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In situ electrochemically mediated oxygen delignification of wood pulp with a manganese (III) aminopolycarboxylate complex

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ABSTRACT

The manganese complex Mn(III)CyDTA [(trans-1,2- cyclohexane-1,2-diamine-N,N,N',N'-tetraaceto)manganate (III)] was used as the redox catalyst for the in situ electrochemically mediated oxygen bleaching of softwood kraft pulp. Three hour bleaching runs at 101 kPa oxygen pressure, pH 9.0, 80°C, 6 mM manganese, with 1 L of pulp suspension at 1% consistency gave the following results: in the presence of an initial concentration of 1.4 mM Mn(III)CyDTA employing a graphite plate anode (A = 58 cm^2) with a current density of 102 A/m^2, the kappa number dropped from 30.0 to 15.0, while the viscosity decreased from 34.6 cP to 20.5 cP. Under similar conditions the "blank" run, i.e., without MnCyDTA and current, brought about only a 9.4% decrease in kappa number, from 30.0 to 27.2, while the viscosity dropped slightly, from 34.6 cP to 30.3 cP. The effects of Mn concentration, CyDTA/Mn molar ratio, oxygen, temperature, pH and current on delignification and carbohydrate degradation, were studied in parametric and factorial experiments. The results show that Mn(III) promotes delignification mainly through second- and third-order interaction with oxygen and a temperature, while CyDTA is working as a carbohydrate protecting agent. The anodic current continuously regenerates the Mn(III) to support the delignification process.

Application:

This work has applications in both the development of novel pulp bleaching processes and the study of catalysts to increase the rate and/or the selectivity of oxygen bleaching.

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, and hydrogen peroxide, to pilot and laboratory scale electrochemical salt splitting or water and air pollution treatments by electrochemical methods *(1)*.

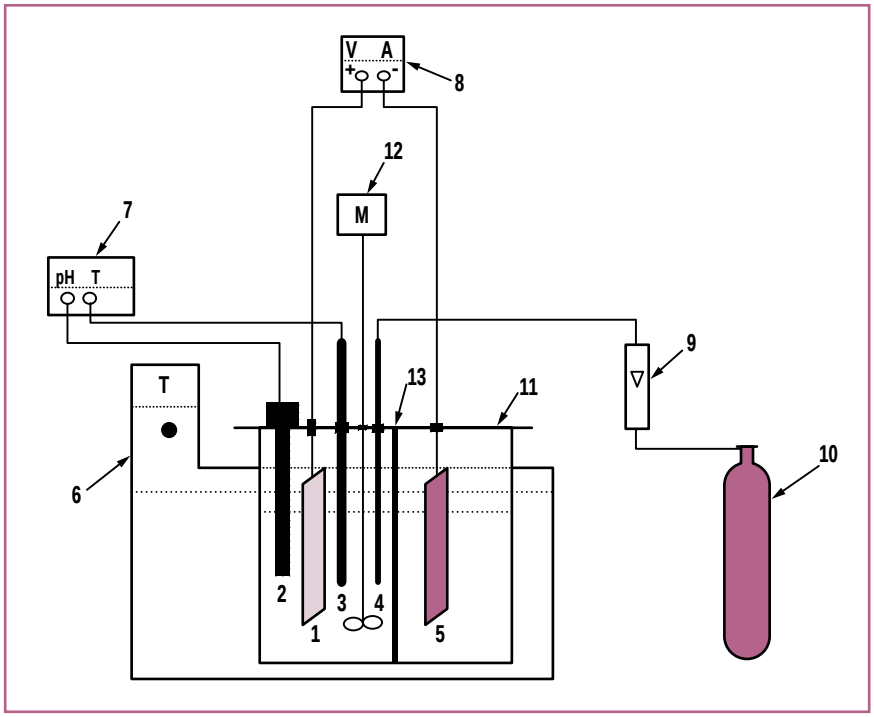
In the area of pulp bleaching, laboratory scale in situ bleaching by electrochemically generated chlorine and hypochlorite ion has received attention *(2, 3)*.

As the pulp and paper industry shifts toward totally chlorine free bleaching processes, under both environmental and economic pressure *(4)*, 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 1990s approximately half of all the kraft pulp produced worldwide was oxygen bleached (~ 35 million tons/year) *(5)*. The ultimate goal would be the development of the "closed cycle pulp mill" based on oxygen delignification.

Unfortunately, at the present stage of development, the oxygen bleaching process alone cannot meet the demanding quality conditions of the "closed cycle pulp mill," i.e., final brightness about 87–90% ISO, final kappa number <1.5 *(5)*, while the viscosity of the pulp should remain high, above 15 cP. It is well documented in the literature that the oxygen delignification cannot remove more than 45–50% of the lignin without significantly damaging the pulp carbohydrates, i.e., reducing the tensile strength of the pulp *(6, 7)*. Due to the low reaction rate between oxygen and lignin, the 50% delignification limit is achieved only under intensive conditions, e.g., oxygen pressure above 0.6 MPa, temperature ~100°C, alkali concentration 2–5% wt in slurry, pulp consistency 25–30% *(7)*.

One way to improve the characteristics of oxygen bleaching is by the development of complex catalytic systems based on transition metal ions to enhance the delignification rate and/or to improve the selectivity of oxygen bleaching *(8–11)*.

