peroxide (Reaction 12) [23]. GH_3^{2-} represents the dianion of the gluconate ion.

$$Mn^{II}_2(GH_3)_4(H_2O)_2^{4-} + O_2 + OH^- \longrightarrow Mn^{III}_2(GH_3)_4(OH)_2^{4-} + HO_2^-$$
$$+ H_2O$$

Rxn 12
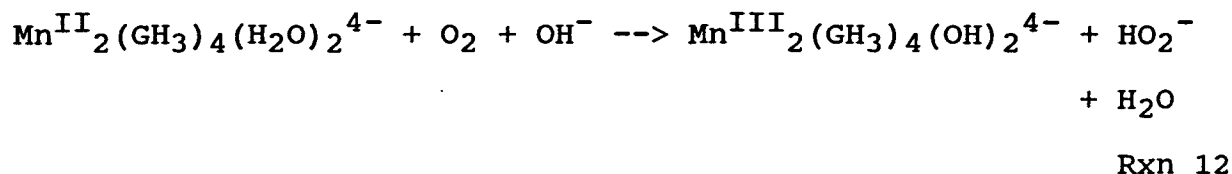
Oxygen also oxidised the manganese(III) complex to produce the manganese(IV) complex (cherry red) and a further peroxide ion (Reaction 13) [23].

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$$Mn^{III}_2(GH_3)_4(OH)_2^{4-} + O_2 + 3OH^- \longrightarrow Mn^{IV}_2(GH_3)_4(OH)_2^{6-} + HO_2^-$$

$$+ H_2O$$

Rxn 13
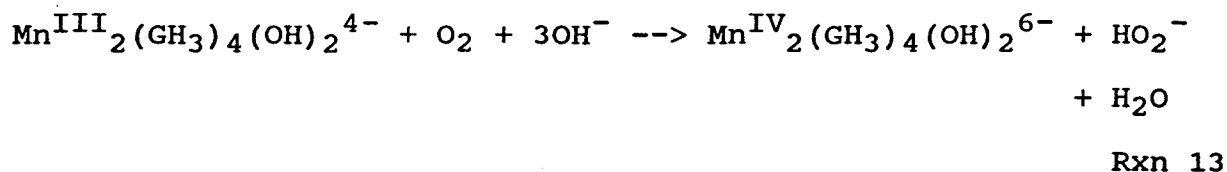
In the reaction scheme proposed by Richens et. al. [22], the manganese (II) gluconate complex reacts rapidly in a binuclear process with $k_{obs} = 2.8E4$ $M^{-1}s^{-1}$ (Rxn 12 in 0.5 M NaOH, 25 ^oC), the manganese(III) gluconate reacting in a slower process with $k_{obs} = 3.9E1$ $M^{-1}s^{-1}$ (Rxn 13 in 0.5 M NaOH, 25 ^oC) [22]. The reaction rate is dependent on pH, temperature, ligand and manganese concentrations [22-25].

The studies also indicated the ability of the lower oxidation states of the manganese complex to be electrochemically regenerated via controlled potential electrolysis on a mercury-pool working electrode [22]. The electrochemical studies indicated the reversibility of the manganese II/III and the manganese III/IV couple [23,24]. The reduction potentials were -0.29 and -0.03 Volts vs SHE respectively for the conditions employed [24].

Studies by Lim et al indicated the ability of these manganese complexes to catalyse high pH oxidation reactions [2]. The peroxide concentration profile during the high pH oxidation of hydrazine catalysed by the manganese complex indicates a rapid formation of hydrogen peroxide at the start of the reaction followed by a steady generation and consumption of peroxide until the reaction is completed [2]. The authors suggest the catalytic activity of the manganese complex is related to its ability to participate in an oxidation-reduction cycle in which hydrogen peroxide is continuously generated from the reaction with oxygen [2].

The steady generation of hydrogen peroxide requires the continuous regeneration of manganese (II) or manganese (III) following its oxidation to the higher valence states. The authors suggest the regeneration occurs through the reaction of the manganese(III) complex and a hydroxy free radical or between the manganese (III) complex and the peroxide sensitive substrate as in the case of hydrazine (Reactions 14,15) [2].

$$Mn^{III}(L^{2-})(OH^-) + OH\cdot \longrightarrow Mn^{II}(L^{2-}) + H_2O_2 \qquad Rxn\ 14$$

$$Mn^{III}(L^{2-})(OH^-) + Mn^{III}(L^{2-})N_2H_4^+ \longrightarrow 2Mn^{II}(L^{2-}) \qquad Rxn\ 15$$
$$+ N_2H_2 + H_2O + H^+$$
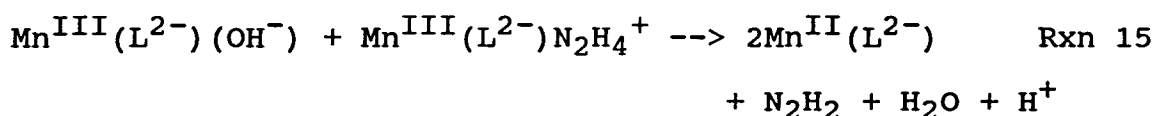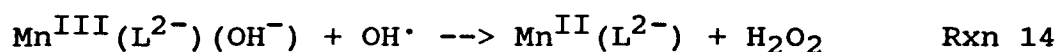
L - denotes gluconate ligand.
N_2H_4 - denotes hydrazine
N_2H_2 - denotes diimine (hydrazine oxidation product [22])

The results of studies on peroxide sensitive substrates appear to indicate the ability of the alkaline manganese complex to promote peroxidation reactions via non-free radical pathways [2]. This result is ascribed to the ability of alkaline manganese to tie up and consume free radical species [2].

2.5 Electrochemistry.

Some chemical reactions can be made to occur via ionic mechanisms by the addition of electrical energy. Electrochemical reactions involve mass transfer, adsorption/desorption, and electron transfer processes at the electrode/electrolyte interface. The rate is dependent on the electrode material, reactant concentration, temperature and electrode potential.

A simple electrochemical system consists of two electrodes and an electrolyte. The electrode at which an electron producing ionic reaction is occurring (eg $M \rightarrow M^+ + e^-$) is the anode, the electrode at which an electron consuming reaction occurs (eg $N^+ + e^- \rightarrow N$) is the cathode.

In most systems multiple reactions at a given electrode are occurring. The electrochemical reactions of interest in the present study are the cathode reactions below (Reactions 16,17,18,19).
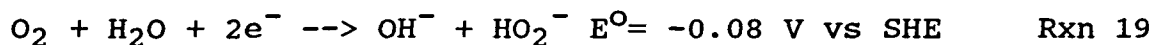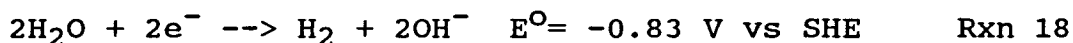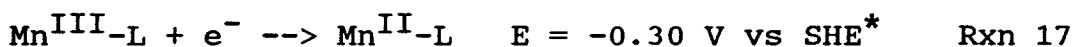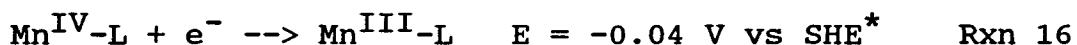
$$Mn^{IV}\text{-}L + e^- \rightarrow Mn^{III}\text{-}L \qquad E = -0.04 \text{ V vs SHE}^* \qquad Rxn\ 16$$

$$Mn^{III}\text{-}L + e^- \rightarrow Mn^{II}\text{-}L \qquad E = -0.30 \text{ V vs SHE}^* \qquad Rxn\ 17$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad E^o = -0.83 \text{ V vs SHE} \qquad Rxn\ 18$$

$$O_2 + H_2O + 2e^- \rightarrow OH^- + HO_2^- \qquad E^o = -0.08 \text{ V vs SHE} \qquad Rxn\ 19$$

(L- denotes gluconate ligand)

(*- measurement for 1 mM Mn, 0.1 M Gluconate, 0.3 M NaOH, 1 atm, 25 °C [25].)

The Nernst equation describes the reversible reduction potential (E^r) of an electrochemical reaction.

$$E^r = E^o - RT\ln Q/zF \qquad (2)$$

Where,
E^o - Standard reduction potential (V vs SHE)
R - Universal gas constant (8.314 J/mole-K)
T - Absolute temperature (K)
z - Electron stoichiometric coefficient
F - Faraday constant (96500 coulombs/g equivalent)
Q - Activity quotient

If the working electrode is a cathode a reaction will occur if the electrode potential (E) is held below the reversible electrode potential (E^r). The overpotential (μ) is described by

$$\mu = E - E^r \qquad (3)$$

The overpotential is related to the current density (i) through the Tafel equation (Equation 4).

$$\mu = a + b\log i \qquad (4)$$

Where, a and b are constants

The limiting current (i_{Lim}) is a mass transfer constraint on the system dependant on a mass transfer coefficient (K), the concentration of the reactant (c) and the transport number (t) as described by Equation (5).

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$$i_{Lim} = zFKc/(1-t) \qquad (5)$$

The transport number is the fraction of the total current carried by the ionic species of interest.

2.6 Cyclic Voltammetry [27].

In cyclic voltammetry the potential applied to an electrode (by means of a potentiostat) is changed linearly with time in a repetitive manner. The current is measured as a function of potential. The basic feature of a voltammogram (ie. a plot of current vs potential during cyclic voltammetry) is the appearance of a current peak at a potential characteristic of an electrode reaction taking place (Figure 4).
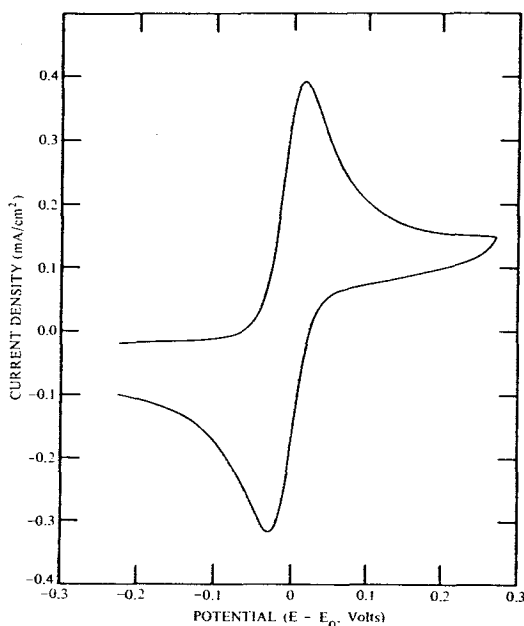
Figure 4. Diagram of Typical CV Result

The position and shape of a given peak depends on such factors as sweep rate, electrode material, solution composition and the concentration of reactants.

In a typical voltammogram a substance being reduced during the cathodic scan (left to right) appears as a positive peak. When the scan is reversed the reduced species which is still at the surface of the electrode is re-oxidised and an anodic peak occurs. For an electrochemically

reversible couple these two peaks should be clear and occur at approximately the same potential.

Cyclic voltammetry is suited to the identification of steps in the overall reaction and of new species which appear in solution during electrolysis. It also gives an indication of the ability of the electrochemical system to promote oxidation or reduction reactions.

2.7 Spectrophotometry [28].

When light falls upon a homogeneous medium a portion of the incident light is reflected, a portion is absorbed within the medium and the remainder is transmitted. The absorbance of a solution is related to the ratio of the transmitted light (I_t) to the incident light (I_o) by Equation 6.

$$A = \log I_o/I_t \qquad (6)$$

The absorbance is related to the concentration (c) of a component as described in Equation 7.

$$A = \epsilon cl \qquad (7)$$

Where,
  l - thickness of the absorbing medium
  ϵ - absorption coefficient
  c = concentration of absorbing component

Through absorbance measurements the predominant ion in the solution can be determined providing the different ions vary in their absorbance at a given wavelength. The wavelength to be used is determined by the construction of a plot of absorption vs wavelength for the different ionic species.

2.8 Factorial Design of Experiments.

Many of the experiments performed in the pulp delignification trials (Section 5.4) utilised factorial design. Factorial design of experiments is a proven technique of obtaining fast accurate results. Its benefits include that it can give more information per experiment than an unplanned approach: it is a simple, organised approach and the reliability of the information can be assessed in the light of experimental and analytical variation [29]. Also such an approach is able to highlight the interaction of experimental variables.

Two-level factorial designs are utilised in this study. A two level design experiment is performed by choosing two fixed levels (denoted -1 for low level and +1 for high level) for each of the variables (factors) to be studied. The arrangement of 2^n experimental runs for n variables is called a "2^n factorial design". The two level factorial design matrices for two and three variables which are utilised in the following experiments are shown in Table 4 below.

2 Variable   3 Variable

X1	X2	R
+1	+1	Y1
+1	-1	Y2
-1	+1	Y3
-1	-1	Y4

X1	X2	X3	R
-1	-1	-1	Y1
+1	-1	-1	Y2
-1	+1	-1	Y3
+1	+1	-1	Y4
-1	-1	+1	Y5
+1	-1	+1	Y6
-1	+1	+1	Y7
+1	+1	+1	Y8

Table 4. Factorial Design Matrices for Two and Three Variables.

The responses (R, dependent variables) are the Kappa number and viscosity of the pulp, the independent variables (X) are current, catalyst concentration, gas purge type etc.

Main Effects.

The main effects (M) of each variable are estimated using the difference between the average high (+1) and low (-1) factor level responses.

ie. for the 2^2 design,

$$M(X1) = ((Y1+Y2)-(Y3+Y4))/2 \qquad (8)$$

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$$M(X2) = ((Y1+Y3)-(Y2+Y4))/2 \qquad (9)$$

Interaction Effects

If the variables are not additive in their effect an interaction occurs. The interaction effect is calculated using the difference between the average response of the high level factorial runs and the low level runs.

ie. for the 2^2 design,

$$I(X1,X2) = ((Y1+Y4)-(Y2+Y3))/2 \qquad (10)$$

Significance of the Effects.

To gauge the significance of an effect confidence intervals are used. The confidence level chosen was the 95% level. The confidence interval (CINT) is calculated from Equation 11 below,

$$CINT = (\text{Effect Estimate}) \pm ts/(N/4)^{1/2} \qquad (11)$$

where,
    s = response error estimate with v degrees of freedom
    N = number of experimental runs in the factorial design
    t = students t statistic with v degrees of freedom at the
           stated confidence interval

Response error is estimated using replicate runs. The error associated with the Kappa number and viscosity measurements are included in this estimate. For duplicates where the responses are denoted V and W,

$$s = ((V-W)^2/2)^{1/2} \qquad (12)$$

Error estimates from several sources may be pooled for a firmer estimate of error. The pooled variance for k separate estimates of error s_i each with r_i replicates is,

$$s^2 = \Sigma(r_i-1)s_i^2/\Sigma(r_i-1) \qquad (13)$$

with degrees of freedom (v),

$$v = \Sigma(r_i-1) \qquad (14)$$

In this study the response error (s) for Kappa No and viscosity was calculated to be 0.21 and 1.21 respectively. The degrees of freedom in both cases was 4 (see Appendix 2).

For a 95% confidence interval the students t statistic with 4 degrees of freedom is 2.776 [30].

Therefore for all the factorial design experiments the 95% confidence intervals were calculated as below,

For Kappa number,

$$\text{CINT} = \text{(Effect Estimate)} \pm 0.58x(N/4)^{1/2} \quad (15)$$

For viscosity,

$$\text{CINT} = \text{(Effect Estimate)} \pm 3.64x(N/4)^{1/2} \quad (16)$$

The confidence intervals for interaction effects were calculated in the same way.

The effects are considered significant if the confidence interval does not contain zero.

For a more complete overview of factorial design a paper by Murphy [29] is recommended.

Chapter 3.

The Proposed System and Research Objectives.

In peroxide and oxygen bleaching of chemical pulps the objective is to lower the lignin content of the pulp whilst minimising the degradation of the cellulose component [15]. An important cellulose degradation reaction pathway involves free radical species [8]. The results of studies on peroxide-sensitive substrates appears to indicate the ability of the alkaline manganese complex/oxygen redox cycle to promote peroxidation reactions via non-free radical pathways [2]. This suggests the possibility of substituting the oxygen and manganese complex system as described above in place of the relatively expensive hydrogen peroxide in the bleaching of chemical pulps.

