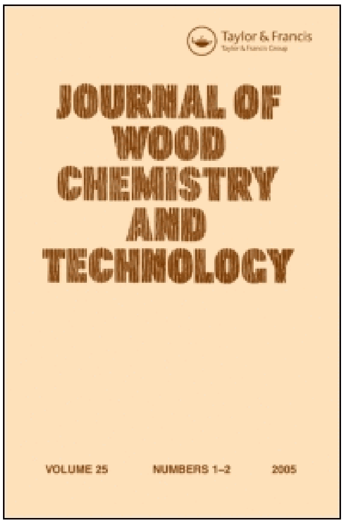

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Danièle Cardona-Barrau[a]; Dominique Lachenal[a]
[a] Domaine Universitaire, Saint Martin d'Hères Cedex, France

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ACTION OF OXYGEN ON THE CARBOHYDRATES OF A KRAFT PULP. THE INFLUENCE OF A SODIUM BOROHYDRIDE PRE-TREATMENT

Danièle Cardona-Barrau and Dominique Lachenal

Ecole Française de Papeterie et des Industries Graphiques,
461, rue de la Papeterie, Domaine Universitaire, BP 65,
38402 Saint Martin d'Hères Cedex, France

ABSTRACT

A fully bleached softwood kraft pulp was chosen as a model for pulp carbohydrates. The pulp was submitted to oxygen bleaching stages, to study the action of oxygen upon carbohydrates in the absence of lignin. The pulp was not degraded under mild conditions. In the presence of several metal ions, the carbohydrates were severely degraded by oxygen. Under these conditions, intermediate HO• radicals were detected. The results suggested an additional pathway to the classical mechanism proposed in the literature. The influence of a pulp pre-treatment with sodium borohydride was studied, and the origin of its protective effect during oxygen bleaching was demonstrated.

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INTRODUCTION

Conventional oxygen bleaching of kraft pulps is usually performed up to 50% of delignification, further development of the process being limited by the lack of selectivity. Previous studies have shown that cellulose degradation is closely related to the extent of delignification.[1] The occurrence of some transition metal ions in the pulp would also promote carbohydrate depolymerization.[2,3] Mechanisms of lignin and cellulose degradation have been well documented in the past.[4,5,6] The generally accepted mechanism to explain carbohydrate degradation proceeds in two steps. At first, molecular oxygen would react with some specific structures in the lignin, mainly the phenolic groups, to produce intermediate peroxides. Secondly, these peroxides would be decomposed according to several pathways into radicals, among which hydroxyl radicals HO• can react directly with carbohydrates to induce their depolymerization. However, most of the conclusions rely on the studies of model compounds,[3,7,8] under operating conditions which differ from a real oxygen bleaching treatment, mainly because of solubility and accessibility factors.

The present study focuses on the impact of the oxygen treatment upon the carbohydrates of kraft pulps. The main purpose is to gain more information about the degradation mechanism of carbohydrates during oxygen bleaching. To eliminate the influence of lignin, a fully bleached softwood kraft pulp is chosen as a model for kraft pulp carbohydrates. This pulp is treated under conventional oxygen delignification conditions. The influence of some metal ions upon pulp degradation is also studied, as well as the role of a specific pulp pre-treatment with sodium borohydride ($NaBH_4$).

RESULTS AND DISCUSSION

Role of the Metal Ions During an Oxygen Treatment

The fully bleached pulp was submitted to bleaching treatments, under the same conditions as a delignification stage, under nitrogen or oxygen atmosphere. The results are presented in Tables 1 and 2.

