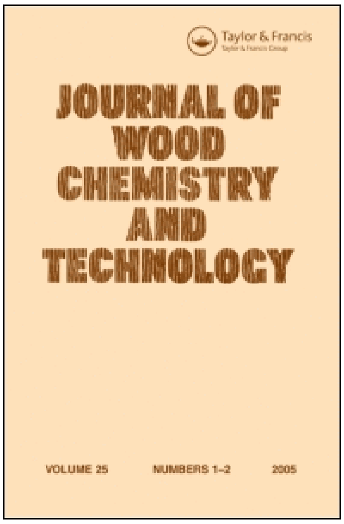

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AFFINITY OF METAL IONS FOR KRAFT PULPS STUDIED BY ESR. INHIBITION OF THEIR CATALYTIC ACTION IN OXYGEN BLEACHING

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ABSTRACT

ESR spectrum of an unbleached kraft pulp exhibits several signals which are attributed to phenoxy or semi-quinone radicals and also to paramagnetic metal ions such as Fe^{III} and Mn^{II}. The same signals are visible on a totally bleached pulp even though their intensity is lower. Analysis of Fe^{III} and Mn^{II} signals reveals that these ions form complexes with lignin or cellulose. Pulp treatment with $NaBH_4$ is followed by ESR spectroscopy. Reduction of the metal ions to

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their lower valence levels is observed ($Fe^{III} \rightarrow Fe^{II}$ or Fe^{0}, $Mn^{II} \rightarrow Mn^{0}$). New complexes are formed with the pulp components. These observations are related to the protecting effect of the $NaBH_4$ pre-treatment, observed during oxygen bleaching.

INTRODUCTION

The development of oxygen bleaching processes is limited by the lack of selectivity of these treatments. Previous studies performed on a fully bleached pulp have demonstrated that the origin of cellulose degradation during oxygen treatment pulp is the presence of metal ions in the pulp.[1] The most harmful metal ions are $Fe^{(II\ or\ III)}$, Mn^{II} and Cu^{II}, which are responsible for $HO^{\bullet}$ radicals formation and reaction on the cellulose chains.[2] Intermediate H_2O_2 would be at the origin of these radicals. During oxygen delignification of an unbleached kraft pulp, the presence of lignin also promotes cellulose degradation.[3] Lignin degradation generates relatively high amounts of intermediate H_2O_2 which partly decomposes into $HO^{\bullet}$ radicals.[2,3] The quantities of H_2O_2 and $HO^{\bullet}$ generated during oxygen delignification of the unbleached pulp are much higher than in the oxygen treatment of a fully bleached pulp. Despite that, the unbleached pulp is comparatively less degraded than the totally bleached pulp, when both pulps are treated by oxygen in the presence of the same amount of metal ions added. The reason for this contradiction is not known.

Several additives and pulp pre-treatments have been investigated[2,3] to minimise the cellulose depolymerization during oxygen treatments. It was found that sodium borohydride ($NaBH_4$) reduction totally suppressed cellulose degradation during the subsequent oxygen treatment of a fully bleached pulp, even in the presence of high amounts of metal ions.[1,3] $NaBH_4$ pre-treatment also partly inhibited pulp degradation during oxygen treatment of an unbleached pulp.[3] A parallel decrease in the formation of $HO^{\bullet}$ radicals was observed.

ESR spectroscopy has been widely used to follow the formation of lignin radicals under mechanical or chemical treatments.[4,5,6] Less work has been done on the interaction of metal ions with pulp components.[7,8] In the present study ESR spectroscopy is used to clarify the fate of metal ions in kraft pulps and their role during oxygen bleaching. Another objective is to understand the effect of a $NaBH_4$ pre-treatment.

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RESULTS AND DISCUSSION

ESR Analysis of the Unbleached and the Totally Bleached Kraft Pulps

Samples of an unbleached and a totally bleached softwood kraft pulp (characteristics given in Table 1) are finely ground and analysed by ESR spectroscopy. Figure 1 represents the spectra given by these two pulps.

