Hydroxyl radical formation during hydrogen peroxide bleaching

Nils-Olof Nilvebrant and Marianne Björklund Jansson

December 2005

According to Innventia Confidentiality Policy this report is public since February 2011
Hydroxyl radical formation during hydrogen peroxide bleaching

Nils-Olof Nilvebrant and Marianne Björklund Jansson

Report no.: 197 | December 2005

Cluster: Chemical pulp, fibre line
Distribution restricted to: AGA, AssiDomän Cartonboard, Billerud, Borregaard, Eka Chemicals, Holmen Iggesund Paperboard, Kemira, Korsnäs, Metsä-Botnia, Mondi Packaging, M-real, Peterson & Søn, Stora Enso, Södra Cell, Voith

According to Innventia Confidentiality Policy this report is public since February 2011
B1 Hydroxyl radical formation during hydrogen peroxide bleaching

Acknowledgements

This work has been performed within the Cluster research program of Chemical pulp - fibre line, during 2004-2005.

The early method development was done together with Filipe de Sousa and Bengt Eriksson. The skilled laboratory work was done by Brita Samuelsson, Pierre Ljungqvist and Rose-Marie Karlsson. Elisabeth Bergnor-Gidnert is thanked for valuable discussions and suggestions during the project.
# Table of contents

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
</tbody>
</table>

## 1 Summary

## 2 Background

## 3 Introduction

## 4 Method for radical determination

### 4.1 Pulp consistency

### 4.2 Radical determination from wet or dry pulp

### 4.3 Reproducibility in hydroxyl radical determination

### 4.4 Units for the determined hydroxyl radical activity

### 4.5 Limitations of the hydroxyl radical determination

## 5 Experimental

### 5.1 Pulp samples

### 5.2 Chemicals

### 5.3 Standard laboratory P-stage bleaching

### 5.4 P-stage bleaching in small scale glass vials

### 5.5 Pulp analysis

## 6 Results and discussion

### 6.1 Formation of radicals from different pulps

### 6.1.1 Screening of the mill pulps

### 6.2 Kinetics of hydroxyl radical formation during a P-stage

### 6.3 Decomposition of H₂O₂ and high end-pH

### 6.4 Catalytic metal ions

#### 6.4.1 Metal removal by different treatments

#### 6.4.2 Formation of radicals after metal ion removal with complexing agents

#### 6.4.3 Accessibility to catalytic metal ions

#### 6.4.4 Activation of catalytic metal ions by acid treatments

### 6.5 Varied Mg-addition

#### 6.5.1 Importance of Q-treatment of acid activated pulps

#### 6.5.2 Addition of manganese ions in different forms before P-bleaching

### 6.6 Scavengers for hydroxyl radicals

#### 6.6.1 Influence of magnesium additions to a P-stage

#### 6.6.2 Radical formation with and without additional magnesium

#### 6.6.3 Displacement of manganese by magnesium

#### 6.6.4 Influence of carry-over in P-stage

---

According to STFI-Packforsk's Confidentiality Policy this report is assigned category 2

B1 Hydroxyl radical formation during hydrogen peroxide bleaching
B1 Hydroxyl radical formation during hydrogen peroxide bleaching

4 (53)

6.7 Sequential peroxide stages ................................................................. 41

7 General discussion of conclusions ....................................................... 42

7.1 General discussion ........................................................................... 42

7.2 Concluding discussion ..................................................................... 42

8 Summarized conclusions .................................................................... 44

8.1 Further work .................................................................................. 45

9 References .......................................................................................... 46

10 Appendixes ....................................................................................... 48

10.1 Appendix: Reproducibility and accuracy ........................................... 48

10.2 Appendix: Additions of magnesium ................................................ 48

10.3 Appendix: Additions to the P-stage .................................................. 50

10.4 Appendix: Synthetic hydroxyl radical generation from peroxynitrite. 50

10.5 Appendix: Complexing agents for metal ion removal ...................... 52

10.6 Appendix: Addition of manganese ions ........................................... 52
1 Summary

Formation of extremely reactive hydroxyl radicals during bleaching of kraft pulp with hydrogen peroxide, i.e. in a P-stage, can be monitored by scavenging the radicals. The hydroxyl radical has the unique ability to convert the low molecular probe isopropyl alcohol (IPA) to acetone, and this has been used to measure the radical activity generated by different pulps under standardised P-stage conditions.

The following results were obtained:

- Hydroxyl radical activities can be quantified during a standardised P-stage.
- Control of manganese is a key to hydroxyl radical formation. However, not only the amount is important, but also in which form or oxidation stage it appears during the P-stage.
  - Removal of catalytic manganese ions with EDTA and DTPA efficiently reduced the hydroxyl radical activity.
  - Pretreatment of the pulp with an acid stage also removed metal ions, but resulted in an increased hydroxyl radical activity.
  - Addition of manganese ions to a pulp before a P-stage had no effect on the measured hydroxyl radical activity – possibly because the added catalytic manganese ions were converted to a less active form by the oxidative and alkaline conditions.
- Addition of magnesium ions did not lower the increased activity caused by an A-stage. Consequently, acidic conditions should be avoided before a P-stage.
- The response from the hydroxyl radical probe, IPA, was very sensitive towards the presence of other substances in the bleaching liquor. For comparisons of pulps and pretreatments the hydroxyl radical formation can thus only be monitored in pure systems under controlled hydrogen peroxide bleaching conditions.
- A lack of residual hydrogen peroxide was indicated by an increase in pH during the bleaching stage. One reason may be the reaction where hydrogen peroxide is decomposed by a transition metal ion to a hydroxyl radical and a hydroxide ion. An increasing pH in the P-stage may be used as an indication of high hydroxyl radical activity.
2 Background

