IN-SITU DELIGNIFICATION OF WOOD PULP BY
ELECTROCHEMICALLY GENERATED Mn(III)CyDTA

by

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We accept this thesis as conforming
to the required standard

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ABSTRACT

The present work consisted of three parts, i.e. cyclic voltammetric investigation of the electrochemical behavior of Mn(III)CyDTA, development of a new, electrochemical method of Mn(III)CyDTA synthesis in alkaline media and in-situ electrochemically mediated oxygen bleaching of softwood kraft pulp with the Mn(III)CyDTA complex.

The cyclic voltammograms of Mn(III)CyDTA were recorded on three electrodes, i.e. graphite disk, stainless steel wire and platinum wire, as a function of pH (5 to 13.5) and scan rate (ν : 33.34 mV/s to 166.67 mV/s) at 25 °C. The presence of sodium bicarbonate (NaHCO₃ 0.1 M) was found to be essential in bringing about the cyclic voltammetry response of Mn(III)CyDTA. The cyclic voltammetry investigations revealed the existence of Mn(II) adsorption on all of the electrodes.

Increasing the pH shifted the cathodic peak potential toward more negative values with simultaneous decrease of the cathodic and anodic peak currents. At pH above 13, the cathodic peak vanishes, due to fast disproportionation of the Mn(III) ion. The actual reduction potential of Mn(III)CyDTA is in the range of +30 to -200 mV/SCE, at pH 10 to 11 and 25 °C.

The electrosynthesis of Mn(III)CyDTA was investigated in a divided batch electrochemical reactor, at 25 °C, in alkaline media, pH 9.0 and 10.5, for two CyDTA/Mn molar ratios, 1/1 and 2/1 respectively. The explored Mn(II) concentration range was between 6 mM and 54 mM. The supporting electrolyte was a 0.1 M NaHCO₃ solution, which contributes to the stabilization of the Mn(III) ion as well. Six anodes were tested.
i.e. stainless steel screen, plus stainless steel, graphite, nickel, lead and platinized titanium plates. It was found that the electrosynthesis is favored by low CyDTA/Mn molar ratio (1/1) and high pH (10.5).

The five anode plates were operated at current densities ranging from 13 A/m$^2$ to 102 A/m$^2$, while on the stainless steel screen electrode the current density ranged from 2.6 A/m$^2$ to 15.5 A/m$^2$. Over the entire domain of explored current densities and Mn(II) concentrations, the anodic oxidation of Mn(II)CyDTA is under different forms of electrode kinetic control. Furthermore, in the case of an equimolar ligand to metal ratio, on the stainless steel and lead anodes a visible, anodic adsorption layer is formed, which modifies the surface and electrochemical properties of the anode and reduces the current efficiency for Mn(III)CyDTA formation.

The graphite and platinized titanium anodes allow for much higher current densities without a visible anodic film formation (the highest current density employed in the present work being 102 A/m$^2$). The current efficiencies for Mn(II) oxidation at pH 10.5 were between 78 and 40 %, for a 18 mM Mn(II) concentration.

In the case of CyDTA/Mn = 2/1 (molar ratio), there was no visible build up of anodic film on any of the anodes. In the investigated range of current densities and Mn(II) concentrations, the current efficiency for Mn(III) electrosynthesis on the graphite anode was below 20 % at pH 10.5 and below 10 % at pH 9.0.

The anolyte obtained after one hour of electrosynthesis, containing various amounts of Mn(III)CyDTA, was employed without further processing in the in-situ electrochemically mediated oxygen bleaching of chemical pulp. Two anodes, i.e. stainless
steel screen and graphite, were tested. The same pulp consistency (1 %) and oxygen pressure (0.1 MPa) were employed in all experiments. Factorial and parametric experiments were performed in order to determine the influence of different process variables on both the Kappa number and pulp viscosity.

In the in-situ electrochemically mediated oxygen bleaching employing a graphite plate anode at a current density of 102 A/m², with an initial Mn(III)CyDTA conc. of 1.4 mM, under milder conditions than in the conventional oxygen bleaching, i.e. pH 9.0, atmospheric oxygen pressure, 80 °C, a 50 % delignification was obtained in 3 hr. (Kappa number dropped from 30.0 to 15.0), while the viscosity decreased from 34.6 to 20.5 cP. Under similar conditions the control experiment (i.e. with oxygen at atmospheric pressure but without catalyst and current) generated only a 3.2 points decrease in the Kappa number.

The half factorial experimental design with six process variables, i.e. oxygen catalyst, current, temperature, pH and CyDTA/Mn molar ratio, at two levels and one centerpoint (2⁶⁻¹ + 1 design) showed that the delignification was mainly due to high second and third order synergistic effects between : catalyst - current, catalyst - oxygen, oxygen - temperature, catalyst - oxygen - temperature and catalyst - current - oxygen.

Also, it was found that carbohydrate protection in the present system was achieved by both, high CyDTA/Mn molar ratio (2 to 4) and by high third order interaction effect between catalyst, pH and temperature. The third order interaction effect actually means that under conditions that cause intensive decomposition of Mn(III)CyDTA (high pH and temperature) the carbohydrates are protected from degradation. Consequently, the Mn(II)
species e.g. Mn(OH)$_2$, Mn(II)CyDTA, are effective cellulose protecting agents. The same conclusion was strengthened by the parametric experiments.

A small, but statistically significant, curvature effect was found proving the existence of a true catalytic interaction between Mn(III)CyDTA, oxygen and temperature.

The stainless steel screen was employed as anode in the in-situ electrochemically mediated oxygen bleaching under conditions where the adsorption does not significantly affect the process—(i.e. at a current density of 2.6 A/m$^2$ and with an initial Mn(III)CyDTA conc. of 0.5 mM). A full factorial experimental design was performed with three process variables, oxygen, catalyst and current, at two levels. The pH and temperature were held constant at 10.5 and 25 °C respectively. Under these conditions the Kappa number dropped from 30.0 to 22.0 in 3 hr. while the viscosity was 24.9 cP. The delignification was mainly due to the additive effect of the catalyst, rather than synergistic effects with other process variables. The presence of 10 % vol dimethylsulfoxide brought about a considerable improvement of selectivity, the final Kappa number after 3 hr. was 22.7 while the viscosity dropped from 34.6 cP to only 27.0 cP.
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NOMENCLATURE

\[ a \] Tafel parameter, \{V\}

\[ a_R \] activity of reactant

\[ a_P \] activity of product

\[ A \] real electrode area, \{cm²\}

\[ A_0 \] surface area of the stainless steel screen, \{cm²\}

\[ A_{mesh} \] real surface area of the meshed part of the stainless steel screen, \{cm²\}

\[ A_{Mn} \] atomic mass of Mn, \{54.94 a.m.u\}

\[ A_{oxygen} \] atomic mass of oxygen, \{16 a.m.u\}

\[ A_{unmesh} \] surface area of the unmeshed part of the stainless steel screen, \{cm²\}

\[ A_{scg} \] electrode area screened by an evolving gas phase, \{cm²\}

\[ b \] Tafel slope, \{V\}

\[ c, C \] concentration, \{M\}

\[ CE \] current efficiency, \{\%\}

\[ d \] impeller diameter, \{m\}

\[ d_b \] bubble break up diameter, \{µm\}

\[ d_0 \] diameter of the anode chamber, \{cm\}

\[ D \] wire diameter for the stainless steel screen, \{m\}; or diffusion coefficient in the Scmidt number \{cm²/s\}

\[ D_P \] degree of polimerization of pulp carbohydrates

\[ D^0 \] diffusion coefficient at infinite dilution, \{cm²/s\}

\[ D_f \] dilution factor
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<tr>
<td>$E$</td>
<td>actual reduction potential, {V/SHE or V/SCE}</td>
</tr>
<tr>
<td>$E_{\text{rev}}$</td>
<td>equilibrium (reversible) electrode potential, {V}</td>
</tr>
<tr>
<td>$E^0$</td>
<td>standard reduction potential, {V/SHE or V/SCE}</td>
</tr>
<tr>
<td>$E^a_p$</td>
<td>anodic peak potential, {V/SHE or V/SCE}</td>
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<tr>
<td>$E^c_p$</td>
<td>cathodic peak potential, {V/SHE or V/SCE}</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday's constant, {\sim 96500 C/equiv}</td>
</tr>
<tr>
<td>$h$</td>
<td>vertical dimension of the impeller blade, {cm}</td>
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<td>$H$</td>
<td>height of the liquid in the electrochemical reactor, {cm}</td>
</tr>
<tr>
<td>$I$</td>
<td>total, applied current, {A}</td>
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<tr>
<td>$I_{\text{oxygen}}$</td>
<td>current consumed by the oxygen evolution reaction, {A}</td>
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<td>$I_v$</td>
<td>intrinsic pulp viscosity, {dm$^3$/kg}</td>
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<td>$i$</td>
<td>total current density, {A/m$^2$}</td>
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<tr>
<td>$i_0$</td>
<td>exchange current density, {A/m$^2$}</td>
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<tr>
<td>$i_{ac}$</td>
<td>activation controlled current density, {A/m$^2$}</td>
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<tr>
<td>$i_L$</td>
<td>limiting current density, {A/m$^2$}</td>
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<td>$i_p^a$</td>
<td>anodic peak current, {mA or $\mu$A}</td>
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<td>$i_p^c$</td>
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<td>$k_C$</td>
<td>rate constant of cellulose degradation during classical oxygen bleaching</td>
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<td>$k_i$</td>
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<td>$k_S$</td>
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<td>$k_{\text{liq}\text{liq}}$</td>
<td>volumetric gas-liquid mass transfer capacity, {s$^{-1}$}</td>
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\( k_d a_s \)  volumetric gas-solid mass transfer capacity, \( \{s^{-1}\} \)

\( K \)  Kappa number

\( K_f \)  Kappa number in the first delignification stage

\( K_m \)  total mass transfer coefficient, \( \{cm/s\} \)

\( K_{mf} \)  mass transfer coefficient due to forced convection, \( \{cm/s\} \)

\( K_{mg} \)  mass transfer coefficient due to gas evolution, \( \{cm/s\} \)

\( K_s \)  Kappa number in the second delignification stage

\( m \)  amount, \( \{g\} \)

\( m_n \)  moles of cellulose per ton of pulp

\( \cdot \)  moles of cellulose per ton of pulp

\( m_g \)  mass rate of oxygen evolved, \( \{g/s\} \)

\( M_{oxygen} \)  molecular mass of oxygen

\( n \)  number of electrons exchanged in the electrochemical reaction

\( O \)  oxidized species

\( P_o \)  oxygen partial pressure, \( \{kPa\} \)

\( P_r \)  electrochemical production rate, \( \{mol/s\} \)

\( Q \)  activity quotient

\( r_{overall,L} \)  overall delignification rate during classical oxygen bleaching

\( r_{overall,c} \)  overall cellulose degradation rate during classical oxygen bleaching

\( R \)  reduced species

\( R_g \)  universal gas constant, \( \{8.314 \text{ J/(mol•K)}\} \)

\( S \)  solubility of oxygen in electrolyte solutions, \( \{mol/l\} \)

\( S_0 \)  solubility of oxygen in pure water, \( \{mol/l\} \)
$SE$ specific energy, \{kWh/kmol\}

$t_R$ transference number of the ionic reactant species

$T$ temperature, \{K\}

$\nu$ pulp viscosity, \{cP\}

$V_{cell}$ cell voltage, \{V\}

$V_v$ volumetric oxygen evolution rate per unit electrode area, \{\(\text{cm}^3/(\text{cm}^2\cdot\text{min})\)}

$V_{oc}$ open circuit potential, \{V\}

$V_{ohm}$ ohmic voltage drop, \{V\}

$z_+; z_-$ the charge of the cation and anion

**Dimensionless numbers:**

$Re$ Reynolds number

$Sc$ Schmidt number

$Sh$ Sherwood number

**Greek symbols:**

$\alpha_A$ anodic charge transfer coefficient

$\alpha_C$ cathodic charge transfer coefficient

$\varepsilon$ gas void fraction

$\eta$ overvoltage, \{V\}

$\eta_{ac}$ activation controlled overpotential, \{V\}

$\lambda^0$ limiting ionic equivalent conductance, \{(mho\cdot cm^2)/equiv\}
 electrolyte conductivity without gas evolution, \{mho\}

\( \Lambda_g \) electrolyte conductivity in the presence of gas evolution, \{mho\}

\( \mu \) electrolyte dynamic viscosity, \{Pa\cdot s\}

\( \theta \) degree of electrode screening by an evolving gas phase

\( \rho \) electrolyte density, \{kg/m\(^3\)\}

\( v \) scan rate, \{mV/s\}

\( \omega \) rotation rate, \{rpm\}

Ligand Nomenclature:

- EDDA ethylenediaminediacetate
- EDTA ethylenediaminetetraacetate
- EDTE ethylenediaminetetraethanol
- EGTA ethylene glycol bis (β-aminoethyl ether) \(N,N'\)-tetraacetate
- EHPG ethylenediaminedi (O-hydroxyphenyl) acetate
- DTPA diethylenetriaminepentaacetate
- HEDTA \(N\)-hydroxyethylethylenediaminetriacetate
- NTA nitrilotriacetate
- TEA triethanolamine

Reference electrodes:

- SCE standard calomel electrode
- SHE standard hydrogen electrode
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INTRODUCTION

Electrochemical technologies have been associated with the pulp and paper industry in several ways. These applications span a wide range of processes from the industrial scale production of basic chemicals for the pulp and paper industry such as sodium hydroxide, chlorine, sodium hypochlorite, chlorine dioxide, hydrogen peroxide to pilot and laboratory scale electrochemical salt splitting or water and air pollution treatments by electrochemical methods [Oloman, 1992].

In the area of pulp bleaching the first electrochemical applications involved the laboratory scale in-situ bleaching by electrochemically generated chlorine [Nassar, 1985]. Recently this method was modified to allow the formation in large amounts of hypochlorite ions, which act together with chlorine as a bleaching agent [Varennes et al., 1994].

As the pulp and paper industry shifts toward totally chlorine free bleaching processes, under both environmental and economic pressure, new possibilities for the application of electrochemical technologies are emerging.

Oxygen bleaching has been investigated at laboratory, pilot and industrial scales, for more than two decades. Due to the intensive research and gradual development of the process, in the early '90-s approximately half of all kraft pulp produced worldwide was oxygen bleached (~ 35 million ton per year) [Croon, 1993]. The advantages of oxygen bleaching can be summarized in one phrase, i.e. suitability for the so-called "closed cycle pulp mill" concept, where all water and effluent lines would be recycled and re-processed. There are studies that indicate considerable economic benefits of this process, beside the obvious environmental gains. For example the total operation costs could be 15 to 30 $US per ton less than the costs of the conventional bleaching stage, due mainly to lower chemical and energy costs [Croon, 1993]. The "closed cycle pulp mill", based on oxygen
bleaching should also be able to deliver very high bleached pulp quality. The oxygen bleached pulp should have a final Kappa number in the range of 6 to 8 while the viscosity of the pulp is maintained at high values, above at least 15 cP. The final brightness of the pulp must be between 85 to 90% ISO.

At this stage it is very difficult to meet these demanding conditions. It is well documented in the literature that the oxygen bleaching cannot remove more than 45-50% of the lignin without significantly damaging the pulp carbohydrates, i.e. reducing the tensile strength of pulp [McGrouther et al., 1994]. Considering that the usual Kappa number of the softwood pulp entering the oxygen bleaching stage is between 25 and 30, a 50% removal generated by oxygen delignification would give a final Kappa number of only 12-13 (at most). Thus, even under the intensive conditions that are common for a mill scale use of the oxygen bleaching process (oxygen pressure above 0.6 MPa, temperature ~ 100 °C, alkali concentration 2 to 5% and pulp consistency ~ 25 to 30%) the quality demand of the modern, "closed cycle mill" cannot be realized.

Two approaches have been undertaken in order to deal with this problem. The first approach involves more efficient pulping of the softwood to generate lower Kappa number pulp that enters the bleaching stage (e.g. 10 to 15) and the second one involves improved oxygen bleaching processes, in order to exceed the 40-50% lignin removal limit.

The pretreatment of pulp with certain chemicals (e.g. sulfuric and peroxy acids, nitrogen oxides) or development of efficient carbohydrate protecting agents (e.g. magnesium compounds, chelating agents) brought about some success in improving the oxygen bleaching stage.

Another research direction is the development of complex catalytic systems for oxygen bleaching, part of which would act as promoter of the delignification reaction while the other part would serve as an inhibitor of the carbohydrate degradation, thus generating a selective delignification [Masura, 1993]. The catalytic systems studied so far are based on transition metal complex compounds, working according to a redox
mechanism (i.e. with the change of the oxidation state of the transition metal ion) [Perng, 1993a; Watson et al., 1993]. Thus, the window for the involvement of electrochemical methods has been opened.

The continuous, electrochemical, \textit{in-situ} regeneration of the active form of the catalyst (usually the higher oxidation state of the transition metal ion) could improve both the delignification rate and the selectivity of the bleaching. The most studied electrochemical mediator (redox catalyst) so far, is the ferri/ferro cyanide couple [Godsay et al., 1988; Perng, 1993a]. These studies showed that under milder conditions than in the conventional oxygen bleaching the delignification rate can be significantly improved in the presence of both ferri/ferrocyanide and current, but unfortunately significant carbohydrate degradation occurred as well, generating unsatisfactory selectivity values.

The objective of the present work was to look at a trivalent manganese complex, with an aminopolycarboxylate ligand, namely Mn(III)CyDTA*, as a potential redox catalytic system at atmospheric oxygen pressure and temperatures between 25 and 80 °C. The Mn(III) would represent the active form in the delignification reaction, while the ligand, CyDTA and eventually the reduced form, i.e. Mn(II), might act as inhibitors of the carbohydrate degradation. The Mn(III)CyDTA is difficult to synthesize (is not available on the market and its classical chemical synthesis is tedious). Thus, its synthesis by a new and more convenient method (e.g. electrochemical route) had to be tackled.

Also electrochemical techniques (e.g. cyclic voltammetry) are helpful in the fundamental investigation of the electrochemical properties of a potential catalytic system of the oxygen bleaching process. The reduction potential of the transition metal compound must be above +0.4 V/SHE** to present any catalytic activity and it must possess fast anodic oxidation kinetics for an efficient \textit{in-situ} regeneration [Perng et al., 1993]. The

* \textit{(trans-Cyclohexane-1,2-diamine-}N,N,N',N''-tetraacetato) manganate (III) 

** standard hydrogen electrode
cyclic voltammetry investigations had to be performed for Mn(III)CyDTA as well, to better predicts its fundamental electrochemical characteristics under the actual bleaching conditions. Furthermore, the cyclic voltammetry studies can supply information about the feasibility of different electrode materials as anodes in the electrochemical production of Mn(III)CyDTA.

The electrochemically mediated oxygen bleaching using Mn(III)CyDTA depends on a large number of process variables such as: temperature, oxygen activity, pH, current, Mn(III) conc. By employing statistical experimental design both the main and interaction effects between variables can be assessed, thus a fairly good representation of the system becomes possible.

Generally speaking the field of in-situ electrochemically mediated oxygen bleaching is new, and there is space for creative and speculative investigations that may lead to new processes.
Chapter 1
BACKGROUND and LITERATURE REVIEW

1.1 Elements of Wood and Pulping Chemistry

Wood is one of the most important renewable resources. Its efficient harvesting and processing, from both economic and environmental point of view, depends on scientific knowledge from various fields such as: wood chemistry, chemical reaction engineering, environmental engineering and others.

On the way from tree to pulp and paper products, the wood fiber goes through several mechanical and chemical stages. Understanding the chemical engineering aspects of processes like mass transport of reactants to and intra-fiber (a gas-liquid-solid system) or the kinetics and mechanism of oxygen bleaching, requires some basic information about the structure and chemical composition of wood and pulp fibers.

This section provides such information as: fiber structure, lignin and carbohydrate structure and distribution in the fiber, kraft pulp and its characteristics and lignin leaching from kraft pulp into electrolyte solutions.

1.1.1 Classification of Wood: Softwood and Hardwood

There are many available criteria for classification of wood, e.g. density, age, cell type etc., [Paszner, 1993]. However the most common classification in the pulping and bleaching literature is: softwood and hardwood.

Conifers or cone-bearing trees are called softwoods, while deciduous trees, those that usually lose their leaves in the autumn, are generally called hardwoods [d'A.Clark, 1985]. There are significant differences between these two categories with respect to the structure, length, diameter and chemical composition of the fiber (Fig.1).
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The longer, thicker, more uniform and with less extractive content, softwood fibers are more suitable for pulping and papermaking than hardwoods [Rydholm, 1965]. However, in recent years, hardwoods are increasingly used in pulping due partly to their abundance, e.g. in Europe there are 10 softwood and 51 hardwood species [Sjostrom, 1993].

**SOFTWOODS**
- Fiber: length (mm): 3-6
- Diameter (mm): 25-60x10^{-3}

**HARDWOODS**
- Length (mm): 0.8-1.5
- Diameter (mm): 10-40x10^{-3}

Figure 1: Fiber dimension and average composition of softwoods and hardwoods (modified after Smook, 1992)

1.1.2 Structure of Wood Fiber

The ultimate structural element of wood is the cell. Varying in shape according to their functions, they provide the necessary mechanical strength of the fiber and also they assure the liquid transport as well as the storage of reserve food supplies in the living tree.

The different parts of the cell wall, containing almost all of the chemical components of the fiber, are the sites of reactions in chemical pulping and bleaching. The cell wall
layers are concentrically arranged because of the differences in chemical composition and orientation of the components (Fig. 2).

**Figure 2**: A scheme of the cell wall structure with the cellulose microfibrils for a softwood tracheids [Rydholm, 1965]; [Fengel and Wegener, 1984].

ML = middle lamella, P = primary wall, S1 = outer secondary wall, S2 = main secondary wall, T = tertiary wall, W = warty layer

The individual cells are connected together by a thin layer, called *middle lamella*. It is mainly composed of lignin, having a thickness of about 0.2-1 micrometers [Sjostrom, 1993]. During the chemical pulping process it is partially dissolved (i.e. delignified), allowing the fibers to separate.

The *primary wall* is only 0.1 - 0.2 μm thick, consisting of cellulose, hemicelluloses, pectin and proteins completely embedded in lignin [Sjostrom, 1993].
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The subsequent two layers (Fig. 2) belong to the *secondary wall*. The outer secondary wall (or S1 layer) is 0.2 - 0.3 μm thick. The main secondary wall (or S2 layer) is the thickest part, about 1-10 μm. It has a high cellulose content and its characteristics (i.e. thickness, orientation angle of cellulose microfibrils) have a strong influence on the fiber stiffness and other papermaking properties [Rydholm, 1965].

The *tertiary wall* (T layer or sometimes called the inner secondary wall, [Sjostrom, 1993]) is of a particular interest from a pulping and bleaching point of view, since it is the first part of the fiber wall to come in contact with chemicals\(^*\). It has a dense microfibrilar structure, resistant to chemicals, although it has a thickness of only 0.07-0.08 μm [Rydholm, 1965].

The *warty layer* (W) is a thin amorphous membrane covering the luminal surface of all softwoods and contains a warty deposit of a still unknown composition.

The distribution of the main chemical components i.e. cellulose, lignin and hemicelluloses in the fiber wall is given in Figure 3.

\(^*\) The chemicals diffuse into the fiber from the lumen (warty layer) toward the primary wall and middle lamella.
1.1.3 Chemical Composition of Wood Fiber

The major components of wood fiber are: cellulose, hemicelluloses, lignin and extractives. In addition small amounts of pectins, starch, proteins and metals can be found. The extractives, low molecular weight organic compounds, being non-structural constituents are completely eliminated in processes prior to bleaching. Thus their chemical structure and properties are not presented in the present work.

a) CELLULOSE

As it can be seen from Figure 1, cellulose is the main constituent of wood. It is a homopolysaccharide composed of β-D-glucopyranose units which are linked together by (1-4)-glycosidic bonds (Fig.4).
The individual chains are held together by hydrogen bonds thus the supermolecular structure of cellulose is formed. There are zones in the fiber where due to a regular system of the H-bonds, the cellulose is organized in crystalline structures. Consequently crystalline and amorphous regions are alternating each other (Fig. 5).

These regions play an important role in the cellulose degradation during bleaching. The more degraded the cellulose the less strength the pulp has. It is assumed that the disordered (i.e. amorphous) parts are the starting point of cellulose degradation [Rydholm, 1965].

Figure 5: a) A model for the arrangement of cellulose in the fiber. Crystalline (ordered) and amorphous (disordered) regions can be identified.

b) Monoclinic crystal space unit of cellulose [Fengel and Wegener, 1984]
b) HEMICELLULOSES (POLYOSES)

The hemicelluloses are heterogeneous polysaccharides with branched and much shorter chains than cellulose. There are structural differences between softwood and hardwood polyoses. The principal softwood hemicellulose is galactoglucomannan (Fig.6):

![Structure of galactoglucomannan]

Figure 6: The structure of galactoglucomannan. Sugar units: β-D-glucopyranose (GlcP); β-D-mannopyranose (Manp); β-D-galactopyranose (Galp). R=CH₃- or H ; Ac=acetyl group [Sjostrom, 1993]

The hemicelluloses are important in bleaching due to their role in swelling and/or contraction of the pulp fiber, they also contribute to the pulp strength and being linked to lignin by chemical bonds, they play a role in the selectivity of delignification.

c) LIGNIN

Lignin is an amorphous, polyphenolic, highly branched polymeric material of phenylpropane units. Its biosynthesis involves two major phases, i.e. the enzymatic synthesis of the lignin precursors (Fig. 7) from D-glucose, followed by a dehydrogenative polymerization of the precursors to form the branched macromolecule. The free radicals involved in the second phase are responsible for the highly branched, random lignin structure.
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Figure 7: The precursors (building units) of lignin: I = p-coumaryl alcohol; II = coniferyl alcohol; III = sinapyl alcohol [Fengel and Wegener, 1984].

There are several classifications of lignins according to their solubility in various solvents or their method of isolation. However, from a bleaching point of view the softwood (or guaiacyl) and hardwood (or guaiacyl-syringyl) lignins are the most common ones [Sarkanen and Hegert, 1971].

A wide variety of linkages are possible between the phenylpropane units. Some of them are presented in Figure 8.

The complete structure of the lignin in various morphological regions of the wood fiber or in different types of pulp is still unknown. However, the general aspects of the lignin structure are known and several models were proposed [Fengel and Wegener, 1984]. One of the most widely accepted structural scheme of softwood lignin is the Adler formula (Fig. 9).
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Figure 8: Common linkages between the phenylpropane lignin units [Sjostrom, 1993].

Figure 9: A structural segment of softwood lignin (Adler formula) [Fengel and Wegener, 1984]
d) LIGNIN - CARBOHYDRATE LINKAGES

Due to the high photo-chemical instability of the lignin structure, to obtain high quality pulp and paper products, the lignin must be eliminated as completely as possible. This task is realized during the pulping and bleaching processes. It is well known that the lignin removal is always accompanied to some extent by carbohydrate degradation as well. Thus the problem of selective delignification arises.

The main reason for this problem is the chemical bonding of lignin with some of the pulp carbohydrates. Lignin-hemicelluloses linkages are by far the most frequent ones, although there are a few lignin-cellulose bonds as well [Tingsvik, 1989].

An example of lignin-hemicellulose association is given in Figure 10.

![Figure 10: Schematic illustration of the connections between softwood hemicelluloses and lignin [Fengel and Wegener, 1984].](image)

1.1.4 Kraft Pulping and Pulps

By definition, pulping is a process by which wood is reduced to a fibrous mass [Smook, 1992]. Chemical, mechanical, thermal or/and combinations of these treatments are in practice today.

In chemical pulping, in order to dissolve away the lignin, the wood chips are cooked in aqueous solution with certain chemicals at elevated temperature and pressure. The kraft
process ("kraft" it means "strong" in German and Swedish), involves cooking the wood chips in a solution of sodium hydroxide and sodium sulfide (Na₂S). Typical conditions are: liquor pH>13; cooking temperature 170-180 °C and cooking time 2-4 hr. [Smook, 1992].

The importance of the kraft process is illustrated in Figure 11.

![Pie chart showing percentages of pulping processes]

Figure 11: The relative contribution of the three major pulping processes to the total North American pulp production in 1990. Total pulp production was 88,509 millions of ton/year [based on data from Smook, 1992].

The trend shown in Figure 11 is representative for the whole, worldwide, pulp market as well.

The most common quantitative variables used to describe the kraft pulp are: Kappa number for lignin content and viscosity for carbohydrate content.

A) Kappa number (TAPPI T236cm-85)

For a softwood kraft pulp:

Lignin content(%)=0.147xKappa number
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The standard method for Kappa number determination is based on the potassium permanganate oxidation of the pulp in acidic media for 10 minutes. The residual KMnO₄ being determined by and iodometric method.

By definition, the Kappa number is the volume (in ml) of 0.1N potassium permanganate solution consumed by 1 gram of moisture free pulp. A decrease in Kappa number it means delignification has occurred.

B) Viscosity (TAPPI T230 cm-82)

The viscosity measures the average degree of polymerization $DP$, of the pulp sample, mainly that of cellulose. Thus, the extent of carbohydrate degradation caused by pulping or bleaching processes can be checked. A decrease in viscosity it means lower average molecular weight and $DP$, consequently pulp degradation has occurred.

The TAPPI viscosity ($v$, cP) is based on the viscosity of 0.5% cellulose solution, using 0.5M cupriethylenediamine(CED) as solvent and a capillary viscometer.

The TAPPI viscosity ($v$, cP) can be converted into intrinsic viscosity ($Iv$, dm³/kg), which is a measure of the effective hydrodynamic volume of the molecule [Sihtola et al., 1963]:

\[
\text{in CED, } \quad Iv = 954 \log(v) - 325 \quad (1)
\]

Furthermore, the intrinsic viscosity gives the viscosity average degree of polymerization, $DP$, according to the following equation [Rydholm, 1965]:

\[
DP^{0.905} = 0.75(Iv) \quad (2)
\]

It must be emphasized that the $DP$ given by eq. (2) has no exact meaning but it is close to the weight average degree of polymerization [Rydholm, 1965].
1.1.5 Chemical Structure of the Residual Lignin in the Kraft Pulp

During the kraft pulping stage the lignin suffers important structural modifications. At the end of this phase its structure can be very different from its original (i.e. unpulped) one. The structural features of the residual lignin in kraft pulp play an important role in how easily it can be further degraded in the next stage, i.e. bleaching.

The most important changes are as follows [Lachenal and Nguyen-Thi, 1993]:
- the residual lignin is much more condensed than the original one, that means an increased number of carbon-carbon bonds (Fig. 8). This makes the bleaching more difficult.
- increased hydrophilicity of residual lignin, due to both the liberation of some phenolic hydroxyl groups and the higher number of alcoholic groups located on side chains. This is an advantage for a subsequent oxygen bleaching in alkaline media
- the number of remaining, easily degradable, β-O-4 linkages (Fig.8) is very small
- there are more double bonds on side chains conjugated to the aromatic ring causing an increased light sensitivity.

1.1.6 Cell Wall Swelling and Lignin Leaching into Electrolyte Solutions

The penetration of bleaching chemicals toward the reaction site and the leaching of lignin from unbleached pulp into electrolyte solutions, depends on the swelling of the cell wall, temperature, pH, concentration and composition of the electrolyte solution.

The cell wall swells about 10 to 20% in the initial stages of delignification during kraft pulping. As the pulping progresses no additional swelling occurs if the majority of hemicelluloses are removed. In the final stages of kraft pulping (at yields below 60%) a
significant contraction of the cell wall volume was observed [von Byrd, 1989]. Thus the cell wall of the kraft pulp that enters the bleaching stage is already in a contracted state.