The spectrum of the unbleached pulp (dotted line) exhibits a characteristic signal for high-spin Fe^{3+} ions, represented by a wide peak at $g = 4.3$, typical[8] of rhombically distorted Fe^{3+}. The elevation of the baseline in the

Table 1. Characteristics of the Softwood Kraft Pulp

	Viscosity (mPa, s)	Brightness (% ISO)	Kappa value	Metal ions content (ppm)			
				Fe	Mn	Cu	Mg
Unbleached softwood kraft pulp	20.2	–	31.9	20	30	< 1	160
Totally bleached softwood kraft pulp	16.7	87.6	–	10	< 1	< 1	30

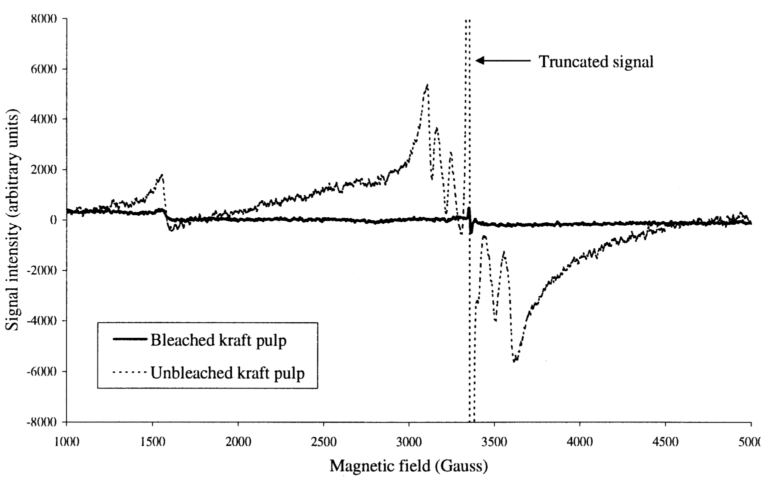


Figure 1. ESR spectra of a fully bleached and an unbleached softwood kraft pulp.

area around 2500–3000 G may indicate the presence of low-spin Fe^{3+}, usually in the pseudo-octahedral conformation[8] in the region around $g = 2$. Mn^{2+} ions are also clearly detected since they give a very well defined 6-peak signal between 3000 and 3600 G. Copper is not detected, maybe because its amount is very low and its signal appears in the same area as Mn^{2+} signal. A typical signal for stable organic radicals R° is seen at $g = 2.004$ (3352 Gauss). This signal is attributed to the presence of lignin, and is due to radicals with semi-quinones or phenoxy structures.[6,7] These radicals are stabilised by the large and rigid polymer matrix,[4] by the resonance effect[9] and also by the presence of metals.[7] Furthermore, the peak is relatively fine, which implies an isotropy of the system: all the radicals have similar structures, so that their superimposed signals provide a peak at the same field value.

In Figure 1, the spectrum of the totally bleached kraft pulp is also represented. The Fe^{3+} signal is still clearly visible, at around $g = 4.3$ (1600 G). Its intensity is lower than for the unbleached kraft pulp, which is in accordance with the fact that the bleached pulp contains less iron than the unbleached one (see Table 1). Neither manganese nor copper are detected (again, this was predictable since Mn^{2+} has disappeared during bleaching). There is still a weak signal corresponding to the $R^{\bullet}$ radicals, 50 times as small as for the unbleached pulp. This signal is very likely due to residual lignin fragments, which remain after the bleaching sequence, but are not abundant enough to be detected by the usual method (micro-kappa). Cellulose is generally supposed to be of non radicalic nature.[4]

The lignin-like residues in fully bleached pulp can be one reason for the light induced brightness reversion of chemical pulps, as these radicals can create coloured structures under the action of light.[6] Furthermore, they could participate in the mechanism by which carbohydrates degradation occurs during oxygen treatment of a totally bleached pulp, as they can be a source of peroxides.

ESR spectroscopy is thus a very powerful tool. Metal ions can be detected in both unbleached and totally bleached pulps, even at very low concentrations. The lignin content in pulp can be at least approached by the intensity of the R° signal, and followed along the bleaching process.