The proposed system involves the use of the manganese gluconate/oxygen redox cycle to delignify chemical pulp through the in-situ production of hydrogen peroxide in an alkaline environment. It is proposed to promote the reduction of the higher oxidation states of manganese via the application of current at a cathode (Reactions 20,21).

$$Mn(IV)\text{-}L + e^- \text{ (from electrode)} --> Mn(III)\text{-}L \quad Rxn\ 20$$

$$Mn(III)\text{-}L + e^- \text{ (from electrode)} --> Mn(II)\text{-}L \quad Rxn\ 21$$

Or through the use of a chemical reductant (Reactions 22,23).

$$Mn(IV)\text{-}L + e^- \text{ (from reductant)} --> Mn(III)\text{-}L \quad Rxn\ 22$$

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Mn(III)-L + e⁻ (from reductant) --> Mn(II)-L   Rxn 23

(-L represents gluconate ligand)

The proposed manganese complex/oxygen redox cycle is as presented in Figure 5.

$$Mn^{II}_2(GH_3)_4(H_2O)_2{}^{4-} + O_2 + OH^- \longrightarrow Mn^{III}_2(GH_3)_4(OH)_2{}^{4-} + HO_2^-$$
$$+ H_2O$$

└──────< + e⁻ (from cathode) <──────┘

$$Mn^{III}_2(GH_3)_4(OH)_2{}^{4-} + O_2 + 3OH^- \longrightarrow Mn^{IV}_2(GH_3)_4(OH)_2{}^{6-} + HO_2^-$$
$$+ H_2O$$

└──────< + e⁻ (from cathode) <──────┘
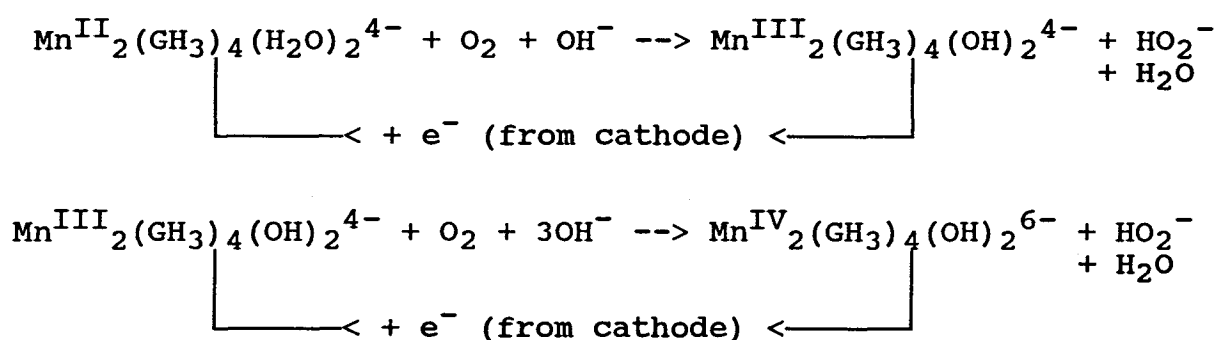
Figure 5. Proposed Redox Cycle for the Continuous Generation of
Hydrogen Peroxide From Manganese Gluconate and Oxygen.

The benefit of such a system would include the generation of the relatively expensive hydrogen peroxide from oxygen [2]. The redox cycle involving manganese gluconate and oxygen may also promote peroxide oxidation reactions via non-free radical pathways [2]. If the proposed redox cycle promotes peroxide oxidation reactions via non-free radical pathways it could minimise the detrimental effect of free radicals on the cellulosic component of the pulps. This would improve the selectivity of the delignification process.

The work described in the following chapters investigates the ability of the proposed manganese complex/oxygen redox cycle to operate in the bleaching environment and to promote, via the peroxide produced, the delignification of chemical pulp.

Chapter 4.

Experimental Apparatus and Procedure.

4.1 Cyclic Voltammetry.

Cyclic voltammograms were determined with a Pine Potentiostat RDE 3 in conjunction with a Watanabe WX446 X-Y recorder. The system used three electrodes. A platinised titanium electrode served as a counter electrode with a saturated calomel electrode (SCE) as the reference electrode. The working electrode consisted of either a graphite rod, a platinum wire, or a copper-mercury amalgam plate electrode.

The set up was as described below (Figure 6).

WE – Working electrode
CE – Counter electrode

N$_2$ or O$_2$
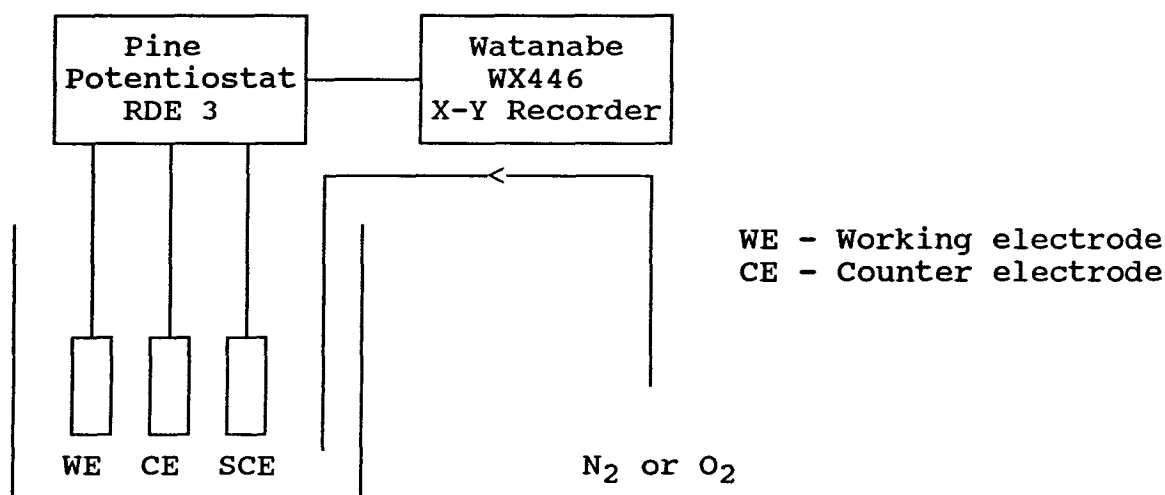
Figure 6. Cyclic Voltammetry Set-up

One liter of sample solution was prepared in air and added to the CV jar. The three electrodes were then placed in the solution The solution was then purged with nitrogen for at least 10

minutes before the measurement was taken. To examine the influence of oxygen on the system oxygen purge was available. After being purged with oxygen for the desired time the solution would be purged with nitrogen and the measurement taken. The oxygen was removed so electrode reactions involving oxygen could be eliminated from the results. All CV measurements were taken at room temperature (23 ^{o}C).

The preparation of the manganese gluconate solutions was a step-wise procedure. First the gluconate ion was formed through the addition of glucono-lactone to an aqueous solution of 1 M sodium hydroxide. For gluconate concentrations greater than 10 mM the gluconolactone was added as a solid and for concentrations of 10 mM and less as a solution (0.1 M). Then the manganese ion was added as a 0.1 M solution of manganese perchlorate. The solution could be prepared under nitrogen if the manganese (II) solution was required. All solutions were prepared at room temperature.

4.2 Spectrophotometry.

The spectrophotometric measurements were made with a HACH DR/2000 Direct reading spectrophotometer. The glass vials containing the solution to be measured were cleaned thoroughly with hot water and distilled water between measurements. The sample absorbance was measured relative to a blank sample solution containing the sodium hydroxide and the ligand components only.

The solutions prepared all contained 1 mM manganese and 5 mM glucono lactone in 1M NaOH. When a manganese II complex was required, to ensure no oxidation of the complex to the III or V forms, the solution was prepared under nitrogen purge. The solutions were prepared using the stepwise procedure described in section 4.1. The manganese III and IV gluconate solutions were prepared through the addition of potassium ferricyanide to a manganese II gluconate solution prepared under nitrogen. The stoichiometry being as shown in Table 5 below [22].

Reaction	Mol of $K_3Fe(CN)_6$/mol of Mn Ion
II --> III	1.0
II --> IV	2.0

Table 5. Stoichiometry for Manganese Complex Oxidations with
   $K_3Fe(CN)_6$.

The samples were measured directly upon removal from the reactor or flask to avoid excessive reaction with oxygen in the air. The path length was 2.5cm.

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For the initial determination of absorption vs wavelength for the system the solutions were prepared as above and their absorption at different wavelengths determined.

For the spectrophotometric experiments the electrochemical cell set up was as for the bleaching runs (Section 4.4). The cathode was a platinised-titanium electrode. The solutions were prepared as above and poured into the catholyte side of the reactor. All experiments were carried out at room temperature, 23 $^{\circ}$C. The 5 experiments utilising spectrophotometric analysis are described in Table 6 below.

Experiment	Initial Manganese Oxidation State	Gas Purge 15 cc/min @ STP	Current Amps	Pulp Present
1	II	O_2	0.0	No
2	III	N_2	1.0	No
3	IV	N_2	1.0	No
4	II/III	O_2	1.0	No
5	II/III	O_2	1.0	Yes

Table 6. Description of Spectrophotometric Experiments.

The solutions for experiments 4 and 5 were prepared in air and therefore contained a mixture of II and III manganese oxidation states.

4.3 Hydrogen Peroxide Analysis.

The reactor set-up was as for the bleaching runs (Section 4.4). All experiments were carried out in the absence of pulp. The solutions were prepared in the stepwise procedure described in Section 4.1.

In Experiment 1 a 1 M solution of NaOH was subjected to O_2 purge and a current of 2.0 A on a graphite cathode and periodically tested for the presence of hydrogen peroxide. In Experiment 2 a 1 M solution of NaOH containing 1 mM manganese and 5 mM gluconate was subjected to O_2 purge and a current of 2.0 A on a graphite cathode and tested for the presence of hydrogen peroxide. Finally, in Experiment 3 a 1 M solution of NaOH containing 1 mM manganese and 5 mM gluconate was subjected to O_2 purge and a current of 2.0 A on a platinised titanium cathode and tested for the presence of hydrogen peroxide.

The solution was periodically analysed for hydrogen peroxide following the titration procedure detailed in Appendix 5.

4.4 Pulp Delignification Trials.

The equipment for the electrochemical bleaching runs was as shown below in Figure 7.
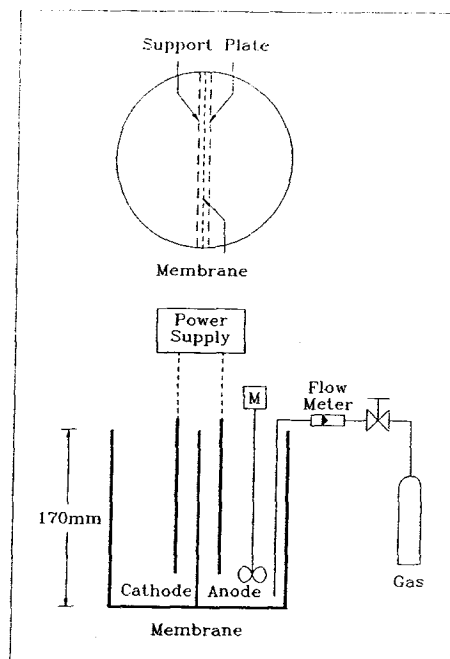
Figure 7. Diagram of Equipment Used in Electrochemical Bleaching
Trials.

The reactor consisted of a cylindrical divided reactor with a diameter and height of 170 mm. The reactor was placed in a constant temperature bath. The reactor was made of stainless steel coated with PTFE to prevent metal ion contamination. The two chambers of the reactor were separated by a cation membrane (Nafion 214) supported by two perforated plexiglass plates. The anode was a 316 stainless steel plate. The cathode material could be varied (graphite, stainless steel, platinised-titanium etc). The cathode area was 140 cm^2. A DC power supply (Anatek 6030) was used for the experiments involving currents of up to and including 4.0 A. Higher currents were obtained through the use of a SORENSEN DCR 40-25B power supply.

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A variable speed motor with a three blade plastic stirrer provided the mixing during the experiments. Gas was purged into the reactor through a glass tube connected to the source cylinder and a flow meter with Teflon tubing. The temperature of the system was regulated by situation of the reactor in a constant temperature bath.

Preparation of Chemicals and Pulp.

The source of the manganese ion was manganese (II) perchlorate hexahydrate obtained from the Aldrich Chemical Company. The gluconate ion was obtained through the reaction of gluconolactone with sodium hydroxide obtained from the Aldrich Chemical Company and Fischer Scientific respectively. The other chemicals used (hydrogen peroxide 30% solution, sodium sulphate, sulphuric acid, magnesium sulphate and sodium silicate) were obtained through BDH Chemicals. All chemicals were reagent grade and were used without further purification.

All solutions were prepared using distilled water to 1 l total volume. For the runs at pH 14 the solution was made up with 40 g/l of sodium hydroxide (NaOH). The gluconate ligand was prepared through the addition of gluconolactone to the sodium hydroxide solution. For ligand concentrations greater than 10 mM the gluconolactone was added as a solid and for concentrations of 10 mM and less as a solution (0.1 M). This solution was then allowed to attain the temperature required in the bleaching run. Finally the desired manganese concentration was attained through the addition of an appropriate amount of 0.1 M manganese perchlorate solution (0.1 M) also at the bleaching run temperature. For the runs at pH 11 the initial solution was 0.5 M in sodium sulphate (Na_2SO_4). The ligand was then added and the

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pH of the solution adjusted to 11 through the dropwise addition of concentrated NaOH. The manganese was then added. Finally the pH of the solution adjusted to 11 through the dropwise addition of concentrated NaOH.

The solution was then placed in the catholyte chamber of the reactor with 10 oven dry grams of unbleached Kraft softwood pulp. The consistency of the pulp suspension was therefore 1 %. The anolyte chamber contained 1 M NaOH. The pulp slurry was purged with gas (O_2 or N_2) at atmospheric pressure, mixed homogeneously and subjected to the desired current for the reaction duration.

For the trials involving chemical reductants the stainless steel reactor was replaced with a glass beaker and the electrode system was not employed.

The pulp used in the experiments was obtained from a previous researcher Mr Yuan-Shing Perng. The original properties were a Kappa No of 28.5 and a viscosity of 32.5 cP. The pulp was a mixture of 35% hemlock, 30% fir and larch, 15% cedar, 10% spruce and balsam fir and 10% lodgepole pine.

The pulp samples were prepared by the weighing of 11.00 $\pm$ 0.01 g of pulp from the conditioning room (= 10 g of oven dry pulp). This was thoroughly dispersed and rinsed, then prepared as a handsheet in the handsheet former.

If a DTPA wash was required the pulp was added to 1 l of distilled water containing 0.4 % DTPA. The mixture was stirred and left to stand for at least 15 minutes at room temperature. The pulp was then rinsed in distilled water and a handsheet was prepared.

After reaction the pulp is removed from the reactor, rinsed thoroughly and formed into a handsheet.

If the colour generation in the reactor indicated a manganese precipitate a sulphurous acid wash was required. The pulp was added to a 0.25 - 0.3 % solution of the acid (approximately 100 ml/g pulp) stirred and left to stand for at least 5 minutes at room temperature. The pulp was then rinsed and a handsheet prepared.

The pulp was then analysed for Kappa number and pulp viscosity using pulp industry standard methods Tappi T236 cm-85 and T230 om-89 respectively [9].

Chapter 5.

Experimental Results and Discussion.

5.1 Cyclic Voltammetry.

5.1.0 Introduction.

Cyclic voltammetry is a useful tool for the investigation of electrochemical systems. The following experiments utilise cyclic voltammetry to investigate the ability of the electrode materials employed in the delignification trials to promote the reduction of the higher oxidation states of the manganese complex. The ability of the electrodes employed to promote that reduction is necessary in the proposed redox cycle for the continuous in-situ generation of hydrogen peroxide. Cyclic voltammetry can also indicate the appearance of new species in the system and therefore may give an indication of the production of hydrogen peroxide.