Results presented in Table 1 indicate that under an inert N_2 atmosphere, all the metal ions promoted a very slight viscosity loss of the pulp, while viscosity remained unaffected during the control experiment. These observations were ascribed to the presence of residual oxygen. Indeed, some O_2 could remain trapped in the fibrous structure, even though the reactor has been evacuated twice with nitrogen, prior to introducing the

Table 1. Pulp Characteristics after Nitrogen Treatments in the Presence of Metal Ions

Treatment	Viscosity (mPa.s)	Brightness (% ISO)
Initial characteristics	*16.7*	*87.6*
Control	16.5	81.8
Fe^{II}, 100 ppm added	14.1	78.3
Cu^{II}, 100 ppm added	14.3	79.5
Mn^{II}, 100 ppm added	14.6	84.0

Table 2. Pulp Characteristics after Oxygen Treatments in the Presence of Metal Ions

Treatment	Viscosity (mPa.s)	Brightness (% ISO)
Initial characteristics	*16.7*	*87.6*
Control	14.5	89.9
Fe^{II}, 100 ppm added	11.8	81.8
Fe^{II}, 500 ppm added	9.4	75.7
Cu^{II}, 100 ppm added	6.2	88.9
Mn^{II}, 100 ppm added	11.4	65.6

final pressure of nitrogen. The small amount of residual oxygen, together with the presence of metal ions, seemed to promote cellulose depolymerization under bleaching conditions. This tendency was confirmed by the experiments carried out under an oxygen atmosphere, presented in Table 2.

The results show a severe viscosity loss occurring during oxygen treatments in the presence of each of the tested metal ions, whereas the control oxygen stage had little effect on pulp viscosity (see Table 2). Furthermore, Cu^{II} ions were the most detrimental for cellulose viscosity, as already described by other authors.[3] Thus, it can be concluded from these experiments that a fully bleached pulp is not degraded by oxygen under classical mild bleaching conditions. But if a sufficient amount of metal ions is present (due for example to a contamination of the bleaching liquor), the carbohydrates will be severely degraded, even in the absence of lignin or lignin-like compounds. The slight degradation observed during the control experiment was assigned to the presence of natural metal ions in the pulp originating from wood (see "Experimental"). The origin of carbohydrate degradation by the oxygen/metal ions system thus needs further investigation, to determine whether the usually believed reaction scheme is still valid under those conditions. In particular, the mechanism of cellulose degradation by oxygen in the presence of metal ions has to be investigated, since it has been reported[2] that Mn^{II} does not catalyse the decomposition of intermediate peroxides into HO• radicals.

Origin of Carbohydrate Degradation During Oxygen Bleaching

In the absence of lignin, carbohydrate degradation may be due to the presence of reducing groups of the carbonyl type present on the polymer itself, as suggested by some authors.[3] Several experiments including a reducing step of the pulp with sodium borohydride ($NaBH_4$) were carried out to check this hypothesis. The results are summarised in Table 3.

Experiments 1 and 2 indicate that the reducing stage improved the pulp viscosity after oxygen treatment, without any indication on the mechanism involved. Washing between R and O was not necessary, since both treatments were carried out under alkaline conditions. 1% $NaBH_4$ was enough to suppress carbohydrate depolymerization almost completely (exp. n°2), and this was effectively achieved with 10% $NaBH_4$ (exp. n°3). Experiment 4 shows that when a high amount of metal ions was present in the bleaching liquor, a treatment of the pulp with 10% $NaBH_4$ suppressed almost completely the detrimental effect of the ions.

Finally, the comparison of experiments 4 and 5 clearly shows that the protective effect of $NaBH_4$ was due to its action upon metal species. Both pulps were treated with $NaBH_4$, 100 ppm of metal ions were added, either

Table 3. Influence of the Reducing Pretreatment upon Pulp Characteristics after Oxygen Bleaching

N°	Initial viscosity (mPa.s)	Added Fe^{II} (ppm)	Reducing R stage (% $NaBH_4$)	Wash	Added Fe^{II} (ppm)	O stage	Final viscosity (mPa.s)
Control	16,7	–	–	–	–	Yes	14,8
1	16,7	–	1	Yes	–	Yes	15,3
2	16,7	–	1	No	–	Yes	16,1
3	16,7	–	10	No	–	Yes	16,7
4	16,7	100	10	No	–	Yes	15,3
5	16,7	–	10	Yes	100	Yes	8,6

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before the $NaBH_4$ stage (n°4) or before the oxygen stage (n°5). During experiment n°4, pulp viscosity remained unaffected after oxygen treatment, showing that $NaBH_4$ has had an action on metal ions. During experiment n°5, the treatment of the pulp by $NaBH_4$ had no effect on carbohydrate degradation during oxygen stage, which indicated that even if carbonyl groups on the polysaccharides have been reduced by $NaBH_4$, the consecutive addition of metal ions still promoted carbohydrate depolymerization. The protective effect of $NaBH_4$ could thus not be attributed solely to the reduction of some reducing carbonyl groups on cellulose chains. Another possibility must be investigated.