Affinity of Metal Ions for Pulps

The affinity of metal ions for kraft pulps is studied by recording the ESR spectra of pulps impregnated with 340 ppm of each metal during 24 h, and then thoroughly washed. Metal ions concentrations in the pulps are also measured by ICP (Table 2). The addition of each metal ion causes an increase in the intensity of the corresponding signal, for each type of pulp (unbleached and bleached). An important result is that the signals of the metals in the pulps (Figures 2, 3 and 4) are different from those observed when solutions of the metals are analysed by ESR (spectra not represented here). This indicates that the metal ions in pulp do not have the same

Table 2. ICP Measurement of Metal Ion Contents in the Bleached and Unbleached Kraft Pulps Impregnated with 340 ppm of Metals

	Fe (ppm)	Mn (ppm)	Cu (ppm)
Totally bleached pulp			
Non washed pulp	340	330	335
Washed pulp	160	170	130
Unbleached pulp			
Non washed pulp	340	353	320
Washed pulp	360	340	290
$NaBH_4$ treated and washed pulp	330	345	290

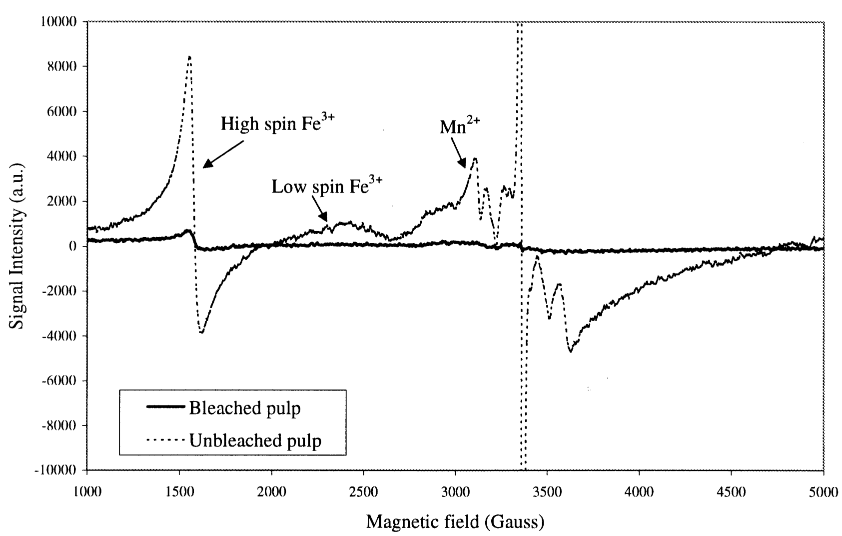


Figure 2. ESR spectra of a fully bleached pulp and an unbleached pulp, enriched with Fe^{3+} ions and then washed.

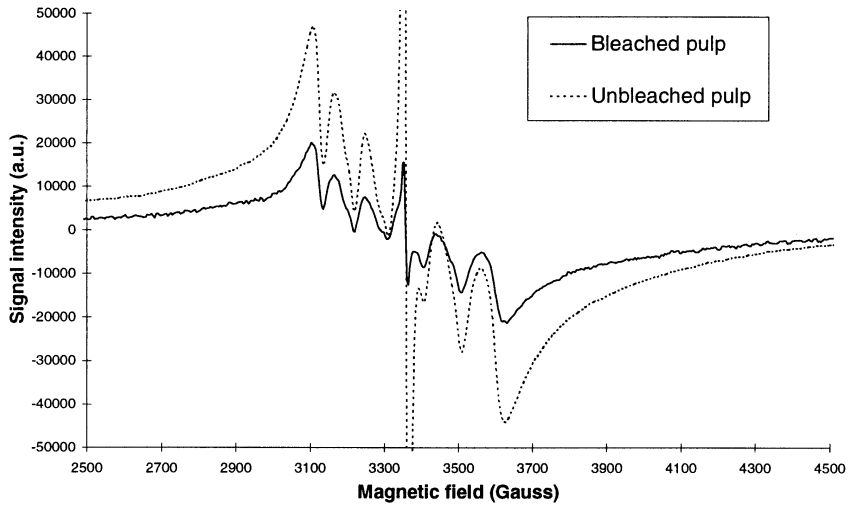


Figure 3. ESR spectra of a fully bleached pulp and an unbleached pulp, enriched with Mn^{2+} ions and then washed.