5.1.1 Results and Discussion.

Results from the use of a platinum wire electrode in a manganese gluconate solution indicate cathodic peaks at -0.19 V vs SHE and -0.51 V vs SHE and anodic peaks at 0.06 V vs SHE and -0.21 V vs SHE (Figure 8).
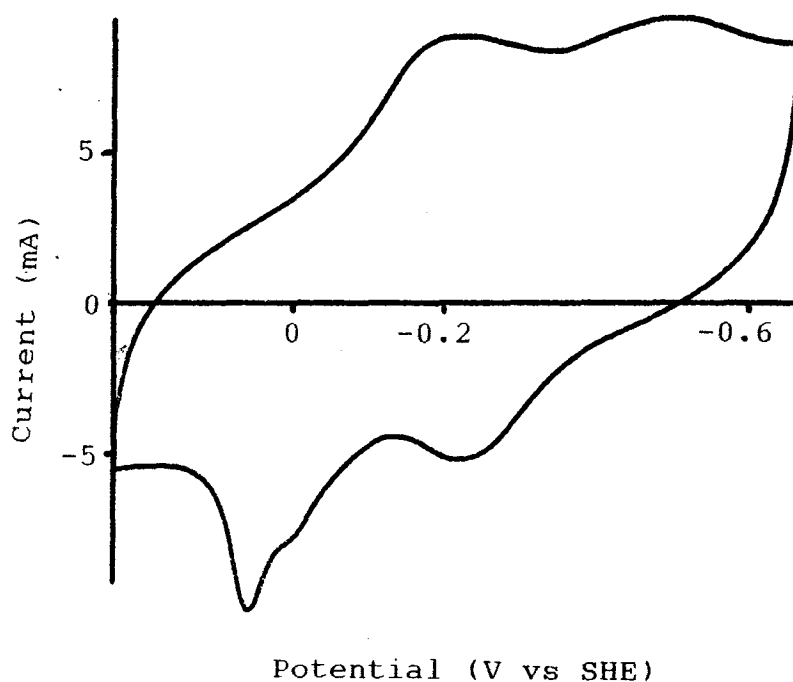
Figure 8. Cyclic Voltammogram for the Manganese Gluconate Complex Formed in the Presence of Oxygen and Deaerated with Nitrogen. (10 mM Mn, 50 mM Gluconate, Platinum Wire Working Electrode, 1 M NaOH, 22 ^{o}C, Scan Rate 5 V/min)

These peaks were not evident in the sodium hydroxide only voltammogram (Figure 9).
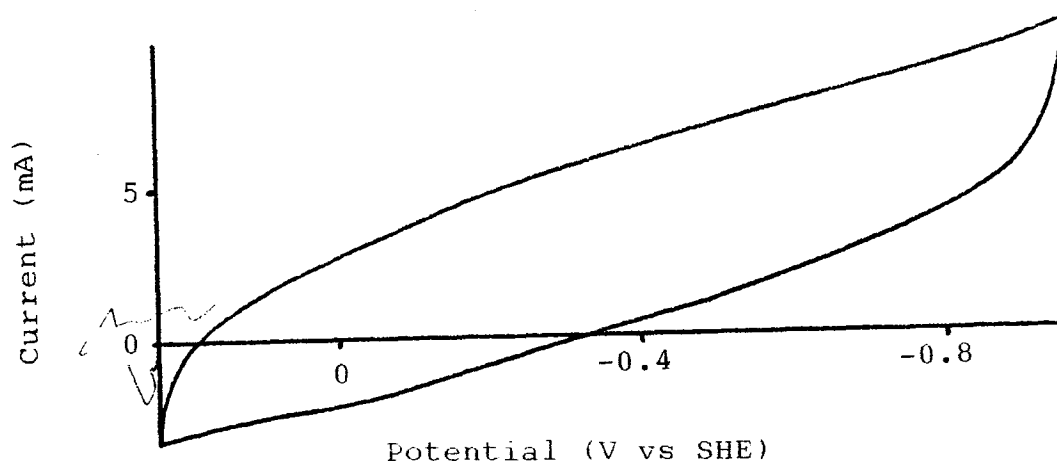
Figure 9. Cyclic Voltammogram for 1 M NaOH Deaerated with Nitrogen. (Platinum Wire Working Electrode, 1 M NaOH, 22 $^\circ$C, Scan Rate 4 V/min)

The peaks evident in Figure 8 are believed to correspond to the oxygen/hydrogen peroxide couple (Reaction 19, -0.19 V vs SHE cathodic / 0.06 V vs SHE anodic) and the manganese III --> IV couple (Reaction 16, -0.51 V vs SHE cathodic / -0.21 V vs SHE anodic).

$$O_2 + H_2O + 2e^- \; <--> \; HO_2^- + OH^- \quad E^o = -0.08 \; V \; vs \; SHE \quad Rxn \; 19$$

$$Mn^{IV}-L + e^- \; <--> \; Mn^{III}-L \quad E = -0.30 \; V \; vs \; SHE^* \quad Rxn \; 16$$

(L- denotes gluconate ligand)

(*- measurement for 1 mM Mn, 0.1 M Gluconate, 0.3 M NaOH, 1 atm, 25 ^{o}C [25].)

The shape of the voltammogram closely resembles a voltammogram presented by Richens et. al. [22] for a similar system.

Although not as clear the cyclic voltammograms on the graphite and copper-mercury electrodes also show peaks in the area of the potential at which the peaks were noted for the platinum wire electrode (Figures 10,11).
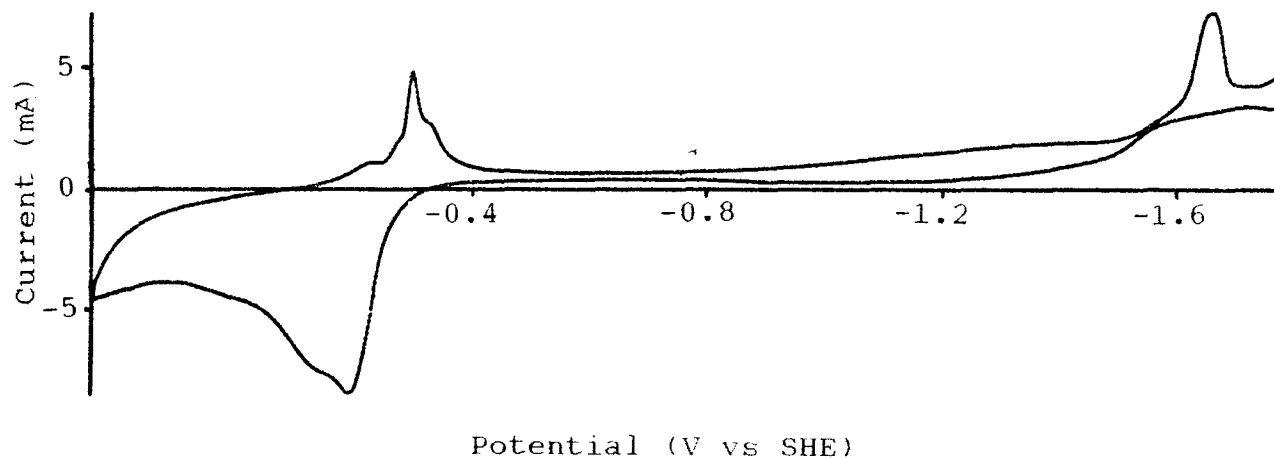
Figure 10. Cyclic Voltammogram for the Manganese Gluconate Complex Formed in the Presence of Oxygen and Deaerated with Nitrogen. (1 mM Mn, 5 mM Gluconate, Copper Mercury Amalgam Working Electrode, 1 M NaOH, 22 °C, Scan Rate 10 V/min)
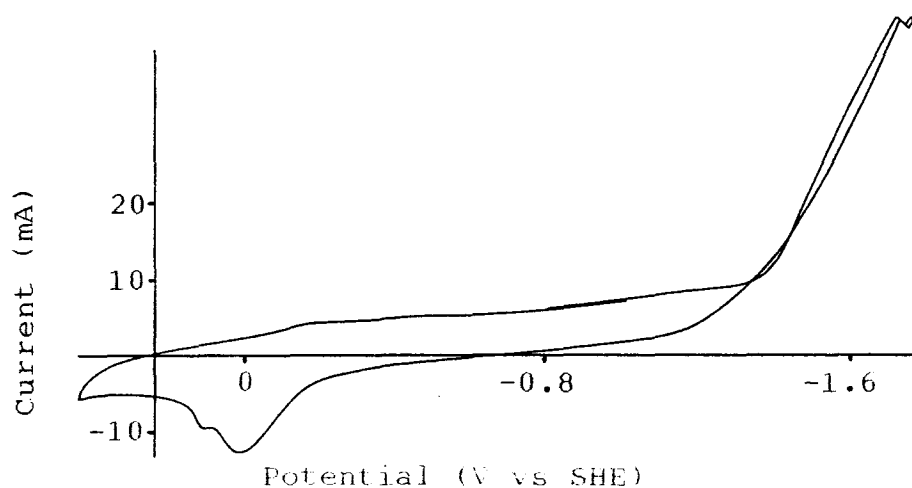
Figure 11. Cyclic Voltammogram for the Manganese Gluconate Complex Formed in the Presence of Oxygen and Deaerated with Nitrogen. (5 mM Mn, 50 mM Gluconate, Graphite Working Electrode, 1 M NaOH, 22 °C, Scan Rate 4 V/min)

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The potential range of the cyclic voltammograms is determined by the hydrogen evolution reaction (Rxn 18). The potential at which this reaction occurs is dependent on the overpotential for that reaction on the electrode material employed.

$$2H_2O + 2e^- <--> H_2 + 2OH^- \quad E^O = -0.83 \text{ V vs SHE} \quad \text{Rxn 18}$$

The hydrogen evolution reaction occurs at approximately -1.8 V vs SHE for both the graphite and copper-mercury amalgam electrodes (Figs 10,11) and approximately -1.0 V vs SHE for the platinum wire electrode (Figure 12). Figure 12 differs from Figure 8 with respect to the scan rate and range. The scan rate and range were altered in Figure 8 to more clearly indicate the peaks indicating electrode reactions.

Current (mA)

5

0

-5

0   -0.4   -0.8

Potential (V vs SHE)
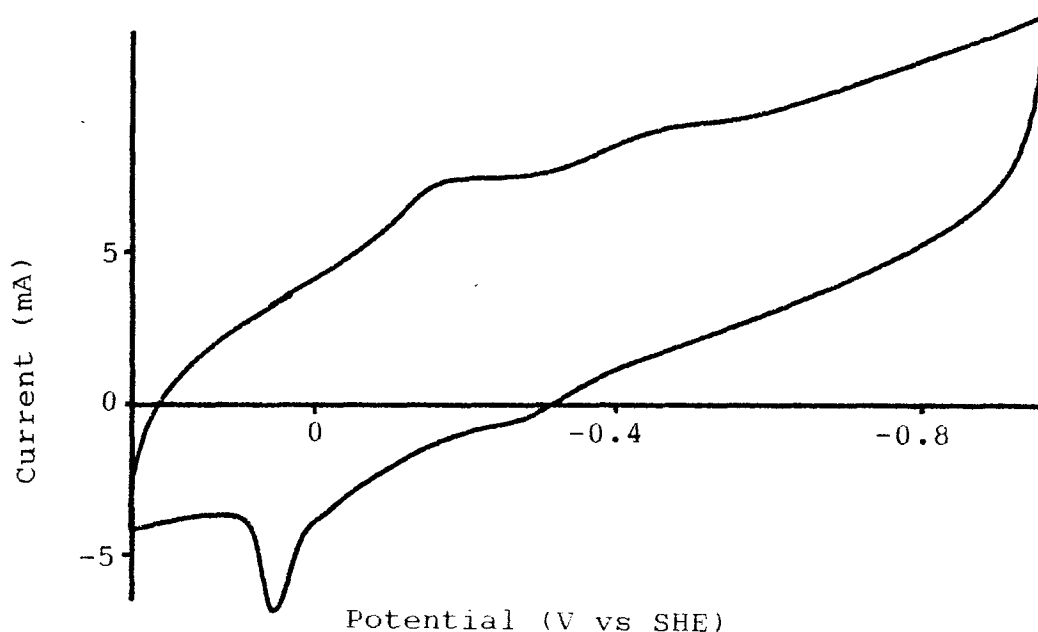
Figure 12. Cyclic Voltammogram for the Manganese Gluconate Complex Formed in the Presence of Oxygen and Deaerated with Nitrogen. (10 mM Mn, 50 mM Gluconate, Platinum Wire Working Electrode, 1 M NaOH, 22 °C, Scan Rate 4 V/min)

The results on the platinum wire electrode clearly indicate the presence of the manganese III/IV couple. This indicates that the reduction of manganese IV to manganese III will occur on the electrode surface. Although not as discernible, peaks evident in the graphite and copper-mercury amalgam results may indicate this couple is also active on their surfaces. There is no indication of the presence of the manganese III/II couple on any of the electrode materials indicating that reaction does not occur readily on those electrode surfaces. The hydrogen peroxide/oxygen couple is evident in the platinum wire results. The solutions are prepared in the presence of oxygen. Upon removal of the oxygen from the solution via nitrogen purge the hydrogen peroxide/oxygen couple is still present. Therefore the hydrogen peroxide is produced

upon preparation of the complex in air. The presence of the couple indicates the production of hydrogen peroxide in the presence of the manganese complex. Again the peaks in the graphite and copper-mercury amalgam results are not as discernible.

The results indicate the presence of hydrogen peroxide and the manganese III <--> IV reaction. This is evidence of the ability of an electrochemical system to influence the reduction of the manganese IV complex to the manganese III form. There is no evidence of the manganese III - II reaction. This may be due to the more negative potential required on these electrode surfaces [22].

5.2 Spectrophotometry.

5.2.0 Introduction.

In the following experiments spectrophotometry will be utilised to further indicate the ability of an electrode employed to promote the necessary reduction of the higher oxidation states of manganese in the complex. Spectrophotometry will also be used to indicate the likely predominant form of the manganese complex (II, III or IV) in the solution under conditions typical of those employed in the pulp bleaching trials.

5.2.1 Results and Discussion.

The results of the absorbance vs wavelength measurements are given in Figure 13 and are similar to results from literature [24]. It can be seen that no separate absorption peaks are evident for the individual oxidation states of the manganese. Therefore the spectrophotometric analysis will be utilised in the following manner.
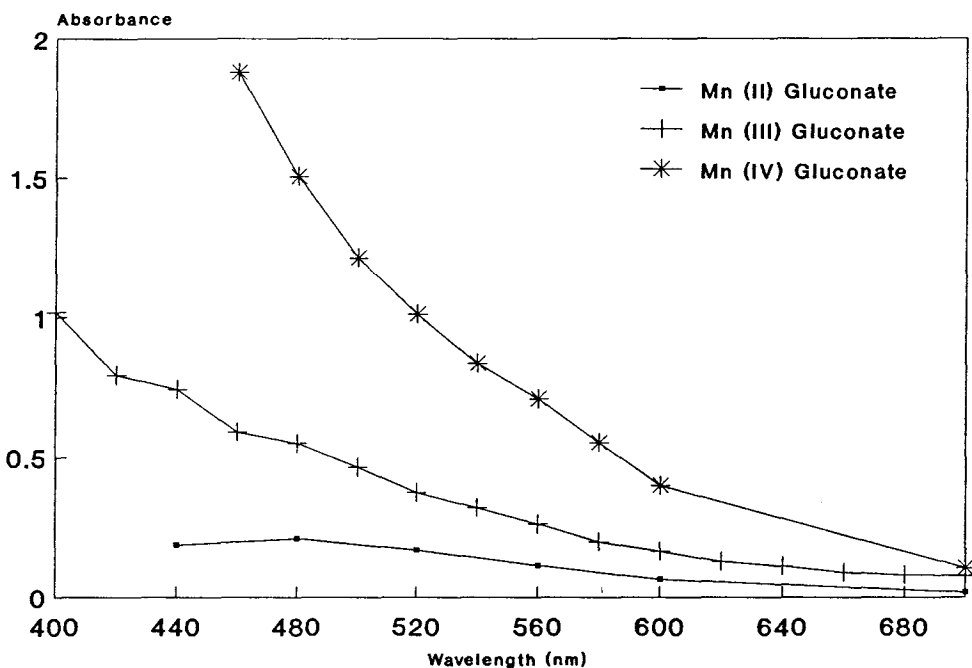
Figure 13. Absorption Spectrograph for Manganese Gluconate Complex. (1 mM Mn, 5 mM Gluconate, 1 M NaOH, 23 $^{\circ}$C, path length 2.5 cm)

The wave length chosen for the following experiments was 520 nm. The absorbance of the manganese II form has to be measured very quickly following its removal from the flask due to its fast reaction with oxygen in the air (absorbance increase over time). The absorbance presented in Table 7 differs from the absorbance in Figure 14. The absorbance given in Table 7 represents the measurement taken as soon as possible after removal from the reactor. The absorbances of the 1 mM manganese complex solutions used in following analysis are given in Table 7 below.

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Manganese Oxidation State	Absorbance @ 520 nm	ϵ (1/mol cm)
II	0.041	16.4
III	0.374	149.6
IV	1.012	404.8

Table 7. Absorbance Values for the Manganese Gluconate Complex (1 mM Mn, 5 mM Gluconate, 1 M NaOH, 23 $^{\circ}$C, path length 2.5 cm)

For the following experiments the predominant oxidation state of manganese will be determined using the above absorbance measurements. If the absorbance of a solution 1 mM in manganese is approximately zero (ie the absorbance of the manganese II complex) the predominant manganese form will be considered to be manganese II. If the absorbance is approximately 0.4 (ie the absorbance of the manganese III complex) the predominant manganese form will be considered to be manganese III. Similarly for an absorbance of approximately 1.0 the predominant form will be considered to be manganese IV.