When unbleached kraft pulp is suspended in water or any other electrolyte solution, some lignin leaches from the pulp into the solution. A schematic representation of this phenomena is given in Figure 12.

![Diagram of lignin leaching](image)

**Figure 12: A schematic representation of lignin leaching [Favis and Goring, 1984]**

The rate of leaching increases with increase in the temperature and decrease in electrolyte concentration. Increased swelling of the fiber at higher temperatures and lower electrolyte concentrations causes an increase in the size of the pulp fiber pores, thus the diffusion of lignin through the fiber wall into solution, is faster [Wilcox and Goring, 1990]. The rate of diffusion of lignin through the fiber wall depends on the interaction of the lignin with the structure of hemicelluloses and cellulose hydrogel which makes up the wet cell wall, on the geometrical configuration of the pores in the cell wall and on the conformation of the lignin macromolecule [Favis and Goring, 1984].

The measured intra-fiber diffusion coefficient of kraft lignin when the pulp is in contact with distilled water, was found to be: $3.5 \times 10^{-18} \text{ m}^2/\text{s}$ at 20°C [Willis and Goring, 1985].
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At a 0.3M NaCl concentration, the leaching was further reduced, while in the presence of a bivalent cation (e.g. Mg$^{2+}$), the leaching was completely eliminated at cation concentrations above 0.01M [Favis and Goring, 1984].

On the other hand the amount of leached lignin from softwood kraft pulp increased with increasing pH (Fig. 13).

![Figure 13: Plot of water retention value (WRV) and leached lignin, after 270 min., vs. pH for softwood kraft pulp [Wilcox and Goring, 1990].](image)

1.2 Oxygen Chemistry and Electrochemistry

The goal of this section is to introduce the "other side" of the oxygen bleaching system, namely, the molecular oxygen (or dioxygen) and the oxygen containing reactive intermediates (e.g. radicals, radical anions etc.). Their chemical and electrochemical properties can partially explain some of the advantages and limitations of the oxygen bleaching process.
1.2.1 Redox Properties of Oxygen Species

Both allotropic forms, O$_2$ and O$_3$ (ozone) are employed as bleaching chemicals.

The oxygen can be reduced to hydrogen peroxide and ultimately to water:

\[ O_2 + 4H^+ + 4e^- \Leftrightarrow 2H_2O ; \quad E_{O_2/H_2O} \]  \hspace{1cm} (3)

The "oxidizing power", expressed by the actual reduction potential, $E_{O_2/H_2O}$, is dependent on the oxygen activity [O$_2$], pH and temperature T, according to the Nernst equation:

\[ E_{O_2/H_2O} = E^0_{O_2/H_2O} + \frac{2.303RT}{F} \left( \frac{1}{4} \log [O_2] - pH \right) ; \quad (4) \]

where $E^0_{O_2/H_2O}$ = standard oxygen reduction potential

(+1.229 V/SHE @ pH= 0)

$F$ = Faraday constant

$R_g$ = universal gas constant

As it can be seen from eq. (4), the reduction potential increases with increasing oxygen activity (or oxygen pressure) and decreasing pH.

A complete diagram of the reduction potentials vs. pH for various dioxygen species involved in oxygen bleaching, is presented in Figure 14.
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Figure 14: Standard reduction potentials vs. pH for oxygen species in aqueous solution @ 25 °C and 1 atm oxygen pressure. In brackets the formal potentials (i.e. for oxygen at unit activity) are presented [Sawyer, 1991].

### 1.2.2 Reactivity of Dioxygen and its Activation

From Figure 14, several important conclusions can be drawn.

First of all, the mechanism of oxygen reduction does not occur in one four electron step, as would be suggested by the overall reaction given by eq. (3). On the contrary, is a sequential, "step-wise", reduction process, involving several one-electron stages and a large variety of reactive, short-lived intermediates. The first step in alkaline and neutral media being the generation of the superoxide radical ion, $O_2^-$. The superoxide radical ion is a weak oxidizing agent in alkaline media ($E^0 = +0.20 \text{ V/SHE} @ \text{pH}=14.0$) when compared with the peroxide ion ($HO_2^-, E^0 = +0.876 \text{ V/SHE} @ \text{pH}=14.0$) or the hydroxyl...
radical (HO•, or H2O + O•-, \( E^0 = 1.77 \) V/SHE @ pH=14.0). These radicals are formed in subsequent steps and in fact most of the oxidation by oxygen is due to these species [Cotton and Wilkinson, 1988]. The efficient decomposition or rather dismutation of the superoxide radical ion into these highly reactive species is of a vital importance for a strong delignification during oxygen bleaching.

This is one point where a carefully selected transition metal coordination compound might help, as a so-called redox catalyst.

1.2.3 Reactivity of Oxygen Species and Interaction with Transition Metal Complexes

A) Catalysis of Superoxide Dismutation by Manganese Complexes

The general scheme of metal ion induced decomposition of superoxide is given by [Gratzl, 1990]:

\[
O_2^- + M^n \rightarrow HOO^- + HO^- + M^{n+1}; \tag{5}
\]

\[
O_2^- + M^{n+1} \rightarrow O_2 + M^n. \tag{6}
\]

The actual mechanism is much more complicated. In the presence of Mn(II) as catalyst, several pathways are possible, leading to Mn(III) or MnO2+. The particular pathway is dependent upon the ligand associated with Mn(I) and pH [Cabelli and Bielski, 1984].

In the case of manganese(II) aminopolycarboxylate complexes, of a special interest in the present work, it was found that most of them (e.g. Mn(II) with EDTA, HEDTA, DTPA, EDDA, EGTA, EHPG and NTA* ) do not catalyze the dismutation reaction efficiently. The catalytic rate constants for MnNTA and MnEDDA complexes decreased with increasing pH, at pH 8 or greater little if any catalysis takes place [Koppenol et al., 1986]. It was proposed that the formation of inactive hydroxo complexes is the main

* please see the ligand nomenclature
reason for the decrease of the catalytic rate constants with pH in the case of superoxide dismutation [Koppenol et al., 1986; Sychev and Isac, 1993].

B) Transition Metal Ion Catalyzed Peroxide Decomposition (Fenton Chemistry)

The other important oxidizing agent in oxygen bleaching system is the peroxide ion, \( \text{HOO}^- \), and its decomposition intermediate, the hydroxyl radical. The peroxide ion decomposes by both autodisproportionation and transition metal ion catalyzed processes:

i) Autodecomposition

\[
\text{HOO}^- + \text{HOOH} \rightarrow \text{HO}^- + \text{HO}^- + \text{HO}^+ \; ;
\]

(7)

ii) Transition metal ion induced decay [Gratzl, 1990]

\[
\text{HOOH} + \text{M}^{n+1} \rightarrow \text{HO}^- + \text{H}^+ + \text{M}^n \; ;
\]

(8)

\[
\text{HOOH} + \text{M}^n \rightarrow \text{HO}^- + \text{HO}^- + \text{M}^{n+1} \; ;
\]

(9)

where reaction (8) is slower than reaction (9).

The autodecomposition is enhanced in alkaline media, with a rate maximum between pH 11 and 12 [Galbacs and Csanyi, 1983] and at high temperatures (e.g. >110-120 °C).

The catalytic decomposition is known for over 100 years as Fenton chemistry [Sawyer, 1991]. The classic catalysts are iron(II) compounds. Various manganese compounds are also known to be effective catalysts of peroxide decomposition. In the presence of MnSO₄ for example, the rate of decay is of the first order vs. peroxide and the pH corresponding to the rate maximum is shifted from the usual range of 11.2 - 12.5 to 9.5 [Galbacs and Csanyi, 1983]. The coordination of Mn(II) ion with aminopolycarboxylate ligands such as CyDTA, EDTA, DTPA, NTA, diminishes the catalytic activity. The aminopolycarboxylate ligand is able not only to deactivate the
catalytically active metallic centers but also acts as a homogeneous sequestering agent, scavenging the hydroxyl radicals which are formed during the peroxide decomposition. This is the reason why the aminopolycarboxylate ligand itself, undergoes decomposition and after a certain time it cannot provide any further inhibiting effect [Galbacs and Csanyi, 1983].

It is interesting to mention that the Mn(II) aqua-ion has no catalytic effect in the peroxide decompostion process, while the Mn(III) aqua-ion catalyses this reaction [Sychev and Isac, 1993].

1.2.4 Oxygen Solubility in Electrolyte Solutions and Mass Transfer in Filamentous Suspensions

The solubility of oxygen in aqueous salt solutions is less than in pure water (salting-out effect). The relationship between the salt concentration ($c_s \text{ mole/l}$) and the solubility of a non-electrolyte (e.g. oxygen) in an electrolyte solution ($S; \text{ mole/l}$), is given by the modified Setchenov equation [Broden and Simonson, 1979]:

$$\log \left( \frac{S_0}{S} \right) = k_s c_s + k_i (S - S_0);$$

where

- $S_0 = \text{solubility of oxygen in pure water (mole/l)}$
- $S = \text{solubility of oxygen in an electrolyte (mole/l)}$
- $c_s = \text{salt concentration (mole/l)}$
- $k_s = \text{salting-out parameter (includes ion - non-electrolyte interactions)}$
- $k_i = \text{non-electrolyte self interaction parameter}$. 
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The salting-out parameter is influenced by temperature, salt concentration and oxygen partial pressure. A regression equation between $k_S$, temperature and NaOH concentration was established [Perng, 1993a].

The non-electrolyte self interaction parameter can be neglected if the solubilities are low [Broden and Simonson, 1979].

In Figure 15, the oxygen solubility at 0.1 MPa is presented, under conditions that are relevant to this work.

![Figure 15: Oxygen solubility at 0.1 MPa vs. temperature at different NaOH concentration levels [Perng, 1993a].](image)

At low oxygen pressures, below 0.5 MPa, and temperatures over 75 °C, the solubility increases linearly with pressure, indicating that Henry's law is obeyed (i.e. close to ideal behaviour). At temperatures below 75 °C and pressures over 2 MPa, a slight deviation from ideality was observed [Broden and Simonson, 1979].

The oxygen bleaching system, besides the electrolytes (e.g. NaOH and other salts), contains various amounts of pulp as well. The presence of the filamentous mass has an important influence on the gas-liquid mass transfer capacity for oxygen. Experiments performed in suspensions of cellulose fibers with concentrations ranging from
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0 to 20 kg/m$^3$, showed a reduction in oxygen transfer rates with increasing fiber concentrations (please see Figure 16) [Svihla and Hanley, 1992].

![Figure 16: Gas-liquid mass transfer capacity for oxygen vs. impeller speed as a function of cellulose fiber concentration (the 10 kg/m$^3$ concentration is representative for the present work). Pressure 1 atm, temperature 20 °C [Svihla and Hanley, 1992].](image)

The mechanism by which the fibers reduce the gas-liquid mass transfer coefficient is not fully understood. They might act as sites for bubble coalescence thereby decreasing the interfacial area or rheological effects can be involved as well [Svihla and Hanley, 1992].

1.3 OXYGEN BLEACHING

The purpose of the bleaching operation is to impart the desired final physical and chemical properties of the pulp. This is usually done by removing or modifying the residual lignin of the unbleached pulp. The operation and processes applied, depend entirely on the character of the unbleached pulp and the desired quality for the bleached pulp.

Two categories of methods can be identified: lignin-preserving and lignin-removing bleaching [Sjostrom, 1993].
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The lignin-preserving bleaching (or brightening) is applied to high-yield mechanical and semichemical pulps were only a moderate brightness increase is desired. In this case just the cromophore groups in the lignin structure are selectively destroyed, while the high pulp yield is preserved.

When high and stable brightness is desired, it is necessary to perform lignin-removing bleaching (or simply bleaching). This is applicable to chemical pulps (e.g. kraft pulp) and some grades of semichemical pulps.

The goal of this section is to present the advantages and disadvantages of the oxygen bleaching (i.e. lignin-removing) process, based on some mechanistic and kinetic aspects of the oxygen reaction in alkaline media with both lignin and carbohydrates.

1.3.1 Classification, General Principles and Evolution of Bleaching Processes

A large number of bleaching processes have been studied and developed, each of which comprises a certain combination of steps, called bleaching sequences. These sequences can span a wide range of pH, from acidic to alkaline and also a large variety of bleaching chemicals from chlorine to oxygen, ozone and even enzymes.

A comprehensive classification of the bleaching methods is further complicated by the fact that during bleaching a large number of oxidative, short-lived species are generated, whose reactions interfere with those of the original bleaching reagent.

One of the most successful rationalization of the complex course of bleaching, divides the reactions in three categories with respect to the initial reacting species (please see Figure 17) [Gierer, 1990].
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The categories are as follows:

i) **cationic processes**: occurring in acidic media, e.g. bleaching with HOCl generates cationic species like Cl\(^{+}\), also ozone bleaching belongs to this category. These processes are oxidative in nature.

ii) **radical processes**: in acidic, neutral or alkaline media, e.g. bleaching with oxygen generates radicals like HO\(^{•}\), HO\(^{2•}\), or bleaching with ClO\(_2\) involves Cl\(^{•}\) radicals. Like cationic processes, radical processes are mostly oxidative in nature, attacking aromatic and olefinic lignin structures.

iii) **anionic processes**: operating in alkaline media, e.g. bleaching with HOO\(^{−}\), HO\(^{−}\) or ClO\(^{−}\)These reactions are reducing carbonyl and conjugated carbonyl structures.

Consequently, it can be stated that oxygen bleaching, occurring in alkaline media is mainly a **radical process**, due to reactive electrophile intermediates like HO\(^{•}\), HO\(^{2•}\), attacking in oxidative manner the aromatic and olefinic structures of lignin. Also **anionic, nucleophile species**, especially HO\(^{−}\) and HOO\(^{−}\), contribute to oxygen bleaching.

The bleaching technologies, involving most of the species presented in Figure 17, have evolved during the years driven by economic, technological and lately, environmental considerations.

<table>
<thead>
<tr>
<th>cationic</th>
<th>radical</th>
<th>anionic</th>
</tr>
</thead>
<tbody>
<tr>
<td>acidic</td>
<td>acidic or alkaline</td>
<td>alkaline</td>
</tr>
<tr>
<td>Cl(^{+}), HO(^{•})</td>
<td>ClO(^{•}), H(_2)O, Cl(^{−}), HO(^{−}), NO(^{•})</td>
<td>S(_2)O(_5^{2−}) → ClO(^{−}), HOO(^{−})</td>
</tr>
<tr>
<td>H(^{+}), NO(_2^{+}), ClO(_2^{•})</td>
<td>NO(_2^{•}), ClO(^{•}), H(^{+})</td>
<td>e(^{−}), H(^{•})</td>
</tr>
<tr>
<td>oxidative</td>
<td>reductive</td>
<td></td>
</tr>
<tr>
<td>- 2 e(^{−})</td>
<td>- 1 e(^{−})</td>
<td>+ 1 e(^{−})</td>
</tr>
<tr>
<td>electrophiles</td>
<td>nucleophiles</td>
<td></td>
</tr>
<tr>
<td>aromatic and olefinic structures</td>
<td>carbonyl and conjugated carbonyl structures</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 17**: Classification of bleaching methods based on three categories [Gierer, 1990]
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As it can be seen from Table 1, the common bleaching sequences of the '60-s, involving large amounts of elemental chlorine and hypochlorite, have been replaced by the mid '80-s and early '90-s with technologies based on oxygen, chlorine dioxide and hydrogen peroxide.

Table 1: The Evolution of Bleaching Sequences [Sjostrom, 1993]. Sequence A was typical during the '60-s, sequence B represents the early '90-s bleaching practice, while sequence C is elementary chlorine free bleaching, representing the choice of the late '90-s

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Stage</th>
<th>Chemicals</th>
<th>Charge (kg/ton pulp)</th>
<th>Consistency (%)</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>C</td>
<td>Cl₂</td>
<td>55</td>
<td>4</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>NaOH</td>
<td>37</td>
<td>10</td>
<td>60</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>NaOCl</td>
<td>12</td>
<td>8</td>
<td>40</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>ClO₂</td>
<td>15</td>
<td>10</td>
<td>70</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>NaOH</td>
<td>7</td>
<td>10</td>
<td>65</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>ClO₂</td>
<td>5</td>
<td>10</td>
<td>70</td>
<td>240</td>
</tr>
<tr>
<td>B</td>
<td>O</td>
<td>O₂ + NaOH</td>
<td>15 + 20</td>
<td>10(30)</td>
<td>100</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>D40C60</td>
<td>ClO₂, Cl₂</td>
<td>12 + 20</td>
<td>4</td>
<td>70</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>EO</td>
<td>NaOH + H₂O₂</td>
<td>15 + 5</td>
<td>10</td>
<td>70</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>ClO₂</td>
<td>17</td>
<td>10</td>
<td>70</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>E + P</td>
<td>NaOH + H₂O₂</td>
<td>8 + 3</td>
<td>10</td>
<td>70</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>ClO₂</td>
<td>5</td>
<td>10</td>
<td>70</td>
<td>180</td>
</tr>
<tr>
<td>C</td>
<td>O</td>
<td>O₂ + NaOH</td>
<td>16 + 18</td>
<td>10</td>
<td>100</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Xe</td>
<td>e.g., EDTA</td>
<td>2</td>
<td>4</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>E + P</td>
<td>NaOH + H₂O₂</td>
<td>14 + 19</td>
<td>10</td>
<td>80</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>ClO₂</td>
<td>32</td>
<td>10</td>
<td>70</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>E + P</td>
<td>NaOH + H₂O₂</td>
<td>11 + 2</td>
<td>8</td>
<td>70</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>ClO₂</td>
<td>8</td>
<td>10</td>
<td>70</td>
<td>180</td>
</tr>
</tbody>
</table>

The old processes using chlorine in the first bleaching stage, generated AOX levels (i.e. the amount of organically bound chlorine) in the range of 7 kg/ton of pulp, composed of very toxic polychlorinated structures and chlorinated dibenzo-dioxins. The total discharge of organic material, COD, was also very high, about 100 kg/t pulp. The modern sequences (please see sequence C in Table 1), being elemental chlorine free (ECF), discharge only 0.1 - 1.0 kg AOX/t pulp while COD is down to about 50 kg/t pulp. The most advanced bleaching technologies are totally chlorine free (TCF), generating no
detectable AOX levels and the discharge of COD is down to below 20 kg/t pulp [Axegard et al., 1993].

Beside these obvious environmental benefits, the presence of oxygen bleaching stages have economic benefits as well. The manufacture of oxygen requires about one-eight of the energy required to make the equivalent amount of chlorine. Other energy related benefits include better recovery of heat from the burning of the material removed from the pulp in the oxygen stage and lower refining energy requirements of oxygen bleached pulps [McDonough, 1990].

Perhaps, most important of all, oxygen bleaching is suitable for the so-called closed cycle mill concept, i.e. closing up the water circuits from bleach plant effluents, condensates etc. It was claimed that the "closed cycle mill", would require a 15 to 25 $US/t of pulp lower operation cost than the existing processes, while producing a very high quality pulp with drastically reduced discharge [Croon, 1993].

Due to the above presented reasons, oxygen becomes widely used as a bleaching agent (please see Figure 18).

Approximately half (i.e. 35 million ton per year) of all kraft pulp produced worldwide is oxygen delignified [Croon, 1993].

![Figure 18: Development and forecast for the use of bleaching chemicals in Sweden [Sjostrom,1993].](image-url)
1.3.2 Mechanism of Oxygen Delignification

Most of the knowledge regarding different aspects of the oxygen delignification mechanism, comes from studies using lignin model compounds. Therefore, these results cannot be regarded as a comprehensive answer to the complex problem of oxygen-lignin reaction. Furthermore, the situation is complicated by the fact that the structure of substrate, i.e. residual lignin which has survived the kraft pulping stage, is virtually unknown. Some basic changes of the lignin structure were presented in section 1.1.5. However, a fairly good representation of the process is still possible.

In alkaline media, the phenolic hydroxyl groups of the lignin structure are ionized, forming phenolate anions. The first step of the oxidative, radical process is the formation of the phenoxy radical from the phenolate anion (please see Figure 19).

It has been suggested in several studies that the abstraction of an electron from the phenolate anion, forming a phenoxy radical, is the rate determining step of the entire lignin oxidation reaction by molecular oxygen [Gersman and Bickel, 1959 and 1962; Johansson and Ljunggren, 1993].

Under the oxygen delignification conditions, the rate constant of the phenoxy radical interaction with oxygen is \( k=10^3 \) l/(mole sec), while for the reaction of molecular phenol compounds with oxygen the rate constant is only \( k=10^{-10} \) l/(mole sec) [Chupka, 1991]. These values of the rate constants are an additional proof that the formation of phenoxy radicals is the rate determining step.
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Figure 19: Possible pathways for the reaction of an intermediate phenoxy radical formed from a phenolate anion. $R =$ the rest of the lignin structure [Johansson and Ljunggren, 1993].

There appears to be a network of autocatalytic oxidation reactions between the starting fragments (i.e. phenoxy radicals) and the oxidation products (Fig. 20). Electron-excited states of organic intermediates like aldehydes, ketones, quinones are involved in this network of radical processes, characterized by non-linear kinetics [Chupka, 1991].

**INITIATION**

\[
\begin{align*}
RH & \quad + \text{HO}^- \rightarrow R^- + \text{HOH} \\
RH & \quad + \text{HOO}^- \rightarrow R^- + \text{HOOH} \\
RH & \quad + \text{O}_2 \rightarrow R^- + \text{HOO}^-
\end{align*}
\]

**PROPAGATION**

\[
\begin{align*}
R^- & \quad + \text{O}_2 \rightarrow \text{ROO}^- \\
\text{ROO}^- & \quad + RH \rightarrow \text{ROOH} + R^-
\end{align*}
\]

**TERMINATION**

\[
\begin{align*}
R^- & \quad + \text{HO}^- \rightarrow \text{ROH} \\
R^- & \quad + \text{HOO}^- \rightarrow \text{ROOH} \\
R^- & \quad + R^- \rightarrow R-R
\end{align*}
\]

Figure 20: Phases of auto-oxidation (chain reactions) in oxygen delignification. $RH =$ lignin (phenolate anion form) [Gratzl, 1990].
The various structural elements (i.e. chemical bonds, functional groups etc.) of the residual lignin structure, present different reactivities against oxygen and other oxidative species during bleaching (please see Figure 21).

The reactivity order given in Figure 21, highlights some important features as follows:
- a high number of free phenolic groups is very important for the delignification to occur
- a hydroxyl or methoxyl group in the ortho position to the free phenolic group enhances the degradation rate
- the presence of carbonyl or hydroxyl groups on the side chain α–carbon has a negative effect
- double bonds on the side chain (especially conjugated double bonds) are very reactive during oxygen bleaching
- the formation of new crosslinkes from radical coupling (e.g. biphenolic structures) are very resistant toward oxygen

![Figure 21: The order of reactivity (on a scale of decreasing reactivities) of different structural elements of lignin under technical oxygen bleaching conditions [Johansson and Ljunggren, 1993].](image)
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In recent years the individual role, during oxygen bleaching, of various radical species received much of attention. Using modern physico-chemical methods such as pulse radiolysis and chemiluminescence, the role of hydroxyl radicals was extensively investigated [Ek et al., 1987; Backa et al., 1989; Giere and Jansbo, 1991; Gierer et al., 1991; Gierer and Yang, 1991]. The role of superoxide anion radicals (O$_2^-$) and their undissociated counterparts, hydroperoxyl radicals (HOO$^-$) were studied as well [Gierer and Yang, 1993].

As a conclusion of this section, the oxygen delignification of kraft pulp leads to the elimination of aromatic units carrying free phenolic hydroxyl groups. Carboxylic groups are introduced into the lignin, thus increasing its water solubility. The biphenolic or other condensed structures in lignin seem to survive the oxygen bleaching stage to a considerable degree [Gellerstedt et al., 1986; Tanada et al., 1993].

1.3.3 Mechanism of Carbohydrate Degradation during Oxygen Bleaching. Selectivity

Due to the same radical species which cause delignification, some of the pulp carbohydrates are degraded during oxygen bleaching. The goal is to minimize the carbohydrate degradation in order to maintain the pulp yield and viscosity in a reasonable range for further utilization. Generally it is considered that a bleached pulp with a viscosity below 12cP is totally unacceptable for commercialization [Paszner, 1993]. Thus the problem of selective delignification must be approached. It is the competition between the reactions of lignin and carbohydrates (especially cellulose) with radicals like HO$^-$ that virtually determines the selectivity (please see Figure 22).
By a "macroscopic definition", the selectivity of the oxygen bleaching process is the ratio between the delignification rate, \( dK/dt \), and the carbohydrate degradation rate, \( dv/dt \), under the same experimental conditions. At a molecular level, the selectivity is expressed as the ratio of rate constants for delignification \( (k_L) \) and carbohydrate degradation\( (k_C) \).

It was experimentally determined that the selectivity vs. \( \text{HO}^- \) attack lies between 5 and 6 [Ek et al., 1989]. Thus the hydroxyl radicals attack the lignin structure about 5-6 times faster than the carbohydrate structure. At pH above 12, the selectivity becomes worse because \( \text{HO}^- \) decomposes to give \( \text{O}^- \cdot \) which attacks the lignin and carbohydrate at about the same rate [Ek et al., 1989]. In practice the selectivity of the oxygen bleaching is even worse than what would be expected on the basis of fundamental studies.

The poor selectivity, made the oxygen bleaching process unfeasible until the early '70s, when Robert et al. discovered the inhibiting effect of Mg(II) compounds (e.g. MgCO₃, MgSO₄) on carbohydrate degradation [Singh and Dillner, 1979]. Two mechanisms were proposed to explain the inhibiting effect of Mg(II) compounds [Sjostrom and Valttila, 1978] :

a) in alkaline media the Mg(II) is precipitated as hydroxide which forms a protecting adsorption layer on the fiber. The magnesium hydroxide being able to deactivate the harmful radical species and also certain damaging traces of transition metal ions.
b) the other mechanism proposes the formation of Mg - Carbohydrate complexes that are stable and not readily oxidizable because the sensitive carbohydrate end groups are linked to Mg(II).

Other studies revealed that using a combination of triethanolamine (0.6 mM/10g of pulp) and Mg(II) (e.g. 0.4% MgCO₃/pulp) gave a better inhibiting effect than that of either of them used separately [Sjostrom and Valttila, 1972]. However, the triethanolamine proved to be ineffective in the presence of manganese.

### 1.3.4 Overall Reaction Kinetics in Oxygen Bleaching

The oxygen bleaching occurs in a heterogeneous, 3-phase, gas-liquid-solid system (i.e. oxygen - electrolyte solution - fiber). The overall kinetics is influenced by both mass transfer and chemical reaction steps. The entire bleaching process can be described as follows (please see Figure 23):

i) oxygen transfer from the bulk gas phase to the gas-liquid interfacial boundary layer
ii) oxygen transfer from the gas-liquid interface to the bulk liquid phase
iii) transfer of oxygen, hydroxyl ion and other chemical species (e.g. redox catalyst) by convection and diffusion from the bulk liquid phase to the liquid film surrounding the fiber
iv) diffusion of oxygen, hydroxyl ion and other species through the liquid film to the fiber
v) intrafiber diffusion of oxygen, hydroxyl ion and other species with simultaneous delignification and carbohydrate degradation at the reaction sites in the fiber
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Figure 23: Schematic representation of the oxygen mass transfer sequences during oxygen bleaching [Hsu and Hsieh, 1988].

According to this model, the overall delignification and cellulose degradation rate of the "pure" oxygen bleaching (i.e. without redox catalyst), can be formulated as follows:

\[ r_{overall,L} = f(k_{liq} a_{liq}, k_s a_s, k_L, [HO^-], [O_2], K, T) \]  \hspace{1cm} (11)

\[ r_{overall,C} = f(k_{liq} a_{liq}, k_s a_s, k_C, [HO^-], [O_2], m_n, T) \]  \hspace{1cm} (12)

Both processes depend on the alkali concentration, \([HO^-]\), oxygen solubility, \([O_2]\), temperature, \(T\), lignin or cellulose content, expressed as Kappa number, \(K\) and moles of cellulose per ton of pulp, \(m_n\), respectively.

The reaction rate constants, \(k_L\), for delignification and, \(k_C\), for cellulose degradation together with the volumetric gas-liquid and gas-solid mass transfer capacitites (i.e. \(k_{liq} a_{liq}\) and \(k_s a_s\)) intervene also.

The development of a comprehensive kinetic model based on eqs. (8) and (9), with a total separation of mass transfer and chemical kinetic effects, is a very difficult task if not impossible. Therefore, apparent kinetic models were proposed, which usually neglect or implicitly incorporate the mass transfer effects. These apparent models are either one
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stage or two stage models. The one-stage models assume no difference in the kinetic behaviour of the oxygen bleaching versus time. The two-stage models consider that the oxygen bleaching process occurs in two different stages (or phases). In the initial phase mainly delignification occurs with little carbohydrate degradation. In the second phase the delignification is slow, reaching a "floor" Kappa number, but significant carbohydrate degradation takes place. There is experimental evidence in favor of this model [Masura, 1993].

The latest two-stage model was developed by Vincent et al., 1994, for the delignification of eucalyptus kraft pulp, and is given by the following equations:

- for the first ("fast" delignification stage):

\[-\frac{dK_f}{dt} = 27.5\exp\left(-\frac{24.2}{R_g T}\right) P_o^{0.4} [HO']^{10.6} K_f ; \quad (13)\]

valid for \( K_f = (K_{initial} \text{ to } 0.79K_{initial}) \)

- for the second ("slow" delignification stage):

\[-\frac{dK_s}{dt} = 7667\exp\left(-\frac{46.3}{R_g T}\right) P_o^{0.38} [HO']^{0.39} K_s ; \quad (14)\]

valid for \( K_s = \{0.79K_{initial} \text{ to } [K_{initial} - 0.9(K_{initial} - K_{floor})]\} \)

In the above equation the activation energies are expressed in kJ/mole, the oxygen partial pressure, \( P_o \), in kPa, the alkali concentration, \([HO']\), in kmole/m³, the temperature, \( T \), in Kelvin, the time, \( t \), in minutes, \( R_g \) in kJ/mole.
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There are significant differences between the two stages as expressed by eqs. (13) and (14). First of all the activation energy and the pre-exponential term are much lower in the first stage than in the second one, indicating that the delignification in the first phase is under mass transfer control, with fast chemical kinetics while in the second phase the chemical kinetics is the rate determining step. However, it was found that the intra-fiber mass transfer may influence the delignification rate in the second stage as well. Consequently, eq. (14) incorporates both the intra-fiber mass transfer and the intrinsic chemical reaction rate [Vincent et al., 1994], still the chemical reaction limitation is considered to be more significant [Myers and Edwards, 1989].

Another striking difference is in the reaction order corresponding to the alkali concentration. A zero order in eq. (13), suggests that in the initial phase the delignification does not depend on the alkali concentration (in the 0.0375 M to 0.2 M range, where the experiments were performed [Vincent et al., 1994]). This result can be attributed also to the mass transfer limitation which predominates in the first stage. As long as there is enough hydroxyl ion, it does not influence the overall kinetics in this stage of the process.

The reaction order of oxygen is the same in both stages. This observation was confirmed by other studies as well [Myers and Edwards, 1989] and it indicates that the oxygen has the same role in both stages, namely, to sustain the non-linear network of oxidative, radical processes.

It must be emphasized that the model described by eqs. (13) and (14) is based on the pseudo-first order approximation with respect to Kappa number [Olm and Teder, 1979].