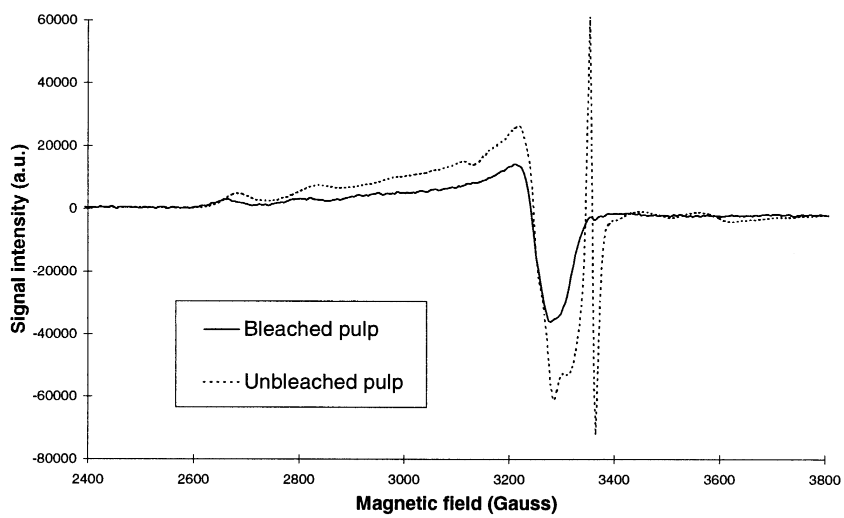


Figure 4. ESR spectra of a fully bleached pulp and an unbleached pulp, enriched with Cu^{2+} ions and then washed.

chemical environment as in solution, which means that they form complexes with pulp components.[10]

Fe^{3+} in the unbleached pulp provides two types of signal corresponding to high and low spin Fe^{3+} (Figure 2), whereas only the high-spin Fe^{3+} signal is visible in the totally bleached pulp spectrum. This indicates that iron finds more possibilities to settle down in the unbleached pulp. Comparison of the Fe^{3+} signal intensities for the unbleached and the bleached pulp after washing is not valid here, because the ESR spectra of the two pulps have not been recorded under identical experimental conditions. Nevertheless, ICP analysis indicates that more Fe^{3+} remains in the unbleached pulp after washing (see Table 2). Mn^{2+} and Cu^{2+} affinity is also higher for the unbleached pulp than for the fully bleached pulp (Table 2). In the case of copper (Figure 4), the typical $(4+1)$-peak signal is observed, with an increasing intensity toward higher field values. This signal was not visible on the original pulp spectrum.

Even though lignin would play a key role in the sequestration of metal ions in the case of unbleached pulps, which has already been proposed by several authors[6,11,12] (Figure 5), these experiments show that the carbohydrates have the ability to form rather stable complexes with the metal ions. Some papers mentioned the high ability of copper to form complexes with carbohydrates in solution.[13] It is shown here that this is also true with the polysaccharides of a fully bleached kraft pulp.

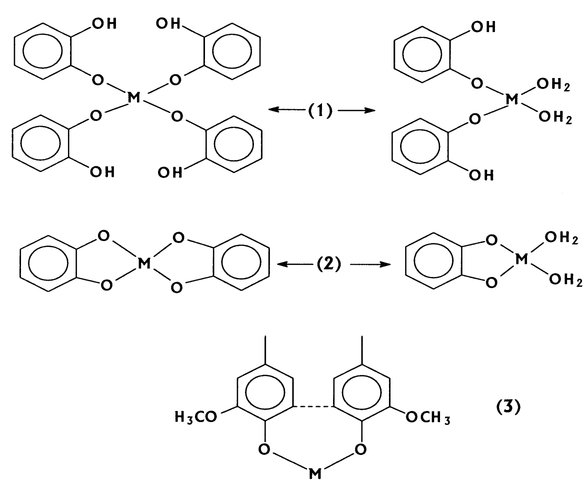


Figure 5. Possible complexes between lignin and metal ions in a mechanical pulp.(1)[13], (2) and (3)[14].