Experiment 1 is designed to determine the predominant ionic form of manganese in a manganese gluconate solution during its oxidation with oxygen in the absence of current. The results shown in Figure 14 indicate the rapid rate of reaction of the manganese II complex with oxygen. After about 1 minute the absorbance of the solution indicates the predominant ionic form of manganese to be manganese IV.
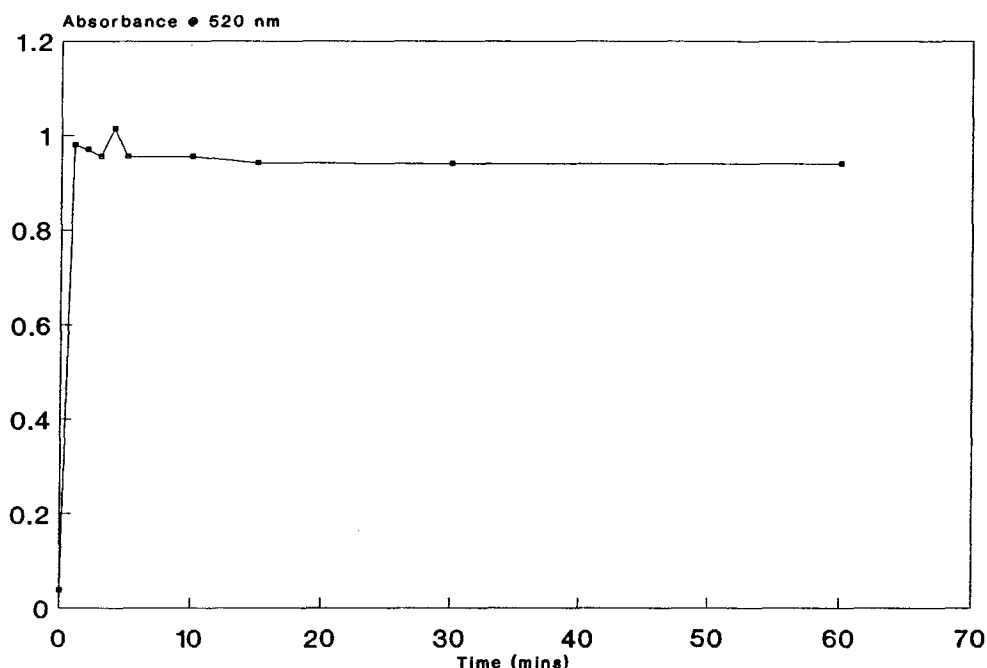
Figure 14. Absorption Profile for Manganese (II) Gluconate Complex in the Presence of Oxygen. (1 mM Mn, 5 mM Gluconate, 0 A, O_2 15 cc/min @ STP, 1 M NaOH, 23 $^{\circ}$C, No Pulp Present)

Experiments 2 and 3 are designed to determine the ability of the platinised titanium cathode employed to reduce the manganese III and IV complex forms. In these two experiments oxidation was suppressed through the use of a nitrogen purge.

The results of experiment 2 (Figure 15) in which the manganese III form was initially present indicate the predominant ionic form to be manganese III throughout. There is no evidence of the reduction of the manganese III complex to the manganese II form.

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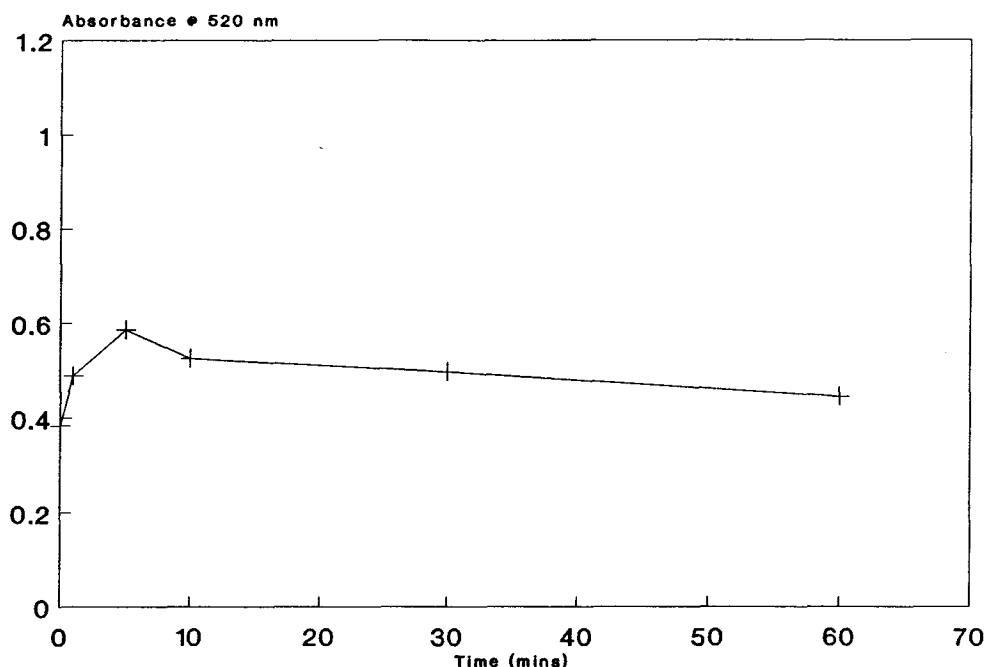
Figure 15. Absorption Profile for Manganese (III) Gluconate Complex in the Presence of Current. (1 mM Mn, 5 mM Gluconate, 1.0 A on Platinised Titanium Cathode, N_2 15 cc/min @ STP, 1 M NaOH, 23 °C, No Pulp Present)

The results of experiment 3 (Figure 16) in which the manganese IV form was initially present indicate the ability of the system to bring about the reduction of the manganese IV complex to the manganese III form. This is indicated by the decrease in absorption of the solution from approximately 1.0 to 0.48. However the results of experiment 3 show no evidence of the reduction of the manganese III complex to the manganese II form. Even after 17 hours (1020 mins) the absorbance measurement (0.486) indicates the predominant ion to be the manganese III form.
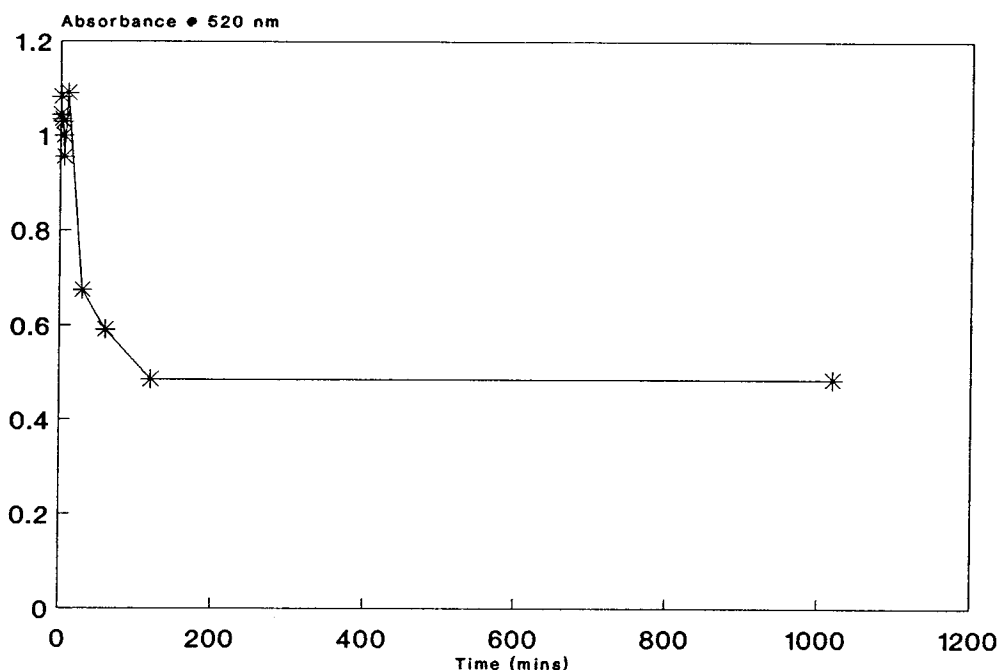
Figure 16. Absorption Profile for Manganese (IV) Gluconate Complex in the Presence of Current. (1 mM Mn, 5 mM Gluconate, 1.0 A on Platinised Titanium Cathode, N_2 15 cc/min @ STP, 1 M NaOH, 23 ^{0}C, No Pulp Present)

The above results correspond to the results from the cyclic voltammetry tests in that they do not indicate the electrochemical reduction of the manganese III complex to the manganese II form at the cathode. The results do indicate the ability of the cathode to reduce the manganese IV form to the manganese III form.

Experiments 4 and 5 were designed to indicate the likely predominant ionic form of the manganese in the reactor during the pulp bleaching trials. In these experiments oxygen purge is employed to promote the oxidation of the manganese complex (as evidenced in experiment 1), also current is applied to promote the reduction of the manganese complex (as evidenced in

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experiment 3). The results presented in Figure 17 indicate the absorbance to be between the values for the manganese III and manganese IV forms both in the presence and absence of pulp and also indicates the likely ionic form of the manganese to be a mixture of the above two forms in the bleaching solution. This is probably due to the combination of the rapid oxidation of the complex by the oxygen and the slower electrochemically promoted reduction of the manganese IV complex to the manganese III form.

Absorbance @ 520 nm
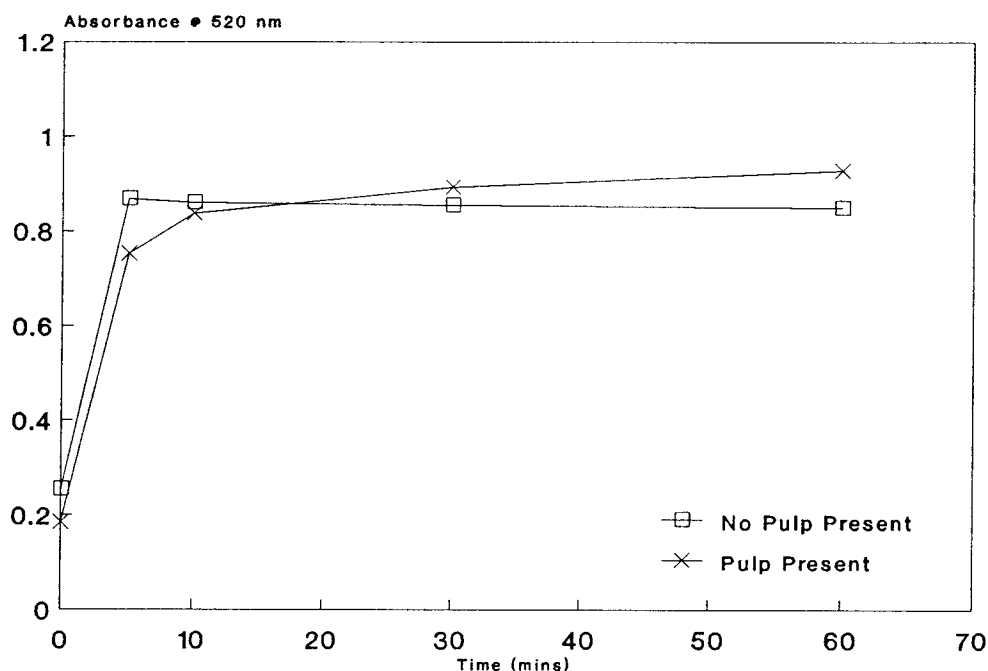
Figure 17. Absorption Profile for Manganese Gluconate Complex in the Presence of Oxygen and Current. (1 mM Mn, 5 mM Gluconate, 1.0 A on Platinised Titanium Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 23 $^{\circ}$C)

The results of the spectrophotometric experiments indicate the electrochemical reduction of the manganese IV complex to the manganese III form. There is no indication of the further reduction of the manganese III complex to the manganese II form. These results support the

results of the cyclic voltammetry tests. The results of the spectrophotometric experiments also indicate the rapid reaction of the manganese complex with oxygen. Furthermore they indicate that in the bleaching system the complex will indeed operate in a cycle in which the manganese III is continuously oxidised to manganese IV by oxygen then reduced electrochemically to the manganese III form. The participation of the manganese complex in this redox cycle is required for the continuous generation of peroxide in the proposed system.

5.3 Hydrogen Peroxide Analysis.

5.3.0 Introduction.

The following experiments involve the analysis of a solution containing the manganese gluconate complex, under conditions typical of those in the bleaching environment, for the presence of hydrogen peroxide.

5.3.1 Results and Discussion.

Experiment 1 was designed to indicate if there would be significant hydrogen peroxide production at the graphite cathode surface during the pulp delignification trials in the absence of the manganese gluconate complex via Reaction 19. The results of Experiment 1 are shown in Table 8. They indicate the presence of hydrogen peroxide in the NaOH solution. As can be seen in Table 8 the results indicate a concentration of 0.0005--> 0.0006 M hydrogen peroxide present in the NaOH solution with no large increase in concentration over time.

Time (mins)	H_2O_2 Concentration (M)
0	0.0005
5	0.0006
30	0.0006

Table 8. Hydrogen Peroxide Concentration in NaOH Solution. (2.0 A on Graphite Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 25 ^{O}C, No Pulp Present)

Under the conditions described above it appears that very little hydrogen peroxide is produced via this route.

The results of Experiment 2 shown in Table 9 indicate the presence of hydrogen peroxide, during electrolysis with oxygen, in the solution containing the manganese gluconate complex. As in Experiment 1 there is no large increase in peroxide concentration over time.

Time (mins)	H_2O_2 Concentration (M)
0	0.001
5	0.0013
30	0.0012

Table 9. Hydrogen Peroxide Concentration in a Manganese Gluconate Complex Under Bleaching Conditions. (1 mM Mn, 5 mM Gluconate, 2.0 A on Graphite Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 25 ^{O}C, No Pulp Present)

It can be seen that a higher concentration of hydrogen peroxide is obtained in the presence of the manganese complex (Table 9) than in the absence of the manganese complex (Table 8).

The results of Experiment 3 which employed a platinised titanium cathode are presented in Table 10.

Time (mins)	H_2O_2 Concentration (M)
0	0.0008
5	0.0012
30	0.0014

Table 10. Hydrogen Peroxide Concentration in a Manganese Gluconate Complex Under Bleaching Conditions. (1 mM Mn, 5 mM Gluconate, 2.0 A on Platinised Titanium Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 25 $^{\circ}$C, No Pulp Present)

The results indicate the presence of hydrogen peroxide in the solution. The concentration of peroxide detected being similar to the concentration detected in Experiment 2 which employed a graphite cathode. Also as in Experiment 2, there is no large increase in peroxide concentration over time.

The results indicate that in the absence of the manganese complex the production of hydrogen peroxide at the graphite cathode was small under the conditions employed. The results indicate the presence of hydrogen peroxide, during electrolysis with oxygen, in the solutions containing the manganese complex under bleaching conditions but in the absence of pulp. There was little difference in the use of a platinised titanium or graphite cathode. However there is not the steady peroxide concentration increase expected. This may be due to the decomposition of the hydrogen peroxide produced into free radical species. The ability of the free manganese ion to catalyse peroxide decomposition is known [20] and may be responsible for the peroxide

decomposition suspected. Decomposition reactions due to the combination of the presence of manganese and the high alkalinity [10] may also be of importance.

5.4 Pulp Delignification Trials.

5.4.0 Introduction.

The results of the cyclic voltammetry and spectrophotometric analysis indicated the ability of an electrode system to promote the reduction of the manganese IV complex to the manganese III form. The literature review indicated that hydrogen peroxide would be continuously generated in such a system via the proposed manganese complex/oxygen redox cycle. The cyclic voltammetry analysis indicated the presence of hydrogen peroxide as did the hydrogen peroxide analysis. The following experiments are designed to investigate the ability of the proposed manganese complex/oxygen redox cycle to delignify chemical pulp and to determine the important variables with respect to this process.

5.4.1 Results and Discussion.

Metal Ion Effect.

Approximately midway through the electrochemical bleaching trials it became necessary to clean the reactor due to suspected metal ion contamination subsequent to the use of a lead cathode. A cleaning procedure, described by Landucci [31], using hot sodium bi-sulphite solution was employed. The results of the bleaching trials prior to the use of the lead electrode and after the hot sodium bi-sulphite wash differed in certain respects. The difference can be explained in terms of metal ion effects; however, it is necessary to separate the bleaching experiments into two groups. Group 1 (Table 12) were the electrochemical bleaching experiments carried out prior to the use of lead cathode. Group 2 (Table 13) were those electrochemical bleaching experiments carried out after the clean with hot sodium bi-sulphite.

Subsequent to the use of a lead cathode it became impossible to reproduce some earlier results as indicated in Table 11.

Run	Notes	Kappa Number
R115	Prior to use of lead cathode	16.9
R157	After use of lead cathode	19.0

Table 11. Results Prior to and After the Use of a Lead cathode. (10 mM Mn, 50 mM Gluconate, 4.0 A on Graphite Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 50 $^{\circ}$C, 3 hours, Pulp DTPA Washed)

The Kappa number of the pulp from a run following the use of the lead cathode was significantly higher than the Kappa number of a run, under identical conditions, carried out prior to the use of the lead cathode. It was thought that some contamination due to the use of the lead cathode was responsible for this effect. The reactor was therefore cleaned using hot sodium bi-sulphite (20 % solution, for 3 hours at 90 °C, finally thoroughly rinsed with distilled water) and a new membrane and support screens installed.