A different approach to the same problem, i.e. the overall behaviour of the oxygen bleaching process, is based on factorial experimental design. Thus the effects of process variables, both main and interaction effects, can be assessed. A factorial study conducted with 10% kraft pulp mixed with 1% (by pulp mass) MgCO₃, showed the following influence of process variables like oxygen pressure, alkali concentration, temperature,
time, initial Kappa number and initial viscosity, on the final Kappa number and viscosity [Irvine et al., 1993]:

I) as long as there is an adequate supply of oxygen, the oxygen pressure is not a critical factor due to its low main effect on the delignification rate. Thus increasing the oxygen pressure above 0.5 MPa had only little benefits.

II) of the five factors studied, the initial Kappa number, alkali concentration and temperature are more significant in determining the final Kappa number and viscosity of the pulp, than reaction time and oxygen pressure. This study concluded that increasing the reaction time past 20 minutes gave no additional benefits.

1.3.5 Improvements to Oxygen Bleaching

The conditions employed for mill scale use of the oxygen bleaching stage are as follows [Masura, 1993]:

- pulp consistency 25 - 30 % wt
- oxygen pressure 0.6 - 1.1 MPa
- temperature 80 - 120 °C
- alkali conc. 2 - 5 % wt
- amount of carbohydrate protecting agent : ~ 0.05 % Mg(II) per mass of pulp

Besides some very important advantages that were previously presented, oxygen bleaching has basically two significant disadvantages, i.e. poor selectivity and/or low delignification rate. It is a generally accepted observation that only a 45 to 50 % delignification can be achieved in the oxygen bleaching stage, before the pulp strength is reduced to unacceptable levels [McGrouther et al., 1994].

A large number of studies were devoted to improve the selectivity and/or the delignification rate of the oxygen bleaching process. These studies were focused on three main aspects, i.e. a proper pretreatment of pulp before the oxygen bleaching stage, finding
better cellulose protecting agents and development of complex catalytic systems based on transition metal ions.

Several pulp pretreatment methods were investigated with some success. Pretreatment with compounds such as chlorine, chlorine dioxide, ozone [Lachenal and de Choudens, 1986], dilute sulfuric acid [Marechal, 1993], peroxymonosulfuric acid [McGrouther et al., 1994] and nitrogen dioxide [Samuelson and Ojteg, 1987] showed improved delignification rates and selectivity in some cases. The nitrogen dioxide pretreatment (with 2% NO₂) followed by the usual oxygen bleaching of the kraft pulp, removed more than 80% of the lignin while still maintaining a high viscosity value (i.e. high selectivity) [Samuelson and Ojteg, 1987]. This process was implemented at a pilot scale in Sweden [Simonson et al., 1987], although the nitrogen dioxide is environmentally hazardous.

The research on carbohydrate protecting agents was concerned with the discovery of more efficient, selective and cheap compounds. One of the problems encountered is the simultaneous decrease in delignification rate as well. Various inorganic salts, such as Ce(SO₄)₂, CaCO₃, Sr(OH)₂, BaCO₃, BeSO₄ and chelating agents like DTPA, EDTA, gluconic acid, KSCN, NTA, sodium oxalate and others, were tested [Sjostrom and Valttila, 1972]. However, the best protecting agent remains the Mg(II) as MgCO₃, MgSO₄ or Mg(OH)₂.

In the last two decades considerable research effort was directed toward the development of complex catalytic systems based on transition metal ions. The role and interaction among the transition metal ion (e.g. manganese), reactive oxygen species and substrate in biochemical systems, represented a serious incentive for these studies. The goal would be the development of a catalytic system in which part of would act as oxygen transfer agent or redox promoter of the lignin oxidation reaction, while the other part would be an effective inhibitor of the polysaccharide degradation [Masura, 1993].

The rest of the present work deals with different aspects of this field.
1.3.6 Transition Metal Ion Catalysis of Oxygen Delignification. Redox Catalysis

In the early '70s it was found that the addition of small amounts of certain transition metal ions in oxygen pulping, significantly influenced the delignification rate and the pulp quality [Landucci and Sanyer, 1974]. Further studies with simple transition metal salts (e.g. sulfates and chlorides) indicated, for pH 9-11, an increased delignification rate in the presence of Cu(II) and Mn(II), while Fe(III), Co(II) and Ni(II) decreased the delignification rate [Landucci and Sanyer, 1975; Landucci, 1975].

A significant contribution of the work done by Landucci and his co-workers was that they recognized the importance of the electrochemical behaviour of a particular transition metal ion in promoting efficient delignification [Landucci, 1979].

The rate determining step of the oxygen delignification in alkaline media, is the formation of phenoxy radicals from the phenolate anion (please see section 1.3.2). It is believed that certain transition metal ions facilitate this process by accepting one electron from the phenolate anion, acting as a redox catalyst (please see Figure 24).

\[
\begin{align*}
\text{Phenol} & \quad + \quad \text{M}^{(n+1)+} \\
& \quad \rightarrow \\
\text{Phenoxy radical} & \quad + \quad \text{M}^{n+}
\end{align*}
\]

Figure 24: A scheme of the redox catalysis of the lignin oxidation in alkaline media.

\[ M = \text{transition metal ion; } R, R' = \text{remaining parts of the lignin structure} \]
The oxidation of the phenolate anion to produce phenoxy radicals is dependent on the redox potential of the $M^{(n+1)+}/M^{n+}$ couple. The actual reduction potential for most lignin model compounds are in the range of 0.427 to 0.676 V/SHE [Bogolitsyn et al., 1993]. Consequently, only those $M^{(n+1)+}/M^{n+}$ redox couples which have an actual reduction potential under the oxygen bleaching conditions at least in the above range are able to oxidize the phenolate anion according to the scheme presented in Figure 24.

Indeed, correlating the electrochemical behaviour, as determined by cyclic voltammetry, with the capability to catalyze oxidative delignification, it was found that only those redox systems which had reduction potentials in the region of -0.06 to +0.54 V/SHE exhibited any catalytic activity [Landucci, 1979]. Recent studies revealed that even higher reduction potentials are required, about or above +0.4 V/SHE [Perng et al., 1993].

It must be emphasized that the discussion based on redox potentials is a thermodynamic point of view and a favorable free energy does not imply efficient kinetics as well.

Beside a proper redox behaviour, other characteristics of the transition metal compound are very important also. It must be soluble and stable under the oxygen bleaching conditions, i.e. at high pH and temperature. Unfortunately most transition metal compounds are precipitated as hydroxides under those conditions, or their redox behaviour is altered, for example the reduction potential drops below +0.4 V/SHE at pH > 9.

The possibility of association of the complex with specific functional groups in the lignin structure is considered to be important as well. Some cobalt complexes (e.g. Co-TEA and Co-EDTEx) by forming coordinative linkages with the substrate, were able to catalyze the guaiacol oxidation (lignin model compound) even though they did not have

* please see the ligand nomenclature
the desired reduction potential [Meguro et al., 1985]. However, this example is rather an exception than a rule.

In summary, the direct redox interaction between the phenolate anion and the transition metal ion (please see Fig. 25), is just one way by which the catalyst can enhance the oxygen delignification. Other possible pathways are as follows [Chupka et al., 1993]:

I) formation of labile complexes between oxygen and catalyst, thus improving the oxygen transfer to lignin (i.e. synergistic effect between oxygen and catalyst)
II) conversion of molecular oxygen by the catalyst into more active forms (e.g. HO', HOO', etc.)

The pivotal role of oxy-heme complexes in the oxidation of biochemical substrates represented an important model for the delignification catalyst development. Also an enzyme ("ligninase") was discovered which uses an oxy-heme complex to destroy lignin by oxidizing the aryl groups [Andersson et al., 1985].

As a result of these biochemical studies, intensive research was carried out to find a "biomimetic" route to delignification, i.e. finding a proper catalyst that can replace the enzyme, while working in a similar manner. In this respect, various water soluble metalloporphyrins received much of attention. They are stable in concentrated sodium hydroxide solutions even at high temperatures. Under alkaline pulping conditions, Co^{III}(TSPP), was found to be an active catalyst working as a one-electron oxidant by cleaving the β-arylether bonds in lignin model compounds [Wright and Fullerton, 1984]. In this case the oxidized form, Co^{III}(TSPP), is only a weak oxidant and the active catalyst is the reduced form, i.e. Co^{II}(TSPP) [Watson et al., 1993a]. Using Fe^{III}(TSPc), a different reaction mechanism was identified. The oxidized form of the iron catalyst is indeed capable of oxidizing the phenolate anion according to the scheme given in Figure 24. Also the reduced catalyst, Fe^{I}(TSPc), is an active delignification agent [Watson et al., 1993b].
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The most efficient metalloporphyrin catalyst of the lignin model compound oxidation was found to be the Rh\textsuperscript{III}(TSPP). This is much more efficient than even antraquinone, which is commonly used to enhance the delignification rate in pulping systems. Again, both the oxidized and reduced forms of the catalyst proved to be active in lignin degradation [Watson et al., 1993c].

Metalloporphyrins and phtalocyanines were employed in oxygen bleaching systems as well. Mn(III), Co(III) and Fe(III) TSPP and TSPc complexes in a concentration of 0.025 g/l (about 2.5x10\textsuperscript{-5} M) at pH=14, T=100 °C and oxygen pressure of 0.8 MPa, were employed. The Mn\textsuperscript{III}(TSPP) generated both a moderate decrease in Kappa number and an increase in viscosity [Perng et al., 1994].

Oxidants other than macrocyclic transition metal complexes have been also investigated. An interesting case being the combination of Mn(II) and Co(II) in acidic media. A treatment of unbleached hardwood kraft pulp (3.3 g), for 1 hr. at 50 °C, in a solution of acetic acid 95% (700 ml) and 150 ml peracetic acid containing 1.5mM Mn(II) acetate and 0.03mM Co(II)acetate, increased the brightness from the initial value of 35% to 80% [Shimada et al., 1989]. Most probably the increased delignification was due to the Mn(III)/Mn(II) redox couple. It is noteworthy that the addition of small amounts of Co(II) as co-catalyst, speeds up the bleaching as compared with the system lacking Co(II).

Another investigation showed that the mixed catalyst, Mn(II)/Co(II) = 9/1 (molar ratio) gave the best selectivity and conversions for lignin model compounds [DiCosimo and Szabo, 1988]. These authors used 80% aqueous acetic acid, 500 psi oxygen pressure and acetaldehyde. The acetaldehyde is oxidized under those conditions to peracetic acid which is capable of reoxidizing Co(II) to Co(III) and Mn(II) to Mn(III).
1.3.7 Influence of Transition Metal Ions on Carbohydrate Degradation

The presence of transition metal ions during oxygen bleaching can cause carbohydrate degradation as well. In the classical oxygen bleaching process, the transition metal ion content is minimized by washing the pulp in acidic solutions in the presence of different chelating agents. However, under carefully selected conditions, transition metal complexes can be effective lignin degradation catalysts, without damaging the carbohydrates (i.e., improving the selectivity). Furthermore, in a few cases they can serve as carbohydrate degradation inhibitors as well.

There are very large differences in the effects on carbohydrates exerted by different transition metal ions. It is not possible to make any generally valid statement that one transition metal is more damaging than another [Samuelson and Stolpe, 1974]. Each situation might be different, depending on the pH, ligand, amount of transition metal ion, its oxidation state, the nature of the pulp, pulp consistency and pretreatment and other factors.

Regarding the manganese compounds the situation seems to be even more intricate than for other metal ions. Some authors reported a slight increase in the viscosity in the presence of 0.1% Mn(II) per pulp, at pH 9 and 150 °C [Landucci and Sanyer, 1974]. On the other hand, in an oxygen bleaching system using 30% consistency kraft pulp at 0.8MPa oxygen pressure and 106.5 °C, with 0.1% Mg(II) content per pulp weight, it was found that the addition of 0.013% MnSO₄ per pulp weight, generated a severe drop of viscosity, about 13% after 2 hours and 18% after 4 hours. However the addition of 0.2% DTPMP* per pulp mass, improved the viscosity, only 6% drop after 2 hours and 8% drop after 4 hours [Larsson and Samuelson, 1981]. Actually without the chelating agent, the presence of both Mn(II) and Mg(II) salts give rise to even a higher viscosity loss than in parallel experiments with the same amount of manganese but without magnesium addition.

* diethylenetriaminepentamethylene phosphoric acid
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[Jarrehult and Samuelson, 1993]. It can be concluded that the magnesium salt, widely employed as protector agent, exerted an opposite effect when small amounts of manganese were added.

These and other results in the literature, show that there is no generally valid correlation between the extent of carbohydrate degradation and the amount of manganese present during oxygen bleaching.

1.4 Electrochemically Mediated Oxygen Bleaching

Intensive research was carried out at the University of British Columbia by the Electrochemical Engineering Group in the emerging field of electrochemically mediated oxygen bleaching and brightening. Several transition metal compounds were tested for their ability to promote electrochemically mediated oxygen bleaching. For the first time rate equations were proposed for both delignification and carbohydrate degradation for this type of bleaching processes [Perng, 1993a].

A manganese gluconate complex was employed to catalyze the hydrogen peroxide formation from oxygen in aqueous alkaline media. The active, low oxidation state manganese ion was continuously regenerated at a cathode of an electrochemical cell, by reducing the higher oxidation state of the manganese complex. For a 1% kraft pulp consistency in 1M NaOH with continuos oxygen purge at atmospheric pressure, for 3 hours at 50 °C, a 10% additional decrease in Kappa number vs. the control experiment (i.e. without catalyst and current) was obtained when a platinized titanium cathode was employed. Unfortunately the selectivity was not satisfactory, due to an increased carbohydrate degradation in the presence of both catalyst and current [Todd, 1993].

Also the in-situ brightening of mechanical pulp using electrochemically generated sodium dithionate [Hu, 1994], hydrogen peroxide in a graphite slurry electrochemical reactor [Srinivasan, 1994] and percarbonate at a water cooled U-anode [Kurniawan,
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[1993] was investigated. In all these studies, under certain experimental conditions, significant brightness gain of 10 to 12 points was achieved.

1.4.1 The Selection of Redox Catalyst

During the mediated oxygen delignification in alkaline media the active form of the redox catalyst (i.e. the higher oxidation state of the transition metal ion, in most cases) is continuously depleted, being reduced by the phenolate anion and/or other reactive species (please see Figure 24). Thus the redox catalytic effect is diminished or completely lost in time. The role of electrochemistry would be to continuously, \textit{in-situ}, generate or re-generate the active, higher oxidation state of the metal complex, thus maintaining a constant amount of active redox catalyst (please see Figure 25). This process involves the oxidation of the reduced transition metal complex at the anode of an electrochemical cell.

\[
\begin{align*}
\text{Phenoxide Radical} & \quad + \quad M^{n+} \\
\text{Phenolate} & \quad + \quad M^{n+} \\
\text{Anion (LIGNIN)} & \quad \text{ANODE}
\end{align*}
\]

\textbf{Figure 25:} Schematic representation of the basic principle of the electrochemically mediated oxygen bleaching in alkaline media. \(M = \text{transition metal.}\)
In order to complete this cycle of redox catalysis - electrochemical regeneration of the catalyst, several demanding conditions have to be met. Some of these requirements are common to all delignification processes catalyzed by transition metal complexes (please see section 1.3.6), but the electrode process imposes further conditions as well. Based on the experience accumulated by the Electrochemical Engineering Group at the U.B.C., the following criteria seem to be decisive in the selection of a proper redox catalyst for electrochemically mediated oxygen bleaching purposes in alkaline media [Perng et al., 1993]:

- hydrolytical stability in alkaline media (at pH>9)
- the reduction potential under the actual bleaching conditions must be greater than +0.4 V/SHE
- ability to activate the oxygen molecule (synergistic effect with oxygen)
- part of the complex catalytic system should act as an inhibitor of the carbohydrate degradation reaction
- must be a reversible redox couple with fast anodic oxidation kinetics, in order to efficiently regenerate the active form of the catalyst.

It is extremely difficult to fulfill all of these conditions. A large number of Fe, Mn, Co, Cr, Cu and V complexes with various ligands such as cyanide, 1,10-phenantroline, 2,2'-dipyridyl, acetylacetonate, sulfonatosalicylate, EDTA, DTPA and others, were tested in oxygen bleaching experiments at pH 9.4, 11.2 and 14. Most of them precipitated as hydroxides at pH >9, the reduction potential dropped below 0.4 V/SHE or they did not have a reversible redox behaviour, as shown by the cyclic voltammetry studies. However, ferricyanide, iron/2,2'-dipyridyl and ferrate (FeO4^{2-}), acting synergistically with oxygen, enhanced significantly the delignification rate [Perng et al., 1993]. Also a strong interaction effect between current and redox catalyst, especially ferrocyanide, was observed, proving the existence of the proposed catalytic cycle.
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Another study employed ferricyanide electrochemically generated outside of the bleaching reactor. The spent bleaching liquor was continuously pumped through the electrochemical cell, consisting of a nickel bed anode and a graphite cathode separated by a semipermeable membrane [Godsay et al, 1988]. Significantly increased delignification was found in this case as well.

Although the ferri/ferro-cyanide redox couple was the most successful electrochemical mediator in all of the previous studies, due to the lack of selectivity and environmental concerns, its use on a larger scale is improbable.

In the present work a manganese aminopolycarboxylate complex, namely Mn(III)CyDTA (please see Figure 26) was investigated as a potential redox catalyst and electrochemical mediator.

![CyDTA ligand structure](image)

**Figure 26**: The CyDTA ligand structure (trans-Cyclohexane-1,2-diamine-N,N,N',N'-tertaacetic acid)

The Mn(III)CyDTA was chosen due to the following characteristics [Hamm and Suwyn, 1967]:

i) due to the rigidity of cyclohexane ring, it is one of the most stable manganese(III) complexes in aqueous alkaline media, being stable up to pH 11 at 25 °C.

ii) it has a standard reduction potential of +0.814 V/SHE at pH ~ 4-5, although the actual reduction potential under alkaline bleaching conditions is lower.

iii) both the ligand CyDTA and Mn(II) might act as carbohydrate protecting agents.
Thus, based on literature data, it can be concluded that Mn(III)CyDTA fulfills some of the conditions that are necessary for a good electrochemical mediator and redox catalyst in oxygen bleaching processes.

1.4.2 Mechanism of the Electrochemically Mediated Oxygen Bleaching

The most investigated redox catalyst in electrochemically mediated oxygen bleaching is the ferri/ferro-cyanide couple. Thus almost all of the known mechanistic and kinetic details of this bleaching process are based on the ferri/ferro-cyanide redox couple.

Surveying the literature, two different models of the reaction mechanism can be identified. Both models agree that the mediator intervenes in the initiation stage of the radical-chain oxidation process, i.e. the formation of phenoxy radicals from phenolate anions. The first model proposes a direct redox reaction between the phenolate anion and the active, higher oxidation state from of the transition metal ion complex as indicated in Figure 25 [Perng et al., 1993; Bogolitsyn et al., 1993]. The oxygen may intervene in the transition state of the reaction, by forming a "triple complex", phenolate anion - catalyst - oxygen. This model can be called the direct redox reaction mechanism of the electrochemically mediated oxygen bleaching.

The second model is based on the fact that in alkaline media in the presence of potassium ferricyanide, spontaneous formation of hydrogen peroxide occurs [Bogolitsyn, 1988]. The most important intermediate of this reaction is the highly reactive hydroxyl radical (eqs. (15) and (16)).

\[
2 \left[ \text{Fe(CN)}_6 \right]^{3-} + 2\text{HO}^- \Leftrightarrow 2 \left[ \text{Fe(CN)}_6 \right]^{4-} + 2\text{HO}^- ;
\]
\[
2\text{HO}^- \Leftrightarrow \text{H}_2\text{O}_2 ; \quad (15&16)
\]
Finally the hydrogen peroxide decomposes in alkaline media under the catalytic action of the transition metal complex to form oxygen and water, through a series of reactive radical intermediates.

Thus this second mechanism proposes that the oxidation of lignin is mainly due to the hydroxyl and other reactive radicals that are spontaneously formed in alkaline ferricyanide solutions (Fig. 27) [Vasil'eva et al., 1993; Shchukin and Babkin, 1993; Shchukin et al., 1990].

\[
\left[ \text{Fe(CN)}_6 \right]^{3-} + \text{HO}^- \Leftrightarrow \left[ \text{Fe(CN)}_6 \right]^{4-} + \text{HO}^- ;
\]

\[
\text{L - O}^- + \text{HO}^- \Leftrightarrow \text{L - O}^- + \text{HO}^- ;
\]

Lignin (Phenolate Anion)

Phenoxyl Radical

\[
\left[ \text{Fe(CN)}_6 \right]^{3-} + 1\text{e}^- \leftarrow \left[ \text{Fe(CN)}_6 \right]^{4-} \text{ at ANODE} ;
\]

**Figure 27**: The indirect redox reaction model of the electrochemically mediated oxygen bleaching

Because this model assumes no direct redox reaction between the redox couple and the phenolate anion, it can be called the indirect redox reaction mechanism.

So far there is not enough experimental evidence to decisively confirm one of the models over the other one.
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The direct redox reaction model seems more general in explaining the effect of other transition metal complexes than ferricyanide. There is too little information about the hydroxyl radical generation in alkaline media promoted by other transition metal complexes.

1.4.3 Kinetics of Electrochemically Mediated Oxygen Bleaching

Perng and Oloman (1994) proposed the first kinetic model which deals with the electrochemically mediated oxygen bleaching system. This study is based on experiments performed with the ferri/ferro-cyanide couple.

They employed a one-stage kinetic model (please see section 1.3.4). The effect of current on the system is reflected by significant changes in the kinetic parameters, such as activation energies and reaction orders.

In the absence of current (i.e. zero ferricyanide concentration) the activation energy values of 60 kJ/mole and 94 kJ/mole for delignification and carbohydrate degradation respectively, indicate a chemical reaction control. However, when current is applied, i.e. ferricyanide is generated, a significant drop in activation energies of both reactions was observed. These, low values about 12 to 15 kJ/mole, show a shift in the rate determining step toward mass transfer control, i.e. intra-fiber diffusion. In the presence of ferricyanide the chemical reaction rates are high and no longer represent a limiting factor.

Regarding the reaction orders, a decreased contribution of oxygen with increased current, indicates the diminished role of oxygen when ferricyanide is generated. The reaction order with respect to the hydroxide ion remains almost unchanged by current (about 0.3-0.4 for delignification reaction). This means that the hydroxide ion plays a similar role in all situations, i.e. generation of the phenolate anion. The hydroxide ion behaves differently with respect to carbohydrate degradation. When current is applied, its role is diminished, the reaction order drops from 0.7 to 0.3, suggesting that the peeling
reaction of carbohydrates losses importance in the presence of the damaging effect due to ferricyanide [Perng and Oloman, 1994].

This study revealed a linear behaviour of the system with respect to ferricyanide concentration, indicating a stoichiometric rather than catalytic interaction between ferricyanide and lignin. In the view of the two discussed mechanisms of electrochemically mediated oxygen bleaching, this observation can be considered as an additional proof in favour of the direct redox reaction mechanism, which is based on a stoichiometric reaction between phenolate anion and mediator. Also the absence of a true catalytic effect, indicates no synergistic interaction of ferricyanide with oxygen in promoting delignification.

1.4.4 A General Scheme of the Reactions Involved in Electrochemically Mediated Oxygen Bleaching

A very large number of radical, redox and electrode reactions are occurring in the electrochemically mediated oxygen bleaching process. They can be classified as reactions at the electrode (i.e. anodic oxidation reactions), reactions in solution (homogeneous reactions) and heterogeneous reactions at the pulp fiber sites (please see Figure 28).

Godsay et al. (1988), made the first attempt to develop a summary of reactions involved in electrochemically mediated oxygen bleaching system using the ferri/ferro-cyanide redox couple.

As it can be seen from Figure 28, there are three potential anodic oxidation reactions, i.e. generation of the higher oxidation state form of the redox catalyst, oxygen evolution and oxidation of the solubilized lignin or lignin fragments. Practically only the first two reactions are significant.

In the aqueous alkaline solution phase, the active form of the redox catalyst, $M^{+1+}Y$, can oxidize soluble lignin or lignin fragments, $L-O_{(aq)}^{-}$, and it might oxidize the hydroxide ion as well, generating hydroxyl radicals.
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The most important reactions regarding pulp bleaching, are those at the pulp fiber sites. Consequently, the intra-fiber diffusion of species like catalyst, hydroxide ions and oxygen plays an important role. The pulp lignin, $L-OH(p)$, is ionized in alkaline media, generating the phenolate anion form, $L-O^-(p)$, some of which (or fragments of it) might leach into the solution phase, $L-O^-(aq)$. The "active" pulp lignin, $L-O^-(p)$, is further engaged in oxidative degradation reactions initiated by the redox catalyst, $M^{n+1}(Y)$, reactive short-lived radical species, e.g. $HO^-$, and oxygen. As a result of these reactions, highly reactive oxidized lignin and lignin fragments are formed, $L-O^-(p)$, which undergo the entire network of radical chain processes. Finally, the outcome of this network are both degradation products and high molecular weight, condensed lignin structures, $L-L(p)$, which are very difficult to eliminate.

In parallel with lignin, the pulp carbohydrates, $C(p)$, are attacked by the same reactive species. As a consequence, the bleached pulp will have a lower viscosity and tensile strength than the unbleached pulp.
Figure 28: A general scheme of reactions involved in electrochemically mediated oxygen bleaching (modified after Godsay et al., 1988)

**ANODE REACTIONS**

\[
M^{n+}Y \rightarrow M^{(n+1)Y} + 1e^{-}
\]

\[
4HO^- \rightarrow 2H_2O + O_2 \uparrow +4e^-
\]

\[
L - O^-(aq) \rightarrow L - O^-(aq) + 1e^-
\]

**REACTIONS in SOLUTION**

\[
M^{n+}Y + L - O^-(aq) \leftrightarrow L - O^-(aq) + M^{(n+1)Y}
\]

**REACTIONS at the PULP FIBER SITES**

\[
L - OH_{(p)} + HO^- \leftrightarrow L - O^-_{(p)}
\]

\[
L - O^-(p) + M^{n+Y} \leftrightarrow L - O^-_{(p)} + M^{(n+1)Y}
\]

\[
O_2^- + L - O^-(p) \leftrightarrow L - O^-(p) + O_{2(aq)}
\]

\[
O_2^- + HO^- \rightarrow [HO^-, HOO^-, HOO^-, etc.]
\]

\[
L - O^-(p) + [HO^-, etc.] \rightarrow \text{Lignin degradation products}
\]

\[
L - O^-(p) + L - O^-(p) \rightarrow L - L_{(p)}
\]

\[
C_{(p)} + [HO^-, M^{(n+1)Y}] \rightarrow \text{Carbohydrate degradation products}
\]
1.5 Electrochemical Processes and Techniques

Electrochemical technologies possess a high "green potential" [Pletcher and Weinberg, 1992]. They are characterized by good control of each reaction through the electrode potential and current density, lower operating temperatures and safer conditions associated with less waste by-products.

In addition to the common aspects of all chemical heterogeneous processes, such as surface properties and concentrations, mass transfer of reactants to the active sites of the catalyst surface etc., electrochemical reactions present some specific problems as well, due to the presence of an electric field and current. Both the electrode kinetics (charge transfer reactions) and the mass transfer of the ions is significantly influenced by the additional independent variable, i.e. cell voltage.

This section provides some elements and fundamental equations of electrode kinetics and mass transfer in electrochemical systems that will be helpful in the "Experimental Results and Discussion" sections of this work. Also elements of the cyclic voltammetry technique, that are necessary in the interpretation of the cyclic voltammograms presented in the "Experimental Results" section, is given.

1.5.1 Electrode Kinetics and Mass Transfer

The rate of an electrochemical reaction (expressed as the current density) is strongly influenced by the electrode potential. The current density dependence of electrode potential can be described for example by recording the polarization curve (please see Figure 29).
Let us consider a simple electrode reaction involving the anodic oxidation of an ionic species, $R$ to its oxidized form, $O$. In the present work the oxidation of $\text{Mn}^{2+}$ to $\text{Mn}^{3+}$ in alkaline media is of a special interest.

$$R \xrightleftharpoons{}^{i_d} i_C \rightarrow O + ne^-$$

At equilibrium, characterized by the reversible potential $E_{\text{rev}}$, there is no net current flowing through the system (please see Figure 29). The reversible (or equilibrium) potential is given by the Nernst equation:

$$E_{\text{rev}} = E^0_{O/R} - \frac{R_g T}{nF} \ln Q$$
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where \( E_{O/R}^0 \) - standard reduction potential of the O/R couple; \( \{ \text{V} \} \)

\( R_g \) - universal gas constant; \( \{ \text{J/mole} \} \)

\( T \) - temperature; \( \{ \text{K} \} \)

\( Q \) - activity quotient

\[
Q = \frac{a_R}{a_o} \frac{c_R}{c_o}
\]

The rate in both directions are equal, \( i_A = i_C \), and can be expressed as the exchange current density, \( i_0 \):

\[
i_0 = nFk_s (c_R)^r (c_O)^{\gamma}
\]

(22)

where \( k_s \) - standard electrochemical rate constant*

\( r, \gamma \) - electrochemical reaction orders with respect to species \( R \) and \( O \)

When a potential \( E \), higher than the reversible potential \( E_{rev} \), is applied, i.e. a positive overpotential \( \eta \) is created (\( \eta = E - E_{rev} \)), the equilibrium in eq. (20) is shifted to the right. Thus, a net anodic oxidation current \( i \), is flowing through the system, causing a gradual consumption of \( R \) and formation of \( O \).

\[
i = i_A - i_C > 0
\]

(23)

As long as the applied potential is low the charge transfer step is slow and the overall electrochemical process is under kinetic (or activation) control (please see Fig. 29). In this region the current - potential dependence is described by the Butler-Volmer equation (the "B-V" equation).

---

* the standard electrochemical rate constant is potential and concentration independent being defined at the standard reduction potential \( E_{O/R}^0 \)
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\[ i = i_0 \left[ \exp \left( \frac{\alpha_A \eta_{ac} F}{R_g T} \right) - \exp \left( -\frac{\alpha_C \eta_{ac} F}{R_g T} \right) \right] \]

(24)

where \( \alpha_A; \alpha_C \) - are the anodic and cathodic charge transfer coefficients

\( (\alpha_A + \alpha_C = n) \)

\( n \) - nr. of electrons exchanged at the electrode

\( \eta_{ac} \) - activation (purely kinetic) overpotential (\( = E - E_{rev} \))

According to eq. (22) the exchange current density and implicitly through eq. (24), the measured current density is a function of the concentration of both reactants (e.g. \( \text{Mn}^{2+} \)) and products (e.g. \( \text{Mn}^{3+} \)). Also is strongly influenced by the electrode material through the standard electrochemical rate constant \( k_s \) (electrocatalysis).

Simplified forms of the Butler-Volmer equation (24) are very popular as well. For example if the overpotential exceeds about +0.1 V, the equilibrium given by eq. (20) is considered completely shifted to the anodic direction. Consequently, the second term in eq. (24) can be neglected and the Tafel equation is obtained:

\[ \eta_{ac} = \frac{R_g T}{\alpha_A F \ln \frac{i}{i_0}} = b \log i - a \]

(25)

where \( b \) - Tafel slope

\( a \) - Tafel parameter

The significance of Tafel constants \( a \) and \( b \) are:

- an increase in overpotential by \( b \) volts generates a current density increase by a factor of 10. Typical values for \( b \) are between 30 to 300 mV [Prentice, 1991].
- the parameter $\alpha$ is the overpotential extrapolated to a high current density of $i = 1.0$ A/cm$^2$.