Table 3. Metal Ions Contents of a Totally Bleached Pulp Impregnated with Three Neutral Solutions of Magnesium and Manganese

Impregnation with:	200 ppm Mg^{2+}	200 ppm Mn^{2+}	200 ppm Mg^{2+} and 200 ppm Mn^{2+}
Before washing	Mn < 1	Mn: 204	Mn: 115
	Mg: 150	Mg: 18	Mg: 120
After washing	Mn < 1	Mn: 195	Mn: 95
	Mg: 125	Mg: 20	Mg: 100

These results suggest that during oxygen treatment the metal ions may behave as organic complexes even when only lignin traces are present and interact with H_2O_2 under this complex form. The protecting effect of the addition of magnesium salts has been attributed to the formation of colloidal co-precipitates of magnesium hydroxyde with the metal ions present in solution or already in the pulp.[14] Another possibility, suggested here, would be that Mg^{2+} would occupy preferentially the possible complexing sites on pulp components. The following experiments support this hypothesis, in the case of a fully bleached pulp: the pulp has been impregnated with three neutral solutions of manganese and magnesium, in various proportions. After 24 h, the metal ions contents of the pulps have been analysed by ICP (Table 3).

When Mg^{2+} and Mn^{2+} ions are introduced simultaneously, half the manganese capable of complexing to the carbohydrates is replaced by magnesium. These experiments demonstrate the aptitude of magnesium to replace manganese on some complexing sites of the carbohydrates.

Figure 6 proposes examples of complexing sites on di-saccharides. As the carbohydrate chain is lengthened, the extent of complexing increases, not only owing to the increasing multiplicity of complexing sites, but also because of possible inter-chain cross-linking. For example, although D-xylose forms only weak complexes, xylans give more stable complexes with a variety of cations.[13] In the pulp, it is supposed that metal ions are caught by several cross-linked polysaccharides chains, forming stable complexes.

Action of a $NaBH_4$ Reducing Treatment

In previous studies, the positive effect of a reducing pre-treatment of the pulp prior to an oxygen stage was demonstrated.[1,3] $NaBH_4$ suppresses

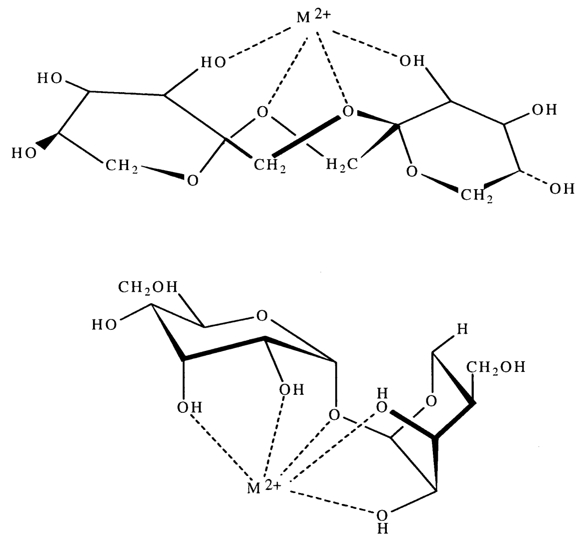


Figure 6. Possibility of metal ion complexation with di-saccharides[15].

the carbohydrates degradation during the oxygen treatment of a totally bleached pulp almost completely, even in the presence of high amounts of metal ions. In the case of the unbleached kraft pulp, pulp degradation was substantially reduced by the pre-treatment with $NaBH_4$ (Table 4).

The influence of the $NaBH_4$ treatment upon metal ions in the unbleached kraft pulp is studied by ESR spectroscopy, on pulp samples enriched in either Fe^{3+}, Mn^{2+} or Cu^{2+}. After the $NaBH_4$ treatment, the pulps are carefully washed, dried and ground. Figure 7 indicates that the $NaBH_4$ treatment of the pulp containing a high amount of Fe^{3+} does not cause any major decrease of the high spin Fe^{3+} signal. Therefore, reduction does not take place to a great extent though the possible reduction of Fe^{III} into Fe^{II} and Fe^{0} proposed by some authors.[7,15] However, the apparition of a large central peak suggests the formation of complexes of low-spin Fe^{3+}. Furthermore, all the *in situ* Mn^{2+} ions of this pulp have disappeared after the $NaBH_4$ treatment.