The results of the Group 2 runs (ie. those completed after the bi-sulphite wash) differed from the Group 1 runs (those completed prior to the use of the lead cathode). Tables 12 and 13 indicate the results of factorial designs and show the differences between the two groups.

Run	Catalyst	Current	Kappa Number	Viscosity (cP)
R115	+	+	16.9	10.1
R112	+	-	19.5	27.9
R140	-	+	18.6	21.2
R107	-	-	19.8	21.7

Table 12. Results of Factorial Experiment.
Catalyst;(+) 10 mM Mn, 50 mM Gluconate, (-) 0 mM Mn, 0 mM Gluconate,
Current;(+) 4.0 A on Graphite Cathode, (-) 0 A,
(Group 1, O_2 15 cc/min @ STP, 1 M NaOH, 50 °C, 3 hours, Pulp DTPA Washed)

Run	Catalyst	Current	Kappa Number	Viscosity (cP)
2-16	+	+	17.5	21.2
2-21	+	-	19.7	32.1
2-18	-	+	19.8	30.6
2-22	-	-	19.6	29.7

Table 13. Results of Factorial Experiment.
Catalyst;(+) 10 mM Mn, 50 mM Gluconate, (-) 0 mM Mn, 0 mM Gluconate,
Current;(+) 10.0 A on Platinised Titanium Cathode, (-) 0 A,
(Group 2, O_2 15 cc/min @ STP, 1 M NaOH, 50 ^oC, 3 hours, Pulp DTPA Washed)

The results indicate the Kappa number responses of the 2 sets of experiments to be similar. In both cases the run with catalyst (+) and current (+) had the lowest Kappa number (Runs R115 and 2-16).

The difference between the two groups lies in the viscosity responses. For Group 2 the viscosity is approximately 30 cP in the runs in the absence of catalyst (Runs 2-18 and 2-22). The viscosity of the run with catalyst but in the absence of current is also similarly high (Run 2-21, 32.1 cP). In the run with both catalyst and current the viscosity falls to approximately 21 cP.

In the Group 1 runs the viscosity is approximately 21 cP for the runs in the absence of catalyst, approximately 28 cP for the run with catalyst but no current and approximately 10 cP for the run with current and catalyst. The catalyst with current runs exhibit the lowest viscosity in both groups.

These effects are explained through the action of hydrogen peroxide thought to be produced via the proposed manganese complex/oxygen redox cycle. It is noted from Chapter 2 that the continuous production of hydrogen peroxide from the manganese complex/oxygen redox cycle requires the combination of 3 components: 1) oxygen, 2) the manganese gluconate complex and 3) a method to reduce the higher oxidation states of the manganese complex (ie, reduction at the cathode). The runs in the factorial experiments in which all 3 components are present (ie. runs R115 in Table 12 and 2-16 in Table 13) exhibit a significantly larger reduction in Kappa number and viscosity than in the runs in which one or more of the components are absent (ie runs R112, R140, R107 in Table 12 and 2-21, 2-18, 2-22 in Table 13).

It is therefore argued that the hydrogen peroxide produced in the manganese complex/oxygen redox cycle is responsible for the larger Kappa number and viscosity reductions observed.

For the runs in the absence of catalyst (with or without current) a significantly higher viscosity is observed in the Group 2 design. It is believed that there was a contaminant absent in the Group 2 design responsible for the viscosity loss evident in the Group 1 design. As noted in Chapter 2, metal ions play an important role in cellulose degradation. The results shown in Table 14 indicate the effect of metal ion addition on runs in the absence of current and catalyst. The reactor system employed in the experiments shown in Table 14 consisted of a glass beaker with O_2 purge and mixing. There was no catalyst (manganese gluconate) present and no current was applied.

Metal Ion Added	Concentration mM	Kappa Number	Viscosity (cP)
None	n/a	19.8	30.6
Fe^{2+}	1.0	19.6	20.0
Fe^{2+}	0.1	20.1	20.8
Mn^{2+}	1.0	19.4	31.5
Mn^{2+}	0.1	19.7	30.8
Cu^{2+}	1.0	19.7	21.1
Cu^{2+}	0.1	19.6	21.5

Table 14. Effect of Metal Ion Addition on Bleaching Result. (Fe^{2+} from $FeSO_4$, Mn^{2+} from $Mn(ClO_4)_2.6H_2O$, Cu^{2+} from $Cu(ClO_4)_2.6H_2O$, O_2 15 cc/min @ STP, 1 M NaOH, 50 ^oC, 3 hours, Pulp DTPA Washed)

The results indicate that small concentrations of iron or copper ions can produce a similar reduction in viscosity to that noted in the Group 1 runs. The metal ions act via their catalytic reaction with oxygen in the system to produce free radicals species responsible for cellulose degradation. It is therefore assumed that a contaminant, likely a metal ion such as copper or iron, was present in the Group 1 runs and that the hot bi-sulphite wash removed that contaminant. The contaminant was responsible for the approximately 10 cP viscosity drop in the Group 1 runs in the absence of catalyst. A similar viscosity loss is not evident in the corresponding Group 2 runs.

This contaminant is also responsible for the larger viscosity drop in the catalyst/current runs in Group 1 when compared to Group 2. In Group 1 the viscosity is affected by both hydrogen

peroxide produced through the combination of catalyst and current and the free radicals produced by the metal ion contaminant present. In Group 2 the viscosity is thought to be affected only by the hydrogen peroxide produced by the catalyst and current.

For the Group 1 set of experiments the higher viscosity of the run with catalyst and no current was probably due to the prevention of cellulose degradation by the free manganese ion. This effect was noted by Gilbert et. al. [32] during oxygen bleaching. This effect is not evident in the Group 2 design as the absence of the contaminant means there is little viscosity loss and therefore no preventative effect is obvious.

In summary the viscosity responses in Group 1 designs are affected by the presence of a contaminant, likely a metal ion such as copper or iron, causing increased viscosity loss. The viscosity responses in Group 2 indicate that this metal ion contaminant is no longer present. With this understanding both groups of experiments can be used to give an indication of the effectiveness of the proposed manganese complex/oxygen redox cycle in pulp delignification.

<u>Evidence of Catalytic Delignification.</u>

The following section indicates the ability of the proposed manganese complex/oxygen redox cycle to bring about significant delignification.

The results of the Group 1 factorial designs presented in Tables 12 and 15 and the Group 2 factorial design presented in Table 13 are at a temperature of 50 °C. The results indicate that for any of the factorial experiments with oxygen, the run combining current and catalyst causes a significantly larger Kappa number reduction than the other runs in that experiment (approximately 29-->17 compared to 29-->20). This Kappa number reduction is accompanied by an increased viscosity loss in both groups (the anomaly for the catalyst/no current run in Group 1 has already been discussed).

Run	Catalyst	Current	Kappa Number	Viscosity (cP)
R111	+	+	17.5	10.9
R112	+	−	19.5	27.9
R116	−	+	19.6	18.2
R107	−	−	19.8	21.7

<u>Table 15.</u> Results of Factorial Experiment.
Catalyst;(+) 10 mM Mn, 50 mM Gluconate, (-) 0 mM Mn, 0 mM Gluconate,
Current;(+) 2.0 A on Graphite Cathode, (-) 0 A,
(Group 1, O_2 15 cc/min @ STP, 1 M NaOH, 50 °C, 3 hours, Pulp DTPA Washed)

The current/catalyst interaction effect is significant in the analyses of the factorial designs presented in Tables 11, 12 and 15 (see Appendix 1). This indicates the combination of current and catalyst is a requirement for the observed Kappa number reduction and viscosity loss.

In the proposed redox cycle the application of current is required for the reduction of the higher oxidation states of the manganese complex to facilitate the continuous generation of hydrogen peroxide. The decomposition of hydrogen peroxide into free radical species is a prerequisite for its delignification reactions [10]. Hydrogen peroxide decomposition products (free radicals) are also responsible for cellulose degradation reactions.

Thus if hydrogen peroxide was being continuously produced by the proposed manganese complex/oxygen redox cycle and then decomposing into free radical species this would explain the significant Kappa number and viscosity reduction with oxygen in the presence of the catalyst and current in both groups.

It therefore appears that the proposed manganese complex/oxygen redox cycle is operating and the hydrogen peroxide produced is capable of delignifying chemical pulp. However the delignification is accompanied by a substantial viscosity loss.

<u>Effect of Cathode Material.</u>

The following section indicates the ability of the cathode material to influence the operation of the proposed manganese complex/oxygen redox cycle.

Table 16 indicates the effect of cathode material in Group 1 experiments. For the cathode materials tested there is a negligible effect on the Kappa number in varying the cathode material. There is however a significant effect in varying the cathode material on the viscosity of the bleached pulp. The use of a graphite cathode resulted in a significantly lower viscosity (10.1 cP) than the use of the other cathode materials. The runs utilising a stainless steel or platinised titanium cathode had a viscosity of approximately double that of the run with the graphite cathode (19.6 and 20.8 cP compared to 10.1 cP).

Run	Cathode Material	Kappa Number	Viscosity (cP)
R115	Graphite	16.9	10.1
R142	Mercury-Copper amalgam	17.4	14.8
R138	Stainless Steel	17.4	19.6
R143	Platinised Titanium	17.5	20.8

Table 16. Effect Cathode Material on Bleaching Result. (Group 1, 10 mM Mn, 50 mM Gluconate, 4.0 A, O_2 15 cc/min @ STP, 1 M NaOH, 50 $^\circ$C, 3 hours, Pulp DTPA Washed)

The results of the Group 2 experiments (shown in Table 17) also indicated that the use of a graphite cathode caused a significantly lower viscosity in the bleached pulp, than the use of a

stainless steel or platinised titanium cathode (17.3 cP compared to 22.4 and 21.1 cP). The difference was smaller than in the Group 1 experiments.

Run	Cathode Material	Kappa Number	Viscosity (cP)
2-15	Graphite	17.6	17.3
2-17	Stainless Steel	17.3	22.4
2-19	Platinised Titanium	17.5	21.1

Table 17. Effect Cathode Material on Bleaching Result. (Group 2, 10 mM Mn, 50 mM Gluconate, 10.0 A, O_2 15 cc/min STP, 1 M NaOH, 50 °C, 3 hours, Pulp DTPA Washed)

This effect may be due to metal ion contaminants in the porous graphite cathode causing greater peroxide decomposition or to the ability of the graphite cathode to catalyse the desired manganese complex reduction reaction to a greater extent than the stainless steel or platinised titanium cathode.

In an alkaline environment the potential a cathode can attain for a given current is limited by the hydrogen evolution reaction (Reaction 18).

$$2H_2O + 2e^- <--> H_2 + 2OH^- \quad E^o = -0.8277 \text{ V vs SHE} \quad \text{Rxn 18}$$

The potential/current profiles for the three electrode materials tested are given in Appendix 3.

For a cathodic reaction the electrode potential must be held at a lower (more negative) potential than the reversible electrode potential. If the reversible potential or overvoltage

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required for the manganese complex reduction and thus continuous hydrogen peroxide generation is very negative then the stainless steel and platinised titanium cathode systems would not be able to promote that reaction to the same extent as graphite. This is because their limiting hydrogen evolution reaction occurs at a higher potential.

<u>Effect of Oxygen.</u>

In the proposed manganese complex/oxygen redox cycle oxygen is required for the continuous generation of hydrogen peroxide. The following section indicates the effect of the oxygen purge.

Table 18 indicates the effect of oxygen on a Group 1 run. It indicates the desired Kappa number reduction (29 --> 17.5) requires oxygen. The viscosity drop also requires the oxygen to be present.

Run	Gas Purge (15 cc/min)	Kappa Number	Viscosity (cP)
R115	Oxygen	16.9	10.1
R136	Nitrogen	22.7	32.6

Table 18. Effect of Oxygen on Bleaching Result. (Group 1, 10 mM Mn, 50 mM Gluconate, 4.0 A on Graphite Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 50 °C, 3 hours, Pulp DTPA Washed)

Table 19 indicates the effect of oxygen on a Group 2 run. Again the observed Kappa number reduction (29 --> 17.5) and the viscosity drop requires the presence of the oxygen.

Run	Gas Purge (15 cc/min)	Kappa Number	Viscosity (cP)
2-16	Oxygen	17.5	21.2
2-35	Nitrogen	22.0	34.0

Table 19. Effect of Oxygen on Bleaching Result. (Group 2, 10 mM Mn, 50 mM Gluconate, 10.0 A on Platinised Titanium Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 50 °C, 3 hours, Pulp DTPA Washed)

These results indicate that oxygen is an essential component of the system causing the observed Kappa number and viscosity reductions. As the proposed manganese complex/oxygen redox cycle requires oxygen for the production of hydrogen peroxide this indicates the proposed redox cycle is indeed operating.

Also the absence of viscosity loss in the Group 1 run in the presence of nitrogen (Table 19) indicates the contaminant also required oxygen to bring about the observed viscosity loss. This supports the view that the contaminant was a metal ion as the metal ion catalysed generation of free radicals from oxygen (Rxn 10) would not occur in the absence of oxygen.

Effect of DTPA Wash.

DTPA (Diethylenetriaminepentaacetic acid (sodium salt)) was utilised in prewashing the pulp due to its known ability to remove metal ions in the unbleached pulp [10]. The effect of the DTPA wash on the important metal ions is indicated in Table 20.

Metal	Metal Content (ppm)	
	Unwashed Pulp	Washed Pulp
Copper	1220	6.05
Iron	36.7	20.0
Manganese	7.1	1.5

Table 20. Effect of DTPA Wash On Metal Content of Pulp.
(Analysis by Quanta Trace Laboratories Inc. (Vancouver))

For the important metals in pulp bleaching (copper, iron and manganese) [16] the DTPA wash brings about a reduction in concentration. In the case of copper, this reduction is especially pronounced (1220 --> 6.05 ppm).

Table 21 indicates the effect of the DTPA wash in Group 1 experiments. It shows the DTPA wash is required to bring about the reduction in Kappa number and viscosity in the runs with current and catalyst.

Run	DTPA Wash	Kappa Number	Viscosity (cP)
R113	Yes	17.8	9.6
R117	No	22.0	20.4

Table 21. Effect of DTPA Wash on Bleaching Result. (Group 1, 1 mM Mn, 5 mM Gluconate, 2.0 A on Graphite Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 50 $^{\circ}$C, 3 hours)

This indicates that for the conditions described the hydrogen peroxide thought to be responsible for the Kappa number and viscosity reductions is not produced in the absence of the DTPA wash. It appears the DTPA wash is necessary to allow the production of hydrogen peroxide from the manganese complex.

Table 22 indicates the effect of the DTPA wash in Group 2 runs. Again it is evident the DTPA wash is required to bring about the Kappa number reduction and viscosity loss.

Run	DTPA Wash	Kappa Number	Viscosity (cP)
2-2	Yes	18.1	20.8
2-67	No	19.4	32.0

Table 22. Effect of DTPA Wash on Bleaching Result. (Group 2, 10 mM Mn, 50 mM Gluconate, 4.0 A on Graphite Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 50 $^{\circ}$C, 3 hours)

Table 23 also indicates the effect of DTPA wash on Group 2 runs but the cathode is made of platinised titanium in this case. The results differ from those utilising a graphite cathode in that the Kappa number reduction and viscosity loss occur in both the washed and unwashed pulp.

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The unwashed pulp exhibits a greater viscosity loss, the Kappa numbers however are comparable. Also Table 23 shows the effect of repeated DTPA washes. It is clear there is no benefit accrued in washing the pulp more than once.

Run	DTPA Wash (Number of Washes)	Kappa Number	Viscosity (cP)
2-31	No	17.1	15.6
2-16	Yes (1)	17.5	21.2
2-60	Yes (5)	17.8	21.1

Table 23. Effect of DTPA Wash on Bleaching Result. (Group 2, 10 mM Mn, 50 mM Gluconate, 10.0 A on Platinised Titanium Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 50 $^{\circ}$C, 3 hours)

The results in Table 23 (platinised titanium cathode) can be explained with reference to Table 20. As discussed in Chapter 2 the catalytic decomposition of oxygen by metal ions is well known. The high concentration of copper in the unwashed pulp and its reaction with oxygen may be responsible for the extra viscosity loss observed. After the DTPA wash the metal ion content of the pulp (especially copper) is reduced and this extra viscosity loss is not observed.

Also as regards the repeated DTPA wash the literature evidence suggests that any metal ions remaining in the pulp after one DTPA wash are likely to be bound to the pulp and are not capable of taking part in the reactions responsible for viscosity loss [18]. Therefore there is no observed benefit in washing the pulp any more than once.