Moving along Figure 29, at higher potentials the measured current density (line $b$) deviates from the values that were expected on a kinetic control basis (line $a$, eq. (24)). The electrode kinetics is fast enough and the effect of mass transport on the rate determining step, becomes significant. Consequently, the electrochemical process is under mixed control. Assuming steady-state, the rate of mass transfer of reactant to the electrode surface is equal to the rate of electrochemical reaction at the electrode surface expressed by the Tafel equation. In the case of a first order electrochemical reaction ($r=1$ and $\gamma=0$ in eq. (22)) we have:

$$i = nFk_m(c_R-c_{R,S}) = nFk_Sc_{R,S} \exp\left(\frac{\alpha_A \eta F}{R_g T}\right); \quad (26)$$

Eliminating the surface concentration $c_{R,S}$, the following equation describing the mixed control is obtained [Oloman, 1992]:

$$i = \frac{nFk_m k_S c_R \exp\left(\frac{\alpha_A \eta F}{R_g T}\right)}{K_m + k_S \exp\left(\frac{\alpha_A \eta F}{R_g T}\right)}; \quad (27)$$

The limiting forms of eq. (27) describe the whole range of kinetic and mass transfer control.

If the overpotential is further increased, the kinetic term in eq. (27) becomes much larger than the mass transfer coefficient $K_m$, i.e. the mass transfer becomes the rate determining step and a limiting current density $i_L$, is achieved (please see Fig. 29).
$i = i_L = nFk_m c_R$ ; \hfill (28)

When the reactant $R$, is an ionic species (e.g. HO⁻) and in the case of an uniform electrolyte composition, eq. (27) can be corrected in a simple way to include the ion migration effect as well, through the ion transference number $t_R$ [Oloman, 1992]:

$$i_L = \frac{nFk_m c_R}{1 - t_R} ; \hfill (29)$$

There is an extensive literature dealing with mass transfer in electrochemical systems of various geometric and fluid dynamic particularities.

The present study is concerned with mass transfer to a vertical electrode in a batch, stirred electrochemical cell, using a propeller axial flow impeller. For this case, the following mass transfer correlation can be employed [Selman and Tobias, 1978; Mizushina et al., 1969]:

$$Sh = 0.228 Re^{2/3} Sc^{1/3} ; \hfill (30)$$

valid for

\begin{align*}
10^2 < Re < 3 \times 10^4 \\
0.2 < h/H < 0.7 \\
d = 6.6 \text{ cm} \\
H = d_o = 10 \text{ cm}
\end{align*}

Where,

$$Sh = \frac{K_m f d}{D} \quad \text{- Sherwood number}$$
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\[ \text{Re} = \frac{\omega d^2}{\nu} \quad \text{- Reynolds number} \]

\[ Sc = \frac{\nu}{D} \quad \text{- Schmidt number} \]

\[ K_{mf} \quad \text{- mass transfer coefficient due to forced convection} \]

\[ D \quad \text{- diffusion coefficient} \]

\[ \omega \quad \text{- rotation rate} \]

\[ \nu \quad \text{- electrolyte kinematic viscosity} \]

\[ h \quad \text{- vertical dimension of impeller blade} \]

\[ H \quad \text{- liquid height} \]

\[ d \quad \text{- impeller diameter} \]

\[ d_0 \quad \text{- cell diameter} \]

The secondary anode reaction in the system under investigation, is oxygen evolution in alkaline media. The electrolytic gas evolution influences the performance of the cell by three effects [Prentice, 1991]:

i) rising gas bubbles enhance the local convection and mass transfer at the electrode

ii) gas bubbles reduce the electrolyte conductivity thus the ohmic resistance of the cell is increased

iii) bubbles that adhere to the electrode surface block the surface and reduce the area available for electrochemical reaction (i.e. electrode screening by gas bubbles).

The mass transfer coefficient due to gas evolution \( K_{mg} \), is given by the following equation [Oloman, 1992]

\[ Sh_g = 0.93 \text{Re}_b^{0.5} Sc^{0.487} \quad ; \quad (31) \]
where $Re_b$ - the bubble Reynolds number \( \left( \frac{d_b \rho V_g}{\mu} \right) \)

$V_g$ - volumetric gas generation rate per unit electrode area

d_b - bubble break up diameter (about 60 \( \mu \)m for O_2 in alkali)

$\rho$ - electrolyte density

$\mu$ - electrolyte dynamic viscosity.

The combined, total mass transfer coefficient $K_m$, due to both forced convection $K_{mf}$ and oxygen evolution $K_{mg}$, is expressed by the following equation [Oloman, 1992]:

$$K_m = K_{mf} \left[ 1 + \left( \frac{K_{mg}}{K_{mf}} \right)^2 \right]^{1/2} \quad (32)$$

The effect of gas evolution on electrolyte conductivity can be described by the Maxwell equation [Sigvist et al., 1980]:

$$\frac{\Lambda_g}{\Lambda} = \frac{1 - \varepsilon}{1 + \frac{\varepsilon}{2}} \quad \text{for} \quad \varepsilon < 0.6 \quad (33)$$

where $\varepsilon$ - gas void fraction

$\Lambda$ - electrolyte conductivity without gas evolution

$\Lambda_g$ - electrolyte conductivity in the presence of gas evolution.
In the electrochemical bleaching cell the electrolyte conductivity, besides temperature, electrolyte concentration and gas evolution, is dependent on pulp consistency as well [Been, 1994].

The degree of screening of an electrode by an evolving gas phase $\theta$, can be defined as the ratio of electrode area screened by an evolving gas phase $A_{SC,g}$, and the total electrode area $A$:

$$\theta = \frac{A_{SC,g}}{A}$$

(34)

The degree of screening increases with increasing current density and it can be minimized by an efficient mixing of electrolyte [Nefedov et al., 1993].

1.5.2 Anodic Oxidation of Cations

When a cation is anodically oxidized, the process takes place against an adverse potential gradient [Wagner, 1954; Oloman, 1993]. This influences both the mass transport of the cation to the anode and the electrode kinetics. Wagner (1954) had shown that the rate of transport of cations toward the anode is appreciably decreased if the potential gradient across the diffusion boundary layer is of the order of or greater than 0.025/z volt. In the case of Mn$^{2+}$ $z=2$, this means 12.5 mV. This limit is low enough in order to be easily exceeded at high, industrially feasible, current densities.

There is an easy way of eliminating this negative effect, by using an excess of supporting electrolyte. For example in the present work a 0.1M NaHCO$_3$ solution is employed in the presence of 6 mM Mn(II) concentration. However, even if the effect of the adverse potential gradient on ionic mass transfer is eliminated, certain kinetic parameters, such as the Tafel slope, might be affected and without a proper correction, their values might be misleading [Gileadi, 1993].
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1.5.3 Factors in the Operation of Electrochemical Reactors

The majority of novel electrochemically processes are initially studied on a small, laboratory scale. The simple batch cell divided by an ion exchange membrane provides a convenient, versatile and easily controlled system for examination of electrochemical characteristics such as electrode material feasibility and kinetics, parametric investigation of the electrochemical process, current efficiency and cell voltage.

One of the most important factors in the operation of an electrochemical reactor is the current efficiency. In an Electrosynthesis process the current efficiency is given by [Oloman, 1992],

\[
CE = \frac{nFPr}{I} \tag{35}
\]

where
- \( n \) - electron stoichiometry of the desired reaction
- \( Pr \) - production rate of desired product (mole/s)
- \( I \) - total applied current (A)
- \( F \) - Faraday constant (C/equivalent).

If the desired product can undergo relatively fast chemical decomposition (e.g. \( Mn^{3+} \) in aqueous alkaline media) the current efficiency given by eq. (35), is rather an apparent value than an absolute one. Because in this case the measured quantity \( Pr \), is the net accumulation rate (i.e. production minus decomposition) instead of the true production rate.

Also in some cases, such as Mn(II) oxidation in alkaline media with high Mn(II)/ligand molar ratio, certain amounts of the desired product can be formed via non-electrochemical pathways as well. In such situations, the true, electrochemical production rate must be carefully determined (please see the "Experimental Results and Discussion" section).
Another important operating variable is the cell voltage $V_{cell}$ given by the following equation (for an electrosynthesis reaction) [Oloman, 1992]:

$$V_{cell} = V_{OC} + \eta_C - \eta_A - V_{ohm}$$  

where $V_{OC}$ - open circuit potential of the full cell reaction

$V_{ohm}$ - ohmic voltage drop through both the electrolyte and separator (e.g. ion exchange membrane)

$\eta_A, \eta_C$ - anodic and cathodic overpotentials respectively

By combining the cell voltage and current efficiency the specific energy of the electrochemical process can be obtained [Oloman, 1992]:

$$SE = \frac{nFV_{cell}}{3600CE} \text{ (kWh/kmole)}$$  

1.5.4 Electrochemical Techniques: Cyclic Voltammetry

Basically, the electrochemical techniques can be classified in two major categories: galvanostatic and potentiostatic ones. In the first category the electrochemical system is disturbed by applying a controlled current impulse and the change in electrode potential is monitored in response. Conversely, in a potentiostatic technique the potential is applied in a controlled manner and the resultant current flow is monitored and employed in electrode kinetics analysis. If the potential is varied in time according to a linear function,
the method is called linear sweep voltammetry while in the case of a triangular potential function, the method is called cyclic voltammetry.

Cyclic voltammetry is one of the basic and most useful tools for analyzing electrode processes. In a typical cyclic voltamrogram (please see Figure 30), two parts can be distinguished: the upper part corresponds to cathodic (reduction) processes while the lower part is given by oxidation (anodic) reactions.

![Figure 30](image)

**Figure 30**: (a) Cyclic potential sweep; (b) Resulting Cyclic Voltammogram [Bard and Faulkner, 1980]

If the scan has started in the cathodic direction (see upper part in Fig. 30) at a potential well positive of the actual equilibrium potential \( E^0 \), a small non-faradaic (capacitive) current will flow for a while. As the potential becomes more negative and reaches the vicinity of \( E^0 \), the reduction begins and current starts to flow. At a certain potential, smaller than \( E^0 \), (i.e. negative overpotential) the current registers a maximum (peak) value, called cathodic peak current \( i_p^c \). The corresponding potential is the cathodic peak potential \( E_p^c \). At this point a steady-state is achieved, i.e. the reduction rate is equal to the rate of diffusion\(^*\). As the potential continues to grow more negative, beyond \( E_p^c \),

\(^*\) Note that cyclic voltammetry is performed in an unsterred,quiescent solution
the kinetic step becomes very fast compared to diffusion. The surface concentration of species $A$ is near to zero. Due to the rapid depletion of the reactive species $A$ in the diffusion boundary layer, the concentration gradient declines and consequently the diffusion controlled current declines as well. This is the reason of the peak behaviour.

In cyclic voltammetry after a certain time, depending on the scan rate $v$, the potential is reversed and is swept in a positive direction (see $E_{sw}$ - switching potential, in Fig. 30). In the anodic, or positive direction the same phenomena will occur but in this case the oxidation processes are detected and the corresponding parameters $E_{p}^a$ and $i_p^a$, are determined.

In practice, as it can be seen in the "Experimental Results and Discussion" section of the present work, the cyclic voltammograms might look somewhat different than the simple "textbook case" presented in Figure 30. The electrode reactions are quite often coupled with homogeneous reactions and/or adsorption processes. Also the nature and concentration of ligand, pH and electrode material significantly influences the shape of the cyclic voltammogram. Very often more than one electroactive species are present thus more than one peak can be observed. Actually the role of cyclic voltammetry is to identify as accurately as possible all these aspects of an electrochemical process offering a reliable insight into the fundamentals of the system. Based on this information certain predictions can be made about the practical suitability of the discussed electrochemical process on a larger scale.

The most important parameters measured from a cyclic voltammogram are the peak currents, their ratio and the peak potentials. Their dependence on scan rate $v$, can be used as a diagnostic criteria to identify various types of charge transfer mechanisms.

In the present work the peak current ratio $i_p^a/i_p^c$, was calculated with the Nicholson equation (please see Figure 31) [Brown and Sandifer, 1986]:

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\[ \frac{i_p^a}{i_p^c} = \frac{(i_{ap})_0}{(i_{cp})_0} + \frac{0.485(i_{sp})_0}{(i_{cp})_0} + 0.086 \]  \hspace{1cm} (38)

The meaning of the parameters in the Nicholson equation are given in Figure 31.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure31.png}
\caption{Cyclic voltammogram showing the parameters necessary to calculate the peak current ratio $i_p^a/i_p^c$, according to the Nicholson equation [Brown and Sandifer, 1986].}
\end{figure}

In Appendix I a summary of cyclic voltammetry diagnostic criteria which is relevant to the present work, is presented.
Chapter 2

EXPERIMENTAL APPARATUS and PROCEDURES

The apparatus employed in this work consisted of cyclic voltammetry equipment with the corresponding three electrode system (i.e. working, counter and reference electrodes), electrochemical reactors, UV-VIS spectrophotometer and standard equipment for pulp analysis.

The procedures involved recording of cyclic voltamograms, development of a new, electrochemical method, of Mn(III)CyDTA synthesis in alkaline media, spectrophotometric characterization of Mn(III)CyDTA, quantitative analysis of Mn(III) by a titrimetric method and several types of bleaching procedures with Kappa number and pulp viscosity determinations.

2.1 Cyclic Voltammetry Apparatus and Procedures

The cyclic voltammetry equipment consisted of a Pine Potentiostat (RDE3), a Goldstar DM-7241 digital multimeter (employed in the high impedance voltmeter mode) and a Watanabe WX446 X-Y recorder (please see Figure 32).

The three - electrode system consisted of a platinized titanium plate counter electrode (area = 10.4 cm²), a saturated calomel reference electrode (SCE, Fisher Scientific) and different types of working electrodes as follows:

- platinum wire (A= 0.76 cm²)
- stainless steel wire (A= 0.34 cm²)
- graphite disk (A= 0.33 cm²)
In order to reduce the ohmic potential drop between the working and reference electrode, the calomel reference electrode was placed in a Luggin capillary filled with saturated KCl solution and having a porous plug at its tip. The Luggin capillary was brought a few millimeter away from the working electrode.
To assure a clean electrode surface, the working electrodes were stored in a weak, (about 5%) HNO₃ solution and they were identically pretreated before each measurement. The stainless steel and graphite electrodes were gently abraded for about one minute with a fine polishing cloth, followed by a thorough rinse with distilled water. After that, all three working electrodes (i.e. including the platinum electrode as well) were electrochemically pretreated by several slow anodic scans in 0.5M H₂SO₄ solution, in order to oxidize the traces of impurities [Gileadi et al., 1975]. Following that, the electrodes were removed from the sulfuric acid solution and thoroughly rinsed with distilled water.

The actual cyclic voltammetry measurement always started with the recording of the background current from the supporting electrolyte. This served as a test for the electrode cleanness as well. The supporting electrolyte in CV tests was 1M KCl or 1M KCl + 0.1M NaHCO₃.

Finally the CV of Mn(III)CyDTA was recorded as follows: in 500 ml supporting electrolyte solution 10 ml Mn(III)CyDTA of 3.6 to 4.6 mM concentration was added. The solution was mixed using a magnetic stirrer and the pH was adjusted to the desired value using a 2M NaOH solution. The oxygen was removed from the cell by purging nitrogen for about 5 to 10 minutes. The three electrodes were placed in the cell which was then closed and the potentiostat was turned on, recording the cyclic voltammograms for different scan rates in the range of 2 to 10 volt/min. The temperature was 20 or 25 °C.

The pH of the solution was gradually increased to study the effect of pH on the electrochemical behavior of the complex compound.

Thus a cyclic voltammetry study of Mn(III)CyDTA, at room temperature, on three different electrode materials (graphite, stainless steel and platinum) as a function of pH and scan rate, was performed.
2.2 Electrochemical Reactor

In all of the electrochemical runs a cylindrical, divided, batch electrochemical reactor was employed (please see Figure 33).

Figure 33: A divided, batch electrochemical reactor

Two electrochemical reactors were employed. One was made of Plexiglas while the other was made of 316 stainless steel with Teflon coated interior. Both reactors were divided in two chambers of 1 liter effective volume each by a cation exchange membrane (Nafion 324) which was held between two perforated Plexiglas support plates. The Plexiglas reactor (diameter = 16.5 cm; height = 15.7 cm) was mainly used for electrosynthesis of Mn(III)CyDTA in alkaline media and occasionally for room temperature bleaching runs. The stainless steel reactor (diameter = 18 cm;
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height = 16.3 cm) was exclusively used for electrochemically mediated bleaching runs. The inside of the reactor was Teflon coated to avoid potential contamination of the pulp slurry with traces of transition metal ions from the stainless steel reactor wall. The temperature during the bleaching runs was controlled by immersing the stainless steel reactor in a water thermobath (Haake E8). The temperature variation inside the reactor was maximum ±1 °C.

During the operation of the reactor, metered gas flow (oxygen or nitrogen, 844 ml/min at 21 °C and 101 kPa) was sparged continuously through the pulp slurry at atmospheric pressure. Also the pH of the pulp suspension was continuously monitored and controlled, by using a pH electrode specially designed for pulp and paper industry (Fisher Scientific Pulp and Paper Combination pH electrode). The most common cause of pH electrode failure in the presence of a pulp suspension is junction clogging. This phenomena is due to the heavy metal ions, Ag(I) or Hg(I), found in the reference electrolyte which can react with the sulfide ions present in the measured pulp samples. Thus insoluble heavy metal sulfides are formed which block the pH electrode junction, causing its failure. The Fisher Pulp and Paper Combination gel-filled electrode, eliminates this problem by having on the reference side a double junction. Consequently, no heavy metal ions are present in the outer gel solution so heavy metal sulfides cannot be formed. This electrode was found to be reliable and fast responding under the conditions employed in this work.

The current was supplied from a DC power supply (XANTREX) with output voltage in the range of 0 to 15 V and current from 0 to 4 A. All electrosynthesis runs were performed under galvanostatic conditions (i.e. at constant current).
2.3 Electrosynthesis of Mn(III)CyDTA in Alkaline Media

Due to the disproportionation of Mn(III) ion in aqueous media,

\[ 2\text{Mn}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Mn}^{2+} + \text{MnO}_2 + 4\text{H}^+; \]
\[ K = 10^9 \text{ (mol/l)}^3 @ 25 \degree \text{C} \]  \hspace{1cm} (39)

which is enhanced at high pH and temperature, all of the existent chemical or electrochemical methods for production of Mn(III) compounds (e.g. sulfate), are carried out in acidic media. The classical chemical method of Mn(III)CyDTA synthesis, developed by Hamm and Suwyn (1967), involves continuous addition of MnO_2 (oxidizing agent) to a slurry at 0 \degree C containing CyDTA and Mn(NO_3)_2 (or MnSO_4) in a 2 : 1 molar ratio. The mixture is vigorously stirred from 0.5 to 1 hour. The remaining MnO_2 is filtered off on a sintered glass filter and a dark red Mn(III)CyDTA solution is the filtrate. From this solution the solid complex compound can be crystallized out. The yield of this method is about 80%.

At the very beginning of the present work, Mn(III)CyDTA was synthesized according to this chemical method. The resulting solution was employed in cyclic voltammetry studies.

However, this chemical method was found to be tedious and inconvenient for frequent production of Mn(III)CyDTA. Thus the need of a new, simple and convenient method, emerged.

The idea was to replace the chemical oxidant (i.e. MnO_2) by a proper anode of an electrochemical cell. Thus, the filtration step of the chemical method would be eliminated. Also keeping in mind that Mn(III)CyDTA in this work is further employed as a redox catalyst in alkaline media, a way to produce this complex directly in alkaline media, instead
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of an acidic slurry, had to be found. For a convenient synthesis, the working temperature must be around 25 °C, instead of the 0 °C employed in the chemical method which requires an ice bath. In conclusion, the main goal of a new method would be the synthesis of Mn(III)CyDTA in the same electrochemical reactor and under similar conditions as for the subsequent oxygen bleaching.

Thus, the following procedure was developed: prepare a 0.1M sodium bicarbonate (NaHCO₃) solution in distilled water. Adjust the pH of this solution to about 11 by adding 2M NaOH. Place this solution in the anode chamber of a Plexiglas electrochemical reactor (Fig. 33). Add the desired amount of ligand, CyDTA and stir vigorously. Add the MnSO₄ as well, stir and adjust the pH to 10.50 ± 0.01 at 25 °C. Prepare the catholyte by adding 75ml 2M NaOH solution and 925 ml distilled water into the cathode chamber (pH=13.5). Connect the electrodes to the DC power supply, set the current to the desired value and run the electrochemical reactor for 1 hour with vigorous stirring of the anolyte. The color of the anolyte gradually becomes yellow-brownish, indicating the formation of Mn(III)CyDTA in alkaline media.

Also oxygen evolution at the anode and hydrogen evolution at the cathode is occurring.

The electrode reactions are as follows:

ANODE (+) \[ \text{Mn}^{2+\text{aq}} - 1e^- \rightarrow \text{Mn}^{3+\text{aq}} \] \hspace{1cm} \text{(40-41)}

\[ 2\text{HO}^- - 2e^- \rightarrow \frac{1}{2}\text{O}_2 \uparrow + \text{H}_2\text{O} \]

CATHODE (-) \[ \text{H}_2\text{O} + 1e^- \rightarrow \frac{1}{2}\text{H}_2 \uparrow + \text{HO}^- \] \hspace{1cm} \text{(42)}

Finally, the anolyte is employed without further processing in subsequent oxygen bleaching or for other purposes (e.g. quantitative and qualitative analysis, CV studies).
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It must be emphasized that the order in which the chemicals are added in this electrochemical procedure, is very important. For instance if the pH of the bicarbonate solution is not increased to about 11, when the ligand, CyDTA is added, due to the carboxylic groups of the ligand the pH will drop to about 6 or 5. Consequently, the bicarbonate ion (HCO$_3^-$) will be decomposed with CO$_2$ evolution. If, under these conditions MnSO$_4$ is added and now the pH is increased to 10.5, an intensive precipitation will occur. The dark brown precipitate is most probably composed of manganese hydroxides. In this case the electrosynthesis becomes impossible.

Thus, it can be concluded that the bicarbonate ion besides its role as a supporting electrolyte and buffer, plays an important role in stabilizing the Mn(II) and Mn(III) ions in aqueous solution.

Various aspects of the electrosynthesis process have been investigated and the findings are presented in the “Experimental Results and Discussion” section of the present work. A typical runs involved the following CyDTA/Mn(II) molar ratio: 1/1 or 2/1.

In order to find the best conditions for electrosynthesis, six anodes were investigated as follows:

a) stainless steel screen (A=232 cm$^2$*)
b) stainless steel plate (A=71 cm$^2$)
c) graphite plate (A=58 cm$^2$)
d) platinized titanium plate (A=71 cm$^2$)
e) nickel plate (A=56 cm$^2$)
f) lead plate (A=56 cm$^2$).

The electrodes were from time to time cleaned in a 5% HNO$_3$ solution.
The cathode in all runs was a platinized titanium plate (A=70 cm$^2$).

* please see Appendix II for the calculation of the area of the screen
2.4 Spectrophotometry of Mn(III)CyDTA

In order to prove the successful electrosynthesis of Mn(III)CyDTA by this new method, the anolyte solution was acidified with 50 ml glacial acetic acid a sample was taken and placed in a quartz SUPRASIL' (200 - 2500 nm) spectrophotometer cell. The spectra in the range of 200 to 900 nm was recorded with a fully automated Varian Spectrophotometer. In the reference cell distilled water was employed.

The spectra for the chemically synthesized Mn(III)CyDTA was recorded under the same conditions as well. These two spectra were compared with each other and with the Mn(III)CyDTA spectra from the literature [Hamm and Suwyn, 1967; Gangopadhyay et al., 1994].

2.5 Quantitative Analysis of Mn(III)CyDTA

The trivalent manganese was quantitatively determined by an iodometric method originally developed by Pribl and Horacek, (1949) and recommended in subsequent literature [Vogel’s, 1978; Kekedy, 1986].

The principle of this method is based on the reduction of Mn(III) in acetic acid media by iodide according to the following equation:

\[
2\text{Mn(III)}Y + 2\text{I}^- \rightarrow 2\text{Mn(II)}Y + \text{I}_2 \uparrow
\]

\[Y = \text{ligand (e.g. CyDTA).}\]

The separated iodine can be titrated with thiosulfate. The volume of thiosulfate consumed can be correlated with the amount of Mn(III) initially present in the sample:

\[5.05 \text{ ml Na}_2\text{S}_2\text{O}_3 \times 0.1\text{N} \Rightarrow 27.5 \text{ mg Mn(III)} ; \text{[Pribl and Horacek, 1949].}\]

The anolyte from the electrochemical reactor was acidified by adding 50 ml glacial acetic acid under moderate stirring. A 50 ml sample was withdrawn from the reactor and transferred quickly in an Erlenmeyer flask containing a mixture of 10 ml glacial acetic acid
and 0.5 g sodium acetate. A 20 ml 10% solution of KI was added to the sample, the flask was closed with a rubber stopper, shaken a couple of times and placed in a dark place for 10 minutes. The separated iodine was titrated with sodium thiosulfate solutions of 0.1N, 0.05N or 0.02N concentration, using a 10 ml burette (the precision of the burette was 0.05 ml). In each case three replicates were made and the average value was reported.

This method is reliable because trivalent iron and cobalt or bivalent copper ions are not reduced in this medium by iodide, consequently they do not interfere with the manganese determination [Pribil and Horacek, 1949].

2.6 Bleaching Procedures

A) Pulp Samples

In all bleaching runs the same softwood kraft pulp was employed. An amount of 11.00 g air-dry (i.e. 10 g oven-dry) kraft pulp was disintegrated in a British Standard Pulp Evaluation apparatus according to TAPPI T205 standard. A handsheet was made in conformity with the TAPPI T218 standard procedure. The resulting handsheet was employed in the bleaching runs. Thus, the pulp consistency in all runs was 1% (i.e. 10 g oven-dry pulp in 1 liter solution).

The initial Kappa number of the pulp $K_0$, was 30.0 and the initial viscosity $v_0$, was 34.6 cP.

The standard deviation of the Kappa number and viscosity tests was found to be ±0.3 and ±0.4 cP respectively.

B) Electrochemically Mediated Oxygen Bleaching

The anode chamber of the electrochemical reactor was filled up with 1 l anolyte from the previous electrosynthesis step. The handsheet was added and the pH adjusted to the desired value with a 2M NaOH solution. The cathode chamber contained the same electrolyte as in the electrosynthesis step.
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In the case when temperature control was required (e.g. factorial experiments) the stainless steel reactor was placed in a water thermobath and the temperature set to the desired value. During the factorial runs the pH was also monitored and controlled with a precision of ± 0.02 pH units. The pH control was performed by measuring the pH each 15 or 20 min., followed by the addition of a couple of drops of NaOH 2 M or glacial acetic acid in order to set the pH to the desired value.

Depending on the experiment, oxygen or nitrogen was purged in the anode chamber at atmospheric pressure. The electrodes were connected to a DC power supply under the galvanostatic operation mode.

In electrochemically mediated oxygen bleaching two anode types were investigated i.e. stainless steel screen and graphite plate. The cathode was unchanged, a platinized titanium plate.

The experimental set-up of the electrochemically mediated oxygen bleaching is given in Figure 34.

In order to avoid the interference of transition metal ions with the Kappa number and viscosity tests, the pulp was thoroughly washed in acidic solutions (e.g. sulfurous acid). For details about the pulp sample preparation and washing please see Appendix IX.

2.7 Statistical Experimental Design Software

The design and data analysis of both the full 3 factors at 2 levels (i.e. $2^3$) run and the half factorial 6 factor at 2 levels and 1 centerpoint (i.e. $2^6 \cdot 1 + 1$) run, was performed by employing the JASS 2.1 software *. The main and interaction effects were calculated.

In Appendix III, some basic elements of factorial experimental design relevant to the present work, are given.

* JASS 2.1 is a licensed product of the Joiner Associates, Madison, Wisconsin, U.S.A
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1. anode; 2. pH electrode; 3. temperature probe; 4. gas inlet tube; 5. cathode; 6. water thermobath; 7. pH meter with "3 in 1"; 8. DC power supply; 9. gas flowmeter; 10. oxygen (or nitrogen) cylinder; 11. electrochemical bleaching reactor; 12. mixer; 13. cation exchange membrane

Figure 34: In-situ electrochemically mediated oxygen bleaching setup
Chapter 3

Experimental Results and Discussion

The objective of the present work was the investigation of a trivalent manganese complex, namely Mn(III)CyDTA*, as a potential electrochemical mediator in the oxygen bleaching of a softwood kraft pulp, at atmospheric pressure and in alkaline media.

To achieve the proposed goal, the fundamental electrochemical behavior of the selected redox catalyst had to be investigated under various conditions (e.g. pH, ligand to metal molar ratio, electrode material). The cyclic voltammetry technique was employed for this purpose. Furthermore, the electrosynthesis of Mn(III)CyDTA in alkaline media had to be approached, due to both the unavailability of the complex on the market and its tedious chemical synthesis. Finally, the electrochemically mediated oxygen bleaching was studied. Parametric and statistical experimental design was employed to evaluate the effects of different variables on the outcome of the bleaching process.

A flowsheet of the experiments performed in the present work is given in Fig. 35.

* (trans-Cyclohexane-1,2-diamine-NN',NN'-tetraacetato)manganate(III)
Chapter 3: Experimental Results and Discussion

Figure 35: The flowsheet of the experimental runs

Investigation of the Mn(III)CyDTA electrochemical behavior (by Cyclic Voltammetry)

Electrosynthesis of Mn(III)CyDTA in alkaline media
- anode selection

In-situ Electrochemically Mediated Oxygen Bleaching at atmospheric pressure using Mn(III)CyDTA
(Parametric and Factorial Experimental Design)

Stainless steel screen anode
- $2^3$ factorial runs
- influence of organic solvents and additives

Graphite plate anode
- Kappa nr. and viscosity profiles (selectivity)
- $2^{6-1}+1$ factorial runs

CONCLUSIONS
3.1 Cyclic Voltammetry Studies of Mn(III)CyDTA

3.1.1 Testing the Cyclic Voltammetry Setup

To assure the proper functioning of the cyclic voltammetry apparatus (Fig. 32) and the reproducibility of cyclic voltammograms, the experimental setup was tested by recording the cyclic voltammogram of a well-documented electrochemical system, i.e. ferri/ferrocyanide redox couple. This system presents an almost perfect reversible behavior in alkaline media and is commonly employed as an "electrochemical standard" in different testing procedures.

The cyclic voltammetry response on a graphite disk electrode of a 1 mM K₃[Fe(CN)₆] in a 0.5 M NaOH solution was recorded as a function of scan rate in the range of 41.67 to 91.67 mV/s (please see Fig. 36). Always the n-th scan (n>1) was recorded.

As it can be seen from Figure 36, the shape of the waves and the peak potentials were independent of scan rate, suggesting a reversible behavior (Table A, Appendix I). The peak potentials are: \( E_p^a = 230 \text{ mV/SCE} \) and \( E_p^c = 171 \text{ mV/SCE} \). Thus, the separation between the peak potentials is \( \Delta E = 59 \text{ mV/SCE} \). This value clearly indicates a reversible (Nernstian) behavior (Appendix I). Furthermore, Fig. 36 shows that the peak current ratio \( i_p^a/i_p^c \), is independent of scan rate as well, its value being close to unity. This finding is representative also for a reversible system as the ferri/ferrocyanide couple.

Based on the results obtained for the ferri/ferrocyanide system, it was concluded that the cyclic voltammetry setup is reliable in predicting the electrochemical behavior of the "test system" and can be employed in the investigation of Mn(III)CyDTA. However,
the non-faradaic (capacitive) current was slightly large under the employed conditions especially at high scan rates*. 

Figure 36: Cyclic voltammogram of 1 mM $\text{K}_3[\text{Fe}(	ext{CN})_6]$ in 0.5 M NaOH solution. Graphite disk working electrode. Temperature 20 °C. Legend: scan rate 1 = 41.67 mV/s, 2 = 58.34 mV/s, 3 = 75.00 mV/s, 4 = 91.67 mV/s.