The transition metal compounds mostly work according to a redox mechanism. The redox catalyst intervenes in the rate determining step of the oxygen delignification, i.e., the formation of phenoxyl radicals from the phenolate anion *(12, 13)*. According to one of the proposed reaction mechanisms *(14, 15)*, the higher oxidation state form of the transition metal ion $M^{(n+1)}$, accepts one electron from the phenolate anion more readily than oxygen, generating the phenoxyl radical and the



1. In situ electrochemically mediated oxygen bleaching setup. Legend: 1 anode, 2 pH electrode, 3 temperature probe, 4 gas sparger, 5 cathode, 6 water thermobath, 7 pH meter, 8 potentiostat, 9 rotameter, 10 gas cylinder (oxygen or nitrogen), 11 batch electrochemical reactor, 12 mixer, 13 cation exchange membrane.

reduced form M^{n+}. The role of electrochemistry would be to continuously, in-situ, regenerate the active form of the redox catalyst at the anode of an electrochemical cell.

Ferricyanide has been the most studied electrochemical mediator for the delignification of chemical pulps *(16–23)*. Regarding manganese compounds as catalysts for oxidative delignification, Landucci and Sanyer *(9)*, had shown that Mn(II) in concentration of 0.1% wt on pulp almost doubled the delignification rate in oxygen pulping at pH 9.0, 150°C, and 140 psi O_2 pressure. Furthermore, the viscosity of the delignified pulp was slightly higher when compared with the control experiment, i.e., without Mn(II), indicating the carbohydrate protecting effect of Mn(II).

Perng *et al.* screened a number of Mn(II) compounds for in situ electrochemically mediated oxygen bleaching at pH 9.4 and 11.2, 1 atm O_2 pressure and temperature between 25-50°C *(19)*. The absence of redox behavior for the Mn complexes as determined by cyclic voltammetry, together with the drop of the reduction potential of the redox couple below 0.4 V(SHE) at pH > 9 and hydrolytical instability at pH > 9, were considered to be the main factors which caused the absence of catalytic activity for the investigated Mn complexes *(19)*.

The finding of redox couples that are stable in alkaline media, electrochemically reversible and that possess a reduction potential above 0.4 V(SHE) *(15, 19)* or between +0.54 V(SHE) and –0.06 V(SHE) *(14)* at pH >9, is crucial for the in situ electrochemically mediated oxygen delignification. In this respect, the work described here is concerned with the investigation of Mn(III)CyDTA [(trans-cyclohexane-1,2-diamine-N, N,-N',N'-tetraacetato)manganate-(III)] as a potential electrochemical mediator of the oxygen delignification. The Mn(III)CyDTA was chosen because of the following characteristics: as a result of the rigidity of the cyclohexane ring, it is one of the most stable Mn(III) complex in aqueous alkaline media, being stable up to pH 11 at 25°C *(24)*, the actual reduction potential of Mn(III)CyDTA in alkaline media at 25°C is approximately +0.2 V(SHE) at pH 10.0 and +0.12 V(SHE) at pH 11 *(25)* and, furthermore, both CyDTA and Mn(II) might act as carbohydrate protecting agents.

The work described below was aimed at testing the ability of Mn(III)CyDTA to promote the delignification of kraft softwood pulp in alkaline conditions.

EXPERIMENTAL APPARATUS AND PROCEDURE

Apparatus

The laboratory scale in situ electrochemically mediated bleaching apparatus is shown in **Fig. 1**. A cylindrical, divided, batch electrochemical reactor, made of 316 stainless steel,was employed. The interior of the reactor was Teflon coated to avoid the contamination of the pulp sample with traces of transition metal ions from the stainless steel wall. The reactor (diameter 18 cm, height 16.3 cm) was divided in two chambers of 1 L effective volume each by a cation exchange membrane (Nafion 324) supported by two perforated Plexiglas plates. Based on studies of the electrosynthesis of Mn(III)CyDTA in alkaline media, two anodes were selected for electrochemically mediated bleaching, i.e., stainless steel (316) screen (with 20 openings per inch, 0.051 cm wire diameter, total area of 232 cm^2) and a graphite plate (A = 58 cm^2). The cathode in all runs was a platinized titanium plate (A = 70 cm^2).

The electrodes were connected to a DC power supply (Xantrex), operated in galvanostatic mode, with an output current from 0 to 4 A and output voltage from 0 to 15 V.

Metered gas flow (oxygen or nitrogen, 844 ml/min at 21°C and

101 kPa) was continuously purged into the anode chamber containing the pulp slurry. Also, the pH of the pulp suspension was monitored by using a pH electrode specially designed for the pulp and paper industry (Fisher Scientific Inc.). The anolyte, containing the pulp slurry, was vigorously mixed using an axial flow impeller connected to a motor with a variable speed (Talboys Inc.). The temperature during bleaching was controlled by immersing the stainless steel reactor in a water thermobath (Haake E8). The temperature variation inside the reactor was ±1° C.