The results in Tables 21 and 22 can not be so easily explained. Although not fully understood it may be the surface of the graphite cathode fouls in the presence of unwashed pulp, affecting the electrode reactions promoting hydrogen peroxide formation (ie. manganese complex reduction). These reactions are suppressed and so the Kappa number reduction and viscosity loss are not observed. In the case of the DTPA washed pulp this fouling does not occur, the reactions proceed and the Kappa number and viscosity are appropriately affected. As the only noted difference between the washed and unwashed pulp is the metal ion content (particularly with regard to copper) it is assumed that the metal ions cause the fouling on the graphite electrode. It may be that the reduction of the copper 2^+ to copper metal occurs on the surface of the graphite cathode. The reduction of manganese (IV) to manganese (III) (Reaction 19) might then not occur on this copper plated surface. This fouling effect (ie. copper reduction) does not appear to occur on the platinised titanium electrode.

The DTPA wash is necessary for the removal of the metal ions. These metal ions are thought to suppress the manganese reduction reactions at the electrode surface or prevent HO_2^- generation on the graphite cathode. On the platinised titanium electrode it is thought the metal ions present in unwashed pulp do not prevent HO_2^- generation by the manganese complex/oxygen redox cycle, but promote viscosity loss through the generation of free radicals in their reaction with hydrogen peroxide.

Effect of Catalyst Concentration.

The following section indicates the effect of the manganese complex concentration on the bleaching system.

Figures 18 and 19 show the results of varying the catalyst concentrations at various currents. The Kappa number (Figure 18) and viscosity (Figure 19) responses for the two catalyst concentrations do not differ significantly. The plots indicate that changing the catalyst concentration from 1 mM to 10 mM does not significantly alter the response. This is evidence of the catalytic ability of the manganese complex in the peroxide generating system.
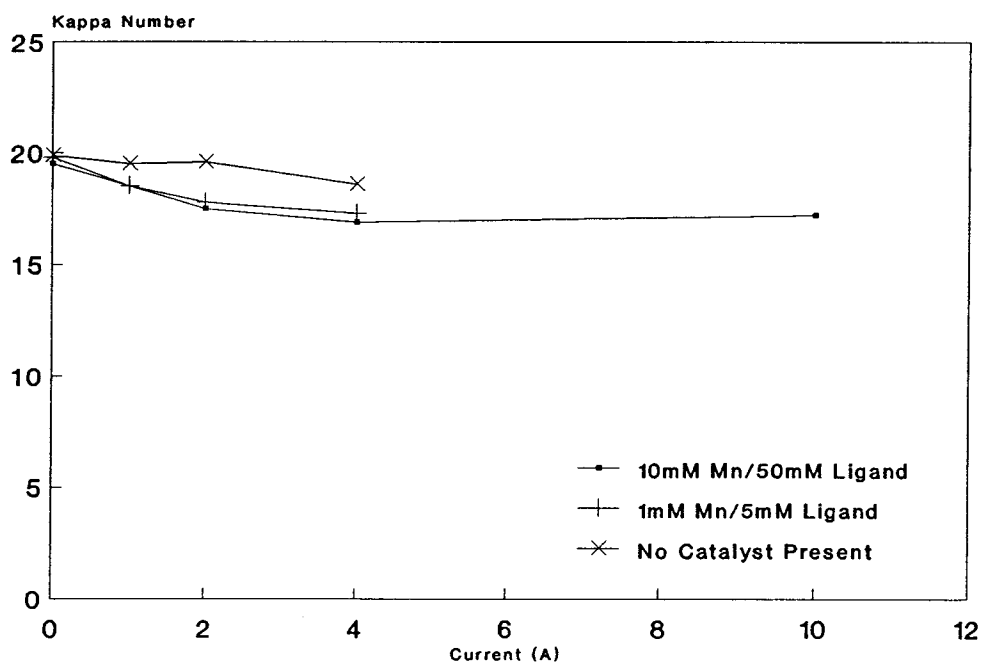
Figure 18. Effect of Catalyst Concentration on Kappa Number. (Group 1, Ligand Gluconate, Graphite Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 50 $^{\circ}$C, 3 Hours, Pulp DTPA Washed)
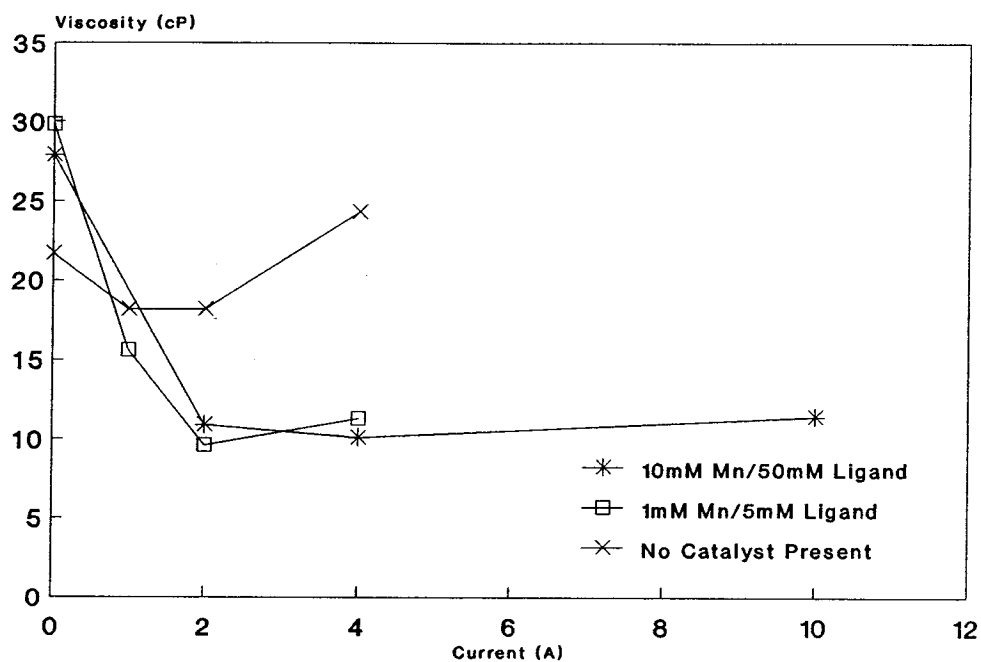
Figure 19. Effect of Catalyst Concentration on Viscosity. (Group 1, Ligand Gluconate, Graphite Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 50 ^{O}C, 3 Hours, Pulp DTPA Washed)

<u>Effect of Hydrogen Peroxide Stabilisers.</u>

The following section indicates the effect of known peroxide stabilisers. The use of chemical stabilisers and the adjustment of the system conditions are examined with respect to their ability to improve peroxide stability. The chemical stabilisers used are sodium silicate and magnesium sulphate, both commonly used in mechanical pulp brightening to stabilise the hydrogen peroxide bleaching solution. Also the temperature and pH of the system are varied as these are factors are known to influence the stability of hydrogen peroxide bleaching solutions.

<u>Effect of Chemical Stabilisers.</u>

Table 24 indicates the effect of the chemical stabilisers. It can be seen the Kappa number and viscosity are both significantly higher in the runs with chemical stabiliser added.

Run	Group	Stabiliser	Kappa Number	Viscosity (cP)
R113	1	None	17.8	9.6
R124	1	0.01 M $Na_2SiO_3.5H_2O$	18.9	21.3
2-14	2	None	18.5	21.1
2-68	2	0.001 $MgSO_4$	19.9	30.0

Table 24. Effect of Chemical Stabilisers. (1 mM Mn, 5 mM Gluconate, 2.0 A (Group 1) and 4.0 A (Group 2) on Graphite Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 50 $^{\circ}$C, 3 hours, Pulp DTPA Washed)

Both the silicate and magnesium stabilisers are thought to act through the removal of the transition metal ions (copper, manganese and iron) responsible for peroxide decomposition reactions via Reaction 8 [15]. Both the stabilisers act therefore to suppress the decomposition of the hydrogen peroxide produced via the manganese complex/oxygen redox cycle [15], in this way preventing the peroxide decomposition necessary for delignification and viscosity loss. Also it may be the stabilisers react with the manganese in the solution and therefore interfere with the formation or action of the manganese complex. This would prevent the generation of hydrogen peroxide via the proposed redox cycle and therefore the associated Kappa number reduction and viscosity loss are not observed.

Effect of pH.

Table 25 indicates the effect of reducing the pH of the solution to pH 11. This is a pH at which the hydrogen peroxide is more stable [17]. (The pK_a of Reaction 1 is 11.6 at 25 ^{o}C [10])

Run	Catalyst	Current	Kappa Number	Viscosity (cP)
2-43	+	+	24.1	33.9
2-40	+	-	24.1	33.8
2-42	-	+	24.6	32.3
2-41	-	-	26.5	35.4

Table 25. Results of Factorial Experiment at pH 11.
Catalyst;(+) 1 mM Mn, 5 mM Gluconate, (-) 0 mM Mn, 0 mM Gluconate,
Current;(+) 0.1 A on Platinised Titanium Cathode, (-) 0 A,
(Group 2, O_2 15 cc/min @ STP, 0.5 M Na_2SO_4 + NaOH to pH 11, 50 ^{o}C, 3 hours, Pulp DTPA Washed)

The results indicate no beneficial effect of the combination of catalyst and current at this lower pH. This may be due to low hydrogen peroxide production at this pH as the peroxide production rate increases with increasing alkalinity [2].

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<u>Effect of Temperature.</u>

Table 26 indicates the results of a factorial experiment at room temperature. The results show

no beneficial effect of catalyst or current at this temperature.

Run	Catalyst	Current	Kappa Number	Viscosity (cP)
R92	+	+	22.9	33.1
R96	+	-	22.3	32.4
R99	-	+	22.3	22.6
R97	-	-	23.1	23.4

Table 26. Results of Factorial Experiment at 20 °C.
Catalyst;(+) 1 mM Mn, 5 mM Gluconate, (-) 0 mM Mn, 0 mM Gluconate,
Current;(+) 1.0 A on Graphite Cathode, (-) 0 A,
(Group 1, O_2 15 cc/min @ STP, 1 M NaOH, 20 °C, 3 hours, Pulp DTPA Washed)

It is likely that at this temperature the decomposition of the peroxide produced via the

proposed redox system is low (decomposition is considered a prerequisite for peroxide

delignification reactions). For this reason the effects on Kappa number and viscosity evident at

the higher (50 °C) temperature are not apparent.

Run	Catalyst	Current	Kappa Number	Viscosity (cP)
2-52	+	+	10.0	11.6
2-53	+	-	11.2	13.3
2-54	-	+	9.2	12.9
2-55	-	-	9.6	14.4

Table 27. Results of Factorial Experiment at 90 $^{\circ}$C.
Catalyst;(+) 10 mM Mn, 50 mM Gluconate, (-) 0 mM Mn, 0 mM Gluconate,
Current;(+) 1.0 A on Platinised Titanium Cathode, (-) 0 A,
(Group 2, O_2 15 cc/min @ STP, 1 M NaOH, 90 $^{\circ}$C, 3 hours, Pulp DTPA Washed)

In the factorial experiments carried out at 50 $^{\circ}$C it was found the current/catalyst run in each factorial experiment had a significantly lower Kappa number than the other runs in the factorial experiment (see Tables 11,12,15). For a 3 hour factorial experiment at 90 $^{\circ}$C (Table 27) the results indicate the current/catalyst run does not have a significantly lower Kappa number than the other runs in the factorial experiment. The viscosity is however slightly lower. Table 27 indicates the catalyst actually slightly inhibits the delignification reaction. It is thought that the production of hydrogen peroxide at 90 $^{\circ}$C is only evident in its effect on the viscosity of the bleached pulp. At this temperature the hydroxide ion/oxygen combination is sufficient to reduce the Kappa number to around 10. At 90 $^{\circ}$C the complex is not stable for 3 hours as evidenced by the observed colour change (red of complex --> green/brown pulp colouration). As this was likely to affect the results a further factorial design for a shorter time period (1 hour) was carried out. The results of which are presented in Table 28.

Run	Catalyst	Current	Kappa Number	Viscosity (cP)
2-58	+	+	16.0	14.6
2-59	+	-	16.8	18.0
2-56	-	+	15.7	19.7
2-57	-	-	15.6	20.8

Table 28. Results of Factorial Experiment at 90 $^{\circ}$C.
Catalyst;(+) 10 mM Mn, 50 mM Gluconate, (-) 0 mM Mn, 0 mM Gluconate,
Current;(+) 1.0 A on Platinised Titanium Cathode, (-) 0 A,
(Group 2, O_2 15 cc/min @ STP, 1 M NaOH, 90 $^{\circ}$C, 1 hour, Pulp DTPA Washed)

As with the 3 hour design the combination of catalyst and current has no effect on the Kappa number although the viscosity is markedly lower. It is believed the hydrogen peroxide produced by the combination of the manganese complex and the current is only evident in its effect on the viscosity of the pulp at this temperature. It was apparent that at this temperature the hydroxide ion/oxygen combination was sufficient to cause the Kappa number reduction observed.

In summary the results indicate the use of the peroxide stabilisers prevents the generation of the hydrogen peroxide in the proposed system or prevents the necessary peroxide decomposition reactions. Lowering the pH to 11 and decreasing the temperature to room temperature had the effect of suppressing the peroxide decomposition rendering the system incapable of promoting delignification. At the higher temperature of 90 $^{\circ}$C the peroxide

generated affected only the viscosity, the hydroxide ion/oxygen combination at this temperature being sufficient to cause the Kappa number reduction observed.

Effect of Current.

This section indicates the effect of current on the proposed system. Figures 20 and 21 give the results of two sets of experiments (Group 1 and Group 2) showing the reduction in Kappa number and viscosity versus the applied current.
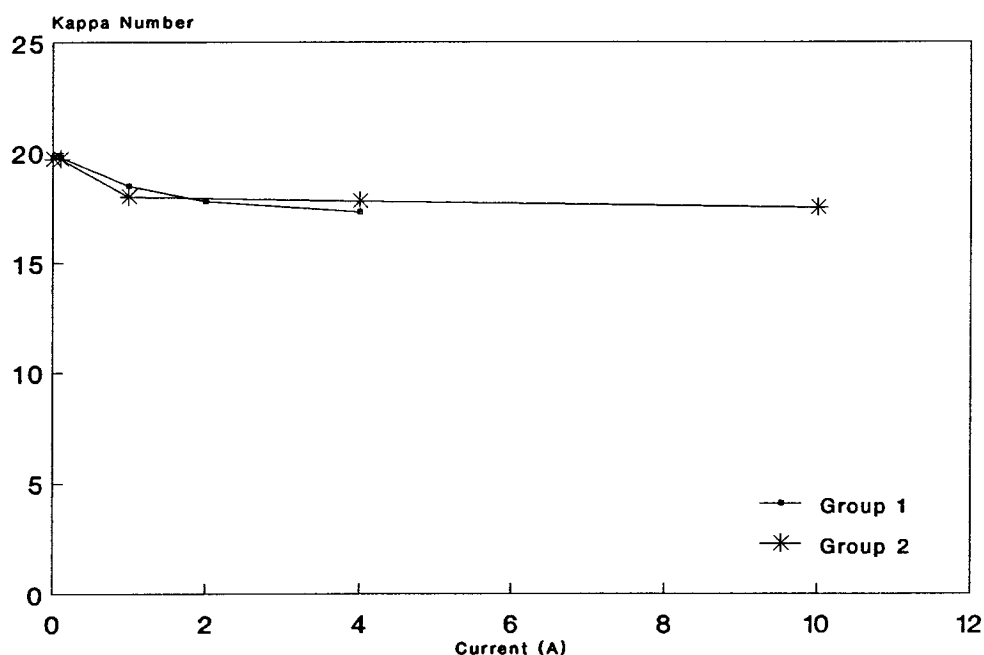
Figure 20. Effect of Current on Kappa Number. (Group 1; 1 mM Mn, 5 mM Gluconate, Graphite Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 50 °C, 3 Hours, Pulp DTPA Washed. Group 2; 10 mM Mn, 50 mM Gluconate, Platinised Titanium Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 50 °C, 3 Hours, Pulp DTPA Washed)
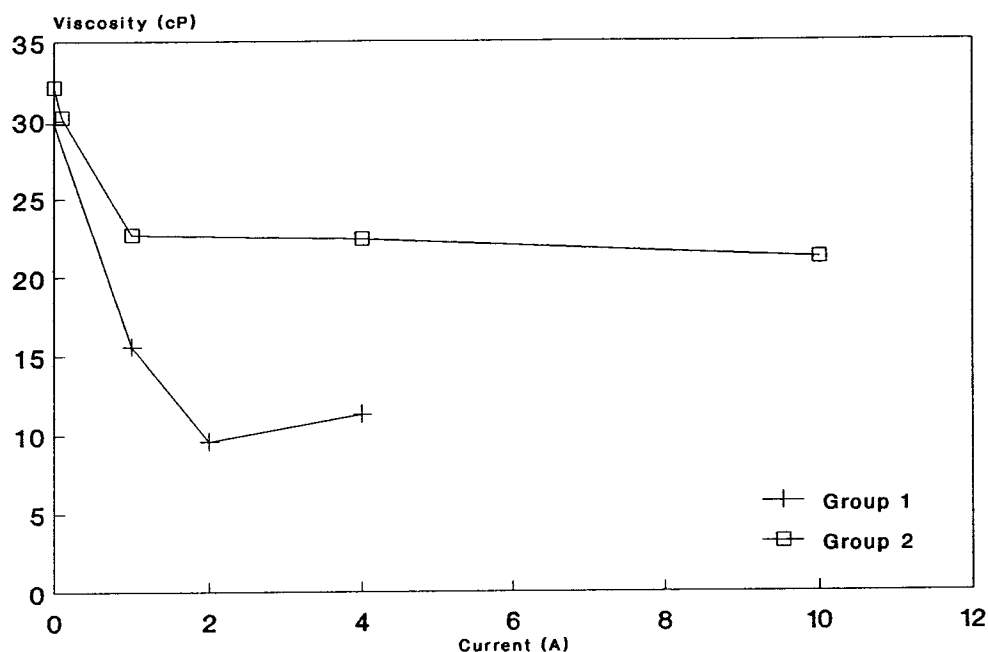
Figure 21. Effect of Current on Viscosity. (Group 1; 1 mM Mn, 5 mM Gluconate, Graphite Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 50 °C, 3 Hours, Pulp DTPA Washed. Group 2; 10 mM Mn, 50 mM Gluconate, Platinised Titanium Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 50 °C, 3 Hours, Pulp DTPA Washed)

The results indicate that in the presence of catalyst, the application of current produces a larger reduction in Kappa number and pulp viscosity than is evident in the absence of current. This indicates that current is required to continuously generate the hydrogen peroxide responsible for these changes through the reaction of the manganese complex and oxygen. The results also appear to indicate that increasing the current above a certain value does not result in any further reduction in Kappa number or viscosity. For the Group 2 results, increasing the current beyond 4.0 A yields little further reduction in Kappa number or viscosity.