The reaction mechanism proposed in the literature involves the occurrence of several intermediate species, the most relevant being peroxides and hydroxyl radicals HO•. Detection of HO• radicals in the bleaching liquor by chemiluminescence measurements were performed by analysing aliquots of the liquor during the bleaching stages, according to the method proposed by Reitberger and Gierer,[9] and are presented in Figure 1.

During the control experiment, no HO• radicals were detected, which was consistent with the fact that the pulp was not degraded under these bleaching conditions. If metal ions were added during oxygen treatment of the bleached pulp, HO• radicals were detected : the higher the amount of HO• radicals in the liquor, the more the pulp was degraded during the bleaching step (see Table 2, experiments with Mn^{II} added, compared to Fe^{II} added). Furthermore, an increasing amount of Fe^{II} in the liquor led to a higher amount of HO• radicals detected and to a more degraded pulp.

An experiment with 100 ppm of Fe^{II} in the bleaching liquor was also carried out in the absence of pulp (see Figure 2.) In these conditions,

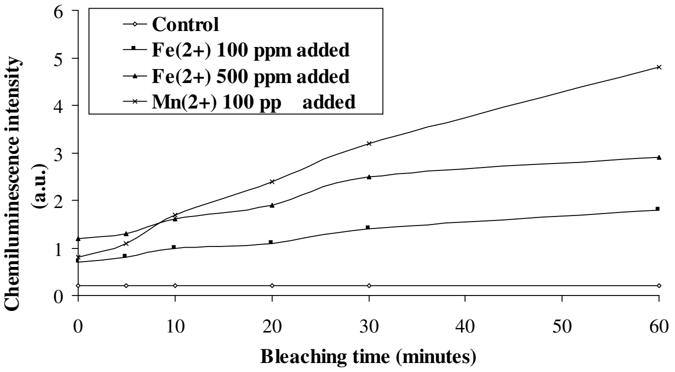

Figure 1. Chemiluminescence measurements on bleaching liquors during oxygen treatments of the fully bleached pulp. Influence of the presence of added metal ions.

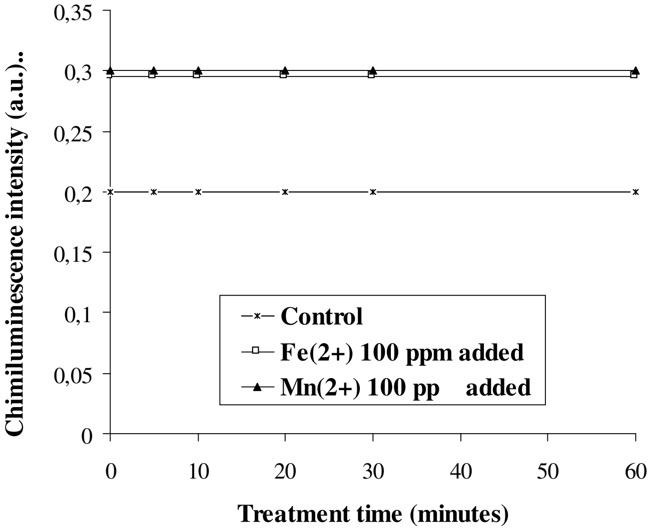

Figure 2. Chemiluminescence measurements on bleaching liquors during oxygen treatments without pulp. Influence of the presence of added metal ions.

no HO• radicals were detected, which proves that their origin was due to the action of oxygen on carbohydrates.