* the capacitive current varies linearly with scan rate while the faradaic current varies with the square root of scan rate [Gileadi, 1993]
3.1.2 Cyclic Voltammetry of Mn(III)CyDTA

The cyclic voltammograms of Mn(III)CyDTA should reflect a large number of phenomena such as: adsorption, complexation, disproportionation, pH dependent electrochemical behavior. By employing different electrode materials, various scan rates and pH values certain aspects of the electrochemical behavior of Mn(III)CyDTA can be revealed. In all cyclic voltammetry experiments the n-th scan was recorded.

A) GRAPHITE disk electrode

The first investigation was performed in a solution containing only 1M KCl as supporting electrolyte. The Mn(III)CyDTA concentration was 0.26 mM. The pH was gradually increased from 5.5 to 9.8 by adding volumes of 2 M NaOH solution. The temperature was 25 °C. The results are presented in Figure 37.

![Cyclic voltammograms of Mn(III)CyDTA in 1M KCl solutions of different pH. Ligand to metal molar ratio: 2/1. Graphite disk working electrode. Scan rate: 33.34 mV/s.](image)

Figure 37: Cyclic voltammograms of Mn(III)CyDTA in 1M KCl solutions of different pH. Ligand to metal molar ratio: 2/1. Graphite disk working electrode. Scan rate: 33.34 mV/s.
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As can be seen from Figure 37, there was no cyclic voltammetry response (i.e. peak currents) due to Mn(III)CyDTA under these conditions. Other authors have also reported the absence of CV response in the case of both manganese(II) 5-sulfonatosalicylate and manganese cyanide, at pH 9.4, borate buffer and 3.75/1 ligand to metal molar ratio [Perng et al., 1993]. Similarly, in the presence of EDTA ligand at pH 9 in borax solution, the manganese(II) exhibited no cyclic voltammetry response on a carbon electrode [Landucci, 1979].

The explanation of Mn(III)CyDTA electrochemical inactivity under the employed conditions, might be found by looking at the structure of the complex compound. In aqueous solutions Mn(III)CyDTA* is engaged in the following acid-base equilibrium:

\[
[Mn(III)CyDTA(H_2O)]^- \rightleftharpoons \frac{K_m}{[Mn(III)CyDTA(HO^-)]^{2-} + H^+}; \quad (40)
\]

the equilibrium constant \(K_m\) is equal to \(7.76 \times 10^{-9}\) mol/l [Gangopadhyay et al., 1994]. In slightly acidic media, pH 4 to 6, the complexation by CyDTA is strong, the equilibrium in eq. (40) being shifted to the left, while with the increase of pH the equilibrium is shifted toward the hydroxo species. Due to the high stability of both Mn(II) and Mn(III) complexes at pH 4 - 6 in the presence of a ligand excess (2:1), the manganese ions cannot participate in electrode reactions, consequently there will be no peak currents. The same

\* Mn(III) forms seven-coordinated complexes with CyDTA, EDTA etc. Six sites are occupied by CyDTA and the seventh by the water molecule, or other species (e.g. hydroxyl ion) [Hamm and Suwyn, 1967].
phenomena was reported for Ni(II) and Cd(II) complexes with other aminopolycarboxylate ligands such as EDTA, DTPA and NTA when the ligand to metal molar ratio exceeded the equivalence point [Piszczek et al., 1988].

At alkaline pH (e.g. 9.8) the complex is less stable, still no electrochemical response was obtained. In this case the inactivity of the hydroxo species toward electron-transfer processes [Gangopadhyay et al., 1994] might be responsible for the absence of the CV response.

The cyclic voltammetry investigation of Mn(III)CyDTA in a supporting electrolyte containing 0.1M NaHCO₃ in addition to 1M KCl, revealed clear anodic and cathodic responses (please see Figure 38).

The cathodic peak belongs to the Mn(III)/Mn(II) reduction, while the anodic peak is given by the Mn(II)/Mn(III) oxidation. It can be argued that on the oxidation scan the Mn(II)/Mn(IV) or/and the Mn(III)/Mn(IV) processes might occur as well. However, the existence of stable Mn(IV) complexes with CyDTA or other EDTA type ligands, has not been reported yet [Cotton and Wilkinson, 1988]. The only stable Mn(IV) in aqueous alkaline media is the MnO₂, which is mainly due its insolubility [Hunter and Kozawa, 1985]. Consequently, the interference of Mn(IV) species in the present CV response was ruled out.

Comparing Figures 37 and 38a, shows that the presence of NaHCO₃ was essential in bringing about the CV response of Mn(III)/Mn(II)CyDTA. A comprehensive explanation of the role played by the bicarbonate ion is not available at this time. However, it can be reasoned that the bicarbonate ion competes with the hydroxyl ion for
the substitution of water molecule in the manganese coordination sphere. The presence of bicarbonate ion might change the stoichiometric equivalence point of the complex or it might facilitate the electron-transfer process.

![Cyclic voltammograms](image)

**Figure 38**: Cyclic voltammograms on a graphite electrode for a) 0.092 mM Mn(III)CyDTA in a 0.1M NaHCO$_3$ and 1M KCl supporting electrolyte. pH=8.0 at 25 °C. CyDTA/Mn=2/1

b) supporting electrolyte only. Scan rate: 66.67 mV/s
Figure 38a reveals some other interesting aspects of the Mn(III)/Mn(II)CyDTA electrochemical behavior as well. As the sweep rate increases, the reduction peak broadens and a second cathodic peak being developed very close to the first one. As a response, on the reverse scan (i.e. anodic) the oxidation peak broadens as well at high scan rates, although not as clearly as the cathodic one (Fig. 38a). This behavior is characteristic for the presence of adsorption processes simultaneously with the electrode reactions [Bard and Faulkner, 1980; Brown and Sandifer, 1986].

The fact that the second reduction peak is developed at high scan rates before the first (diffusion controlled) peak, i.e. "pre-peak behavior", indicates that the product of the reduction reaction, i.e. Mn(II) species is adsorbed on the surface of the graphite electrode [Bard and Faulkner, 1980].

Thus, the "pre-peak" represents the reduction of Mn(III) to form a layer of adsorbed Mn(II). The adsorption controlled "pre-peak" occurs at potentials more positive than the usual diffusion-controlled peak (please see Fig. 38a) because the reduction of Mn(III) to adsorbed Mn(II) is easier than to Mn(II) species in solution [based on Bard and Faulkner, 1980].

The cyclic voltammogram of Mn(II) (18 mM) oxidation at a glassy carbon electrode (scan rate 2 mV/s), in 6.15 M H₂SO₄ was consistent with film formation as well [Kuhn and Randle, 1983].

Another relevant factor to electrochemically mediated oxygen bleaching is the pH dependence of the electrochemical behavior of Mn(III)/Mn(II)CyDTA. The CV response
(i.e. peak potentials and currents) are significantly influenced by pH, in the case of metal-polycarboxyl ligand systems [Gampp, 1987].

For the investigation of pH influence on CV, a low scan rate was selected (33.34 mV/s) to avoid complications due to the presence of adsorption peaks (Fig. 38a). At this scan rate only the soluble Mn(III) and Mn(II) species are detected. The pH was varied in the range of 11.1 (curve 1, Fig. 39) and 13.4 (curve 3, Fig. 39). Increasing the pH generated a decrease in the cathodic and anodic peak currents, and a shift of the peak potentials toward more negative values. At pH 13.4 the cathodic peak basically vanishes due to the extremely fast decomposition (disproportionation) of Mn(III)CyDTA and the formation of inactive Mn(IV) oxides and hydroxides. The anodic peak is still present, this means that the oxidation of Mn(II)CyDTA is possible, furthermore is even easier at high pH (the anodic peak potential is shifted toward more negative values (Fig. 38a). However, the electrochemically generated Mn(III)CyDTA is not stable and consequently it cannot be used in subsequent homogeneous oxidation reactions.
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Figure 39: Cyclic voltammogram of Mn(III)CyDTA (0.092 mM) in 0.1M NaHCO₃ and 1M KCl as a function of pH at 25 °C. Graphite disk electrode, scan rate 33.34 mV/s.

B) STAINLESS STEEL wire electrode

The cyclic voltammetry responses on a stainless steel wire working electrode showed both similarities and slight differences in comparison with the graphite electrode.

The first investigation employing the stainless steel electrode was concerned with the scan rate influence. Figure 40a shows that increasing the scan rate from 33.34 mV/s to 66.67 mV/s did not bring about a clear, distinct second peak as in the case of graphite (Fig. 38a). However, this does not mean that there is no adsorption phenomena on stainless steel. It means only that the dynamics of adsorption could not be properly detected under the employed conditions. It might well be, that the time scale of the adsorption on stainless steel is out of range compared with the time scale of the CV experiment (i.e. scan rate)..
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Figure 40: Cyclic voltammogram of:

a) Mn(III)CyDTA (0.092 mM) in a 0.1 M NaHCO₃ and 1 M KCl solution at pH = 8.1, 25°C

b) supporting electrolyte only

The peak current ratio \( i_p/\bar{i}_p \), determined from eq. (38), has a value of 4.27 for a scan rate of 33.34 mV/s and 4.22 for \( v = 66.67 \) mV/s, thus it is virtually independent of scan rate. The smaller cathodic peak current compared with the anodic one, is a reflection of a lower Mn(III)CyDTA concentration than Mn(II)CyDTA conc. due the Mn(III)CyDTA decomposition in alkaline media.

The peak potential separation is large, \( E_{p}^{a} - E_{p}^{c} = 274 \) mV for both scan rates. The ohmic potential drop contributes to this value as well.
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The pH dependence of the electrochemical behavior on stainless steel, was investigated in the range of pH 10.5 to 13.4 at 25 °C. The scan rate was maintained constant at 66.67 mV/s.

![Cyclic voltammogram of Mn(III)CyDTA (0.092 mM) in 0.1 M NaHCO₃ and 1 M KCl as a function of pH at 25 °C. Scan rate 66.67 mV/s. Stainless steel electrode](image)

**Figure 41**: Cyclic voltammogram of Mn(III)CyDTA (0.092 mM) in 0.1 M NaHCO₃ and 1 M KCl as a function of pH at 25 °C. Scan rate 66.67 mV/s. Stainless steel electrode

- **a)** pH: 10.5 to 11.1
- **b)** pH: 12.9 to 13.4.
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Increasing the pH generated the same effect as in the case of a graphite electrode, i.e. a shift of the cathodic peak potential toward more negative values and a decrease of both the cathodic and anodic peak currents (Fig. 41). At pH 13.4 the cathodic peak current disappears as an indication of the fast and complete disproportionation of Mn(III)CyDTA in strong alkaline media. Thus, at this pH the Mn(II)CyDTA oxidation becomes irreversible.

C) PLATINUM wire electrode

The question of Mn(II) adsorption on metal electrodes remained somewhat unresolved in the studies involving the stainless steel electrode. Therefore, a comparison between the CV response on platinum and stainless steel have been made. The cyclic voltammograms were recorded on the same chart (Fig. 42). Also, a four times more sensitive current measurement has been made compared with the sensitivity employed in the CV test presented in Figure 40 (i.e. 5 µA/V (Fig. 42a) vs. 20 µA/V (Fig. 40a)).

Figure 42a clearly shows the existence of adsorption on both stainless steel and platinum electrodes at low scan rate (33.34 mV/s). The “pre-peak“ on platinum is better separated than the one on stainless steel. On the reverse scan, a broad anodic response, composed of two peaks can be identified as well. The anodic “pre-peak“ corresponds to the oxidation of the adsorbed Mn(II) layer. On platinum the separation of diffusion peaks is 136 mV, higher than the 59 mV which is characteristic for a perfect reversible behavior. Thus, the CV response is quasi-reversible (i.e. between reversible and irreversible behaviour) [Appendix I].
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Figure 42: Cyclic voltammogram of:

a) Mn(III)CyDTA on platinum and stainless steel electrodes at pH=10.0, 20 °C. \([\text{Mn(III)}]= 0.092 \text{ mM, CyDTA/Mn (molar ratio)}=2/1.\)

Supporting electrolyte: 0.1 M NaHCO\(_3\) and 1 M KCl solution. Scan rate: 33.34 mV/s

b) supporting electrolyte only on Pt as a function of scan rate
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From the point of view of Mn(III)CyDTA electrosynthesis and its further role as a redox catalyst in oxygen bleaching a couple of important conclusions can be drawn from the cyclic voltammetry data.

First of all the CV results have shown the paramount importance of the bicarbonate ion in bringing about the electrochemical response of the Mn(III)/Mn(II)CyDTA system in alkaline media. Based on this evidence, in all of the subsequent electrosynthesis and bleaching runs a 0.1 M NaHCO$_3$ concentration was employed.

It is known from the literature that the complexation of Mn(III) with CyDTA reduces significantly the standard reduction potential of the Mn(III)/Mn(II) couple. For example in strong acidic media, pH 0 and below, $E^\circ_{Mn(III)/Mn(II)} = +1.5$ V/SHE [Hunter and Koziawa, 1985] while for Mn(III)/Mn(II)CyDTA at pH 4 - 5, $E^\circ_{Mn(III)/Mn(II)}$ is only +0.814 V/SHE [Hamm and Suwyn, 1967]. This is due to the stronger complexation of the higher oxidation state of the metal ion [Ibanez et al., 1988]. On top of this, the CV data has shown that the reduction potential of the Mn(III)/Mn(II)CyDTA is further decreased with increasing pH. The cathodic peak potential was shifted toward more negative values with the increasing pH. Unfortunately the actual reduction potential could not be calculated from the presented CV data, because of the deviation from ideal reversible behavior. At pH greater than 11, the cathodic peak current is significantly reduced and at pH~13, it vanishes due to the fast disproportionation of Mn(III) and formation of inactive hydroxo species. Thus, in order to obtain a reasonable oxidizing power the pH should not exceed the value of 11.
In order to present any catalytic activity in electrochemically mediated oxygen bleaching, the required reduction potential of the redox couple should be greater than +400 mV/SHE [Perng et al., 1993] or it should be in the range of -60 to +540 mV/SHE according to Landucci, (1979) (please see section 1.3.6 of Chapter 1). The presented cyclic voltammograms have shown that in alkaline media, in the presence of NaHCO₃, the cathodic peak potential for Mn(III)CyDTA reduction is in the range of 40 to 160 mV/SHE while the anodic peak potential is between 200 to 270 mV/SHE (please see Fig. 37 to 42) for a pH range of 10 to 11 at 25 °C. Thus, the actual reduction potential is roughly around 215 mV/SHE (pH=10) and 120 mV/SHE (pH=11). Consequently, the electrochemical behavior of Mn(III)CyDTA fits in the range established by Landucci but does not satisfy the more demanding condition determined by Perng et al.

The fact that in all cases the anodic peak was present at potentials lower than the oxygen evolution peak potential indicates that the generation of Mn(III)CyDTA by electrochemical oxidation of Mn(II)CyDTA is possible and is favored by a high pH. The anodic peak potential was found to decrease with increasing pH and the values obtained in alkaline media were significantly lower than those reported in the literature for the oxidation of Mn(II) in acidic media (pH=4.5), in the presence of other strong ligands [Cui and Dolphin, 1990]. However, the existence of adsorption phenomena, clearly indicated by the CV data, has to be taken into account during the electrosynthesis.

* Note that these values are approximate, being calculated by assuming perfect reversible behaviour
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3.2 Electrosynthesis of Mn(III)CyDTA in Alkaline Media

3.2.1 Spectrophotometry of Mn(III)CyDTA

The absorption spectra were recorded for both electrochemically and chemically synthesized Mn(III)CyDTA in the range of 340 to 900 nm, with a speed of 2.0 nm/s (Fig. 43 and 44). The pH of the electrochemically synthesized Mn(III)CyDTA was 4.5 while for the chemically synthesized Mn(III)CyDTA was 2.6 at 25 °C.

A single, broad peak was observed in both spectra, with an absorption maximum between 480 to 518 nm (Fig. 43 and 44). This is the reason of the dark red color of Mn(III)CyDTA in acidic media. Both spectra matched perfectly the Mn(III)CyDTA absorption spectra presented in the literature [Hamm and Suwyn, 1976; Gangopadhy et al., 1994], indicating the successful electrochemical synthesis of this complex compound.

When the pH is increased, the complex changes color, becoming yellow and yellow-brownish in alkaline media.
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Figure 43: Absorption spectra of electrochemically synthesized Mn(III)CyDTA at pH=4.5, 20°C.

Figure 44: Absorption spectra of chemically synthesized Mn(III)CyDTA at pH=2.5, 20°C.
3.2.2 Spontaneous, Aerobic Generation of Mn(III)CyDTA in Alkaline Solutions

In alkaline solutions, in the presence of dissolved oxygen, the Mn(II)CyDTA might undergo spontaneous chemical oxidation to form Mn(III)CyDTA. Such reactions were described for the Mn(II) sorbitol and gluconate complexes [Bondini and Sawyer, 1976; Richens et al., 1979]. Therefore, in the case of electrochemical synthesis of Mn(III)CyDTA, it is very important to know if or how much Mn(III)CyDTA is formed by a parallel, non-electrochemical route. This will affect the current efficiency calculation, where the electrochemical production rate must be taken into account only (please see section 1.5.3 of Chapter 1).

“Blank” synthesis runs (i.e. without current) were performed by employing the same concentrations of Mn(II) and CyDTA, under the same conditions as in the electrosynthesis runs (pH=10.5, 25 °C, dissolved oxygen from the air). The CyDTA/Mn molar ratio was 1/1 and 2/1 respectively. The desired amounts of Mn(II) and CyDTA were added to a 1 l solution containing 0.1 M NaHCO₃. The pH was set to 10.5. The solution was mixed with a magnetic stirrer for 1 hour. At the end three samples were taken and analyzed for the Mn(III)CyDTA content. The results are presented in Figure 45.

The problem of spontaneous Mn(III)CyDTA formation in alkaline media, is related to the superoxide dismutation catalysis, presented in section 1.2.3 of Chapter 1. There it was pointed out that Mn aminopolycarboxylate complexes, at high ligand to metal ratio, do not catalyze the dismutation reaction efficiently at pH above 8. This is what was found for Mn(II)CyDTA oxidation by dissolved oxygen, when CyDTA/Mn molar ratio was 2/1.
2/1. There was no measurable amount of Mn(III)CyDTA formed (please see Fig. 45).

However, for an equimolar ligand to metal ratio, the situation is different.

![Figure 45: Aerobic formation of Mn(III)CyDTA at pH=10.5, 25 °C. Reaction time 1 hr.](image)

For an equimolar CyDTA/Mn molar ratio, the concentration of Mn(III)CyDTA produced, followed a parabolic shape as a function of Mn(II) concentration. The increase, leveling and subsequent drop in the Mn(III)CyDTA formation indicates a catalyst - inhibitor conversion of Mn(II)CyDTA in alkaline media. Similar behavior was observed in the case of manganese(II)-sorbitol (1/1) catalyzed aerobic oxidation of hydrazine at pH=12.1 [Lim et al., 1988]. The aerobic oxidation of Mn(II)CyDTA involves various oxygen containing free radical species. After exceeding an induction concentration of
Mn(II), i.e. 18 mM, the Mn(II) catalyzes the oxygen reduction to form Mn(III) and hydrogen peroxide. However, at concentrations above 27 mM, both the Mn(II) and CyDTA act as sequestering agents, tying up and scavenging the free radicals (e.g. hydroxyl and peroxy radicals).

When pure oxygen was purged into the system at atmospheric pressure, virtually the same data as those in Fig. 45, were obtained.

It is considered that the aerobic oxidation of Mn(II)CyDTA, generates Mn(III)CyDTA only. Generally the Mn(III) complexes react with O$_2$ much slower than the Mn(II) complexes [Richens et al., 1979] and the formation of Mn(IV)CyDTA is highly unlikely.

3.2.3 Electrosynthesis of Mn(III)CyDTA on a Stainless Steel Screen Anode in Alkaline Media

The literature survey indicates that the electrolytic oxidation of Mn(II) to Mn(III) was mainly studied in strong acidic media, e.g. in sulfate, phosphate, pyrophosphate solutions. A variety of anodes was tested, e.g. platinum, PbO$_2$, Au, boron carbide, paraffin-impregnated carbon and glassy carbon. Usually very high current efficiencies were obtained (> 99%) [Kuhn and Randle, 1983]. The presence of carboxyl and polycarboxyl ligands was found to decrease the current efficiency of Mn(III) electrosynthesis in sulfuric acid slurry [Comminellis and Plattner, 1984].

There is very little information about the electrosynthesis of Mn(III) complexes, particularly Mn(III)CyDTA, in alkaline media. The present work tries to contribute some
information to this area. The first investigated anode was a stainless steel screen. The
electrochemical reactor presented in Fig. 33 was employed in all of the electrosynthesis
runs.

A) Current Efficiency vs. Mn(II) concentration. The Mechanism of Electrosynthesis

The Mn(III)CyDTA electrosynthesis was investigated for five different Mn(II)
concentrations, from 6 mM to 54 mM, and at two CyDTA/Mn molar ratio, 1/1 and 2/1
respectively. The initial pH was 10.5 at 25 °C. The applied current density was 2.6 A/m²
(i.e. 0.06 A) for a 1 hour period. The resulting electrolyte was analyzed for
Mn(III)CyDTA content. A plot of Mn(III)CyDTA conc. vs. the Mn(II)CyDTA conc. is
given in Figure 46.

In order to calculate the true current efficiency for CyDTA/Mn = 1/1, the
electrochemically generated Mn(III)CyDTA had to be calculated by subtracting from the
total amount of Mn(III)CyDTA formed (given in Fig. 46), the Mn(III)CyDTA generated
by the non-electrochemical, aerobic, oxidation (given in Fig. 45). A detailed sample
calculation of current efficiency is given in Appendix IV. The calculated current efficiency
was plotted against the Mn(II) concentration for both cases : CyDTA/Mn 1/1 and 2/1
respectively (Fig. 47).

There are significant differences in the outcome of electrosynthesis as a function of
CyDTA/Mn molar ratio.
Figure 46: Mn(III)CyDTA conc. vs. Mn(II) conc. Electrosynthesis at pH_{in} = 10.5, 25 °C, \( i = 2.6 \text{ A/m}^2 \), time 1 hr. Stainless steel screen anode.

Figure 47: Current efficiency vs. Mn(II) conc. Electrosynthesis at pH_{in} = 10.5, 25 °C, \( i = 2.6 \text{ A/m}^2 \), time 1 hr. Stainless steel screen anode.
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In the case of equimolar ligand to metal ratio, three different phases can be observed (Fig. 47). In the range of 6 mM to 36 mM Mn(II), the current efficiency increases up to ~96%. In the subsequent Mn(II) conc. range, 36 mM to 45 mM, the current efficiency is leveled off at ~96%, while at even higher reactant concentrations, the current efficiency drops to 89%. This intricate behavior is determined by the significant changes of the electrode surface. Beginning with the 18 mM Mn(II) conc. level, a brownish deposit (adsorbed layer) was formed on the stainless steel screen. The higher the Mn(II) conc., the thicker the adsorption layer was, and its formation was faster. At the end of electrolysis, the electrolyte was acidified in the reactor with the anode present. In this acidic media (pH ~ 4 - 5, 50 ml glacial acetic acid added), under mixing, the adsorption layer was washed from the anode surface, generating the same red color as the rest of the electrolyte. Thus, the analyzed samples contained Mn(III)CyDTA from both, the electrolyte and the adsorbed layer.

The formation of anodic films during the oxidation of manganese compounds in alkaline media, is dependent on the electrode surface, pH of the solution, local pH at the vicinity of the electrode and the polarization of the electrode [Ivanova and Ivanov, 1993].

For a proper further discussion of the electrosynthesis mechanism and the implications of the adsorption layer, the effect of convective mass transfer, due to both mixing and oxygen evolution, has to be determined. The limiting current density was calculated for each concentration level (please see Appendix V for detailed calculation). The calculated limiting current density together with the actual, measured current density

\[ i_{\text{meas}} = \text{CE} \times i; \text{ where } i=2.6 \text{ A/m}^2 \]
adsorption phenomena. At higher concentrations, starting with 18 mM, the anodic film becomes significant modifying both the surface and the electrochemical properties of the stainless steel electrode. In the 18 mM to 36 mM Mn(II) conc. range (Fig. 47), the electrosynthesis is under a different kind of kinetic control, namely, kinetic control on the modified stainless steel surface. The adsorption layer acts as a "new" electrode material. At even higher concentrations, 36 mM to 45 mM, the current efficiency is leveled off, the anodic film is formed very fast and is thick. The oxidation process takes place almost entirely in the adsorbed layer through the interconversion of different adsorbed species:

\[
\begin{align*}
\text{Mn(II)CyDTA}_{(aq)} & \rightarrow \text{Mn(II)CyDTA}_{(ads)} \\
& \quad \downarrow -1e^- \\
& \quad \text{Mn(III)CyDTA}_{(ads)} \\
\text{Mn(OH)}_2_{(ads)} & \rightarrow -1e^- \text{MnOOH}_{(ads)} \rightarrow -1e^- \text{MnO}_2_{(ads)}
\end{align*}
\]

The adsorption layer hinders the transport of Mn(II) ions from the bulk of the electrolyte to the electrode surface. Thus, the film acts as an "electrolyte" (ionic conductor) as well, having its own conductance. The leveled off current efficiency
suggests that in this range the rate of diffusion of Mn(II)CyDTA through the anodic film is equal to the rate of electrochemical consumption of the adsorbed species. Consequently, a steady-state has been achieved.

At the highest Mn(II) conc. level (i.e. 54 mM) the current efficiency dropped to about 89%. The anodic film is very thick and the entire electrosynthesis is controlled by the diffusion of the reactant through the anodic film.

Processes such as product desorption or dissolution might further complicate the overall kinetic behavior of the Mn(III)CyDTA electrosynthesis on stainless steel.

Due to the fact that the anodic film acts as both electrode and "electrolyte", in the literature this behavior is sometimes called "bifunctional electrochemical system" [Ivanova and Ivanov, 1993].

In the case of a CyDTA excess (CyDTA/Mn = 2/1), the electrosynthesis behaves differently. There was no visible evidence of any deposit on the stainless steel screen. However, the CV results have shown the existence of adsorption phenomena at this ligand to metal ratio, but rather a microscopic, more or less, monolayer is formed than a visible, thick film. The electrosynthesis is under kinetic control, the virtual independence of the Mn(III)CyDTA conc. and current efficiency on Mn(II) conc. (Fig. 46 and 47) indicates an apparent zero order kinetics*

* for detailed discussion of this aspect please see section 3.2.5
B) Current Efficiency vs. Current Density

The current density used in the runs presented above was low, 2.6 A/m². The electrosynthesis of Mn(III)CyDTA on stainless steel was further investigated at higher current densities as well (Fig. 49 and 50). A concentration of 18 mM Mn(II) was chosen.

At the *equimolar* CyDTA/Mn ratio for current densities above 5.8 A/m², the electrode reaction is fast, the anodic film is formed very rapidly but the diffusion of Mn(II)CyDTA through the thick anodic film is very slow, becoming the rate controlling step. As a consequence, the current efficiency drops dramatically.

In the presence of an *excess* CyDTA, the Mn(III)CyDTA concentration slightly increases with current density (Fig. 49). Again, there was no visible evidence of anodic film.

![Graph showing Mn(III)CyDTA conc. vs. current density](image)

**Figure 49**: Mn(III)CyDTA conc. vs. current density. [Mn(II)] = 18 mM. Electrosynthesis at pH_{in} = 10.5, 25 °C, time 1 hr. Stainless steel screen anode.
Figure 50: Current efficiency vs. current density. Electrosynthesis at pH_{in} = 10.5, 25 °C, [Mn(II)] = 18 mM, time 1 hr. Stainless steel screen anode.

The data presented so far, show that the stainless steel screen can be employed as an anode for Mn(III)CyDTA electrosynthesis only at low Mn(II) conc. (e.g. 6 mM), low current density (i.e. 2.6 A/m^2) and equimolar CyDTA/Mn ratio.

3.2.4 Comparison Among Various Anode Materials

To find a better anode, with better electrocatalytic properties for Mn(III)CyDTA electrosynthesis in alkaline media, four additional materials were tested as anodes. These are: platinized titanium, Pb/PbO_2, Ni and graphite. Also, a stainless steel plate was investigated.

In all runs equimolar concentrations of 18 mM Mn(II) and CyDTA were employed. The initial pH was 10.5 and the temperature 25 °C. Reaction time was 1 hour.
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Because the electrodes had different areas (please see Chapter 2), for a proper comparison the normalized Mn(III)CyDTA conc. to the unit electrode area, \( \{M/m^2\} \) is reported.

A) Current Efficiency vs. Current Density

In Figure 51 the Mn(III)CyDTA conc. per unit electrode area is plotted as a function of current density. The calculated current efficiency (please see Appendix IV) is plotted vs. current density in Fig. 52.

![Graph of Normalized Mn(III)CyDTA vs. Current Density](image)

**Figure 51:** Normalized Mn(III)CyDTA conc. vs. current density for various anodes. 
CyDTA/Mn (molar ratio) = 1/1, \([\text{Mn(II)}]\) = 1.8 mM, pH\textsubscript{a} = 10.5 at 25 °C. Time 1hr.
A1) Stainless Steel Plate

The adsorption on the stainless steel plate was found to be significant as well. Comparing the plate with the screen (Fig. 52 with Fig. 50), it can be seen that on the screen anode a current density of 15.5 A/m\(^2\) gave a 2 % current efficiency, while on the plate the same, very low current efficiency, was obtained at much higher current density, i.e. 76 A/m\(^2\). In other words, the build-up of the anodic film, which is the cause of the significant current efficiency drop, occurs faster on the screen than on the plate at the same mixing power. This indicates the effect of local turbulence created around the fine meshes of the screen on the film formation. The deposition of Mn(II)CyDTA is facilitated by an enhanced local mass transfer.
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Comparing the stainless steel plate with the other anodes (Fig. 51 and 52), it gave the worst response, thus is not recommended for further use.

A2) Platinized titanium (Pt/Ti) Plate

On the Pt/Ti plate there was no visible deposit at any of the employed current densities. However, the CV data has shown the existence of adsorption on Pt wire, but it might be that the adsorbed layer remains microscopic without growing to a thick, visible film.

The current efficiency was good, ranging from 66 % to 32 %. At high current densities the oxygen evolution becomes significant.

A3) Ni Plate

The Ni anode had an interesting behavior. At the lowest current density explored, i.e. 13 A/m², the Ni gave the highest Mn(III)CyDTA conc. and current efficiency (84 %). As the current density increased, the current efficiency dropped dramatically, to 12 % at 102 A/m². On the Ni anode there was no visible deposit formation. However, at high current densities the Ni anode, initially silvery, turned rapidly dark gray, due to the formation of Ni hydroxides and oxides on its surface. Thus, the electrosynthesis occurred on a “modified “Ni surface (i.e. Ni(OH)₂, NiO, NiOOH etc.) rather than on a “pure “Ni metal surface. This has an important effect on the kinetics of the process being responsible for the current efficiency drop.
Due to the electrochemical instability of the Ni anode in alkaline media, is not recommended for use in this particular process.

A4) Pb Plate

In alkaline media and under anodic conditions, the Pb surface is instantaneously covered with an oxide layer, thus the active electrode is PbO₂.

Even at the lowest current density, a brownish deposit was formed on the electrode surface. The deposit was washed off with great difficulty.

The current efficiency values were high in the range of 35 % to 60 % (Fig. 52). However, due to a strong adsorption of Mn(II) and Mn(III) species is not considered as a proper choice.

A5) Graphite Plate

Over the entire range of explored current densities the graphite anode gave the best current efficiency values (from 41 % to 78 %)*. These values were obtained without observing any modification on the graphite surface. However, the graphite has a porous structure where adsorption could have occurred. The CV data also showed the existence of adsorption phenomena. Still, at a macroscopic level, macroscopic parameters like current efficiency were not affected.