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The current above which further Kappa number reduction and viscosity loss are not observed corresponds to the current required to promote the regeneration of the manganese complex and thus continuously generate the hydrogen peroxide responsible for the Kappa number and viscosity reductions.

At very high currents (10.0 A) it should be noted the production of hydroxide ions via the hydrogen evolution reaction (Rxn 18) may be of importance. Table 29 indicates the results of the addition of hydroxide ion to simulate the production of that ion at a current of 10.0 A (see Appendix 4). The total amount of hydroxide added was 1.12 mols, added as 11 equal additions of 0.108 mols (added as solid NaOH) at time t = 15, 30, 45,..,165 mins. It shows that the addition of 1.12 mols of hydroxide ion (Run 2-33) brings about a similar Kappa number reduction to that observed in the 10.0 A run (Run 2-16) without the viscosity loss associated with the current/catalyst combination.

Run	Conditions	Kappa Number	Viscosity (cP)
2-18	10 A, No Catalyst	19.8	30.6
2-16	10 A, Catalyst	17.5	21.2
2-37	0 A, No Catalyst, OH⁻ Added	17.8	28.2
2-33	0 A, Catalyst, OH⁻ Added	16.9	30.8

Table 29. Effect of Hydroxide Addition on Bleaching Result. (Group 2, Catalyst 10 mM Mn, 50 mM Gluconate if used, Total OH⁻ Added 1.12 mols if added, Platinised Titanium Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 50 °C, 3 hours, Pulp DTPA Washed)

In the presence of catalyst, if no current flows, none of the manganese complex is regenerated to participate in the continuous generation of hydrogen peroxide. Therefore in the absence of current (Run 2-33) the viscosity is high compared to the run in the presence of current (Run 2-16) where the production of peroxide affects the viscosity.

The amount of hydroxide ion added is calculated from the theoretical production of that ion, via the hydrogen evolution reaction, at a current of 10.0 A. It can be seen that the addition of this hydroxide ion can produce a Kappa number reduction similar to the reduction evident in the catalyst/current run. It would seem that the hydroxide ion produced at 10.0 A is responsible for the Kappa number reduction. It should be noted however that in the absence of catalyst, a current of 10.0 A does not produce the reduction in Kappa number (Run 2-18, Kappa No = 19.8) evident when the theoretical amount of hydroxide produced at that current is added (Run 2-37 Kappa No = 17.8). This implies that the actual production of hydroxide ion via the hydrogen evolution reaction is much smaller than the theoretical production and does not influence the Kappa number reduction. The actual production of hydroxide ions may be affected by electrode reactions involving the pulp extractives (ie. those compounds extracted from the pulp fibres during the bleaching reaction) [33].

To investigate the effect of the hydroxide ions thought to be generated at 10.0 A, Table 30 shows the result of the addition of the stoichiometric requirement of acid to neutralise the theoretical production of hydroxide ions produced at 10 A (see Appendix 4). The acid (H_2SO_4) was added to a current/catalyst run at 10.0 A.

Run	Conditions	Kappa Number	Viscosity (cP)
2-16	10 A, Catalyst	17.5	21.2
2-61	10 A, Catalyst, H^+ Added	20.6	22.4

Table 30. Effect of Acid Addition on Bleaching Result. (Group 2, Catalyst 10 mM Mn, 50 mM Gluconate if used, Total H^+ Added 1.12 M, if added, Platinised Titanium Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 50 °C, 3 hours, Pulp DTPA Washed)

Table 30 indicates that the run involving the neutralisation of the OH^- ions (generated by the current) by the acid (Run 2-61) does not exhibit the reduction in Kappa number evident in the current/catalyst run (Run 2-16). There was significant viscosity loss apparent in both runs.

As noted above, the actual production of hydroxide ions is thought to be lower than the theoretical value. Therefore the addition of 1.12 mols of H^+ ions would affect the alkalinity of the bleaching solution (ie. lower the alkalinity) producing the effects on Kappa number and viscosity noted [5].

The factorial experiment shown in Table 31 is designed to determine the importance of oxygen and catalyst with respect to the OH^- thought to be produced at 10.0 A. It is apparent that oxygen is required for the added OH^- to be effective in reducing the Kappa Number. It should be noted that in the absence of the peroxide producing catalyst/current combination no viscosity loss is evident.

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Run	Gas Purge	Added Hydroxide	Catalyst	Kappa Number	Viscosity (cP)
2-36	-	-	-	23.9	37.1
2-27	+	-	-	20.1	28.7
2-35	-	+	-	22.0	34.0
2-37	+	+	-	17.8	28.2
2-34	-	-	+	24.3	39.9
2-28	+	-	+	19.7	29.9
2-29	-	+	+	22.2	38.1
2-33	+	+	+	16.9	30.8

Table 31. Results of Factorial Experiment.
Catalyst;(+) 10 mM Mn, 50 mM Gluconate, (-) 0 mM Mn, 0 mM Gluconate,
Added Hydroxide;(+) 1.12 mols, (-) 0 mols,
Gas Purge; (+) Oxygen, (-) Nitrogen,
(Group 2, O_2 15 cc/min @ STP, 1 M NaOH, 50 °C, 3 hour, Pulp DTPA Washed)

Also it can again be seen that the addition of 1.12 mols of hydroxide ion can produce a Kappa number reduction similar to the reduction evident in the catalyst/current run at 10.0 A (compare Runs 2-16 Table 29 and 2-33 Table 31). The presence of catalyst has little effect on the results of the hydroxide ion addition (Runs 2-37 and 2-33).

It is thought then, that the production of hydroxide ions at 10.0 A is smaller than the theoretical production and that the reduction in Kappa number and viscosity, noted in runs where the manganese complex and current are combined, is due to the peroxide continuously produced in the proposed redox cycle.

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Table 32 indicates the effect of hydrogen peroxide addition on the bleaching result. The peroxide was added to simulate the effect of the production of peroxide in the bleaching environment. The total amount of peroxide added was 0.15 mols, added as 3 equal additions of 0.05 mols (5 ml of 10 M H_2O_2) at time t = 0, 1, 2 hours. It can be seen that in the presence of catalyst the addition of the peroxide (Run 2-30) brought about a similar reduction in both Kappa number and viscosity to the reductions noted in the catalyst/current run (Run 2-16). This is very strong evidence that the proposed redox couple is operating and the peroxide produced is capable of causing the results attributed to it.

Run	Conditions	Kappa Number	Viscosity (cP)
2-16	10 A, Catalyst	17.5	21.2
2-30	0 A, Catalyst, H_2O_2 Added	17.2	18.8

Table 32. Effect of Hydrogen Peroxide Addition. (Group 2, Catalyst 10 mM Mn, 50 mM Gluconate, Total H_2O_2 Added 0.15 mols (if added), Platinised Titanium Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 50 $^{\circ}$C, 3 hours, Pulp DTPA Washed)

The results indicate the production of hydrogen peroxide via the current/catalyst interaction and show the ability of this peroxide to affect both the Kappa number and viscosity of the bleached pulp.

<u>Time Dependence.</u>

The following experiments examine the effect of reaction time upon the bleaching results.

Figure 22 indicates the change in Kappa number and viscosity over an 8 hour period. They show an initial sharp decrease in both Kappa No and viscosity followed by a levelling off. Because of this effect there is little benefit in continuing the reaction beyond 5 --> 6 hours. It should be noted that the complex does not remain stable beyond approximately 5 --> 6 hours at 50 ^{o}C. Therefore shown in Figure 22 is a run (Run R137) in which the catalyst is renewed after 3 hours so the complex is present throughout a 6 hour reaction period. There is no increase in delignification evident in this action.
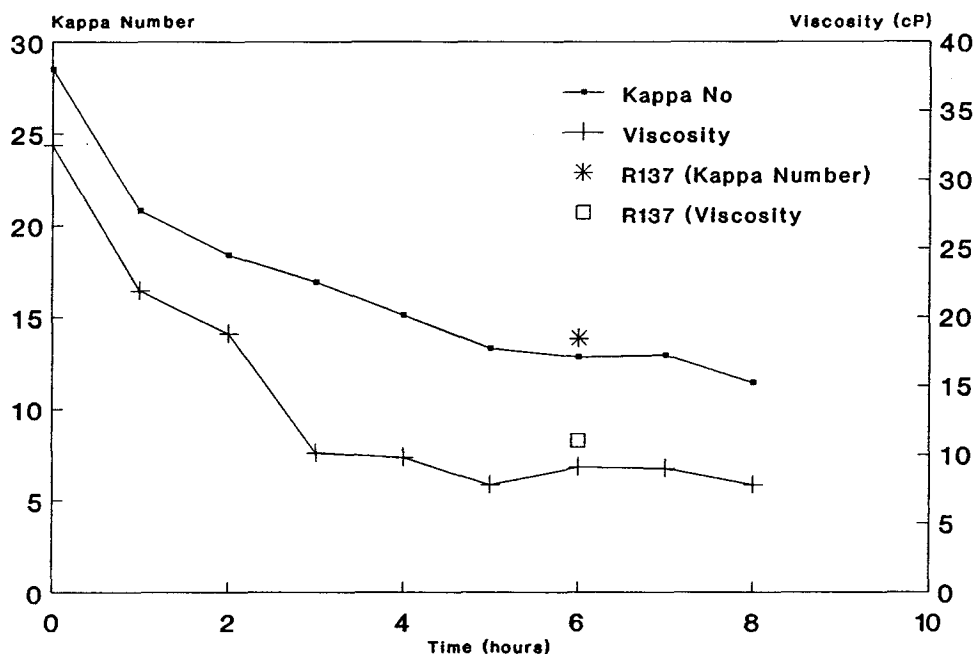
Figure 22. Time Dependance. (Group 1, 10 mM Mn, 50 mM Gluconate, 4.0 A on Graphite Cathode, O_2 15 cc/min @ STP, 1 M NaOH, 50 °C, 3 Hours, Pulp DTPA Washed)

It would appear that under these conditions the catalyst/current combination is not effective in promoting Kappa number reduction (or viscosity loss) beyond 5-6 hours. It is thought that this is because the peroxide generated is incapable of reducing the Kappa number (or viscosity) beyond a certain value. That value representing the limit of reaction under the conditions described.

Effect of Manganese and Ligand Only.

The following experiments investigate the ability of the manganese complex to prevent the viscosity loss evident in Group 1 runs in the absence of current as described earlier.

From Table 33 it can be seen that the protection of viscosity under the prescribed conditions (R112) also occurs when the metal alone (R119) or ligand alone (R123) are present. The metal is more effective in this respect.

Run	Conditions	Kappa Number	Viscosity (cP)
R107	No Metal, No Ligand	19.8	21.7
R112	Metal, Ligand	19.5	27.9
R119	Metal, No Ligand	20.1	31.4
R123	Ligand, No Metal	19.9	26.5

Table 33. Effect of Metal and Ligand on Bleaching Result.
Metal; 10 mM Mn added as a solution of 0.1 M $Mn(ClO_4)_2.6H_2O$,
Ligand; 50 mM Gluconate added as a 0.1 M solution,
(Group 1, O_2 15 cc/min @ STP, 1 M NaOH, 50 ^oC, 3 hours, Pulp DTPA Washed)

The noted effect of manganese protection is known and described earlier (Chapter 2). The mechanism of ligand only protection is thought to be due to its action as a sacrificial protector. It is a sacrificial protector as the viscosity-degrading free radicals attack both the free ligand and the cellulose structures effectively reducing the damage to the cellulose.

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The protection effect of the manganese complex is therefore ascribed to a combination of the ability of its 2 components to protect against cellulose degradation.

Use of Chemical Reductants.

This section examines briefly the use of chemical reagents to reduce the higher oxidation states of manganese rather than the use of the electrochemical method. Ascorbic acid and hydrazine sulphate were tested as potential candidates due to their known ability to reduce the manganese complex [2].

The results of the factorial design experiments are given in Tables 34 and 35. The ascorbic acid trials (Table 34) indicate no benefit in the use of the reductant, the blank run (R85) having the lowest Kappa number. It would appear that the ascorbic acid is incapable of participating in the reduction of the manganese complex to generate hydrogen peroxide under these conditions.

Run	Catalyst	Reductant	Kappa Number	Viscosity (cP)
R88	+	+	25.5	29.3
R83	+	−	24.4	28.8
R90	−	+	25.7	29.2
R85	−	−	24.4	28.1

Table 34. Results of Factorial Experiment.
Catalyst;(+) 2.5 mM Mn, 25 mM Gluconate, (-) 0 mM Mn, 0 mM Gluconate,
Reductant;(+) 0.1 M Ascorbic Acid, (-) 0 M Ascorbic Acid,
(O_2 15 cc/min @ STP, 0.5 M NaOH, 30 $^{\circ}$C, 1 hour)

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Table 35 for the hydrazine sulphate indicates that the reductant alone (R84) exhibits the largest Kappa number reduction and that the viscosity of R84 is also affected detrimentally. In the absence of the reductant the manganese complex does not improve the bleaching response (Runs R83 and R85). Where the catalyst and reductant are both present (Run R82) the effect of the catalyst is to retard Kappa number reduction and viscosity loss when compared to the reductant only run (Run R84).

Run	Catalyst	Reductant	Kappa Number	Viscosity (cP)
R82	+	+	23.5	11.8
R83	+	-	24.4	28.8
R84	-	+	20.8	7.2
R85	-	-	24.4	28.1

Table 35. Results of Factorial Experiment.
Catalyst;(+) 2.5 mM Mn, 25 mM Gluconate, (-) 0 mM Mn, 0 mM Gluconate,
Reductant;(+) 20 mM Hydrazine Sulphate, (-) 0 mM Hydrazine Sulphate,
(O_2 15 cc/min @ STP, 0.5 M NaOH, 25 ^{b}C, 1 hour)

Shown in Table 36, Run 2-62 shows the effect of hydrazine in the absence of oxygen and indicates that oxygen is a requirement for the Kappa number and viscosity reductions evident in Run R84.

Run	Conditions	Kappa Number	Viscosity (cP)
R84	No Catalyst, Reductant, O_2	20.8	7.2
2-62	No Catalyst, Reductant, N_2	24.7	28.1

Table 36. Effect of Nitrogen on Bleaching Result.
Reductant;(+) 20 mM Hydrazine Sulphate,
(O_2 or N_2 15 cc/min @ STP, 0.5 M NaOH, 25 $^{\circ}$C, 1 hour)

It appears that the hydrazine sulphate is also incapable of operating in a cycle with the manganese complex to generate hydrogen peroxide. The presence of the manganese complex has the effect of reducing the viscosity drop (compare Runs 82,83). This is probably due to the ability of the manganese complex to protect against cellulose degradation. However, the presence of the manganese complex also reduces the Kappa number drop (compare Runs 82,83). It appears the action of the hydrazine sulphate alone with oxygen is responsible for the Kappa number and viscosity reductions evident in the factorial experiment.