Procedure for in situ electrochemically mediated oxygen delignification

The anode chamber of the electrochemical reactor was filled with 1 L electrolyte containing Mn(III)CyDTA (0.5–3 mM) electrochemically generated from $MnSO^4$ and CyDTA *(25, 26)* and Mn(II)CyDTA (3–5.5 mM), in 0.1 M $NaHCO^3$ at pH ~10.0, 25°C. The CyDTA/Mn molar ratio was in the range of 1/1 to 4/1.

An amount of 10 g ovendry softwood kraft pulp was disintegrated in a British Standard Pulp Evaluation apparatus according to TAPPI T 205 Method. A handsheet was made in conformity with the TAPPI T 218 Method. The resulting handsheet was added to the anolyte and both the pH and temperature were adjusted to the desired values, in the range of 9.0 to 10.5 and 25 to 80°C, respectively. The pulp consistency in all runs was 1% (i.e., 10 g o.d. pulp in 1 L solution). The initial kappa number of the pulp was 30.0±0.3 and the initial viscosity was 34.6±0.4 cP.

The cathode chamber was filled with 1 L NaOH solution at pH 13.5. The pulp suspension was purged with gas (O_2 or N_2) at atmospheric pressure, mixed continuously and subjected to electrolysis at a constant current (in the range of 0 to 1 A) for up to 3 h reaction time. During the factorial runs, the pH of the pulp slurry was also controlled, by measuring it every 15 or 20 min and adjusting it to the desired value by addition of 2M NaOH or glacial acetic acid.

Washing type	Washing procedure (for 1L volume & 1% kraft pulp consistency)	Kappa number	Viscosity, cP
I	3 times, 5 min each with H_2SO_3 0.25% @25-30°C	30.0	34.6
II	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[a] (i.e., 25 mL 40%) @ pH 4-5 (adjusted with glacial acetic acid) and 20-25°C	30.0	34.6

[a] DTPA = diethylenetriaminepentaacetic acid (chelating agent)

I. Pulp washing procedures and their influence on the unbleached kraft pulp (pulp before washing: K = 30.0 and viscosity = 34.6 cP)

At the end of the bleaching, the pulp was filtered and thoroughly washed in sulfurous acid solution **(Table I)** in order to wash out the manganese which might interfere with the kappa number and viscosity determinations. As can be seen from Table I, the washing procedures based on dilute H_2SO_3 (0.25%), did not affect the kappa number or the viscosity, thus the results obtained were solely determined by the bleaching methods. The washing method I (Table I) was successful in the presence of small amounts of manganese (< 1.5 mM), while in the case of higher concentrations a more effective method, based on H_2SO_3 and a chelating agent (DTPA), had to be employed.

After washing, a handsheet was made from the bleached pulp and placed in the conditioner room (i.e., at constant temperature and humidity) for 24 h. Finally, the kappa number and viscosity of the bleached pulp were determined, according to TAPPI Methods T 236 cm-85 and T 230 cm-82, respectively.

EXPERIMENTAL RESULTS

The electrode reactions are: Mn(II)CyDTA oxidation to Mn(III)CyDTA with parallel oxygen generation from alkaline media at the anode and hydrogen evolution at the cathode:

$$\text{ANODE (+): Mn(III)CyDTA} + 1e^- \leftarrow \text{Mn(II)CyDTA}$$

$$1/2O_2 + H_2O + 2e^- \leftarrow 2OH^-$$

$$\text{CATHODE (–): } H_2O + 1e^- \rightarrow 1/2\ H_2 + OH^-$$

Stainless steel screen anode: full factorial experimental design using 3 factors at 2 levels (i.e., 23 design)

The electrosynthesis studies have shown the possibility of electrochemical generation of Mn(III)-CyDTA on a stainless steel screen anode, but the current efficiency for Mn(III) was satisfactory (i.e., between 20 and 96%) only for an equimolar CyDTA/Mn molar ratio and furthermore low current density (e.g., 2.6 A/m^2) and low Mn(II) concentration (e.g., 6 mM) have to be employed in order to avoid the anodic deposition of diverse manganese oxides and hydroxides *(25, 26)*.

A full factorial experimental design at two levels was performed to determine the main and interaction effects for three process variables, i.e., oxygen, redox catalyst (Mn(III)CyDTA) and current, on both

Variables	Variable - ("Low")	Level + ("High")
Oxygen (MPa) (O)	0[a]	0.1[b]
Mn(III) (mM) (C)	0	0.5[c]
Current density (A/m^2) (**I**)	0	2.6[d]

[a] N_2 Purge
[b] O_2 Purge (844 mL/min., 21 C, 101 kPa)
[c] Initial concentration
[d] On a stainless steel screen anode

II. Variables and their levels in the 2^3 factorial experiment

NO.	VARIABLES	VARIABLE - ("Low")	VARIABLE 0 ("Center")	LEVEL + ("High")
1	Oxygen (mL/min.) (**O**)	0[a]	422	844
2	Mn(III) (m*M*) (**C**)	0	0.7 m*M*[b]	1.4 m*M*[b]
3	Current density (A/m^2) (**I**)	0	25[c]	51[c]
4	Temperature (C) (**T**)	25	53	80
5	pH (**P**)[d]	9.0	9.8	10.5
6	CyDTA/Mn (mol. ratio)(**L**)	2	3	4

[a] N2 Purge
[b] Initial concentration
[c] On the graphite plate anode
[d] pH control

III. Variables and their levels in the 2^{6-1} + 1 factorial experiment

kappa number and viscosity. The temperature and pH were held constant at 25°C and 10.5, respectively. The levels of the variables employed are given in **Table II**.