* except the 13 A/m² current density, where on the Ni anode the current efficiency was 84 %
B) Cell Voltage and Specific Energy vs. Current Density

The energy requirements of an electrochemical process are of paramount importance in determining its viability. The overall cell voltage and specific energy are two key parameters used in evaluating the energy consumption of an electrochemical process (please see section 1.5.3 of Chapter 1).

The electrosynthesis of Mn(III)CyDTA was carried out under galvanostatic conditions, i.e. the cell voltage slightly changed (i.e. ± 0.5 V) in order to supply a constant current all the time. Still, an average cell voltage could be calculated. Considering that the ohmic voltage drop across both the membrane and the electrolytes, together with the voltage change on the cathode (Pt/Ti) were the same in all runs, the differences in the required cell voltage were due to the different anode materials tested, more exactly to the different overvoltages on the tested anodes (please see eq. (36) in section 1.5.3).

The required cell voltage $V_{\text{cell}}$, was plotted against the current density as a function of the five investigated anodes (Fig.53). The specific energy was calculated from the cell voltage and current efficiency by using eq.(37). The specific energy $SE$, was plotted against the current density in Figure 54.

Both the cell voltage and specific energy increased with increasing current density. The cell voltage values varied between 1.6 and 5.6 V, while the specific energy was between 62 and 8259 kWh/(kmol of Mn(III)CyDTA), depending on the anode material. Among the five tested anodes graphite gave the lowest specific energy values due to the low required cell voltages and high current efficiencies.
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The highest cell voltages were measured when the anode was a Pt/Ti plate. This is partly due to the high oxygen overpotential on platinum [based on Oloman, 1992]. However, the relatively high current efficiency on Pt generated lower specific energy values than those on stainless steel for example.

Taking into account all the investigated factors, current efficiency, cell voltage, specific energy, surface properties together with the cost of the electrode material*, it was concluded that the graphite is the most appropriate anode for this process. Consequently, the electrosynthesis of Mn(III)CyDTA on graphite plate was subjected to further investigations.

* the price of Pt/Ti is ~ 1,000 - 2,000 $/m², while the price of graphite is only ~ 50 - 100 $/m² [Oloman, 1992]
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Figure 53: Cell voltage vs. current density. CyDTA/Mn (molar ratio) = 1/1, [Mn(II)] = 18 mM, pH_{in} = 10.5 at 25 °C. Reaction time 1 hour.

Figure 54: Specific energy vs. current density. CyDTA/Mn (molar ratio) = 1/1, [Mn(II)] = 18 mM, pH_{in} = 10.5 at 25 °C. Reaction time 1 hour.
3.2.5 Electrosynthesis of Mn(III)CyDTA on Graphite Plate Anode

A) Current Efficiency vs. Mn(II) concentration

The electrosynthesis was carried out at a current density of 25 A/m$^2$, for 1 hour, with an initial pH of 10.5 at 25 °C, with various initial Mn(II) concentrations ranging from 6 mM to 36 mM, for two CyDTA/Mn molar ratio, 1/1 and 2/1 respectively. The results are presented in Figures 55 and 56.

There was no visible evidence of anodic film formation at any of the concentrations employed. Just like in the previous studies (e.g. stainless steel screen), the electrogenerated Mn(III)CyDTA conc. and the current efficiency were considerably higher for an equimolar CyDTA/Mn ratio than in the case of CyDTA/Mn = 2/1. The strong complexation of Mn(II) by CyDTA makes the electrochemical oxidation more difficult. This implies that the actual reactant at the anode surface is rather the uncoordinated Mn(II) ion than the Mn(II)CyDTA itself. Thus, the Mn(II) inside the electric double layer must be free of the voluminous CyDTA ligand and approaches the anode surface in an uncoordinated form.

As long as the CyDTA/Mn molar ratio remains 2/1, by increasing the Mn(II) conc., the generated Mn(III)CyDTA conc. and the current efficiency remained unchanged (Fig. 55 and 56), i.e. apparent zero order behavior. The reason for this is that the concentration of uncoordinated Mn(II) inside the electric double layer actually remains the same if the ligand to metal molar ratio is unchanged, i.e. 2/1. However, more studies are needed in order to clarify this aspect of the process.
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Figure 55: Mn(III)CyDTA conc. vs. Mn(II) conc. Electrosynthesis at $\text{pH}_{\text{in}} = 10.5$, 25 °C, $i = 25 \text{ A/m}^2$, time 1 hr. Graphite plate anode.

Figure 56: Current efficiency vs. Mn(II) conc. Electrosynthesis at $\text{pH}_{\text{in}} = 10.5$, 25 °C, $i = 25 \text{ A/m}^2$, time 1 hr. Graphite plate anode.
B) Current Efficiency vs. Current Density

Increasing the current density at the 6 mM Mn(II) conc. level, generated increased concentrations of Mn(III)CyDTA as well (Fig. 57). Again, there was no visible sign of anodic film formation. The limiting current density is about 74 A/m$^2$ (Appendix V), while the actual current density corresponding to Mn(III)CyDTA generation $i_{\text{meas}} = CE*i$, is much lower, thus the synthesis on graphite is under kinetic control.

As the current density increases, the oxygen evolution predominates more and more over the Mn(III)CyDTA electrosynthesis, causing a gradual drop in current efficiency (Fig. 58).

![Figure 57: Mn(III)CyDTA conc. vs. current density. Electrosynthesis at pH$_{in} = 10.5$, 25 °C, $[\text{Mn(II)}] = 6$ mM, time 1 hr. Graphite plate anode.](image)
Figure 58: Current efficiency vs. current density. Electrosynthesis at pH_{in} = 10.50, 25 °C, [Mn(II)] = 6 mM, time 1 hr. Graphite plate anode.

C) The Influence of pH and the Importance of pH Control during Mn(III)CyDTA Electrosynthesis

The electrosynthesis on graphite anode was investigated as a function of current density by starting at two different pH values, i.e. 10.5 and 9.0 respectively (Figs. 59 and 60). It was found that the process is favored by a higher pH, giving higher Mn(III)CyDTA concentrations and better current efficiencies (please see Figs. 59 and 60).

The complexation of Mn(II) by CyDTA is stronger at pH 9.0 than at pH 10.5, consequently the formation of uncoordinated Mn(II) inside the electric double layer is much more difficult, hindering the electrosynthesis. The upper limit of the operational pH is determined by the Mn(II) and Mn(III)CyDTA stability.
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Figure 59: Mn(III)CyDTA conc. vs. current density as a function of pH. CyDTA/Mn (molar ratio) = 2/1, [Mn(II)] = 6 mM, 25 °C. Graphite plate anode.

Figure 60: Current Efficiency vs. current density as a function of pH. CyDTA/Mn (molar ratio) = 2/1, [Mn(II)] = 6 mM, 25 °C. Graphite plate anode.
Due to the parallel oxygen evolution on the anode, the pH of the anolyte decreases during the electrosynthesis (Fig. 61). This has an important effect upon the outcome of the electrosynthesis, especially when the process is prolonged e.g. over 1 hour*. In the absence of pH control, beyond 1 hour, the Mn(III)CyDTA concentration decreased in the electrochemical reactor (Fig. 62). Bearing in mind that the measured Mn(III)CyDTA conc. is always the net, accumulated Mn(III)CyDTA conc. (i.e. electrochemically synthesized minus decomposed), beyond 1 hour, the decomposition exceeded the electrosynthesis rate, the decreased pH (i.e. < 10.0) slowed down the electrochemical process more than the complex decomposition.

In the case of pH control at 10.5, the Mn(III)CyDTA conc. remained high even after 1 hour, being somewhat leveled off, indicating that the electrosynthesis rate exceeded the decomposition rate (Fig. 62). The pH was controlled by measuring it every 15 min. and correcting it to the desired value by addition of a couple of drops of NaOH 2 M.

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* this is the case during electrochemically mediated oxygen bleaching which last usually 3 hours
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Figure 61: pH profile during the Mn(III)CyDTA electrosynthesis. $i = 51$ A/m$^2$, $[\text{Mn(II)}] = 6$ mM, CyDTA/Mn (molar ratio) = 2/1. Graphite plate anode.

Figure 62: The influence of pH control (at 10.5) on the Mn(III)CyDTA electrosynthesis. $i = 51$ A/m$^2$, $[\text{Mn(II)}] = 6$ mM, CyDTA/Mn (molar ratio) = 2/1. Graphite plate anode.
3.2.6 The Stability of Mn(III)CyDTA in Alkaline Media

The stability of Mn(III)CyDTA depends on a number of factors such as: pH, temperature, ligand to metal ratio.

The Mn(III)CyDTA stability was investigated at pH = 10.5 for the two ligand to metal molar ratios, 1/1 and 2/1 respectively. The anolyte from the electrosynthesis step was placed in a thermobath with the pH set to 10.5. Samples were taken and analyzed for Mn(III)CyDTA content from time to time. The half-life time of the complex was calculated (Appendix VIII).

At 25 °C, CyDTA/Mn = 2/1, initial Mn(III)CyDTA conc. 1.4 mM, pH 10.50, the half life time was about 40 minutes. Increasing the temperature generated a faster decomposition. At 40 °C the half life time dropped to about 30 minutes while at 80 °C is about 10 minutes. For an equimolar CyDTA/Mn ratio, the decomposition at pH 10.5 was even more significant. The half-life time was about 30 min. at 25 °C, dropping to about 20 min. at 40 °C and about 5 min. at 80 °C.

By increasing the CyDTA/Mn molar ratio and decreasing the pH (e.g. pH 9.0) the Mn(III)CyDTA stability increases considerably. No measurements were made for this case.
3.3 \textit{In-situ} Electrochemically Mediated Oxygen Bleaching using Mn(III)CyDTA

The electrosynthesis studies proved the possibility of electrochemical Mn(III)CyDTA generation in alkaline media. Out of the six investigated anodes, only two were retained for the bleaching runs, namely the stainless steel screen (under conditions where adsorption does not influence the process) and graphite. The rest of them were discarded on the basis of poor electrochemical performance, chemical instability under the employed conditions or high cost (please see section 3.2.4).

The softwood kraft pulp was added to the anolyte from the electrosynthesis step (1\% consistency), the pH and temperature were adjusted to the desired values and different types of bleaching runs were performed. The employed apparatus and procedures were presented in Chapter 2, section 2.6 (please see Fig. 34 as well).

3.3.1 Stainless Steel Screen Anode

The initial Mn(III)CyDTA concentration in the present series of bleaching runs was 0.5 mM, being generated from an equimolar 6 mM Mn(II) and CyDTA solution at pH 10.5 and \( i = 2.6 \text{ A/m}^2 \). The current efficiency of the electrosynthesis step was 19 \% (please see Figs. 46 and 47).

The electrochemically mediated bleaching was performed at the same, low current density (2.6 A/m\(^2\)), to avoid excessive adsorption on the screen.

Also an \textit{equimolar} CyDTA/Mn ratio was used in all of the bleaching runs
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employing stainless steel screen, due to an unsatisfactory electrochemical performance at higher CyDTA/Mn ratio (please see section 3.2.3).

The counter electrode was a platinized titanium plate in all cases.

A) Full Factorial Experimental Design using 3 Factors at 2 Levels

The goal of the present investigation was to determine the effects (main and interaction) of three process variables, i.e. oxygen, catalyst and current, on both Kappa number and viscosity. The temperature and pH were held constant at 25 °C and 10.5 respectively. The levels of the employed variables are given in Table 2.

Table 2: Variables and their levels in the $2^3$ factorial run

<table>
<thead>
<tr>
<th>VARIABLES</th>
<th>VARIABLE</th>
<th>LEVEL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- ('LOW')</td>
<td>+ ('HIGH')</td>
</tr>
<tr>
<td>OXYGEN (MPa) (O)</td>
<td>0*</td>
<td>0.1**</td>
</tr>
<tr>
<td>CATALYST (mM) (C)</td>
<td>0</td>
<td>0.5***</td>
</tr>
<tr>
<td>CURRENT DENSITY (A/m²) (I)</td>
<td>0</td>
<td>2.6****</td>
</tr>
</tbody>
</table>

Eight runs (i.e. $2^3$) were performed in random order according to the design created by the JASS 2.1 software (Table 3). Some of the runs were replicated three times in order to estimate the experimental error for both Kappa number and viscosity. From the

* Nitrogen purge  
** Oxygen purge (844 ml/min, 21 °C, 101kPa)  
*** Initial concentration  
**** On a stainless steel screen anode
replicated runs, Appendix VI, the response errors are: for Kappa number \( s_k \approx \pm 0.43 \) and for viscosity \( s_v = \pm 0.47 \) cP.

The experimental results are plotted as cube plots in Figures 63a and 63b respectively.

Table 3: Design of the \( 2^3 \) full factorial experiment

<table>
<thead>
<tr>
<th>I.D.</th>
<th>OXYGEN</th>
<th>CATALYST</th>
<th>CURRENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>2</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
</tbody>
</table>
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Figure 63: Cube plot of Kappa number and viscosity as a function of oxygen, catalyst and current density levels. Bleaching time 3 hr., pH 10.5, 25 °C. Unbleached pulp: \( K = 30.0 \) and \( v = 34.6 \) cP.
Figure 63a, shows that the best delignification $K=22.0$, was obtained at the highest level of all three factors. Also, in this case the carbohydrate degradation was the most intense, the viscosity dropped to 24.9 cP (Fig. 63b).

The JASS 2.1 software supplied the main and interaction effects as well (Table 4).

### Table 4: Main and Interaction Effects in the $2^3$ factorial experiments

<table>
<thead>
<tr>
<th>EFFECTS</th>
<th>FACTORS</th>
<th>KAPPA number</th>
<th>VISCOSITY (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAIN</td>
<td>OXYGEN (O)</td>
<td>-0.725</td>
<td>-0.950</td>
</tr>
<tr>
<td>MAIN</td>
<td>CATALYST (C)</td>
<td>-4.875</td>
<td>-2.050</td>
</tr>
<tr>
<td>MAIN</td>
<td>CURRENT (I)</td>
<td>-1.125</td>
<td>-1.250</td>
</tr>
<tr>
<td>INTERACTION</td>
<td>OC</td>
<td>-0.475</td>
<td>-0.150</td>
</tr>
<tr>
<td>INTERACTION</td>
<td>CI</td>
<td>-0.575</td>
<td>-0.850</td>
</tr>
<tr>
<td>INTERACTION</td>
<td>OI</td>
<td>0.175</td>
<td>-1.050</td>
</tr>
</tbody>
</table>

The effects presented in Table 4, shows that oxygen at 25 °C, pH 10.5 and atmospheric pressure had a statistically insignificant effect on delignification, its main effect being -0.725 while the confidence interval is $\pm 0.785$. This result is consistent with other studies as well [Perng, 1993a]. Figure 63a indicates that the runs with oxygen

---

* The confidence intervals at a 95% level are: $W(K,\text{effect})=\pm 0.785$ for Kappa number and $W(v,\text{effect})=\pm 0.869$ for viscosity. Please see Appendix VI for detailed calculation.
** The interaction effect between 2 factors assumes that the remaining factors are at an average, middle level.
generated Kappa numbers just slightly lower than the runs with nitrogen purge. However, oxygen had a statistically significant, damaging effect on carbohydrates causing a viscosity drop of 0.95 cP when the oxygen 'level' was increased from 'low' to 'high'. The interaction effect between oxygen and current (OI) is significant as well. Considering the catalyst at an average, middle level, increasing the current at its 'highest' level (i.e. 2.6 A/m$^2$) when oxygen is present, caused a full point decrease in viscosity (OI = -1.05 cP). This is due to the damaging effect of the high amount of Mn(III) (when current is present) acting synergistically with oxygen.

The redox catalyst, Mn(III)CyDTA, had a very significant main effect on both delignification and carbohydrate degradation. However, its main effect on Kappa number exceeded the main effect on viscosity (-4.875 vs. -2.050), indicating a certain degree of selectivity. The interaction effects on Kappa number between catalyst and both oxygen and current are statistically insignificant under the employed conditions, suggesting that Mn(III)CyDTA acts on delignification additively rather than synergistically (i.e. in interaction). Still, the negative sign of the interaction effects shows a tendency of improving the delignification.

Similarly, the interaction effect between catalyst and oxygen upon viscosity is insignificant when current is absent or is at a middle level (OC = -0.150 cP). This result is interesting, because it shows that the Mn(II) form of the catalyst, which predominates in the absence of current, does not interact with oxygen in destroying the pulp carbohydrates.
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The high main effect of current on both Kappa number and viscosity is a reflection of its role in continuously generating the active form of the redox catalyst, i.e. Mn(III)CyDTA, thus it cannot be analyzed as an individual contribution.

B) The Influence of Organic Solvents

From the factorial experiments it was learned that Mn(III)CyDTA, even in low amounts (i.e. 0.5 mM) was the single most important factor in promoting delignification. However, neither the extent of delignification nor the selectivity were satisfactory. Under the employed conditions the oxygen had an insignificant effect on delignification.

In organic solvents, the solubility of oxygen is increased at least two times vs. its solubility in pure water [Sawyer. 1991]. Also, the solubility of certain high molecular weight, crosslinked lignin structures is enhanced in organic solvents, thus an improved delignification might be possible [Ljunggren, 1990; Ljunggren and Johansson, 1990].

In the present work two organic solvents were employed, i.e. dimethylsulfoxide (DMSO) in a 10% vol. proportion and acetonitrile (MeCN) in a 50% vol. proportion. The oxygen solubility at 25 °C and 1 atm in DMSO is 2.1 mM while in MeCN is 8.1 mM [Sawyer, 1991]. These values are approximately 2 and 8 times respectively higher than the oxygen solubility in pure water.

The electrosynthesis of Mn(III)CyDTA was performed under similar conditions with the previous factorial runs.

In order to prepare the desired mixture of bleaching solution (i.e. electrolyte-organic solvent) 500 ml of anolyte containing 0.5 mM Mn(III)CyDTA was retained in the
anode chamber and either a volume of 500 ml MeCN or 100 ml DMSO with 400 ml distilled water was added. Thus, the content of organic solvent was 50% vol of MeCN and 10% vol of DMSO. The initial Mn(III)CyDTA concentration in the MeCN run was 0.27 mM and 0.48 mM in the DMSO run. Current was supplied from the stainless steel anode ($i = 2.6 \text{ A/m}^2$). The bleaching time was 3 hours at 25 °C, with a 1% pulp consistency and atmospheric oxygen pressure. The Teflon coated stainless steel reactor was employed to avoid the dissolution of Plexiglas by the organic solvents (Chapter 2, section 2.5). The results are presented in Table 5.

Table 5: The effect of organic solvents (DMSO and MeCN) on in-situ electrochemically mediated oxygen bleaching using a stainless steel screen anode ($i = 2.6 \text{ A/m}^2$, $T = 25 ^\circ \text{C}$, $t = 3 \text{ hr.}$, oxygen = 1 atm). Unbleached pulp: $K = 30.0$, $v = 34.6 \text{ cP}$.

<table>
<thead>
<tr>
<th>Run #</th>
<th>CONDITIONS</th>
<th>KAPPA nr.</th>
<th>VISCOSITY (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMSO 10% vol, initial Mn(III)CyDTA conc. 0.48 mM</td>
<td>22.7</td>
<td>27.0</td>
</tr>
<tr>
<td>2</td>
<td>MeCN 50% vol, initial Mn(III)CyDTA conc., 0.27 mM</td>
<td>21.2</td>
<td>21.2</td>
</tr>
<tr>
<td>3</td>
<td>without organic solvent initial Mn(III)CyDTA conc., 0.5 mM</td>
<td>22.0</td>
<td>24.9</td>
</tr>
</tbody>
</table>
In the presence of 10% vol DMSO the viscosity improved considerably, compared with the run without organic solvent. At the same time the delignification was slightly slower than in the absence of the solvent, but this might be due the lower initial Mn(III) conc. Overall the selectivity of the process was much better (compare runs # 1 and 3), the DMSO contributed mainly to the carbohydrate protection while it did not significantly affect the delignification.

In the case of 50% vol MeCN both the delignification and carbohydrate degradation was intensified. This is probably due to the increased role of oxygen according to its high solubility. Unfortunately, the intense viscosity drop causes a poor overall selectivity.

C) The Influence of Additives

In order to improve the outcome of the in-situ electrochemically mediated oxygen bleaching certain additives were tested to check if they are able to assist the redox catalyst in promoting selective delignification. In the present work the effects of a nitroxyl radical (4-carboxy TEMPO*) and of nitrous oxide (N₂O) were investigated.

The nitroxyl radicals are known to catalyze the chlorine dioxide oxidation of certain oxygen-containing organic substrates [Golubev et al., 1991], while the nitrous oxide has radical scavenging properties [James, 1992], thus it might improve the viscosity of the resulting pulp.

Most of these runs were identical with the ones performed as part of the factorial runs. The additive 4-carboxy-TEMPO was added to the anolyte in a 0.25 mM concentration, before bleaching. The nitrous oxide was purged at atmospheric pressure in

* 4-carboxy-TEMPO = 4 - carboxy - 2,2,6,6 - tetramethylpiperidinyloxy free radical
the anode chamber for 1 hour. During this time oxygen was not purged. After the first hour oxygen was purged for the last 2 hours, thus the total bleaching time was 3 hr., as usual. The experimental results are given in Table 6.

Table 6: The effect of additives on in-situ electrochemically mediated oxygen bleaching using a stainless steel screen anode (i = 2.6 A/m², initial Mn(III)CyDTA conc. 0.5 mM, pH 10.5, T = 25 °C, t = 3 hr.). Unbleached pulp : K = 30.0 and v =34.6 cP.

<table>
<thead>
<tr>
<th>Run #</th>
<th>CONDITIONS</th>
<th>KAPPA nr.</th>
<th>VISCOSITY (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-carboxy-TEMPO (0.2 mM)</td>
<td>22.3</td>
<td>21.6</td>
</tr>
<tr>
<td>2</td>
<td>N₂O purge (1 hr.)</td>
<td>21.7</td>
<td>18.1</td>
</tr>
<tr>
<td>3</td>
<td>without additives</td>
<td>22.0</td>
<td>24.9</td>
</tr>
</tbody>
</table>

Both additives had damaged the pulp carbohydrates without improving the delignification (Table 6). Surprisingly, the nitrous oxide instead of protecting the carbohydrates by scavenging the free radicals, caused the most severe viscosity drop.

The absence of lignin oxidizing power of 4-carboxy-TEMPO is due to its diminished reduction potential at high pH*.

* E(R₂NO./R₂NOH) = 0.608 - 0.059pH V/SHE [Golubev et al., 1991]
3.3.2 Graphite Plate Anode

By employing a stainless steel screen anode, the electrochemically mediated oxygen bleaching was confined to low current densities and therefore to low redox catalyst concentration (~ 0.5 mM). Although this demonstrated the role of Mn(III)CyDTA in promoting bleaching, the extent of delignification was not satisfactory.

Replacing the stainless steel screen anode with a graphite plate allows for much higher current densities without significant complications due to adsorption. Also, a 2/1 CyDTA/Mn molar ratio can be explored due to better electrosynthesis on graphite (please see section 3.2.5). Therefore, the improved electrochemical performance might bring about an enhanced delignification process.

A) The Influence of Ligand to Metal Molar Ratio

The electrosynthesis of Mn(III)CyDTA is strongly dependent on the CyDTA/Mn molar ratio (please see section 3.2.5), thus it should influence the outcome of the bleaching process. Also, the CyDTA might act as a carbohydrate protecting agent, consequently its concentration during the bleaching can be a significant process variable.

Two CyDTA/Mn molar ratios were investigated, i.e. 1/1 and 2/1 respectively. The initial Mn(II) conc. (as MnSO₄) was 6 mM. The applied current density was for both cases 51 A/m², at pH 10.5, 25 °C. The current efficiency and Mn(III)CyDTA conc. after 1 hour of electrosynthesis were: 28 % and 3 mM for CyDTA/Mn = 1/1, and 13 % with 1.4 mM for CyDTA/Mn = 2/1 (please see section 3.2.5).
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At the end of electrosynthesis the pH of the anolyte was adjusted to 10.5, pulp was added (1% consistency), the current was applied (51 A/m²) and the bleaching process was performed with continuous oxygen purge at atmospheric pressure (844 ml/min @ 21 °C and 101 kPa). The temperature was held constant at 25 °C. In order to determine the time profile of both Kappa number and viscosity, the bleaching time was varied as follows: 15 min, 30 min, 1 hr, 2 hr, and 3 hr.

To assess the role of both catalyst and current, two parallel experiments were performed under similar bleaching conditions (pH, T, O₂ and pulp consistency). The first one was a 'thermocatalysis', i.e. with redox catalyst but without current, while the second one was a 'classical' oxygen bleaching ('blank' run), without both catalyst and current.

The Kappa number and viscosity values were plotted vs. time for both CyDTA/Mn ratios in Figures 64 and 65 respectively.

At a first glance it can be seen from Figure 64, that in both cases the best delignification was obtained in the electrochemically mediated bleaching runs, thus putting into evidence the role of the anodic current in the regeneration of the active form of the redox catalyst, i.e. Mn(III)CyDTA. However, there are significant differences between the two ligand to metal ratios.

In the case of an equimolar CyDTA/Mn ratio, the Mn(III)CyDTA concentration was higher but the stability of the complex is lower. From Fig. 64a it can be seen that in the presence of current, after a fast delignification in the first 20 minutes, the Kappa number was leveled off for the next two to three hours at a value of about 23 to 22.4.
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Figure 64: KAPPA number profiles in time as a function of CyDTA/Mn ratio. pH 10.5, 25 °C, O₂ 0.1 MPa, i = 51 A/m² (where applicable).

A) CyDTA/Mn = 1/1 (molar ratio); initial Mn(III)CyDTA conc. 3 mM

B) CyDTA/Mn = 2/1 (molar ratio); initial Mn(III)CyDTA conc. 1.4 mM
Chapter 3: Experimental Results and Discussion

The leveled Kappa number in the equimolar case (curve # 1, Fig. 64a), can be explained by the fast decomposition of the electrogenerated Mn(III)CyDTA and the formation of electrochemically inactive hydroxo species, at high Mn(III) concentrations (e.g. above 3 mM)*. When the CyDTA was in excess (i.e. CyDTA/Mn = 2/1), again the fastest delignification occurred in the first 30 min, K dropped from 30 to 23.5. However, due to the presence of an anodic current (curve # 1, Fig. 64b), the Kappa number gradually decreased during the entire bleaching period, from 23.5 at 30 min. to 19.8 after 3 hours, in a sharp contrast with the equimolar case. In this situation the stability of Mn(III)CyDTA is higher than in the equimolar case, consequently the Mn(III) decomposition rate is lower. The rate determining step being the reaction kinetics, thus a continuous anodic generation of Mn(III)CyDTA helps the delignification over the entire period. The extended lifetime of Mn(III), i.e. higher stability of the complex, contributes to the sustained delignification over a longer period of time.

The runs performed without current (thermocatalysis) but with initial conc. of Mn(III)CyDTA (curves # 2, Fig. 64a and 64b), for CyDTA/Mn 2/1, showed a rapid delignification in the first 15 minutes, followed by a leveling off for the rest of the time (curve #2, Fig. 64b). The Mn(III) is continuously consumed in both the delignification reaction and by decomposition in alkaline media, without a continuous regeneration its concentration falls and cannot further promote delignification. Consequently, the Mn(III) form is the active delignification promoting agent in the present system.

The Kappa number profile of the thermocatalytical bleaching was different for an equimolar CyDTA/Mn ratio (please see curve #2, Fig. 64a). The delignification was

*usually a first order kinetics is assumed for the Mn(III)CyDTA decomposition [Hamm and Suwyn, 1967]
Chapter 3: Experimental Results and Discussion

characterized by an initial lag period (about 30 min) followed by a rapid delignification between 30 min and 1 hour and a leveling off for the remaining period. The existence of an induction phase when CyDTA/Mn was 1/1 and the absence of it when CyDTA/Mn was 2/1 (compare curves #2 from Fig. 64a and 64b respectively), indicates two different reaction mechanisms. When CyDTA/Mn is 1/1, the complex is easily disproportionated generating Mn(II) species and MnO₂. The competition between the Mn(III)CyDTA - lignin and Mn(III)CyDTA disproportionation is shifted toward the disproportionation, thus almost no further delignification occurs in the first 30 minutes (induction period). However, after a certain period of time, the accumulated Mn(II) species can assist oxygen in promoting a moderate delignification, K drops from 29.1 to 25.2 between 30 min and 1 hour. Thus, a true thermocatalysis takes place. The extent of thermocatalysis did not improve in time, the Kappa number reached a floor value of 24.1. When CyDTA/Mn is 2/1, the stability of the complex is much higher (please see section 3.2.6), in the initial 30 minutes the Mn(III) has enough life time to attack the lignin (phenolate anion) via a direct redox mechanism. In time the active Mn(III)CyDTA is depleted in this case as well, however due to an excess of CyDTA the active sites of Mn(II) are completely blocked, thus a further true thermocatalysis does not takes place.

The viscosity profiles (Figs. 65a and 65b) revealed some other interesting aspects of the process as well. The viscosity drop was the most severe during the electrochemically mediated bleaching runs, indicating that Mn(III) attacks both the lignin and carbohydrates.
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A) CyDTA/Mn = 1/1 (molar ratio); initial Mn(III)CyDTA conc. 3 mM

B) CyDTA/Mn = 2/1 (molar ratio); initial Mn(III)CyDTA conc. 1.4 mM

Figure 65: VISCOSITY profiles in time as a function of CyDTA/Mn ratio. pH 10.5, 25 °C, O₂ 0.1 MPa, i = 51 A/m² (where applicable).
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The extent of carbohydrate degradation was significantly alleviated when CyDTA was in excess (please see curves #1 in Figs. 65a and 65b).

After 3 hours, for CyDTA/Mn = 2/1, $v = 20.5$ cP, while for CyDTA/Mn = 1/1, $v = 13.2$ cP. Consequently, the CyDTA indeed acts as carbohydrate protecting agent in the presence of Mn(III).

During the runs without current (thermocatalysis) high viscosity values were obtained in both cases (curves # 2, Figs. 65a and 65b). These values are almost independent of CyDTA/Mn molar ratio.

Furthermore, over an extended period of time (e.g. 3 hours) there was no difference between the viscosity values obtained in the blank runs (curves # 3) and the thermocatalytical experiments. The fact that the results were similar for the two different CyDTA/Mn ratios, shows that in this case not the CyDTA but rather the Mn(II) species e.g. Mn(OH)$_2$, Mn(II)CyDTA, were responsible for the carbohydrate protection. These results are in agreement with the work of Landucci, 1975, which indicates as well the protecting role of Mn(II) compounds.

The mechanism by which both the Mn(II) species and CyDTA protect the carbohydrates cannot be fully explained at this time. Efficient free radical scavenging coupled with other possible factors such as complexation of the reducing ends of carbohydrates, adsorption on the fiber, deactivation of the harmful effect of Mn(III) by an excess of CyDTA etc., might contribute to the overall protecting effect.

The Kappa number and viscosity profiles showed the multiple and complex functions played by the \{(Mn(III)/Mn(II))\}CyDTA redox couple. The Mn(III) is active in
promoting delignification, while CyDTA and Mn(II) species are effective carbohydrate protecting agents.

The 'blank' experiments (curves #3, Figs. 64 and 65) showed once again that at 25 °C, pH 10.5 and atmospheric oxygen pressure, the oxygen itself cannot induce a reasonable delignification.

**B) The Combined Effect of pH and Temperature on Delignification**

From the previous studies it was learned that the CyDTA/Mn = 2/1 molar ratio gave the best Kappa number and viscosity values, in the case of electrochemically mediated oxygen bleaching using a graphite plate anode. Therefore, the 2/1 CyDTA/Mn ratio was retained for further investigations.