The influence of the $NaBH_4$ treatment on the pulp enriched in Mn^{2+} ions is represented in Figure 8. The 6-peak signal of Mn^{2+} is substantially decreased after $NaBH_4$ treatment, though the manganese content of this pulp does not change (Table 2). It is roughly estimated that about 40% of the Mn^{2+} ions is reduced by $NaBH_4$.

Table 4. Influence of a Reducing Pre-Treatment R on the Cellulose Degradation of Kraft Pulps During Consecutive Oxygen Bleaching

	Viscosity (mPa. s)	ISO brightness (%)	Kappa value
Initial totally bleached pulp	16.7	87.6	–
O	14.4	90.4	–
R/O	16.7	91	–
(100 ppm Fe)/O	8.3	85.3	–
(100 ppm Fe)/R/O	15.3	88.3	–
Initial unbleached pulp	20.2	–	31.9
O	14.6	–	14.9
R/O	18.2	–	14.8

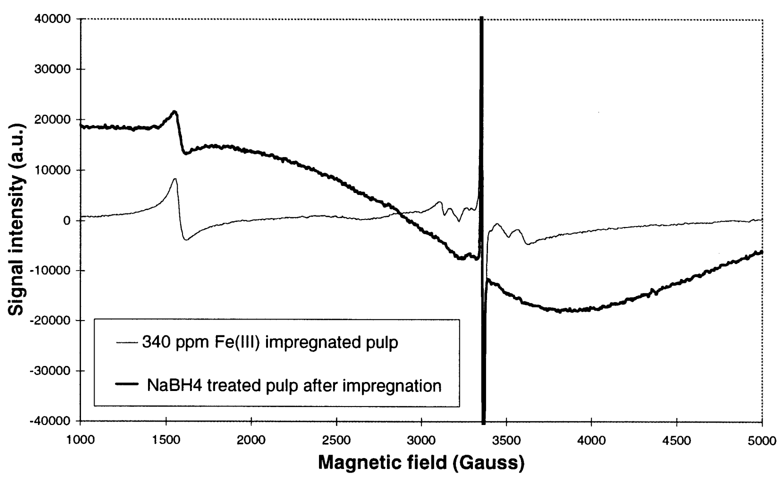


Figure 7. Influence of the $NaBH_4$ treatment on the ESR spectrum of Fe^{3+} ions in an unbleached pulp.

In the case of Cu^{2+} ions, the results are even more spectacular. Though $NaBH_4$ does not seem to modify the content in Cu^{2+}, the spectrum after the reducing treatment shows dramatic changes (Figure 9). Instead of $(4+1)$ peaks, the Cu^{2+} signal consists now of 8 peaks $(4+4)$. The last peak (for the highest field value) is split into an hyperfine structure of 4 new peaks. This indicates that the chemical environment of the cations has changed to a

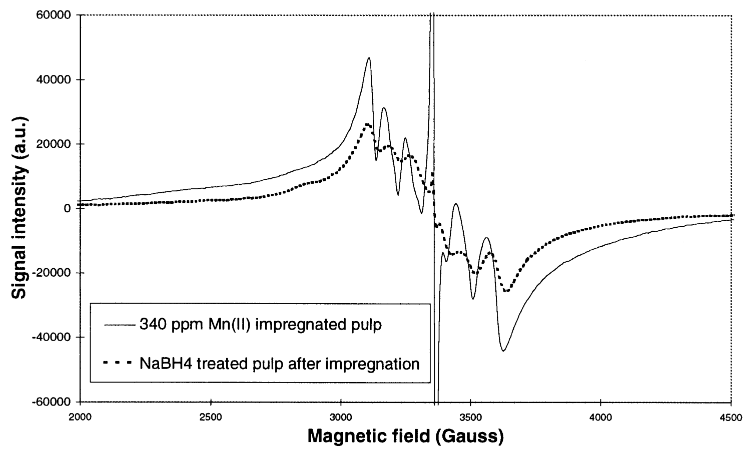


Figure 8. Influence of the $NaBH_4$ treatment on the ESR spectrum of Mn^{2+} ions in an unbleached pulp.