Eight runs were performed in random order, according to the experimental design created with the Jass 2.1 software *(27)*. Some of the runs were replicated to estimate the experimental error for both kappa number and viscosity. The results are given as cube plots in **Fig. 2**.

As can be seen from Fig. 2A, the best delignification run was obtained at the highest level of all three factors, i.e., in the in situ electrochemically mediated bleaching run, in which the kappa number dropped from 30.0 to 22.0 in 3 h, at 1 atm oxygen pressure, 25°C, pH 10.5. The same conditions, but without Mn(III)CyDTA and current ("conventional" oxygen bleaching), brought about a decrease in kappa number from 30.0 to 28.3.

Regarding the viscosity (Fig. 2B), the most severe carbohydrate degradation occurred in the in situ electrochemically mediated bleaching where the viscosity dropped from 34.6 to 24.9 cP. Interestingly, the run without current but with [Mn(III)/Mn(II)]CyDTA and oxygen (i.e., thermocatalytical bleaching), caused only a 6.9 cP decrease in viscosity, from 34.6 to 27.7 cP. This suggests that the Mn(III), continuously regenerated by the current, attacks both the lignin and the carbohydrates, while the Mn(II) which predominates in the absence of current (due to the depletion of Mn(III) in reactions with the pulp and in disproportionation in alkali media), has a milder effect on carbohydrates.

From the factorial experiments performed on the stainless steel screen anode, it was learned that Mn(III)CyDTA even in low concentrations (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. Replacing the stainless steel anode with graphite allows the exploration of higher CyDTA/Mn molar ratios (e.g., 2/1) which would assure an increased stability of the complex, and also current densities up to 100 A/m^2 can be employed without complications due to anodic deposit formation *(25, 26)*.

Graphite plate anode: the influence of CyDTA/Mn molar ratio

The CyDTA stabilizes the Mn(III) in aqueous alkaline media and might also act as a carbohydrate protecting agent through a strong chelation of Mn(III) and Mn(II) and, finally, influences the outcome of the electrochemical generation of Mn(III)-CyDTA *(26)*. Consequently, the CyDTA concentration during the in situ electrochemically mediated oxygen bleaching can be a significant process variable.

Two CyDTA/Mn molar ratios were investigated, i.e., 1/1 and 2/1, respectively. In both cases the current density was 51 A/m^2, the pH 10.5, 25°C, 1 atm O_2 pressure and 1% pulp consistency. To assess the role of both Mn and current, two further parallel experiments were performed under similar bleaching conditions (i.e., pH, T, O_2 pressure and pulp consistency). The first was with [Mn(III)/Mn(II)]CyDTA but without current, while the second was a "conventional" oxygen bleaching ("blank" run) without Mn and current.

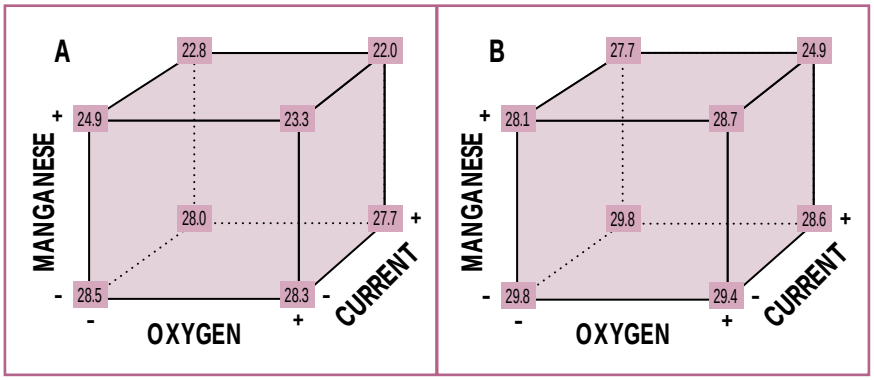
The kappa numbers and viscosities were plotted vs. time in **Figs. 3 and 4**, respectively. At first glance it can be seen from Fig. 3 that for both CyDTA/Mn molar ratios, the best delignification was obtained in the in situ electrochemically mediated runs (i.e., curves No.1 in **Figs. 3A and**

3B), putting into evidence the role of the anodic current in the regeneration of the active form of the redox couple, i.e., Mn(III)CyDTA. Nevertheless, there are significant differences between the two ligand to metal ratios as well.

In the case of an equimolar CyDTA/Mn ratio, the stability of the complex is lower, at 25°C, pH 10.5; the half-life time of Mn(III) for CyDTA/Mn 1/1 is about 30 min, while for CyDTA/Mn 2/1 is about 40 min *(25)*. As can be seen from Fig. 3A (curve No. 1) when current was applied, after a fast delignification in the first 15–30 min, when the kappa number dropped from 30.0 to 24.2, the delignification leveled off for the next 2–3 h, at a kappa number of 23–22.4. The leveled kappa number in the equimolar case can be explained by both the depletion of the easily oxidizable lignin functional groups in the first 20 min and the fast decomposition of the electrogenerated Mn(III)CyDTA with the formation of inactive hydroxo and oxo species (e.g., $Mn(OH)_2$, MnO(OH), MnO_2).