The severe viscosity loss of the bleached pulp during oxygen treatment in the presence of metal ions can be attributed to the degradation of carbohydrates by HO• radicals, which is in accordance with the mechanism proposed in the literature. Several observations suggested that new reaction pathways must not be neglected, such as the creation of HO• radicals from the carbohydrates, and not solely from the lignin, but the carbohydrate degradation was not due to the direct reaction of oxygen upon reducing carbonyl groups present on the polysaccharides chains. Furthermore, it was demonstrated that even Mn^{II} can decompose the peroxides to produce HO• radicals. This reaction needs further explanation, and is discussed in the next part of this study.

Influence of a $NaBH_4$ Pre-Treatment of the Pulp

The protective effect of $NaBH_4$ upon carbohydrate viscosity is not due to its action upon cellulose reducing groups. Thus, another possibility is an action upon the metal ions. Initially, the behaviour of $NaBH_4$ was studied by chemiluminescence on metal ion solutions, without pulp (see Figure 3). In these experiments, H_2O_2 was simply added to metal ions solutions, at room temperature, under atmospheric pressure.

As expected, a huge amount of HO• radicals was produced when H_2O_2 and Fe^{II} were mixed together and 20% of H_2O_2 was consumed. The addition of $NaBH_4$ to the Fe^{II} solution before H_2O_2 suppressed HO• formation, and in these conditions, no H_2O_2 was consumed, indicating that $NaBH_4$ did not react with H_2O_2. Consequently, the catalytic role of iron in H_2O_2 decomposition was lost after $NaBH_4$ treatment. Chemiluminescence measurements were also made on bleaching liquors during oxygen treatment of the fully bleached pulp under various conditions (see Figure 4).

As shown previously, the presence of metal ions in the liquor generated HO• radicals. It is further demonstrated in Figure 4 that the treatment by $NaBH_4$ of the pulp containing a high amount of metal ions totally suppressed the formation of HO• radicals during the bleaching stage, which explained the fact that the pulp was not degraded by oxygen. The protective effect of $NaBH_4$ was efficient throughout the oxygen treatment. This suggested the formation of metal species stable under these conditions.

To check the behaviour of metal ions in the pulp itself (cations which have moved from the liquor to the core of the pulp), and the role of $NaBH_4$ upon these cations, ESR spectra were recorded. Only the results concerning Cu^{II} ions are presented here (see Figure 5), but the following observations

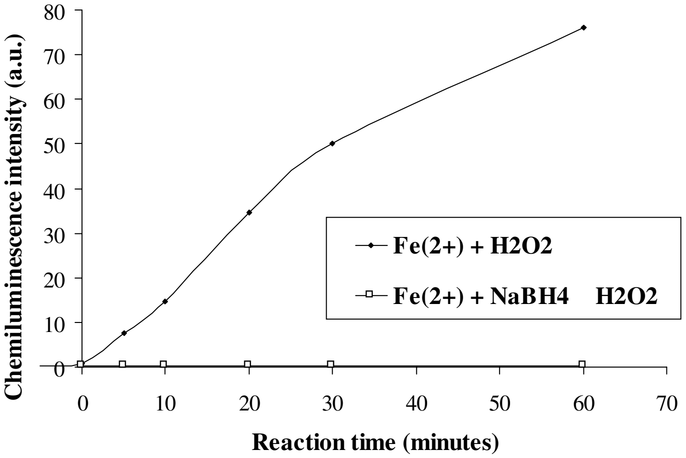

Figure 3. Chemiluminescence measurements on Fe^{II} solutions. Influence of the addition of $NaBH_4$ and H_2O_2. 3 mg/l Fe^{II}, 350 mg/l H_2O_2, 5 g/l $NaBH_4$, room temperature, pH 10.