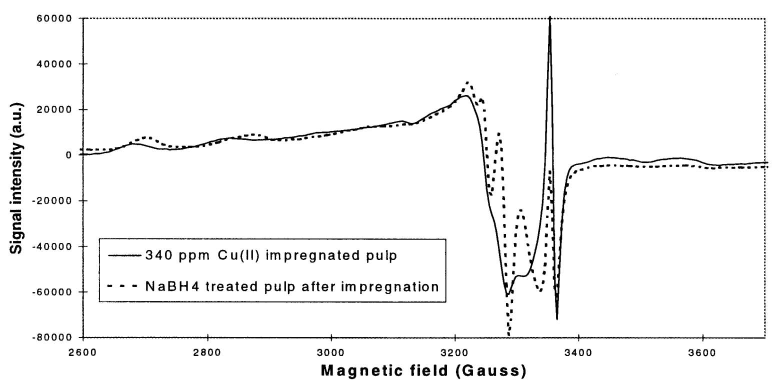
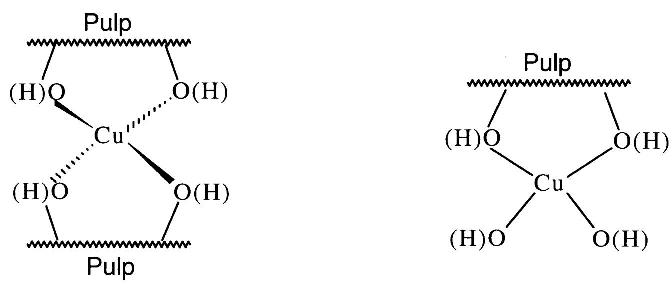


Figure 9. Influence of the $NaBH_4$ treatment on the ESR spectrum of Cu^{2+} ions in an unbleached pulp.

great extent, suggesting that new complexes are formed. Considering the spectroscopic characteristics measured on the spectra and former studies,[16] it is proposed that the Cu^{2+} complexes have moved from a tetrahedral distortion to a square-planar structure. Possible structures are suggested on Figure 10. Previous work[15] showed that Cu^{II} ions could be reduced to Cu^0 by $NaBH_4$. This is not clearly visible here.

The unbleached kraft pulp (without any added metal) is also treated by $NaBH_4$ (Figure 11). It is shown that after the $NaBH_4$ treatment the high-spin Fe^{3+} signal is unchanged. The intensity of the low-spin Fe^{3+} peak ($\approx 3000\,G$) is lowered. An important part of the Mn^{2+} signal disappears (50%). These ions are certainly reduced to lower valence levels. The $R^{\bullet}$ signal is still of the same intensity. Some authors have observed a decrease of the amount of $R^{\bullet}$ radicals by $NaBH_4$ treatment of isolated lignin.[7] They suggested that the semi-quinones radicals are reduced into catechol structures. In our case there is no evidence of this phenomenon, maybe because



Tetrahedral distorted structure

Square-planar structure

Figure 10. Hypothesis of Cu^{2+} complexes in the unbleached kraft pulp.

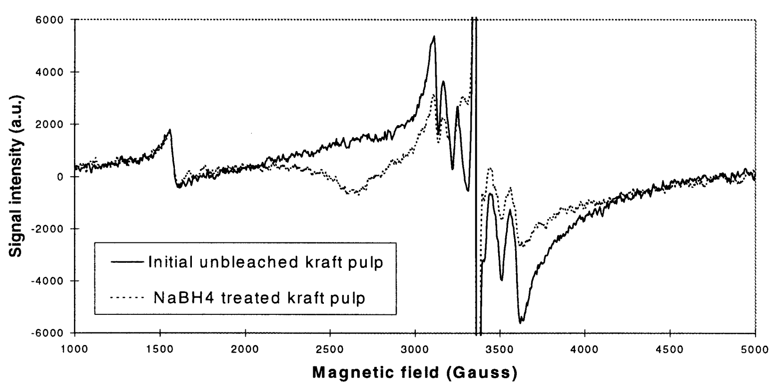


Figure 11. Influence of the $NaBH_4$ treatment on the ESR spectrum of a rough kraft pulp.

of accessibility factors, or because $R^{\bullet}$ species mainly consist of phenoxy radicals.