All the experiments presented so far, were performed at 25 °C and pH 10.5. The conventional oxygen bleaching is carried out at temperatures ~ 100 °C (section 1.3.5). Previous electrochemically mediated bleaching studies have shown significant delignification enhancement at high temperatures [Perng, 1993a; Todd, 1993]. Therefore, the role of temperature in this process, required a closer look.

The electrochemically mediated oxygen bleaching employed a CyDTA/Mn = 2/1 molar ratio, a current density of 51 A/m² on a graphite plate anode. Oxygen was purged at atmospheric pressure, with a 1 % pulp consistency. The bleaching time was 3 hours. The initial Mn(III)CyDTA conc. was 1.4 mM.

The bleaching runs were performed at two pH levels, 10.5 and 9.0 respectively. The effect of temperature was investigated in the range of 25 to 80 °C.
Unfortunately, for all these experiments, the bleached pulp was washed according to the procedure # III (based on sulfuric acid, please see Appendix IX.). This washing procedure significantly damaged the pulp carbohydrates, causing altered and unreproducible viscosity values. These values were found unreliable and not worth for interpretation and analysis. Consequently, the Kappa numbers are reported and analyzed only.

In Figure 66 the Kappa number is plotted as a function of temperature and pH for the electrochemically mediated oxygen bleaching.

![Figure 66](image)

Figure 66: The combined influence of pH and temperature on delignification. CyDTA/Mn 2/1, graphite plate anode, 51 A/m², oxygen 0.1 MPa, t = 3 hr.
Chapter 3 : Experimental Results and Discussion

At the pH 10.5 level, the increased temperature generated a retardation of delignification, the Kappa number increased from 19.8 at 25 °C to 24.5 at 80 °C. This is due to the fast, enhanced complex decomposition with temperature.

At pH 9.0 the trend is reversed. Increasing the temperature improved the delignification process. At 80 °C the Kappa number dropped from 30.0 to 17.1 in 3 hr. The stability of Mn(III)CyDTA is greatly improved by lowering the pH while the rate of the kinetic controlling step for delignification is increased by the high temperature. These combined effects are responsible for the extended delignification.

Although no experiments were performed, it can be reasoned that a further lowering of pH below 9.0, would give greater stability of the complex but would not improve the delignification because it will negatively affect both the electrochemical Mn(III)CyDTA generation and the ionization of the phenol units in lignin to form the phenolate anion.

C) Half Factorial Experiments with 6 Factors at 2 Levels and 1 Centerpoint (2^6 + 1)

In addition to oxygen, catalyst and current, the investigations previously reported, revealed the importance of three other factors, i.e. temperature, pH and CyDTA/Mn molar ratio, on the outcome of electrochemically mediated oxygen bleaching. Therefore, a factorial design involving all six variables would give a fairly good overall picture of the process. Furthermore, the centerpoint result would supply information about the linearity or non-linearity of the system. The employed apparatus in Fig. 34 was presented.
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The pulp consistency was the usual 1 % and the bleaching time 3 hr. for all experiments. The employed levels of the six variables are given in Table 7.

A number of 33 experiments were performed in random order, according to the experimental design created with the JASS 2.1 software. The experiments and the results obtained are given in Table 8. Selected runs were replicated and the response errors together with the confidence intervals were calculated, for both Kappa number and viscosity (please see Appendix VI part B). By performing half-factorial design instead of the full factorial one, only the 4-th and higher order interactions are not estimable.

Table 7: Variables and their levels in the \(2^{6-1} + 1\) factorial experimental design

<table>
<thead>
<tr>
<th>Nr.</th>
<th>VARIABLES (variable symbols)</th>
<th>- ('LOW')</th>
<th>0 ('CENTER')</th>
<th>+ ('HIGH')</th>
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<tr>
<td>1</td>
<td>OXYGEN (ml/min) (O)</td>
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<td>422</td>
<td>844</td>
</tr>
<tr>
<td>2</td>
<td>CATALYST (M) (C)</td>
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<td>0.7 mM**</td>
<td>1.4 mM**</td>
</tr>
<tr>
<td>3</td>
<td>CURRENT DEN. (A/m²) (I)</td>
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<td>25***</td>
<td>51***</td>
</tr>
<tr>
<td>4</td>
<td>TEMPERATURE (°C) (T)</td>
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<td>53</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>pH (P)</td>
<td>9.0</td>
<td>9.8</td>
<td>10.5</td>
</tr>
<tr>
<td>6</td>
<td>CyDTA/Mn (mol. ratio) (L)</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

* Nitrogen purge (844 ml/min 21 °C, 101 kPa)
** Initial concentration
*** on the graphite plate anode
\(\text{pH control}\)
Chapter 3 : Experimental Results and Discussion

Table 8 : Design and outcome of the $2^6 + 1$ factorial experiments

<table>
<thead>
<tr>
<th>I.D.</th>
<th>C</th>
<th>I</th>
<th>O</th>
<th>P</th>
<th>L</th>
<th>T</th>
<th>Kappa</th>
<th>Viscosity (cP)</th>
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<td>-</td>
<td>-</td>
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<td>+</td>
<td>26.1</td>
<td>31.1</td>
</tr>
<tr>
<td>19</td>
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<td>+</td>
<td>+</td>
<td>-</td>
<td>28.8</td>
<td>30.5</td>
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</table>
The response errors are: for Kappa number \( s_K = \pm 0.379 \); for viscosity \( s_v = \pm 0.388 \) cP.

The confidence intervals at 95 % level are: \( W(K,\text{effect}) = \pm 0.366 \); \( W(v,\text{effect}) = \pm 0.374 \).

Please see Appendix VI part B for detailed calculations of these statistical parameters.

---

* Table 8 (CONTINUATION)
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The results presented in Table 8 are difficult to analyze on an individual basis. Therefore, with the help of the JASS 2.1 software, the main and interaction effects were calculated (Table 9). The highest order of estimable interaction was three.

Table 9: Main and interaction effects for the ‘2⁶⁺¹’ factorial experiments

<table>
<thead>
<tr>
<th>EFFECTS MAIN &amp; INTERACTION*</th>
<th>KAPPA number</th>
<th>VISCOSITY (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CATALYST (C)</td>
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<td>-1.981</td>
</tr>
<tr>
<td>CURRENT DENS. (I)</td>
<td>-1.925</td>
<td>-2.549</td>
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<tr>
<td>OXYGEN (O)</td>
<td>-2.006</td>
<td>-1.269</td>
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<tr>
<td>pH (P)</td>
<td>-0.705</td>
<td>-0.616</td>
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<tr>
<td>CyDTA/Mn (L)</td>
<td>0.981</td>
<td>1.244</td>
</tr>
<tr>
<td>TEMPERATURE (T)</td>
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<tr>
<td>CI</td>
<td>-1.744</td>
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<tr>
<td>CO</td>
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<td>-1.756</td>
</tr>
<tr>
<td>CP</td>
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<tr>
<td>CL</td>
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<td>CT</td>
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<td>IL</td>
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</table>

* Note: the interaction effects between two or three variables assume that the remaining variables are at an average, middle level.
**Chapter 3 : Experimental Results and Discussion**

<table>
<thead>
<tr>
<th>EFFECTS**</th>
<th>KAPPA number</th>
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<td>MAIN &amp; INTERACTION*</td>
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<tr>
<td>OT</td>
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<td>CLT</td>
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</tbody>
</table>

---

**Table 9 (CONTINUATION)**

* Note: the interaction effects between two or three variables assume that the remaining variables are at an average, middle level.
From Table 9 it can be seen that among the investigated variables, the redox catalyst, Mn(III)CyDTA, had the most profound effect on delignification, its main effect being -2.9. This main effect cannot be analyzed separately, because the catalyst is involved in statistically significant second and third order interaction effects with almost all of the process variables. The second order interaction between catalyst and current (CI), is especially important. When the catalyst is at its highest level, by increasing the current from ‘low’ to ‘high’ the Kappa number is further reduced with 1.7 units. This proves the significance of the in-situ regeneration of the Mn(III)CyDTA. In a sharp contrast with the findings of the full factorial runs performed at 25 °C employing the stainless steel screen electrode, the interaction between catalyst and oxygen (CO) is statistically very significant in this case, being equal to -1.4. This is due to the increased importance of oxygen in the high temperature runs, e.g. OT = -2.0, coupled with the presence of a higher Mn(III)CyDTA concentration as a result of a more efficient electrosynthesis on graphite than on stainless steel. Under these conditions Mn(III)/Mn(II)CyDTA and oxygen acted synergistically to delignify the pulp.

The third order interaction between Mn(III)CyDTA, oxygen and temperature (COT) has a value of -1.0, and it shows that actually all three factors act in synergy to promote delignification. The same is true for the Mn(III)CyDTA, oxygen and current (COI) third order interaction, however this interaction parameter is only -0.5.

The large main effect of oxygen is due actually to its interaction with temperature and catalyst, consequently it does not has the meaning of a single, additive effect.
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Similarly, the main effect of current $I = -1.9$, is a reflection of its role in the generation of the Mn(III)CyDTA, is not an additive effect as well.

The pH has a significant main effect on Kappa number $P = -0.7$, while most of its second order interaction parameters are statistically insignificant, being of the order of the confidence interval, i.e. $W(K, effect) = \pm 0.366$. Consequently, increasing the pH improves the delignification through an additive rather than an interaction effect. However, certain third order interactions between pH and other variables require a closer look. For instance, the interaction between catalyst, pH and temperature (CPT) has a value of 0.9, indicating a severe retardation of delignification. This result is due to the rapid decomposition of the active form of the catalyst, when pH and temperature are at a 'high' level. Thus, in the absence of current and oxygen the delignification is slowed down at high pH and temperature.

The CyDTA/Mn molar ratio ($L$) has a significant retarding main effect on delignification. Increasing the ligand to metal ratio from 2 to 4, generates an increase in Kappa number with 1.0 units. At high $L$, the Mn(III) is strongly bonded (or is not electrogenerated at all), consequently its catalytic activity being greatly diminished. Thus, the interaction effect between catalyst and ligand to metal ratio (CL), has a positive value of 0.6, indicating a reduced delignification rate. Interestingly, the interaction parameter between oxygen and CyDTA/Mn ratio (OL) has a positive value as well, i.e. 0.8, proving that the CyDTA scavenges the free radicals involved in promoting the oxygen delignification. Following the same pattern, the third order interaction between catalyst,
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oxygen and ligand (COL) has a value of +0.8, summarizing the fact that a 'high' concentration of CyDTA blocks both the Mn(III) and the oxygen containing free radicals.

Regarding the viscosity (i.e. carbohydrate degradation), a high concentration of CyDTA has a beneficial effect on pulp carbohydrates $L = +1.2$, which is due exactly to the same reason why CyDTA hinders the delignification. Still, the third order interaction effect between catalyst, pH and temperature (CPT), outweighs the protection effect due to CyDTA only, $CPT = +1.5$ vs. $L = +1.2$. It can be concluded that the Mn(II) species like Mn(OH)$_2$, Mn(II)CyDTA, which are predominating at 'high' pH, temperature and catalyst levels, are more efficient carbohydrate protecting agents than CyDTA itself. This conclusion is further supported by the second order interaction effects such as $CL = 0.6$ while $CT = 1.0$. Put in simple words, the disproportionation of Mn(III) at high temperatures generates a more effective carbohydrate protection than its strong complexation with a large excess of CyDTA. Obviously, a unilateral carbohydrate protection without delignification improvement, as in the case of Mn(III) disproportionation, is of no use.

The Mn(III)CyDTA in itself and especially in second and third order interactions with current and/or oxygen damaged the carbohydrates as well. Still, for the best run from a delignification point of view (please see I.D. 14 in Table 8) where $K = 16.7$, the viscosity value is fairly high, being equal to 21.5 cP.

The curvature effects were calculated for both delignification and carbohydrate degradation as the difference between the average of the centerpoint response and the average of factorial points. For Kappa number the factorial points gave an average of
Chapter 3: Experimental Results and Discussion

26.3 while the centerpoint average was 23.5 (please see Table 10). Thus, a curvature of -2.8 Kappa number points was obtained. This effect is statistically significant, the confidence interval of the Kappa number curvature effect at a 95 % level being ±1.1 (please see Appendix VI part B).

In the case of viscosity, the average value of the factorial responses was 29.2 cP while the centerpoint gave a value of 26.9 cP, generating a curvature of -2.3 cP. This result is statistically significant as well, the confidence interval of the viscosity curvature effect at a 95 % level being ±1.1 cP (Appendix VI part B).

Consequently, the system presented a small but statistically significant non-linear behavior which might be attributed to the complex interdependence of the investigated process variables. It also reveals the existence of a true catalytic effect rather than stoichiometric interaction only.

The best result so far, was obtained at 80 °C, pH 9.0, 0.1 MPa oxygen pressure, CyDTA/Mn = 2/1, with an initial Mn(III)CyDTA conc. of 1.4 mM, by employing a graphite plate anode at a current density of 51 A/m² (please see I.D. 14, Table 8). Under these conditions, with a 1 % pulp consistency, after 3 hours, the Kappa number dropped from 30.0 to 16.7 while the viscosity changed from 34.6 cP to 21.5 cP. At the employed current density value, the actual current density due to the anodic oxidation of Mn(II)CyDTA is still far from its limiting value, which is about 74 A/m² (Appendix V).

Thus, the following question arises: by further increasing the current density and consequently the in-situ concentration of Mn(III)CyDTA, is still possible to further improve the delignification? In order to answer this question an additional experiment was
Chapter 3: Experimental Results and Discussion

performed under the same conditions but a current density of 102 A/m² was employed during the 3 hour bleaching. The bleached pulp had a Kappa number of 15.0 and a viscosity of 20.5 cP. Consequently, under much milder conditions than in the conventional oxygen bleaching, i.e. pH 9.0, atmospheric oxygen pressure, 80 °C, a 50 % delignification was possible in 3 hours at 1 % pulp consistency, while the viscosity of the bleached pulp was still slightly above 20 cP.
Chapter 4

CONCLUSIONS and RECOMMENDATIONS

4.1 CONCLUSIONS

A trivalent manganese aminopolycarboxylate complex, i.e. Mn(III)CyDTA*, was investigated as a potential redox catalyst in the *in-situ* electrochemically mediated oxygen bleaching of kraft pulp. The present study consisted of three major parts: the fundamental investigation of the electrochemical behavior of Mn(III)CyDTA as a function of pH and electrode material by employing the cyclic voltammetry technique, the development of a new, electrochemical method, of Mn(III)CyDTA synthesis in alkaline media and investigation of the *in-situ* electrochemically mediated oxygen bleaching using Mn(III)CyDTA by employing both parametric and factorial experiments.

The cyclic voltammetry studies revealed the paramount importance of sodium bicarbonate (NaHCO₃) in bringing about the cyclic voltammetry response of Mn(III)CyDTA with CyDTA/Mn molar ratio equal to 2/1. Also a strong pH dependency of the redox behavior of Mn(III)CyDTA was found. By increasing the pH, the cathodic peak potential shifts toward more negative values. At pH above 13, the cathodic peak vanishes due to the fast disproportionation of Mn(III)CyDTA. Although the actual reduction potential could not be determined (because the redox behavior was not perfectly reversible), from the position of the peak potentials it can be concluded that the actual reduction potential of Mn(III)CyDTA for a pH between 10 to 11, is in the range of +40 to

* (trans-Cyclohexane-1,2-diamine-\(N,N,N',N\)-tetraacetato) manganate (III)
Chapter 4: Conclusions and Recommendations

270 mV/SHE. Thus, Mn(III)CyDTA does satisfy the ‘required’ reduction potential of a redox catalyst in the oxygen bleaching system according to the conditions set by Landucci (1979) \[ E_{\text{red}} \text{ between } -60 \text{ to } +540 \text{ mV/SHE} \], however does not comply with the more demanding criteria established by Perng et al. (1993), which asks for a reduction potential above +400 mV/SHE.

The dependence of cyclic voltammograms on scan rate revealed a ‘pre-peak’ behavior, indicating the existence of Mn(II) adsorption on all the investigated electrode materials, i.e. graphite, stainless steel and platinum.

The classical, chemical synthesis of Mn(III)CyDTA was found to be tedious and inconvenient. A new, electrochemical method of Mn(III)CyDTA synthesis in alkaline media (pH 10.5 and 9.0) was developed and tested. A variety of anodes were investigated, i.e. stainless steel screen, stainless steel, graphite, nickel, lead and platinized titanium plates. It was found that the electrosynthesis is favored by a high pH and low CyDTA/Mn molar ratio. For an equimolar CyDTA/Mn ratio a visible anodic adsorption layer is formed on stainless steel and lead electrodes, causing significant changes in the electrode kinetics of the oxidation reaction. On both graphite and platinized titanium anodes there was no visible deposition, while the nickel anode was found to be chemically unstable in alkaline media. The current efficiency for Mn(III) electrosynthesis ranged from as high as 84 % on nickel to as low as 3 % on stainless steel plate when the initial Mn(II) concentration was 6 mM, CyDTA/Mn = 1/1, and a current density of 13 A/m² was applied for 1 hour at a pH of 10.5.
Chapter 4: Conclusions and Recommendations

When CyDTA was in excess, i.e. CyDTA/Mn = 2/1 (molar ratio), there was no visible sign of adsorption on any of the investigated anodes. Also, significantly lower current efficiencies were obtained, e.g. at pH 10.5, Mn(II) conc. 6 mM at 25 A/m² on graphite plate, the current efficiency was 16% only. By decreasing the pH to 9.0, the current efficiency dropped below 10%.

During a prolonged electrosynthesis, as in the case of electrochemically mediated oxygen bleaching (3 hr.), the control of pH at 10.5 was necessary to maintain the desired Mn(III)CyDTA concentration in the electrochemical reactor.

Two anodes were retained for in-situ electrochemically mediated oxygen bleaching, i.e. the stainless steel screen at low current density and Mn(II) concentrations and graphite plate. The bleaching results obtained by employing the stainless steel screen anode, employing an equimolar CyDTA/Mn ratio, showed a moderate decrease in Kappa number only, from 30.0 to 22.0 in 3 hours at 25 °C, pH 10.5, while the viscosity dropped from 34.6 to 24.9 cP.

The electrochemically mediated oxygen bleaching employing a graphite anode was much more successful. Under milder conditions than in the conventional oxygen bleaching, i.e. pH 9.0, atmospheric oxygen pressure, 80 °C, 1 % pulp consistency, in 3 hr. a 50 % delignification was possible, K dropped from 30.0 to 15.0, while the viscosity dropped from 34.6 cP to 20.5 cP, when the initial Mn(III)CyDTA conc. was 1.4 mM, CyDTA/Mn (molar ratio) 2/1 and a current density of 102 A/m² was applied. The factorial experiments revealed the multiple functions played by the [Mn(III)/Mn(II)]CyDTA catalytic system. The Mn(III)CyDTA is active in promoting delignification through second
Chapter 4: Conclusions and Recommendations

and third order interactions with current, oxygen and temperature (synergistic effects), while both the Mn(II) species, e.g. Mn(OH)$_2$, Mn(II)CyDTA, and CyDTA itself, were found to be effective carbohydrate protecting agents. At high pH and temperature, the protection due to Mn(II) species outweighed the effect of CyDTA.

The system presented a small but statistically significant non-linear behavior (i.e. curvature effect), reflecting the existence of a true catalytic interaction between the electrochemical mediator, oxygen and temperature.

One might speculate about the role of sodium bicarbonate (NaHCO$_3$, 100 mM) on the outcome of the delignification reaction. Aimoto et al., (1985) had shown that the catalytic activity of certain Co(III) complexes (e.g. [Co(salen)]$^+$) in the oxidative degradation of lignin model compounds decreases in the order of additives in aqueous solution: NaHCO$_3$ > Na$_2$CO$_3$ > NaOH. These authors showed the intercalation of CO$_3^{2-}$ as the fifth and sixth ligand in the coordination sphere of the cobalt ion. The high catalytic activity in the presence of sodium bicarbonate was attributed to the high liability of the carbonate ion when the complex is attacked by the phenolate anion. One might wonder if in the case of Mn(III)CyDTA a similar effect exists.

* salen = N,N'-disalicylideneethylenediamine anion
4.2 RECOMMENDATIONS

The present study represents rather a beginning than an end. The starting point for any further investigation should be the 50 % delignification result. Any additional delignification would mean an improvement with respect to the conventional oxygen bleaching. The following recommendations are made for future in work in the area of in-situ electrochemically mediated oxygen bleaching using Mn(III)CyDTA:

1. At atmospheric oxygen pressure, 80 °C, pH 9.0, CyDTA/Mn (molar ratio) 2/1, with an initial Mn(III)CyDTA conc. of 1.4 mM, by further increasing the current density to 200 or 300 A/m² on a graphite anode, it might be possible to lower the Kappa number below 15. As long as the reaction between lignin and Mn(III)CyDTA is under kinetic control and the limiting current density of Mn(II)CyDTA oxidation has not been achieved, any increase in current density and consequently in the Mn(III)CyDTA conc. generated in-situ, in the case of a 2/1 CyDTA/Mn molar ratio, might bring about a certain decrease in Kappa number.

2. Investigation of the process at superatmospheric oxygen pressures, e.g. 0.2, 0.5 MPa. Increasing the oxygen pressure, proved to be beneficial in the case of ferricyanide mediated oxygen bleaching [Perng, 1993].

3. The statistical experimental design was able to reveal the range of process variables in which their main and interaction effects were statistically significant. From here on, an optimization of the process variables should be performed (e.g. Simplex
optimization) in order to find the ‘best’ conditions which leads to both the lowest Kappa number and highest selectivity.

4. So far the electrochemically mediated oxygen bleaching studies have been confined to low, usually 1 %, pulp consistency due to both high ohmic voltage drops and more difficult mixing in laboratory scale electrochemical reactors, at high consistencies. In order to approach industrially feasible pulp consistencies (~ 20 - 25 %), a new design of the electrochemical reactor is required.

5. The oxygen bleaching kinetics are strongly dependent on the initial Kappa number of the pulp (please see section 1.3.4). Thus, by employing pulp samples with different initial Kappa number and viscosity, other aspects of the electrochemically mediated oxygen bleaching can be revealed.

6. Regarding the electrosynthesis of Mn(III)CyDTA, other anodes, such as glassy carbon, should be investigated in the search for better electrochemical performance. Also, a 3-D graphite felt anode could be employed.

7. Cyclic voltammetry studies in the presence of both Mn(III)CyDTA and lignin or Mn(III)CyDTA and cellulose, would provide further insights in the intricate details of the mechanism of electrochemically mediated oxygen bleaching.
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APPENDIX I

A summary of diagnostic criteria for cyclic voltammetry
[based on Brown and Sandifer, 1986]

A) REVERSIBLE Charge Transfer

- the peak potentials are independent of scan rate

- \( |E_p^e - E_p^a| = 59/n \) mV @ 25 °C

- \( i_p^a / i_p^c = 1 \), being independent of scan rate

- the cyclic voltammetry wave shape is independent of scan rate as well

B) QUASI-REVERSIBLE Charge Transfer

- the peak potentials shift with the scan rate

- \( |E_p^e - E_p^a| > 59/n \) mV

- \( i_p^a / i_p^c \neq 1 \)

- the cyclic voltammetry response broadens with the increase of the scan rate

C) IRREVERSIBLE Charge Transfer

- the peak potentials are cathodically shifting with an increase in scan rate

- there is no response on the reverse scan, the wave shape is independent of scan rate
APPENDIX II

The calculation of stainless steel screen anode area

- dimensions of the meshed part: 13 cm x 13 cm - $2\pi^2 = A_0 = 163 \text{ cm}^2$

- mesh characteristics: $M = 20$ openings per inch ($L = 2.54 \text{ cm}$)
  
  \[ D = 0.051 \text{ cm wire diameter} \]

- the real surface area of the meshed part (Tyler standard sieve) $A_{mesh}$, is given by:
  
  \[ \frac{A_{mesh}}{A_0} = \left[ \frac{6.28DL(M+1) - (M+1)^2 D^2}{12.9} \right] \]

  \[ \text{[Perng, 1993a].} \]

- substituting the numerical values in the above equation, gives: $A_{mesh}/A_0 = 1.236$

- thus, the area of the meshed part is: $A_{mesh} = 201 \text{ cm}^2$

- the area of the unmeshed part of the anode is: $A_{unmesh} = 31 \text{ cm}^2$

- the total area of the stainless steel screen anode is given by:
  
  \[ A = A_{mesh} + A_{unmesh} = 201 + 31 = 232 \text{ cm}^2 \]
APPENDIX III

Elements of factorial experimental design

[based on Murphy, 1977]

In order to filter out the individual and interaction effects between a large number of variables that might influence the outcome of a process, several experimental designs are available. Among them, the two level designs are the most common ones. Considering \( n \) factors, a full factorial design at two levels for each factor it means \( 2^n \) experimental runs. However, the actual size of design depends on the desired precision of an estimate of the effects and/or the physical possibility of performing all of the required runs. Thus, sometimes the need of a so-called fractional factorial design arises. In this procedure some higher order interaction effects are lost. Stepping forward from the two level designs, centerpoints might be added to investigate the possible non-linear behavior of the system.

The factorial experimental design allows for the calculation of main, interaction and curvature effects.

A) Main effects

Consider \( n \) variables \( (X_1, \ldots) \) at two levels, i.e. 'low'(-) and 'high'(+). The main effect is calculated as the difference between the average 'high' and 'low' level responses.

\[
\text{Main effect of } X_i = \frac{\sum (\text{responses at 'high' } X_i - \text{responses at 'low' } X_i)}{(\text{half the number of factorial runs})} \tag{1}
\]
Appendix III

B) Interaction effects

The interaction effect is the average response difference between one half of the factorial runs and the other half. To illustrate the calculation of interaction effects a $2^2$ design is considered. The design table includes the interaction column as well, formed from the columns of the two factors that comprise the interaction, by multiplying the entries in the factor column.

<table>
<thead>
<tr>
<th>Run</th>
<th>$X_1$</th>
<th>$X_2$</th>
<th>$X_1^*X_2$</th>
<th>Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>$Y_1$</td>
</tr>
<tr>
<td>2</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>$Y_2$</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>$Y_3$</td>
</tr>
<tr>
<td>4</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>$Y_4$</td>
</tr>
</tbody>
</table>

\[
\text{Interaction effect} = \frac{\left[(Y_1 + Y_4) - (Y_2 + Y_3)\right]}{2} \quad (2)
\]

C) Curvature effects

The curvature effect is given by the deviation of the average centerpoint responses from the average factorial responses.

The statistical significance and the confidence intervals of the effects is discussed in connection with an example calculation in Appendix VI.
APPENDIX IV

Current efficiency sample calculation

EXAMPLE:

After one hour of electrosynthesis of 27 mM MnSO$_4$ in the presence of 27 mM CyDTA, on a stainless steel screen anode, I = 0.06 A at pH 10.5, 25 °C, the anolyte obtained was acidified with 50 ml glacial acetic acid and three samples were taken, of 50 ml each. They were titrated with sodium thiosulfate (0.05 N) according to the procedure described in section 2.5 of Chapter 2. The following results were obtained:

- the total volume $V_{tot}$, at the end of electrosynthesis is the sum of the anolyte volume $V_{anolyte}$, plus the volume of the added glacial acetic acid $V_{HAc}$. Thus,

$$V_{tot} = V_{anolyte} + V_{HAc} = 1000\text{ml} + 50\text{ml} = 1050\text{ml}.$$  

- the dilution factor due to the addition of acetic acid is:

$$D_f = \frac{V_{anolyte}}{V_{tot}} = \frac{1000}{1050} = 0.9523.$$ 

- consequently, the 'true' volume of the analyzed sample is given by:

$$V_{true} = V_{sample} \cdot D_f.$$ 

the 50 ml sample $\Rightarrow$ 'true' volume of $47.6$ ml.

- the volume of thiosulfate consumed is correlated with the Mn(III) conc. according to the following relationship (please see section 2.5 of Chapter 2 as well):

$$10.1\text{ml Na}_2\text{S}_2\text{O}_3, 0.05\text{ N} \Rightarrow 27.5\text{ mg Mn(III)}.$$
### Appendix IV

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Sample volume (ml)</th>
<th>'True' sample volume (ml)</th>
<th>Volume of thiosulfate consumed (ml)</th>
<th>Amount of Mn(III) in the sample (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>47.6</td>
<td>3.00</td>
<td>171.5</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>47.6</td>
<td>2.95</td>
<td>168.4</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>47.6</td>
<td>2.90</td>
<td>165.8</td>
</tr>
</tbody>
</table>

An average Mn(III) conc. was calculated from the three values, i.e.

\[ m_{\text{Mn(III)}} = 168.6 \text{ mg/l}. \]

The Mn(III)CyDTA conc. is : ( 1mol Mn(III)CyDTA \( \Rightarrow \) 54.94 g Mn(III))

\[ C_{\text{Mn(III)CyDTA}} = 3.1 \text{ mM}. \]

- however, in this case some of the Mn(III) is formed by a parallel non-electrochemical route. To find the 'true', electrochemically generated Mn(III)CyDTA a 'blank' run (without current) was performed and the samples were similarly analyzed (please see section 3.1 as well). Thus, the non-electrochemical Mn(III) conc. was found to be :

\[ m_{\text{Mn(III) non-electr.}} = 70 \text{ mg/l}. \]

Consequently, the 'true', electrochemically produced Mn(III) conc. is :

\[ m_{\text{Mn(III) electr.}} = m_{\text{Mn(III)}} - m_{\text{Mn(III) non-electr.}} = 168.6 - 70 = 98.6 \text{ mg/l}, \]

\[ C_{\text{Mn(III)CyDTA electr.}} = 1.8 \text{ mM}. \]
- the current efficiency \( CE (\%) \), was calculated from Faraday's law:

\[
CE = \frac{zFM_{\text{Mn(III)electr.}}/(A_{\text{Mn}} \cdot t)}{I} \cdot 100,
\]

where \( A_{\text{Mn}} \) = atomic mass of Mn (i.e. 54.94)

\( t \) = time of electrosynthesis \( \text{(sec)} \)

\( I \) = applied current \( \text{(A)} \)

\( m_{\text{Mn(III)electr.}} \) = amount of electrochemically produced Mn(III) \( \text{(g)} \)

\( F \) = Faraday's constant \((-96500 \text{ C/equiv})\)

\( z \) = nr. of electrons transferred (i.e. 1, Mn(II)/Mn(III)).