When the CyDTA was in excess (i.e., CyDTA/Mn 2/1), in the presence of current, although the fastest delignification occurred again in the first 30 min (i.e., the kappa number dropped from 30.0 to 23.5, Fig. 3B, curve No. 1), the delignification progressed over the entire bleaching period, from a kappa number of 23.5 at 30 min to 19.8 after 3 h. This result is in a sharp contrast with the equimolar case. The extended life time of Mn(III), in aqueous alkaline media in the presence of a CyDTA excess, makes it possible for the Mn(III) to attack the more resistant lignin structures which remain after the first 30 min of fast delignification.

The runs performed without current but with initial concentration of Mn(III)CyDTA, for a 2/1 CyDTA/Mn molar ratio (curve No. 2, Fig. 3B), showed a rapid delignification in the first 15 min, followed by a leveling off for the rest of the time. The



2. Cube plot of kappa number (A) and viscosity (B) as a function of oxygen, manganese complex and current density levels. Bleaching time 3 h, pH 10.5, 25°C, stainless steel screen anode (where applicable). Unbleached pulp: K = 30.0 and viscosity = 34.6 cP. Response errors: ± 0.4 for kappa number and ± 0.5 cP for viscosity.

Mn(III) is continuously consumed by both the delignification reaction and by decomposition in alkaline media, and, although the Mn(III) concentration during the bleaching runs was not measured, it is hypothesized that without an anodic regeneration the Mn(III) concentration is diminished to levels which are not able to further promote delignification.

The viscosity profiles (Fig. 4) revealed some interesting aspects regarding the carbohydrate degradation during the three different oxygen bleaching methods (i.e., in situ electrochemically mediated, with Mn but without current and "conventional" oxygen bleaching). As can be seen from Fig. 4, the viscosity drop was the most severe during the in situ electrochemically mediated bleaching runs, as a result of a high concentration of Mn(III) ions. Still, an excess of CyDTA significantly alleviated the extent of carbohydrate degradation, e.g., after 3 h, for CyDTA/Mn 2/1 (molar ratio) the viscosity was 20.5 cP, while for a CyDTA/Mn 1/1 (molar ratio) it was 13.2 cP (curves No. 1, Figs. 4A and 4B).

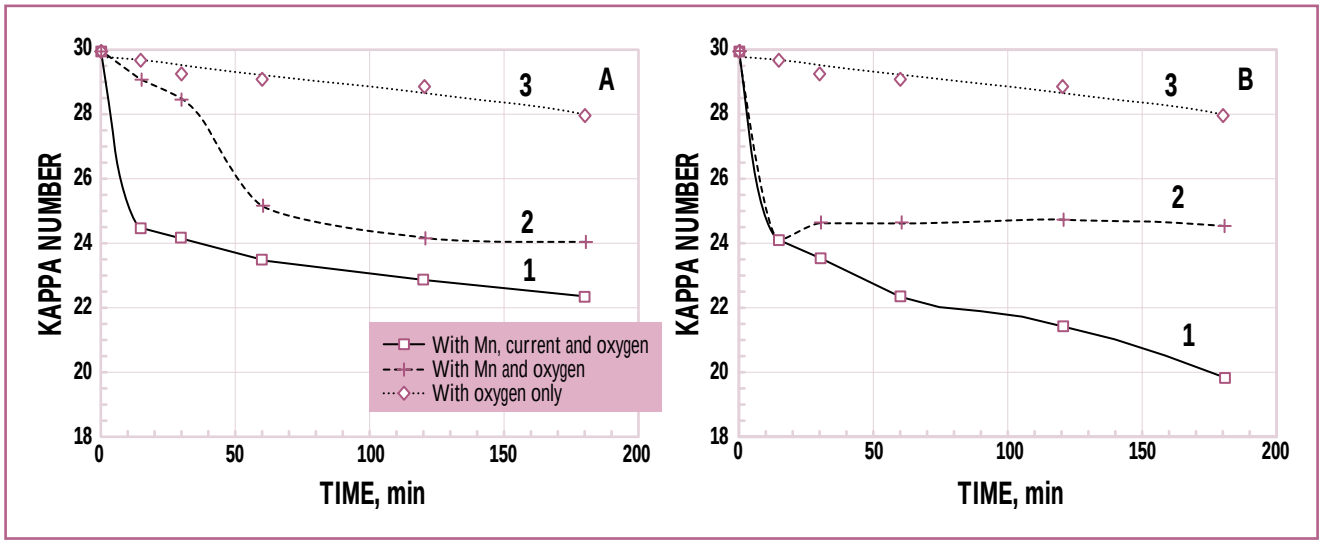
During the runs without current but with Mn, the viscosity remained high for both CyDTA/Mn molar ratios, i.e., above 29 cP (curves No. 2 Figs. 4A and 4B). Furthermore, these values are almost independent of the CyDTA/Mn molar ratio. This suggests that the Mn(II) species formed by the decomposition of Mn(III)CyDTA are not responsible for the carbohydrate degradation. The viscosity profiles obtained during these runs were almost identical with the one obtained for the conventional oxygen bleaching (compare curves No. 2 and 3 in Figs. 4A and 4B).