Chapter 6.

General Discussion.

The proposed manganese complex/oxygen redox couple involved the use of the manganese gluconate complex to delignify chemical pulp through the in-situ production of hydrogen peroxide from oxygen in an alkaline environment. It was proposed to bring about the reduction of the higher oxidation states of manganese via the use of an electrode system. The ability of this redox couple to operate in the bleaching environment was examined and the following observations were made.

The experiments employing cyclic voltammetry indicated the presence of the manganese III/IV couple; this indicated the manganese IV->III reduction would take place on the cathode surface. There was no evidence of the manganese II/III couple. The experiments employing cyclic voltammetry indicated the presence of hydrogen peroxide in the sample solution. Analysis of the bleaching solution also indicated the presence of hydrogen peroxide in the solution. The ability of a cathode to promote the reduction of manganese IV to the manganese III form was evidenced in the experiments employing spectrophotometric analysis. Similarly, spectrophotometric experiments showed no evidence of the manganese III to manganese II reduction. The experiments indicated the predominant forms of the manganese gluconate complex in the bleaching environment were likely to be the manganese III and IV forms.

It was found that the combination of the manganese gluconate complex, oxygen and sufficient current in an alkaline environment produced a significantly larger Kappa number and viscosity

reduction in the chemical pulp, than in the absence of the manganese gluconate complex. Analysis of the factorial design experiments indicated the combination of catalyst and current had a significant effect on Kappa number and viscosity reduction. This effect is attributed to the action of the peroxide produced in the proposed redox cycle. Free radical species generated from the peroxide are thought to be responsible for the effects on Kappa number and viscosity noted, as peroxide stabilisers added to prevent peroxide decomposition inhibited the delignification and cellulose degradation reactions. Metal ions were found to be very important with respect to the delignification process. The addition of Cu^{2+} or Fe^{2+} ions to runs in the absence of the manganese complex was found to promote viscosity loss in the pulp, probably due to free radical generation catalysed by the metal ions. It is believed a metal ion contaminant such as Cu^{2+} was responsible for increased viscosity loss in certain experimental runs. The addition of Mn^{2+} ions in the absence of the manganese complex was found to inhibit viscosity loss, an effect attributed in the literature to the adsorbtion of transition metal ions on the surface of precipitated manganese oxides.

In summary, the evidence presented in this study suggests the proposed manganese gluconate complex/oxygen redox cycle is indeed operating to delignify the pulp. It appears the manganese III and IV forms of the manganese gluconate complex are involved in the redox cycle. Oxygen is required to oxidise the manganese III form to the manganese IV form and the peroxide anion while sufficient current is required to bring about the reduction of the manganese IV form to the manganese III form. It is noted that free radicals species, thought to be generated in the bleaching environment from the peroxide, are probably responsible for the delignification and cellulose degradation reactions observed.

Chapter 7.

Conclusions and Recommendations.

Conclusions.

It was found that the combination of the manganese gluconate complex, oxygen and sufficient current in an alkaline environment produced a significantly larger Kappa number and viscosity reduction in the chemical pulp, than in the absence of the manganese gluconate complex. This effect is attributed to the action of the peroxide produced in the proposed manganese gluconate/oxygen redox cycle. It had been hoped the manganese complex/oxygen redox cycle would promote the delignification of chemical pulp via non-free radical pathways, thus reducing cellulose degradation. No evidence of this effect was noted; indeed, it is likely that the hydrogen peroxide produced via the manganese gluconate complex was decomposed to free radical species causing the delignification and cellulose degradation observed.

The manganese gluconate complex/oxygen redox cycle proved to be a capable oxidising system which had a significant effect on both the cellulose and lignin components of pulp. However the redox couple was not particularly selective compared to conventional oxygen bleaching. Further research may improve the effectiveness and selectivity of the manganese gluconate complex/oxygen redox cycle.

Recommendations.

The following recommendations are suggested for future work in the delignification of chemical pulp utilising the manganese gluconate/oxygen redox couple:

1) Investigation of the reduction of the manganese III complex to the manganese II form. This reduction would increase the potential peroxide production.

2) Further investigation of the reduction of the manganese (IV) complex to the manganese (III) form. Improvement would increase the potential peroxide production.

3) Incorporation of a method of measuring the production of, and type of, free radical species in the reactor chamber. This may indicate conditions promoting more selective delignification.

4) An in-situ method of measuring the peroxide concentrations within the reactor would be helpful in determining the optimum operating conditions.

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Appendix 1. Analysis of Factorial Designs.

The analyses presented in this appendix tabulate the effects (as calculated from Equations 8,9 and 10, Section 2.8) of the variables in the factorial experiments presented in Chapter 5.4. Below the table of effects the significant effects on the measured response (Kappa number and viscosity) are noted. The significant effects are those for which the confidence interval does not contain zero.

For all the analyses presented, except the analysis in Table 44, the 95% confidence intervals for Kappa number and viscosity were ±0.58 and ±3.64 cP respectively. The 95% confidence intervals for Kappa number and viscosity for Table 44 were ±0.82 and ·±5.15 cP respectively.

Main Effects	Kappa Number	Viscosity (cP)
Catalyst (C)	-1.0	-2.5
Current (I)	-1.9	-9.2
Interaction (C*I)	-0.7	-8.7

Table 37. Factorial Analysis of Data from Table 11.

Significant Effects.

Kappa Number: catalyst, current and catalyst/current interaction

Viscosity: current and catalyst/current interaction

Main Effects	Kappa Number	Viscosity (cP)
Catalyst (C)	-1.1	-3.5
Current (I)	-1.0	-5.0
Interaction (C*I)	-1.2	-5.9

Table 38. Factorial Analysis of Data from Table 12.

Significant Effects.

Kappa Number: catalyst, current and catalyst/current interaction

Viscosity: current and catalyst/current interaction

Main Effects	Kappa Number	Viscosity (cP)
Catalyst (C)	-1.2	-0.6
Current (I)	-1.1	-10.3
Interaction (C*I)	-0.9	-6.8

Table 39. Factorial Analysis of Data from Table 15.

Significant Effects.

Kappa Number: catalyst, current and catalyst/current interaction

Viscosity: current and catalyst/current interaction

Main Effects	Kappa Number	Viscosity (cP)
Catalyst (C)	-1.5	0.0
Current (I)	-1.0	-1.5
Interaction (C*I)	1.0	1.6

Table 40. Factorial Analysis of Data from Table 25.

Significant Effects.

Kappa Number: catalyst, current and catalyst/current interaction

Viscosity: none

Main Effects	Kappa Number	Viscosity (cP)
Catalyst (C)	-0.1	9.8
Current (I)	-0.1	-0.1
Interaction (C*I)	0.7	0.8

Table 41. Factorial Analysis of Data from Table 26.

Significant Effects.

Kappa Number: catalyst/current interaction

Viscosity: catalyst

Main Effects	Kappa Number	Viscosity (cP)
Catalyst (C)	1.2	-1.2
Current (I)	-0.8	-1.6
Interaction (C*I)	-0.4	-0.1

Table 42. Factorial Analysis of Data from Table 27.

Significant Effects.

Kappa Number: catalyst and current

Viscosity: none

Main Effects	Kappa Number	Viscosity (cP)
Catalyst (C)	0.8	-4.0
Current (I)	-0.4	-2.3
Interaction (C*I)	-0.5	-1.2

Table 43. Factorial Analysis of Data from Table 28.

Significant Effects.

Kappa Number: catalyst

Viscosity: catalyst

Main Effects		Kappa Number	Viscosity (cP)
Gas Purge	(G)	-4.5	-7.9
Added Hydroxide	(H)	-2.3	-1.1
Catalyst	(C)	-0.2	-2.7
Interaction	(G*H)	-0.3	+1.3
Interaction	(G*C)	-0.5	-0.8
Interaction	(H*C)	-0.2	-0.7
Interaction	(G*H*C)	-0.1	-0.0

Table 44. Factorial Analysis of Data from Table 31.

Significant Effects.

Kappa Number: gas purge and added hydroxide

Viscosity: gas purge

Main Effects		Kappa Number	Viscosity (cP)
Catalyst	(C)	-0.1	0.4
Reductant	(R)	1.2	0.8
Interaction	(C*R)	-0.1	-0.3

Table 45. Factorial Analysis of Data from Table 34.

Significant Effects.

Kappa Number: reductant

Viscosity: none

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Main Effects	Kappa Number	Viscosity (cP)
Catalyst (C)	1.4	2.7
Reductant (R)	-2.3	-19.0
Interaction (C*R)	1.4	2.0

Table 46. Factorial Analysis of Data from Table 35.

Significant Effects.

Kappa Number: catalyst, reductant and catalyst/reductant interaction

Viscosity: reductant

Appendix 2. Calculation of Response Error.

Runs	Kappa Number	Viscosity (cP)	s_k	s_v	r
R100, R106	18.26, 18.76		0.354		2
R101, R105	19.71, 19.93		0.156		2
R110, R104	19.42, 19.59		0.120		2
R103, R107	19.99, 19.83		0.1131		2
R139, R140		21.22, 24.27		2.157	2
R138, R141		19.55, 21.08		1.082	2
2-11, 2-12		22.43, 22.21		0.156	2
2-16, 2-19		21.16, 21.07		0.064	2

Table 47. Table for Response Error Calculation.

The response error for duplicate runs (Y1, Y2) for Kappa number and viscosity (s_k and s_v) are calculated from

$$s = ((Y1-Y2)^2/2)^{1/2}$$

The pooled estimation of response error for both Kappa Number and viscosity responses is calculated from

$$s^2 = \Sigma(r_i-1)s_i^2/\Sigma(r_i-1)$$

With, Degrees of Freedom (v),

$$v = \Sigma(r_i-1)$$

For Kappa Number response,

$$s=0.21, v=4$$

For viscosity response,

$$s=1.21, v=4$$

Appendix 3. Electrode Studies.

To determine the effect of electrode material on the electrode potential resulting from an increase in current the following experiment was carried out.

The equipment used in these experiments was as shown in Figure 6. A Standard Calomel Electrode (SCE) was held close to the cathode in the reactor. A high impedance voltmeter was connected to the SCE and the cathode. In this way measurements of electrode potential were taken.

The solution in the reactor was prepared as described in Section 4.4. The applied current was set at the desired level (as read from the power supply), 1 minute was allowed to elapse and then the electrode potential (vs the SCE) was read from the voltmeter. The results are indicated in Figure 23.
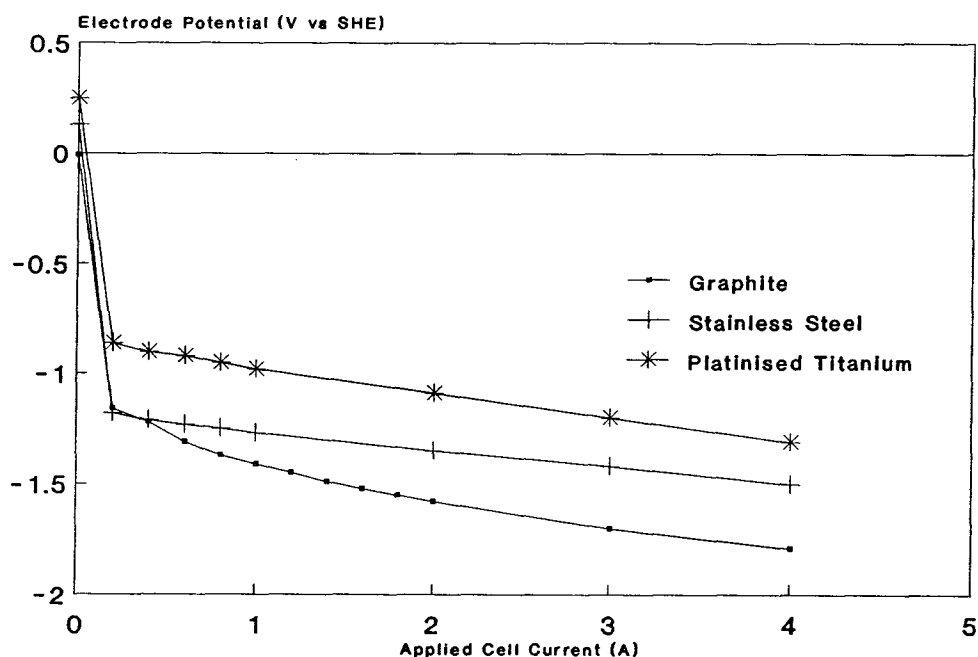
Figure 23. Electrode Potential vs Applied Current. (1 mM Mn, 5 mM Gluconate, 1 M NaOH, 23 ^{o}C, No Pulp Present)

Figure 23 indicates that for the cathode materials tested the limiting hydrogen evolution reaction (Reaction 18) occurred at different electrode potentials. The hydrogen evolution reaction on the graphite electrode occurred at the most negative electrode potential.

Appendix 4. Hydroxide Ion Production at 10.0A.

Hydroxide ions are produced at the cathode via the hydrogen evolution reaction (Reaction 18).

$$2H_2O + 2e^- <--> H_2 + 2OH^- \qquad Rxn\ 18$$
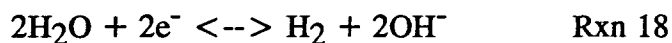
The theoretical production of hydroxide ions is calculated from,

$$OH^-\ produced\ =\ It/zF \qquad (17)$$

where t - duration of reaction (s)

    z = electron stoichiometric coefficient

    I = current (A)

    F = Faraday Constant (= 96500 c/mol)

At 10.0 A for 3 hours, the hydroxide ion production is,

OH^- produced = $10.0x(3x3600)/1x96500$ = 1.119 mols

The production of hydroxide ion is simulated through the addition of a total of 1.119 mols of NaOH (corresponds to 44.77g NaOH) to the bleaching solution.

As the production of hydroxide ions is 1.119 mols, the acid (H^+) required to neutralise the OH^- produced is 1.119 mols (corresponds to 1.119/2 mols of sulphuric acid)

Appendix 5. Hydrogen Peroxide Titration Calculation [28].

Hydrogen peroxide reacts with permanganate via Reaction 24.

$$2MnO_4^- + 5H_2O_2 + 6H^+ <--> 2Mn^{2+} + 5O_2 + 8H_2O \qquad \text{Rxn 24}$$

The titration procedure described below is based on the above equation and a method presented in literature [28].

A 5 ml sample of solution was drawn from the reactor.

This was added to 200ml of ice-cold 0.5 M H_2SO_4 in a 250 ml flask.

2 drops of ferroin indicator were then added.

The sample was then titrated with 0.01 N $KMnO_4$ where, 1ml of 0.01N $KMnO_4$ titrated corresponds to a sample concentration of 0.001M H_2O_2.

Glossary.

Cellulose : The main chemical component in the cell walls of plants. It is the fibrous substance that remains after the non-fibrous portions, such as lignin , have been removed from the pulp during the cooking and bleaching operations.

Chemical Pulp : Wood pulp produced by removing lignin during the cooking of wood chips in a digester. The Kraft or sulpite processes are examples of processes producing chemical pulp.

Consistency : A measure of the fibrous material in pulp suspensions. It is expressed as a weight percentage.

DTPA : Diethylenetriaminepentaacetic acid.

EDTA : Ethylenedinitrilotetraacetic acid.

Fibre : An elongated, tapering, thick walled cellular unit which is the structural component of woody plants.

Handsheet : A single sheet of pulp prepared in the laboratory by draining water from a pulp suspension on a screen-covered sheet mould. It is used in testing the properties of pulp.

Kappa Number : A value obtained using a standard test procedure which indicates the lignin content of pulp.

Kraft Pulp : Wood pulp produced by the sulphate chemical process using cooking liquor composing primarily of sodium hydroxide and sodium sulphide.

Lignin : A coloured organic substance which acts as an interfiber bond in woody materials. It is removed along with other organic materials during the pulping and bleaching stages.

Mechanical Pulp : Pulp produced by reducing pulpwood logs and chips into their fibre components by the use of mechanical energy. eg via the use of a grinding stone.

Pulp Extractives : The products of lignin and cellulose oxidation, found in the bleaching solution.

PTFE : Polytetrafluoroethane.

Redox Cycle : Chemical/electrochemical process involving oxidation and reduction reactions.

SCE : Saturated Calomel Electrode, V(vs SCE) = 0.24 + V(vs SHE) at 25 ^{o}C.

SHE : Standard Hydrogen Electrode.

TAPPI : Technical Association of the Pulp and Paper Industry.

<u>Viscosity</u> : A value obtained using a standard test procedure involving the measurement of the viscosity of the pulp in a solvent. This indicates the length of the cellulose molecules in the pulp sample.