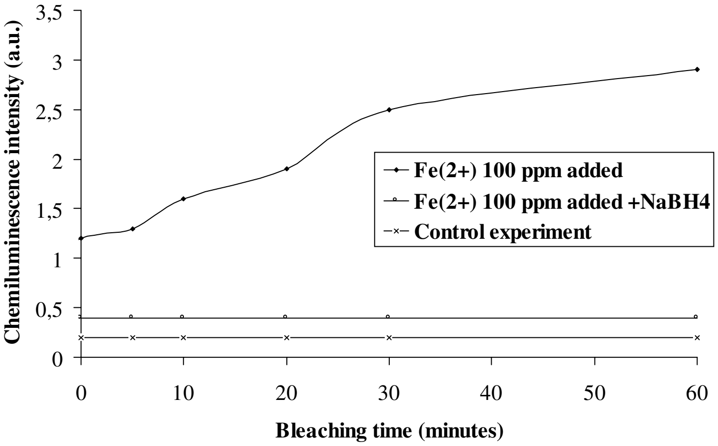

Figure 4. Chemiluminescence measurements on bleaching liquors during oxygen treatments of the fully bleached pulp. Influence of a pulp pre-treatment with $NaBH_4$ before the addition of metal ions.

and conclusions were also valid for Fe^{II} and Mn^{II} ions, and will be presented in a next paper.

Figure 5 shows ESR spectra of a fully bleached pulp, impregnated by a Cu^{II} solution and subsequently treated by a $NaBH_4$ solution. The addition of Cu^{II} caused an increase in the corresponding signal ($4+1$ peaks between 2550 and 3300 Gauss), even after an intensive wash of the pulp. This indicated that the cations can form stable bonds with pulp carbohydrates, presumably of the coordination complex type. Indeed, the Cu^{II} signal in the pulp differed from that of Cu^{II} in solution, mainly by the "g factor" value, which confirmed that the Cu^{II} environment in the pulp was different from that in solution.[10] Then, it was suggested that during the oxygen stage, catalytic reactions induced by the metal ions would take place immediately on the carbohydrate chains, thus causing severe damage. Figure 5 shows that after the $NaBH_4$ pre-treatment of the pulp containing an excess of Cu^{II}, the corresponding ESR spectrum changed dramatically. Instead of $4+1$ peaks, the Cu^{II} signal consisted of $4+4$ peaks, the last peak being decomposed into a hyperfine structure of four new peaks. This means that the chemical environment of the Cu^{II} cation has changed to a great extent, suggesting that new complexes were formed. Cu^{II} in these complexes must have been less active during consecutive oxygen bleaching, since carbohydrates were less degraded. The nature of these complexes is not known.

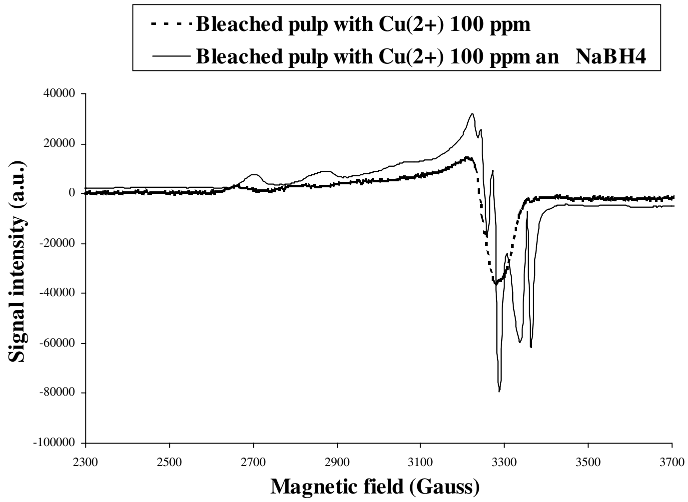

Figure 5. ESR spectra of the fully bleached pulp containing 340 ppm of Cu^{II}. Influence of a pulp treatment with $NaBH_4$.