The kappa number and viscosity profiles (Figs. 3 and 4), showed the multiple and intricate functions played by the [Mn(III)/Mn(II)]-CyDTA redox couple during bleaching. The Mn(III) form is active in promoting delignification while it attacks the pulp carbohydrates as well. Furthermore, CyDTA is functioning as carbohydrate protecting agent.

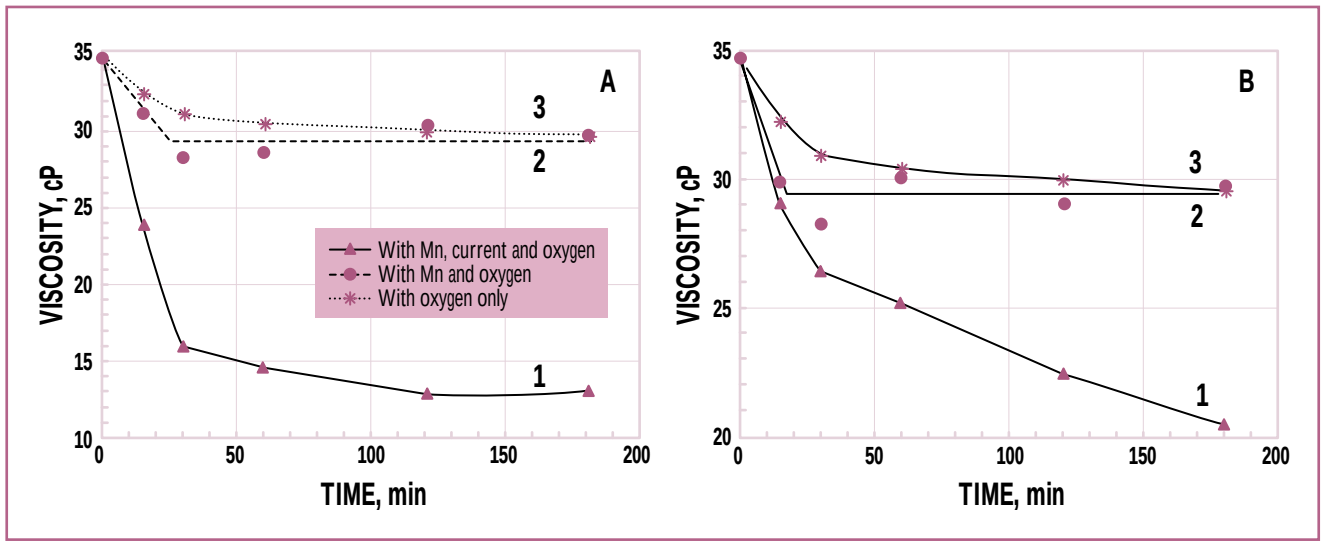
The combined effect of pH and temperature on delignification

From the previously presented investigations, it was learned that the 2/1 CyDTA/Mn molar ratio gave the lowest kappa number and the highest viscosity, in the case of in situ electrochemically mediated oxygen bleaching employing a graphite plate anode. Therefore, the 2/1 CyDTA/Mn ratio was adopted in further experiments.

All the investigations presented so far were performed at 25°C and pH 10.5. Other electrochemically mediated bleaching studies revealed significant delignification enhancement at temperatures above 50°C



3. Kappa number profiles in time as a function of CyDTA/Mn molar ratio. pH 10.5, 25°C, O_2 0.1 MPa, i = 51 A/m² on a graphite plate anode (where applicable). A. CyDTA/Mn = 1/1 (molar ratio); initial Mn(III)CyDTA concentration 3 mM. B. CyDTA/Mn = 2/1 (molar ratio); initial Mn(III)CyDTA concentration 1.4 mM.



4. Viscosity profiles in time as function of CyDTA/Mn molar ratio. pH 10.5, 25°C, O_2 0.1 MPa, i = 51 A/m² on a graphite plate anode (where applicable). A. CyDTA/Mn = 1/1 (molar ratio); initial Mn(III)CyDTA concentration 3 mM. B. CyDTA/Mn = 2/1 (molar ratio); initial Mn(III)CyDTA concentration 1.4 mM

(15, 28). Consequently, the role of temperature in the present system required a closer look.

The bleaching runs were performed at 1 atm oxygen pressure, at two pH levels, 9.0 and 10.5, respectively, with an initial Mn(III)CyDTA concentration of 1.4 mM, at an anode current density of 51 A/m², employing a graphite plate anode. The effect of temperature was investigated in the range of 25 to 80°C **(Fig. 5)**.

As can be seen from Fig. 5, at pH 10.5, increasing the temperature from 25 to 80°C caused a retardation of the delignification, the kappa number of the bleached pulp increased from 19.8 to 24.5. This is due to the enhanced decomposition of the Mn(III)CyDTA at temperatures above 25°C. However, at pH 9.0 the trend is reversed: the delignification improved significantly with increasing temperature, at 80°C the kappa number dropped from 30.0 (i.e., unbleached pulp) to 17.1 in 3 h. The stability of Mn(III)CyDTA is improved by lowering the pH, while the rate of the kinetic controlling step for delignification is increased at high temperatures. These combined effects are responsible for the extended delignification at pH 9.0 and 80°C.