To summarise former results, the effect of $NaBH_4$ on metal ions in the pulp is double: on one hand, some Fe^{3+} and Mn^{2+} ions are reduced to lower valence levels. This is especially true for Mn^{2+}. On the other hand, after the $NaBH_4$ treatment, the ions form new complexes with the pulp, which must be less active during consecutive oxygen bleaching, since cellulose is less degraded.

Practical Relevance

From these observations, some conclusions of practical importance can be proposed. This study demonstrates the high affinity of transition metal ions for chemical pulps. If the bleaching liquor is contaminated by metal ions for any reason (effluent recycling, corrosion, chemicals...), stable complexes will easily form with pulp components. These metal complexes must be stabilised by a cage effect, due to the large size of the lignocellulosic matrix.[5] Affinity of metal ions for lignin is much higher than for carbohydrates. Therefore, pulp-metal complexes will be more likely in an unbleached pulp.

The following mechanism is proposed to account for cellulose degradation during oxygen bleaching: as the metal ions are complexed with lignin or carbohydrates, they can be more easily stabilised at several oxidation levels. They can then promote H_2O_2 decomposition into $HO^{\bullet}$ radicals, according to the Fenton reaction. This reaction will occur at the site of the metal complexes, i.e. on lignin or cellulose:

$$M^{(n)} + HOOH \longrightarrow M^{(n+1)} + HO^{-} + HO^{\bullet}$$

$$M^{(n+1)} + HOO^{-} \longrightarrow M^{(n)} + HOO^{\bullet}$$

In the case of the fully bleached pulp, the creation of the $HO^{\bullet}$ radicals will take place on the cellulose molecules. This explains the severe cellulose depolymerization observed during oxygen treatment when metal ions are added to the pulp.[1,3] Furthermore, the persistence of some phenoxy radicals in the fully bleached pulp was demonstrated. They can be a source of H_2O_2. On the contrary, when the metal ions are added to an unbleached kraft pulp, they preferentially form complexes with the lignin. The $HO^{\bullet}$ radicals, even if they are formed in larger quantities, are created rather on the lignin than on the cellulose. This may explain why the unbleached kraft pulp is comparatively less degraded than the totally bleached pulp during the O stage, for the same amount of metal ions added.[1,3]

The protective effect of the $NaBH_4$ pre-treatment has at least two origins. On one hand, $NaBH_4$ reduces a part of the metal ions in the pulp to lower valence levels. In these oxidation levels, the ions may have less affinity for pulp components, so that less complexes are formed with pulp after $NaBH_4$ treatment. On the other hand, new types of complexes are formed between metal ions and pulp components after $NaBH_4$ treatment. It is proposed that $NaBH_4$ has reduced some lignin structures, mainly quinone-type into catechols. These structures become new acceptation sites for metal ions. As metal ions have more affinity for such structures than for carbohydrates, they can move from the cellulose chains to the lignin, to create new complexes. Cellulose chains are thus less degraded during consecutive oxygen treatment. Furthermore, complexing reactions or chelation is known to alter the redox potential of a metal couple.[17] The new complexes formed after $NaBH_4$ treatment may modify the redox potential of the studied metal so that they become less active during oxygen bleaching.

EXPERIMENTAL

A Scandinavian softwood kraft pulp was used in this study (characteristics given in Table 1). The pulp was also fully bleached according to a DEDED sequence.

ESR spectra were recorded at room temperature on a Brücker ESP 300E operated at X-band, working at 9.4 GHz with 100 kHz modulation. Magnetic field varied between 1000 and 5000 Gauss.

Metal ions were added to the pulp as solutions of their sulfate form (for Fe^{3+}, Cu^{2+}, Mn^{2+} and Mg^{2+}). The reducing R stages on the fully bleached pulp were performed with 1 to 10% $NaBH_4$, during 30 min, at 10% pulp consistency and 25°C. The reducing R stages on the unbleached pulp were performed with 5% $NaBH_4$, 1% Na_2CO_3, during 3 h at 50°C and 10% pulp consistency. The oxygen treatments were carried out at 100°C with 1.5% NaOH and 0.5% $MgSO_4$, at 10% pulp consistency, during 1 h, with $P_{O2} = 5$ bar.

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