CONCLUSIONS

A fully bleached kraft pulp is useful for studying the behaviour of kraft pulp carbohydrates during oxygen treatment. It is shown that the degradation of carbohydrates by oxygen is very small under conventional mild bleaching conditions. However, if some transition metal ions (Fe^{II}, Cu^{II} and Mn^{II}) are present in the pulp, they enhance the carbohydrate degradation to a great extent, Cu^{II} being the most detrimental. This demonstrates that the presence of lignin is not necessary to induce carbohydrate degradation, and that an additional reaction pathway exists, together with that described in the literature.[4,5] This mechanism involves the same intermediate species, such as hydroxyl radicals. It is demonstrated that at higher levels of metal ions, more HO• radicals are created. This is in accordance with the usual reaction scheme, except that intermediate species are not created by the reaction of oxygen with lignin, but with carbohydrates. The mechanism by which oxygen leads to the formation of peroxides remains unclear. The direct action of oxygen on aldehyde groups would not be the explanation since the same degradation is observed after pre-treatment with $NaBH_4$ and further addition of metal ions. Furthermore, the hypothesis that the metal ions which form complexes with the pulp can take a sufficiently high oxidation level to attack the cellulose chains directly cannot be excluded.

With the use of the ESR technique, it is shown that metal ions easily form strong complexes with pulp carbohydrates, which implies that they can get stabilised at different oxidation levels all along the bleaching stage, and then participate to Fenton-type reactions. So, the manganese would exist under the stable Mn^{III} form (which is not possible in bleaching liquor), and would thus promote the decomposition of hydrogen peroxide into HO• radicals, due to the Mn^{III}/Mn^{II} redox activity. As the metal ions can form complexes with pulp carbohydrates, the creation of the harmful radicals certainly takes place on the cellulose molecules. This explains the very important degradation observed during oxygen treatment in the presence of metal ions, contrary to what can be seen with an unbleached kraft pulp treated in the same conditions, where the lignin seems to have a protecting effect.[11]

A pretreatment of the fully bleached kraft pulp with sodium borohydride $NaBH_4$ prevents carbohydrate degradation during the consecutive oxygen stage, even if the pulp contains a high amount of metal ions before the $NaBH_4$ treatment. It is demonstrated that even though $NaBH_4$ reduces the reducing carbonyl groups on the carbohydrate molecules, its protective action is mainly due to its reaction with metal ions. After the $NaBH_4$ treatment, new complexes are formed between pulp carbohydrates and metal ions. This leads to an inhibition of the metal ions during the whole bleaching treatment by oxygen. Indeed, it seems that they are not capable of further catalysing the formation of HO• radicals. The hypothesis of a reduction of some of the transition metal ions to lower valence state is not excluded,[12,13] other results which are not presented here suggest this phenomenon and will be published later.

EXPERIMENTAL

The fully bleached pulp was a French softwood kraft pulp, bleached according to a DEDED sequence. Initial viscosity was 16.7 mPa.s, and the brightness was 87.6% ISO. Its metal content measured by ICP at CNRS, Vernaison, France, was Fe : 10 ppm, Cu $<$ 1 ppm, Mn $<$ 1 ppm and Mg : 30–50 ppm.

Oxygen treatments were performed in stainless steel autoclaves on 50 g o.d. pulp or on 500 mL of liquor. The operating conditions were : temperature 100°C, 1.5% NaOH charge on pulp, 0.5 MPa nitrogen or oxygen pressure, 20 min to temperature and 60 min at temperature, 10% pulp consistency. No $MgSO_4$ was added. NaOH was of high purity grade (RectaPur). Reducing $NaBH_4$ pre-treatments were carried out at room temperature, 10% pulp consistency, for 30 min with 1 to 10% $NaBH_4$ and 0 to 1% Na_2CO_3 on pulp.

Metal ions were added to the pulp as solutions of their sulfates (Fe^{II}, Cu^{II}, Mn^{II}). Chemiluminescence measurements were performed with a 1250-001 BioOrbit chemiluminometer, according to the method described by Reitberger and Gierer.[9] ESR spectra were recorded at room temperature on a Brüker ESP 300E spectrometer, working at 9.4 GHz.

Standard procedures were applied for viscosity (TAPPI T230om-82, accuracy 0.5 mPa.s) and brightness (ISO 2470, accuracy 0.5 point) measurements.

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