I.D.	Mn(III)	Current density	Oxygen	pH	CyDTA/Mn molar ratio	Temp.	Kappa[a] number	Visc.[b], cP
1	+	+	+	-	-	+	16.7	21.5
2	-	-	+	-	-	+	27.2	30.3
3	+	+	-	+	-	+	26.1	31.1
4	+	+	-	-	+	+	27.6	31.1
5	+	+	+	+	-	-	19.9	20.6
6	+	-	+	+	-	+	22.4	31.4
7	+	+	+	+	+	+	21.6	24.1
8	0	0	0	0	0	0	23.5	26.9

[a]the response error for kappa number is 0.4.
[b]the response error for viscosity is 0.4 cP.

IV. Selected results from 2^{6-1} + 1 factorial experiments. Reaction time 3 h, pulp consistency 1%. Unbleached pulp: K = 30.0, viscosity = 34.6 cP.

KEYWORDS
Bibliographies, catalysts, delignification, electrochemistry, kraft pulps, manganese compounds, oxygen, oxygen bleaching, redox reactions, softwood pulps, transition metals.

Half factorial experiments with 6 factors at 2 levels and 1 centerpoint (2^{6-1} + 1 design)

Finally, a fractional factorial experimental design was performed to evaluate the main and interaction effects of Mn, oxygen, temperature, current, CyDTA/Mn molar ratio and pH on delignification and carbohydrate degradation.

The employed levels of the six variables are given in **Table III**. Thirty-three experiments were performed in random order, according to the experimental design created with the Jass 2.1 software. Selected runs were replicated and the response errors together with the confidence intervals were calculated *(29)* for both kappa number and viscosity. By performing half-factorial design for 6 variables, instead of the full factorial ones, only the 4th and higher order interaction effects are not estimable.

Selected experimental results are given in **Table IV**. The pulp consistency was 1% and the reaction time was 3 h at atmospheric pressure.

Effects[a] (Main and interaction[b])	Kappa number	Viscosity, cP
Mn(III) (**C**)	-2.9	-2.0
Current density (**I**)	-1.9	-2.5
Oxygen (**O**)	-2.0	-1.3
pH (**P**)	-0.7	-0.6
CyDTA/Mn (**L**)	+1.0	+1.2
Temperature (**T**)	-1.2	-0.1
CI	-1.7	-2.6
CO	-1.4	-1.8
CL	+0.6	+0.6
CT	+0.1	+1.0
OT	-2.0	-1.2
CIO	-0.5	-1.9
CIT	+0.3	+0.7
COT	-1.0	0.0
CPT	+0.9	+1.5
COP	+0.6	+0.6
COL	+0.8	+0.8

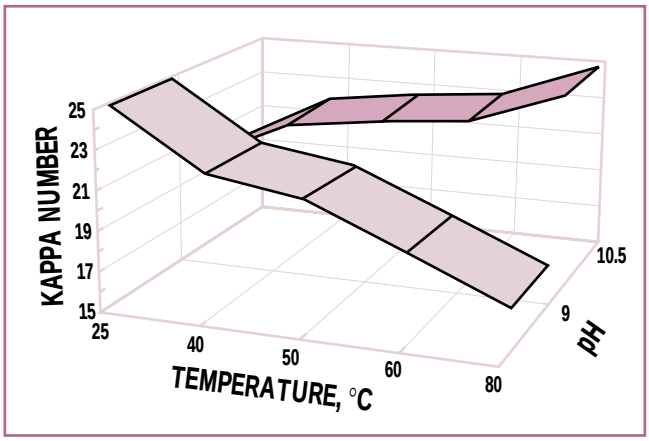
[a]The confidence intervals at 95% level are: 0.4 for both kappa number and viscosity.
[b]The interaction effect between 2 or 3 factors assumes that the remaining factors are at a middle level.

V. Selected main and interaction effects for the 2^{6-1} + 1 factorial experiment

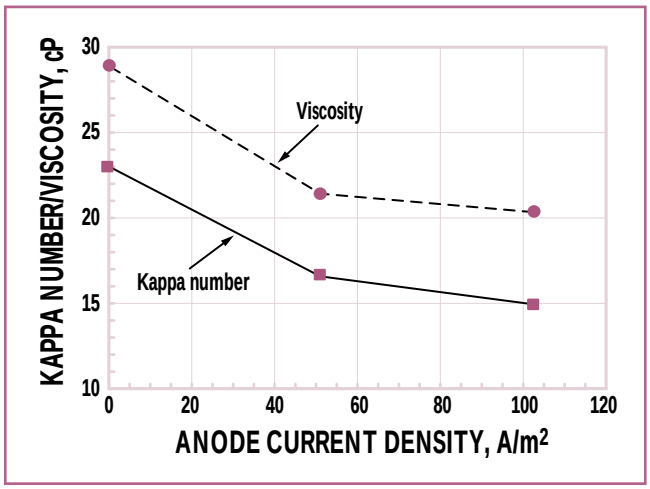
Table IV shows that the best delignification was obtained at "high" levels of Mn, current, oxygen and temperature but at "low" levels of both pH and CyDTA/Mn molar ratio (entry No. 1, Table IV).