By substituting in the above equation we have:

\[
CE = \frac{96500 \cdot 0.0986/(54.94 \cdot 3600)}{0.06} \cdot 100 = 80 \%
\]

Note: when electrodes of different area are to be compared (please see section 3.1 of Chapter 3) in order to have a fair comparison, the Mn(III)CyDTA concentrations per unit electrode area has to be calculated and compared.
APPENDIX V

The calculation of the limiting current density for Mn(III)CyDTA electrosynthesis on a stainless steel screen anode

Physico-chemical data:

- electrolyte density at 25 °C: (~ρ_{water}), \( ρ = 10^3 \text{ kg/m}^3 \)
- electrolyte dynamic viscosity at 25 °C: (~μ_{water}), \( μ = 9.5 \times 10^{-4} \text{ Pa•s} \) [Perry's*, 1984]
- limiting equivalent conductance of Mn(II) in aqueous solutions at 25 °C:
  \[
  \lambda^0_{\text{Mn(II)}} = 53.5 \text{ mho} \cdot \text{cm}^2/\text{equiv}, \quad \text{[Lange's**}, 1992]\]
- limiting equivalent conductance of CyDTA in aqueous solutions at 25 °C:
  (~ with the value for the cyclohexane carboxylate anion) [Lange's 1992],
  \[
  \lambda^0_{\text{CyDTA}} = 28.7 \text{ mho} \cdot \text{cm}^2/\text{equiv},
  \]
- impeller diameter: \( d = 4.4 \times 10^{-2} \text{ m}^2 \)

A) Estimation of the Mn(II)CyDTA diffusion coefficient in aqueous solution, 25 °C

The diffusion coefficient of a binary electrolyte in dilute aqueous solutions \( D^0 \), is given by the following equation [Prentice, 1991]:

\[
D^0 = \frac{Z_+ \lambda^0_+ D^0_+ + Z_- \lambda^0_- D^0_-}{Z_+ \lambda^0_+ + Z_- \lambda^0_-},
\]

where the diffusion coefficients of both the cation \( D^0_+ \) and anion \( D^0_- \), can be calculated from the Nernst-Einstein equation [Oloman, 1992]:

---

* Handbook of Chemical Engineering (please see the Reference list)
** Handbook of Chemistry (please see the Reference list)
Appendix V

\[ D_i^0 = \lambda_i \frac{R_i T}{Z_i F^2} , \]

with \( i = ' + ' \) (cation) or ' - ' (anion). \hspace{1cm} (2)

Substituting the numerical values in eq. (2), for Mn(II) (i.e. \( z_+ = 2 \)) we have:

\[ D_{\text{Mn(II)}}^0 = 53.5 \frac{8.314 \cdot 298}{2 \cdot 96500^2} = 7.1 \cdot 10^{-6} \text{ cm}^2 / \text{s}, \]

similarly, for CyDTA (\( z_+ = -4 \)) eq. (2) gives:

\[ D_{\text{CyDTA}}^0 = 28.7 \frac{8.314 \cdot 298}{4 \cdot 96500^2} = 1.9 \cdot 10^{-6} \text{ cm}^2 / \text{s}. \]

From eq. (1) the diffusion coefficient of Mn(II)CyDTA in dilute solutions is:

\[ D_{\text{Mn(II)CyDTA}}^0 = \frac{2 \cdot 53.5 \cdot 1.9 \cdot 10^{-6} + 4 \cdot 28.7 \cdot 7.1 \cdot 10^{-6}}{2 \cdot 53.5 + 4 \cdot 28.7} = 4.6 \cdot 10^{-6} \text{ cm}^2 / \text{s}. \]

In the present work the employed Mn(II) conc. is between 6 mM and 54 mM. In the absence of a better approximation than the 'infinite dilution' one, it is assumed that the value for the Mn(II)CyDTA calculated above, is still valid in the range of employed concentrations. Thus,

\[ D_{\text{Mn(II)CyDTA}}^0 \approx D_{\text{Mn(II)CyDTA}}. \]

B) Calculation of the convective mass transfer coefficient \( K_{mf} \)

The rotation rate of the mixer was \( \omega = 2833 \text{ rpm} = 47 \text{ rps} \). The convective mass transfer coefficient in the present system is given by the following equation (please see eq. (30) in Chapter 1, for a more detailed discussion):

\[ Sh = 0.228 \text{ Re}^{2/3} \text{ Sc}^{1/3}. \]  \hspace{1cm} (3)

The Reynolds number can be calculated as follows:
Re = \frac{\omega d^2 \rho}{\mu} = \frac{47 \cdot (4.4 \cdot 10^{-2})^2 \cdot 10^3}{9.5 \cdot 10^{-4}} = 9.62 \cdot 10^4.

The Schmidt number is: \( \text{Sc} = \frac{\mu}{\rho D_{\text{Mn(U)}} \text{CODTA}} = \frac{9.5 \cdot 10^{-4}}{10^3 \cdot 4.61 \cdot 10^{-10}} = 2.06 \cdot 10^3. \)

By substituting in eq. (3), it results:

\[ Sh = 0.228 \cdot (9.62 \cdot 10^4)^{2/3} \cdot (2.06 \cdot 10^3)^{1/3} = 6.09 \cdot 10^3. \]

Thus, the mass transfer coefficient due to forced convection \( K_{m,f} \), is:

\[ K_{m,f} = Sh \frac{D_{\text{Mn(U)}} \text{CODTA}}{d} = 6.09 \cdot 10^3 \cdot \frac{4.6 \cdot 10^{-10}}{4.4 \cdot 10^{-2}} = 6.4 \cdot 10^{-5} \text{ m/s}. \]

C) Calculation of the mass transfer coefficient due to gas evolution \( K_{m,g} \)

The mass transfer coefficient due to the anodic oxygen evolution on a stainless screen was calculated, instead of eq. (31) given in Chapter 1, with an equation specifically determined for oxygen evolving mesh electrodes [Sedahmed and Shemilt, 1984]:

\[ K_{m,g} = 3.228 \cdot 10^{-3} \cdot \left( \frac{V_g}{d} \right)^{0.469} \]  \hspace{1cm} (4)

where \( V_g \) - gas (i.e. oxygen) volume discharge rate per unit electrode area \( \{ \text{cm}^3/(\text{cm}^2\text{min}) \} \)

\( K_{m,g} \) - mass transfer coefficient due to oxygen evolution \( \{ \text{cm/s} \} \).

The gas discharge rate was calculated by subtracting the current consumed in oxidizing the Mn(II) from the total current passing through the cell, thus the current
consumed in the oxygen evolution reaction was found, $I_{\text{oxygen}}$. Then, Faraday's law was applied to obtain the mass rate of oxygen evolved. This mass rate was then converted into volumetric rate by employing the gas law. Putting it into mathematical equations, we have:

$$I_{\text{oxygen}} = (1 - CE)I,$$

(5)

where: $CE$ - current efficiency

$I$ - total, applied current.

The mass rate of oxygen evolved, $m_g$, is given by:

$$m_g = m_{\text{oxygen}} = \frac{A_{\text{oxygen}}}{zF} I_{\text{oxygen}},$$

(6)

where: $A_{\text{oxygen}}$ - atomic mass of oxygen

$z = 2$ (nr. of electrons exchanged)

$F$ = Faraday's constant (~96500 C/equiv).

By applying the gas law, the volumetric discharge rate at $25^\circ$C and 1 atm can be calculated by:

$$V_g = \frac{24462 \cdot m_g}{M_{\text{oxygen}}} \quad \{\text{cm}^3/\text{s}\}$$

(7)

Substituting eq. (6) in eq. (7), the gas discharge rate is given by:

$$V_g = \frac{24462 \cdot (1 - CE)I}{2zF} \quad \{\text{cm}^3/\text{s}\}$$

(8)

Substituting $F \approx 96500$ C/equiv, $z = 2$ and converting to $\{\text{cm}^3/\text{min}\}$, equation 7 becomes:

$$V_g = 3.8024(1 - CE)I \quad \{\text{cm}^3/\text{min}\}$$

(8)
Appendix V

Thus, the gas discharge rate per unit electrode area $A$, expressed in $\{\text{cm}^3/\text{cm}^2\cdot\text{min}\}$ is given by:

$$
V_g^* = \frac{3.8024(1-CE)I}{A} \quad \{\text{cm}^3/\text{cm}^2\cdot\text{min}\} \quad (10)
$$

Equation 10 was employed in the calculation of the mass transfer coefficient due to oxygen evolution according to eq. (4).

D) Calculation of the combined, global, mass transfer coefficient $K_m$

The combined, global, mass transfer coefficient $K_m$, is given by eq. (32) of Chapter 1, i.e.:

$$
K_m = K_{m,f} \left[ 1 + \left( \frac{K_{m,g}}{K_{m,f}} \right) \right]^{1/2} \quad \{\text{cm/s}\} \quad (11)
$$

E) Calculation of the limiting current density $i_L$

Consequently, the limiting current density $i_L$, is expressed by:

$$
i_L = zF K_m c_{Mn(II)} \quad (12)
$$

F) SAMPLE CALCULATION:

For a Mn(II) concentration of 6 mM, at $I = 0.06\text{A}$, on a stainless steel screen of $A = 232 \text{ cm}^2$, the current efficiency was $CE = 19 \%$ (i.e. 0.19) (please see Fig. 47). By substituting in eq. (10), the gas discharge rate per unit electrode area is:
Thus, from eq. (4) the mass transfer coefficient due to oxygen evolution is equal to:

\[ K_{m,g} = 1.1 \times 10^{-6} \text{ m/s.} \]

By substituting in eq. (11) both \( K_{mf} \) and \( K_{m,g} \), the combined mass transfer coefficient has a value of:

\[ K_m = 6.4 \times 10^{-5} \text{ m/s.} \]

The limiting current density for \( c_{Mn(II)} = 6 \text{ mol/m}^3 \) is:

\[ i_L = 2 \cdot 96500 \cdot 6.383 \cdot 10^{-5} \cdot 6 = 74 \text{ A/m}^2. \]

Similarly, for the rest of the concentration values the following limiting current densities were obtained (these values were plotted in Fig. 48):

<table>
<thead>
<tr>
<th>Mn(II) conc. (M) x 10^2</th>
<th>Limiting current density (A/m^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>222</td>
</tr>
<tr>
<td>2.7</td>
<td>333</td>
</tr>
<tr>
<td>3.6</td>
<td>444</td>
</tr>
<tr>
<td>4.5</td>
<td>554</td>
</tr>
<tr>
<td>5.4</td>
<td>665</td>
</tr>
</tbody>
</table>
APPENDIX VI

Calculation of the pooled response errors for Kappa number and viscosity.

Estimation of the confidence intervals of main effects

A) *For the $2^3$ full factorial experiments*

The following replicated runs were performed (please see Table 3 of Chapter 3 for experimental details):

<table>
<thead>
<tr>
<th>Run #</th>
<th>Kappa nr.</th>
<th>Average Kappa nr. ($\bar{K}$)</th>
<th>Viscosity (cP)</th>
<th>Average viscosity ($\bar{v}$)</th>
<th>Nr. of replicated runs ($r$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22.0 ; 22.4 ; 21.4</td>
<td>22.0</td>
<td>24.9 ; 25.5 ; 24.2</td>
<td>24.9</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>28.0 ; 28.6</td>
<td>28.3</td>
<td>29.2 ; 29.6</td>
<td>29.4</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>27.7 ; 28.3</td>
<td>28.0</td>
<td>30.1 ; 29.5</td>
<td>29.8</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>28.2 ; 28.8</td>
<td>28.5</td>
<td>29.6 ; 29.9</td>
<td>29.8</td>
<td>2</td>
</tr>
</tbody>
</table>

The response error of each run was calculated with the following equation [Murphy, 1977]:

$$S_i = \sqrt{\frac{\sum_j (Y_j - \bar{Y})^2}{r-1}}$$  \hspace{1cm} (1)
By substituting the corresponding Kappa number or viscosity values in eq. (1), the following estimates of the standard deviation were obtained:

<table>
<thead>
<tr>
<th>Run #</th>
<th>$s^{(a)}$</th>
<th>$s^{(b)}$</th>
<th>$r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.45</td>
<td>0.65</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>0.42</td>
<td>0.28</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>0.42</td>
<td>0.42</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>0.42</td>
<td>0.21</td>
<td>2</td>
</tr>
</tbody>
</table>

The pooled variance for $k = 4$ separate estimates of error $s_e$ each with $r_i$ replicates, is given by [Murphy, 1977]:

$$s^2 = \frac{\sum (r_i-1)s_i^2}{\sum (r_i-1)}$$

(2)

I) the pooled estimate of Kappa number response error

$$s_K^2 = \frac{2 \cdot (0.45)^2 + (0.42)^2 + (0.42)^2 + (0.42)^2}{2+1+1+1} = 0.187$$

$$s_K = \pm 0.432$$
II) the pooled estimate of viscosity response error

\[ S_v^2 = \frac{2 \cdot (0.65)^2 + (0.28)^2 + (0.42)^2 + (0.21)^2}{2 + 1 + 1 + 1} = 0.229 \]

\[ S_v = \pm 0.478 \text{ cP} \]

The CONFIDENCE INTERVAL of the effects is given by the following equation [Murphy, 1977]:

\[ W(\text{effect}) = \frac{ts}{\sqrt{N/4}} \] (3)

where \( s = \) response error (or pooled response error) with \( \nu \) degrees of freedom

\( t = \) student's 't' statistics with \( \nu \) degrees of freedom

\( N = \) number of factorial runs in the design.

The total degrees of freedom is \( \nu = 5 \). For a 95 % confidence level, at \( \nu = 5 \), \( t \) is equal to 2.571 [Murphy, 1977]. Thus,

I) the confidence interval for Kappa number main effects is :

\[ W(K, \text{effect}) = \pm 0.785 \]

II) the confidence interval for viscosity main effects is :

\[ W(v, \text{effect}) = \pm 0.869 \text{ cP} \]
B) For the \( (2^{k-1} + 1) \) factorial runs

The following replicated runs were performed (please see Table 7 of Chapter 3 for experimental details):

<table>
<thead>
<tr>
<th>Run #</th>
<th>Kappa nr.</th>
<th>( \bar{K} )</th>
<th>Viscosity (cP)</th>
<th>( \bar{v} )</th>
<th>Nr. of replicated runs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>17.1 ; 16.3 ; 16.8</td>
<td>16.7</td>
<td>21.4 ; 21.6 ; 21.5</td>
<td>21.5</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>23.3 ; 23.7</td>
<td>23.5</td>
<td>27.4 ; 26.4</td>
<td>26.9</td>
<td>2</td>
</tr>
<tr>
<td>(centerpoint)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>28.6 ; 28.0</td>
<td>28.3</td>
<td>29.3 ; 29.7</td>
<td>29.5</td>
<td>2</td>
</tr>
</tbody>
</table>

The standard deviations are as follows:

<table>
<thead>
<tr>
<th>Run #</th>
<th>( s_{\bar{K}} )</th>
<th>( s_{\bar{v}} )</th>
<th>( r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>0.40</td>
<td>0.10</td>
<td>3</td>
</tr>
<tr>
<td>3 (centerpoint)</td>
<td>0.28</td>
<td>0.71</td>
<td>2</td>
</tr>
<tr>
<td>23</td>
<td>0.42</td>
<td>0.28</td>
<td>2</td>
</tr>
</tbody>
</table>

The pooled variance are:

1) for Kappa number

\[ s_K = \pm 0.379 \]
II) for viscosity

\[ s_v = \pm 0.379 \text{ cP}. \]

The CONFIDENCE INTERVALS are obtained by substitution in eq. (3):

\[ N = 33 \text{ runs in the factorial run, total degrees of freedom } \nu = 4, \text{ for a 95 \% confidence level the student's parameter } t = 2.776 [\text{Murphy, 1977}]. \]

I) for Kappa number main effects

\[ W(K, \text{effect}) = \pm 0.366 \]

II) for viscosity main effects

\[ W(v, \text{effect}) = \pm 0.374 \text{ cP} \]

The CONFIDENCE INTERVAL for the curvature effect is given by:

\[ W(c.\text{effect}) = \pm ts\sqrt{\frac{1}{N} + \frac{1}{C}}, \quad (4) \]

where \( s \) = pooled variance of the entire factorial design

\( t = \) student’s statistical parameter

\( C = \) number of centerpoints

\( N = \) number of factorial points in the design.
Example: in the $2^{6-1} + 1$ design, $C=1$, $N = 32$ (i.e. factorial runs other than the centerpoint). The total degree of freedom is four. Consequently, for a 95 % confidence level $t = 2.776$ [Murphy, 1977].

- for Kappa number: $s = 0.379$

From eq. (3) we have: $W(c.\text{Kappa nr.}) = \pm 1.1$

- for viscosity: $s = 0.388$

consequently $W(c.\text{viscosity}) = \pm 1.1 \text{ cP.}$
Table A: Spontaneous, chemical generation of Mn(III)CyDTA in alkaline media
(related to Fig. 45)

<table>
<thead>
<tr>
<th>I.D.</th>
<th>Mn(II) conc. (mM)</th>
<th>Mn(III)CyDTA conc. (mM)</th>
<th>Mn(III)CyDTA conc. (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CyDTA/Mn = 2/1</td>
<td>CyDTA/Mn = 1/1</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>0</td>
<td>0.11</td>
</tr>
<tr>
<td>2</td>
<td>18</td>
<td>0</td>
<td>0.17</td>
</tr>
<tr>
<td>3</td>
<td>27</td>
<td>0</td>
<td>1.3</td>
</tr>
<tr>
<td>4</td>
<td>36</td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>5</td>
<td>45</td>
<td></td>
<td>0.76</td>
</tr>
<tr>
<td>6</td>
<td>54</td>
<td></td>
<td>0.39</td>
</tr>
</tbody>
</table>
Table B: Electrochemical synthesis of Mn(III)CyDTA on a stainless steel screen

(related to Figs. 46 and 47)

<table>
<thead>
<tr>
<th>I.D.</th>
<th>Mn(II) conc. (mM)</th>
<th>Mn(III) conc (mM)</th>
<th>Mn(III) conc (mM)</th>
<th>CE (%) CyDTA/Mn 1/1</th>
<th>CE (%) CyDTA/Mn 2/1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>0.53</td>
<td>0.14</td>
<td>19</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>18</td>
<td>1.28</td>
<td>0.15</td>
<td>49</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>27</td>
<td>3.10</td>
<td>0.16</td>
<td>80</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>36</td>
<td>3.35</td>
<td>0.16</td>
<td>96</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>45</td>
<td>2.92</td>
<td>0.17</td>
<td>97</td>
<td>9</td>
</tr>
<tr>
<td>6</td>
<td>54</td>
<td>2.33</td>
<td>0.17</td>
<td>89</td>
<td>9</td>
</tr>
</tbody>
</table>

Table C: Current efficiency vs. current density on a stainless steel screen anode

(related to Fig. 50)

<table>
<thead>
<tr>
<th>I.D.</th>
<th>Current density (A/m²)</th>
<th>CE (%) CyDTA/Mn = 1/1</th>
<th>CE (%) CyDTA/Mn = 1/1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.6</td>
<td>49</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>5.2</td>
<td>62</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>10.3</td>
<td>23</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>15.5</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>
Table D: Comparison among various anodes. Normalized Mn(III)CyDTA conc. (mM/cm^2) (related to Fig. 51)

<table>
<thead>
<tr>
<th>I.D.</th>
<th>Current Density (A/m^2)</th>
<th>Stainless steel</th>
<th>Graphite</th>
<th>Pt/Ti</th>
<th>Ni</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13</td>
<td>37.8</td>
<td>399.5</td>
<td>337.4</td>
<td>427</td>
<td>315.2</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>51.4</td>
<td>639.7</td>
<td>580</td>
<td>301.8</td>
<td>496.5</td>
</tr>
<tr>
<td>3</td>
<td>51</td>
<td>56.8</td>
<td>1047</td>
<td>894.7</td>
<td>354.3</td>
<td>1000</td>
</tr>
<tr>
<td>4</td>
<td>76</td>
<td>79.6</td>
<td>1361</td>
<td>1198</td>
<td>384.7</td>
<td>1384</td>
</tr>
<tr>
<td>5</td>
<td>102</td>
<td>85.4</td>
<td>1575</td>
<td>1245</td>
<td>487.4</td>
<td>1345</td>
</tr>
</tbody>
</table>

Table E: Comparison among various anode plates. Current efficiency (%) (related to Fig. 52)

<table>
<thead>
<tr>
<th>I.D.</th>
<th>Current Density (A/m^2)</th>
<th>Stainless steel</th>
<th>Graphite</th>
<th>Pt/Ti</th>
<th>Ni</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13</td>
<td>3</td>
<td>78</td>
<td>66</td>
<td>84</td>
<td>.60</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>3</td>
<td>64</td>
<td>59</td>
<td>29</td>
<td>49</td>
</tr>
<tr>
<td>3</td>
<td>51</td>
<td>3</td>
<td>54</td>
<td>46</td>
<td>17</td>
<td>51</td>
</tr>
<tr>
<td>4</td>
<td>76</td>
<td>2</td>
<td>47</td>
<td>41</td>
<td>12</td>
<td>48</td>
</tr>
<tr>
<td>5</td>
<td>102</td>
<td>1.6</td>
<td>41</td>
<td>32</td>
<td>12</td>
<td>35</td>
</tr>
</tbody>
</table>
Table F: Specific energy (kWh/kmol) vs. current density for various anode plates
(related to Fig. 54)

<table>
<thead>
<tr>
<th>I.D.</th>
<th>Current Density (A/m²)</th>
<th>Stainless steel</th>
<th>Graphite</th>
<th>Pt/Ti</th>
<th>Ni</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13</td>
<td>2209</td>
<td>62</td>
<td>102</td>
<td>66</td>
<td>101</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>2141</td>
<td>96</td>
<td>144</td>
<td>256</td>
<td>148</td>
</tr>
<tr>
<td>3</td>
<td>51</td>
<td>3127</td>
<td>147</td>
<td>236</td>
<td>563</td>
<td>181</td>
</tr>
<tr>
<td>4</td>
<td>76</td>
<td>6042</td>
<td>220</td>
<td>311</td>
<td>851</td>
<td>265</td>
</tr>
<tr>
<td>5</td>
<td>102</td>
<td>8259</td>
<td>302</td>
<td>458</td>
<td>1024</td>
<td>382</td>
</tr>
</tbody>
</table>

Table G: Electrosynthesis of Mn(III)CyDTA on a graphite plate anode. (related to Figs. 55 and 56)

<table>
<thead>
<tr>
<th>I.D.</th>
<th>Mn(II) conc. (mM)</th>
<th>Mn(III) conc. (mM)</th>
<th>Mn(III) conc. (mM)</th>
<th>CE (%) CyDTA/Mn</th>
<th>CE (%) CyDTA/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CyDTA/Mn 1/1</td>
<td>CyDTA/Mn 2/1</td>
<td>CyDTA/Mn 1/1</td>
<td>CyDTA/Mn 2/1</td>
<td>CyDTA/Mn 2/1</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>2.50</td>
<td>0.90</td>
<td>42</td>
<td>16</td>
</tr>
<tr>
<td>2</td>
<td>18</td>
<td>4.00</td>
<td>0.81</td>
<td>64</td>
<td>14.5</td>
</tr>
<tr>
<td>3</td>
<td>36</td>
<td>4.60</td>
<td>0.83</td>
<td>61</td>
<td>15</td>
</tr>
</tbody>
</table>


### Table H: Electrosynthesis of Mn(III)CyDTA on a graphite plate anode (related to Figs. 59 and 60)

<table>
<thead>
<tr>
<th>I.D.</th>
<th>Current density (A/m²)</th>
<th>Mn(III) conc. (mM)</th>
<th>Mn(III) conc. (mM)</th>
<th>CE (%) CyDTA/Mn 1/1</th>
<th>CE (%) CyDTA/Mn 2/1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>2.46</td>
<td>0.90</td>
<td>42</td>
<td>16</td>
</tr>
<tr>
<td>2</td>
<td>51</td>
<td>3.11</td>
<td>1.41</td>
<td>28</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>76</td>
<td>3.42</td>
<td>1.62</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>102</td>
<td>3.84</td>
<td>1.83</td>
<td>17</td>
<td>8</td>
</tr>
</tbody>
</table>

### Table I: The influence of pH on Mn(III)CyDTA electrosynthesis on graphite plate anode (related to Fig. 59)

<table>
<thead>
<tr>
<th>I.D.</th>
<th>Current density (A/m²)</th>
<th>Mn(III)CyDTA conc (mM)</th>
<th>Mn(III)CyDTA conc (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>pH = 9.0</td>
<td>pH = 10.5</td>
</tr>
<tr>
<td>1</td>
<td>51</td>
<td>0.50</td>
<td>1.41</td>
</tr>
<tr>
<td>2</td>
<td>76</td>
<td>0.60</td>
<td>1.62</td>
</tr>
<tr>
<td>3</td>
<td>102</td>
<td>0.63</td>
<td>1.83</td>
</tr>
</tbody>
</table>
Table J : The influence of pH control on Mn(III)CyDTA electrosynthesis on a graphite plate anode (related to Fig. 62)

<table>
<thead>
<tr>
<th>I.D.</th>
<th>Time (min)</th>
<th>Mn(III)CyDTA conc (mM) without pH control</th>
<th>Mn(III)CyDTA conc (mM) pH control (10.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>0.76</td>
<td>0.76</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>1.05</td>
<td>1.05</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>1.21</td>
<td>1.25</td>
</tr>
<tr>
<td>5</td>
<td>120</td>
<td>0.75</td>
<td>1.33</td>
</tr>
<tr>
<td>6</td>
<td>180</td>
<td>0.52</td>
<td>1.11</td>
</tr>
</tbody>
</table>

Table L : Kappa nr. profiles (related to Fig. 64a)

<table>
<thead>
<tr>
<th>I.D.</th>
<th>Time (min)</th>
<th>with catalyst, current and oxygen</th>
<th>with catalyst and oxygen</th>
<th>with oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>30.0</td>
<td>30.0</td>
<td>30.0</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>24.5</td>
<td>29.1</td>
<td>29.7</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>24.2</td>
<td>28.5</td>
<td>29.3</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>23.5</td>
<td>25.2</td>
<td>29.1</td>
</tr>
<tr>
<td>5</td>
<td>120</td>
<td>22.9</td>
<td>24.2</td>
<td>28.9</td>
</tr>
<tr>
<td>6</td>
<td>180</td>
<td>22.4</td>
<td>24.1</td>
<td>28.0</td>
</tr>
</tbody>
</table>
### Table M: Kappa nr. profiles (related to Fig. 64b)

<table>
<thead>
<tr>
<th>I.D.</th>
<th>Time (min)</th>
<th>with catalyst, current and oxygen</th>
<th>with catalyst and oxygen</th>
<th>with oxygen</th>
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<tbody>
<tr>
<td>1</td>
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<td>30.0</td>
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<td>15</td>
<td>24.1</td>
<td>24.1</td>
<td>29.7</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>23.5</td>
<td>24.6</td>
<td>29.3</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>22.3</td>
<td>24.6</td>
<td>29.1</td>
</tr>
<tr>
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<td>120</td>
<td>21.4</td>
<td>24.7</td>
<td>28.9</td>
</tr>
<tr>
<td>6</td>
<td>180</td>
<td>19.8</td>
<td>24.5</td>
<td>28.0</td>
</tr>
</tbody>
</table>

### Table N: Viscosity profiles (cP) (related to Fig. 65a)

<table>
<thead>
<tr>
<th>I.D.</th>
<th>Time (min)</th>
<th>with catalyst, current and oxygen</th>
<th>with catalyst and oxygen</th>
<th>with oxygen</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>34.6</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>23.9</td>
<td>31.0</td>
<td>32.3</td>
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<td>3</td>
<td>30</td>
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<td>31.0</td>
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<td>14.7</td>
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<td>30.4</td>
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<td>120</td>
<td>13.0</td>
<td>30.3</td>
<td>30.0</td>
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<tr>
<td>6</td>
<td>180</td>
<td>13.2</td>
<td>29.7</td>
<td>29.6</td>
</tr>
</tbody>
</table>
Table O : Viscosity (cP) profiles (related to Fig. 65b)

<table>
<thead>
<tr>
<th>I.D.</th>
<th>Time (min)</th>
<th>with catalyst, current and oxygen</th>
<th>with catalyst and oxygen</th>
<th>with oxygen</th>
</tr>
</thead>
<tbody>
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<td>34.6</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>29.0</td>
<td>29.9</td>
<td>32.3</td>
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<td>31.0</td>
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<td>120</td>
<td>22.5</td>
<td>29.1</td>
<td>30.0</td>
</tr>
<tr>
<td>6</td>
<td>180</td>
<td>20.5</td>
<td>29.8</td>
<td>29.6</td>
</tr>
</tbody>
</table>

Table P : The combined influence of pH and temperature on Kappa number (related to Fig. 66)

<table>
<thead>
<tr>
<th>I.D.</th>
<th>Temperature (°C)</th>
<th>pH 9.0</th>
<th>pH 10.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>24.9</td>
<td>19.8</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>22.0</td>
<td>22.2</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
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</tr>
<tr>
<td>5</td>
<td>80</td>
<td>17.1</td>
<td>25.0</td>
</tr>
</tbody>
</table>
APPENDIX VIII

The stability of Mn(III)CyDTA in alkaline media

The stability of Mn(III)CyDTA was investigated for two ligand to metal ratio (i.e. 1/1 and 2/1 respectively) at pH 10.5 in the range of temperatures between 25 °C and 80 °C. The samples were placed in a water thermobath at the desired temperature and they were analyzed from time to time to check the remaining amount of Mn(III). The initial Mn(III) conc. was 1.41 mM. The following experimental results were obtained:

A) 25 °C

After 30 min. for CyDTA/Mn 1/1 the remaining Mn(III) conc. was 0.69 mM. In the case of CyDTA/Mn 2/1 a conc. of 0.72 mM Mn(III) conc. was obtained in 40 min. Thus, the half-life time was considered to be around 30 min. for CyDTA/Mn 1/1 and around 40 min. for CyDTA/Mn 2/1.

B) 40 °C

For CyDTA/Mn 1/1 after 20 min. the remaining Mn(III) was 0.68 mM, while for CyDTA/Mn 2/1 after 30 min. the Mn(III) conc. was 0.71 mM. The half-life times are about 20 min. for equimolar ligand to metal ratio and 30 min. for CyDTA/Mn 2/1.

C) 80 °C

For CyDTA/Mn 1/1 after 5 min. the Mn(III) conc. was 0.70 mM, while in the case of CyDTA/Mn 2/1 after 10 min. the Mn(III) conc. is 0.73 mM. The half-life times are about 5 min. for CyDTA/Mn 1/1 and 10 min. for CyDTA/Mn 2/1.
APPENDIX IX

Preparation of pulp samples for Kappa number and Viscosity Tests

At the end of bleaching runs, all pulp samples were subjected to acidic washing in order to remove the transition metal ions that might interfere with the Kappa number and viscosity determinations.

Three washing procedures were employed and their influence on the initial, unbleached kraft pulp is presented in Table IXA. The ability of the chemicals presented in Table IXA to remove the transition metal ions from pulp suspensions, is well documented in the literature and it was demonstrated by atomic spectroscopy [Perng, 1993a].

The washing method I, is successful when relatively small amounts of manganese are present. However, in the case of higher amounts of manganese, e.g. high temperature runs with intensive manganese decomposition, a more effective method must be employed. The washing method III, although successful in removing the transition metal ions, had a disastrous effect on pulp viscosity (please see Table IXA) and consequently is not recommended.

Method II, was found to be suitable in most cases, even in the case of intensive precipitation, without damaging the pulp carbohydrates (i.e. the viscosity remains unaffected by washing).

After washing, a handsheet was made which was placed in the pulp conditioner room (i.e. constant temperature and humidity) for 24 hours. Finally the Kappa number (TAPPI standard T236) and viscosity (TAPPI standard T230) were determined.
Table IXA: Pulp washing procedures and their influence on the unbleached kraft pulp

<table>
<thead>
<tr>
<th>WASHING TYPE</th>
<th>WASHING PROCEDURE (for 1 l volume &amp; 1% kraft pulp consistency)</th>
<th>Kappa number</th>
<th>Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>3 times, 5 min. each with H_2SO_3 0.25% @ 25-30 °C</td>
<td>30.0</td>
<td>34.6</td>
</tr>
<tr>
<td>II</td>
<td>washing 2 times, 5 min each with H_2SO_3 0.25%, followed by a 30 min washing with H_2SO_3 0.25% + 1% DTPA* (i.e. 25 ml DTPA 40%) @ pH 4-5 (adjust with glacial acetic acid) and 20-25 °C</td>
<td>30.0</td>
<td>34.6</td>
</tr>
<tr>
<td>III</td>
<td>washing type I, followed by washing 2 times 15 min each with H_2SO_4 0.5M @ 60 °C</td>
<td>28.6</td>
<td>11.1</td>
</tr>
</tbody>
</table>

*DTPA = diethylenetriaminepentaacetic acid (chelating agent)