Generally, the runs performed at "high" levels of Mn, pH and temperature but without current, generated viscosities above 30.0 cP (e.g., entry No. 6, Table IV). This confirms once again that the Mn(II) species formed by the rapid decomposition of Mn(III)CyDTA at pH 10.5 and 80°C did not damage the pulp carbohydrates.

A better insight into the system is gained by analyzing some of the main and interaction effects (2nd and 3rd order) of the 2^{6-1} + 1 factorial design (**Table V**). From Table V it can be seen that among the investigated variables, the Mn had the most profound effect on delignification, its main effect being –2.9. However, this value cannot be separately analyzed because the Mn is involved in statistically significant second- and third-



5. 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 h.



6. The effect of anode current density on the kappa number and viscosity, pH 9.0, 80°C, O_2 0.1 MPa, initial Mn(III)CyDTA conc. 1.4 mM, CyDTA/Mn (molar ratio) 2/1, 1% pulp consistency, graphite plate anode, bleaching time 3 h.

order interaction effects with almost all of the process variables. The second-order interaction between Mn and current (CI) is especially important. When Mn is at a "high" level, by increasing the current from "low" to "high" the kappa number is further reduced by 1.7 units (Table V). This proves the significance of the in situ anodic (re)generation of Mn(III)-CyDTA.

Furthermore, the second-order interaction between Mn and oxygen (CO) and the third-order interactions among Mn, oxygen and temperature (COT) and Mn, oxygen and current (COI) upon delignification is statistically significant. Thus, it can be concluded that Mn(III)CyDTA and oxygen acted synergistically to delignify the wood pulp. However, Mn and oxygen may not act simultaneously, in the same reaction step but rather consecutively. For instance, the Mn(III)CyDTA may promote the phenoxyl radical formation which is followed by the reaction of oxygen with the phenoxyl radicals leading to lignin degradation products. According to this scenario, Mn(III) is an initiator of the network of radical chain processes involving various free radicals, lignin fragments and oxygen.

Increasing the CyDTA/Mn molar ratio from 2 to 4 slows the delignification L = +1.0. Both the second-order interaction effect between Mn and ligand (CL) and the third-order interaction among Mn, ligand and oxygen (COL) shows delignification retardation at "high" concentrations of CyDTA (Table V). At a 4/1 CyDTA/Mn molar ratio, both the Mn(II) and Mn(III) ions are strongly chelated and also the electrochemical (re)generation of Mn(III) is inefficient *(25,26)*.

Regarding the carbohydrate degradation, a high concentration of CyDTA has a beneficial effect, its main effect being L = + 1.2 cP, which is due to the same reason that CyDTA hinders the delignification. The Mn(III) itself, especially through second- and third-order interactions with current and/or oxygen, damages the pulp carbohydrates (Table V).

The influence of the anode current density on the kappa number and viscosity

As can be seen from **Fig. 6**, increasing the anode current density during bleaching from zero (i.e., initial Mn(III)CyDTA concentration of 1.4 mM) to 51 A/m², at pH 9.0, 80°C, atmospheric oxygen pressure and 1% pulp consistency brought about a 6.4 points decrease in kappa number and an 8.5 cP decrease in viscosity, in 3 h. By further increasing the anode current density to 102 A/m², the kappa number drops an additional 1.7 points, to 15.0, while the viscosity is still slightly above 20 cP. The required cell voltage was 4 V.

The dependence of both delignification and carbohydrate degradation on current density is actually a dependence on the in situ concentration of Mn(III)CyDTA. Figure 6 clearly shows a tendency toward reaching a "floor" kappa number (between 13 and 15) by increasing the current density above 102 A/m².

CONCLUSIONS

Under milder conditions than in the conventional industrial practice of oxygen bleaching *(30)*, i.e., 1 atm oxygen pressure, pH 9.0, 80°C and 1% kraft pulp consistency, a 50% delignification was obtained in 3 h by in situ electrochemically mediated oxygen bleaching based on the [Mn(III)/Mn(II)]CyDTA redox couple (initial concentration of Mn(III) 1.4 mM) and a graphite plate anode operated at a current density of 102 A/m². The kappa number dropped

from 30.0 to 15.0 and the viscosity from 34.6 cP to 20.5 cP.

The parametric and factorial experiments revealed the multiple functions played by the [Mn(III)/Mn(II)]CyDTA redox couple. The Mn(III) is the active form in promoting delignification, acting mainly through second- and third-order interactions with oxygen and temperature, while CyDTA is an effective carbohydrate protecting agent. The Mn(II) species do not damage the pulp carbohydrates or promote delignification.

The anodic current has the role to continuously, in situ (re)generate the active form of the redox couple, i.e., Mn(III)CyDTA. The in situ electrochemically mediated oxygen bleaching employing Mn(III)CyDTA presented a small but statistically significant nonlinear behavior, reflecting the existence of a catalytic interaction between [Mn(III)/Mn(II)]-CyDTA, oxygen, and temperature.

The practical application of in situ electrochemically mediated bleaching requires overcoming a number of problems related to the scale-up of such a system. These problems include the need for mixing and the high specific energy consumption in pulp slurries above 1% consistency, along with cathodic hydrogen evolution and the process requirements for recycling the electrochemical mediator. However, these problems are not insurmountable and there is strong motivation to continue this line of study into the improvement of oxygen bleaching technology. **TJ**

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