Radicals are involved during bleaching with oxygen containing reagents (Gellerstedt and Petterson 1982, Gierer 1997, Ek et al. 1989, Gierer et al. 2001). In this context the hydroxyl radicals have to be considered, since they often are held responsible for the loss of pulp strength in a P-stage. Therefore, the first objective of this project was to develop a method to quantify hydroxyl radical activity (Laine 2000). These efforts are reported in “Measurement of hydroxyl radicals in hydrogen peroxide bleaching of softwood kraft pulp” (Nilvebrant and Björklund-Jansson, 2003).

The degradation of cellulose, the most important component in pulps, must be avoided in the processes used for production of fully bleached kraft pulp. Severe acidic conditions are efficient in cleaving the glycosidic bonds and are avoided. Severe alkaline conditions cause peeling reactions leading to a lower pulp yield and cause alkaline hydrolysis of the cellulose chains. At pH conditions within the wide range between too high and too low, hydroxyl radicals are the only reactant present in the technical processes that have the power to degrade cellulose.

The need to remove transition metals before a P-stage is now general knowledge and a part of the modern bleaching processes. The results from fundamental research made by Gellerstedt and Petterson (1982) and Basta et al. (1991) followed by Troughton et al. (1992) and the application reported by Fastén (1993) point to the beneficial removal of manganese in pulps before a P-stage. The beneficial effect by magnesium addition is a fact (J. Devenyns and L. Plumet 1994), and its formation of stabilizing solid-solutions (Lidén 1994, Norberg 2003) is established. A confusing conclusion has been made by Chirat and Lachenal (1994), namely that Fe and Cu, but not Mn, are the problematic metal ions. They found no negative effects on viscosity and no formation of hydroxyl radicals after addition of Mn$^{2+}$ ions. Their experiments, using gamma irradiation to generate hydroxyl radicals, can be questioned (Merényi et al. 1997) and a method to directly quantify hydroxyl radicals has been needed. However, Chirat and Lachenal observed a decomposition of hydrogen peroxide and a lower brightness but low carbohydrate degradation after the P-stage. On the contrary, traces of manganese in a pulp entering a P-stage is usually considered to be detrimental for the cellulose and to cause lower viscosity. This was one observation that needed to be reinvestigated. The positive effect of Q-stages and a direct determination of hydroxyl radical activity also needed to be confirmed. How the removal of transition metal ions by an A-stage, with or without addition of additional magnesium ions, affected the hydroxyl radical activity was one aim for a direct determination of the often accused hydroxyl radicals.
3 Introduction

The present report focusses on quantification of hydroxyl radical activity from pulps collected at different positions in a mill using a TCF bleaching sequence, and on the individual mill pulps samples treated in different ways in the laboratory. The method developed earlier has been used (Nilvebrant and Björklund-Jansson, 2003).

Except for water, carbohydrates are stoichiometrically the most abundant component in a bleaching stage. Formation of non-selective species, such as the hydroxyl radical, leads to attacks on and the inevitable degradation of polysaccharide chains. The hydroxyl radical can abstract hydrogen atoms from cellulose leading to loss of pulp viscosity. A way to reduce the effects of hydroxyl radicals formed during bleaching is to add a radical scavenger to the bleaching liquor mixture. Such a concept is not valid if the detrimental reaction takes place in the fibre wall, due to the extremely short lifetime of the hydroxyl radical.

All reactions introduced by hydroxyl radicals are detrimental on pure cellulose. The reactions result in cleavage of glycosidic bonds and loss of polymer strength, measured as its viscosity. Thus, hydrogen peroxide bleaching needs a very pure substrate, with few catalytic metal ions, to limit the damage of the polymer chains.

A chemical pulp is sensitive towards hydroxyl radicals, especially at the end of a bleaching sequence. Here the aim is to increase the brightness and thus to attack chromophoric structures in the pulp. Such structures are sensitive to nucleophilic attacks by the hydroperoxy anion, which has a stronger nucleophilicity than the hydroxide anion. The higher basivity of the latter leads to other reactions forming coloured structures, so-called yellowing. Generation of hydroxyl radicals will instead lower the quality of other pulp properties like strength (Grönroos et al.1998). This is particularly important if the radicals are formed locally with repeated generation at a specific site (Johansson 2003). On the other hand, the first hydrogen peroxide bleaching stage in a TCF bleaching sequence does not only focus on selective chromophore elimination but also on improved delignification. Then some hydroxyl radical activity may have a positive effect by increasing reactivity of residual lignins.

Hydroxyl radicals cannot be directly observed since they are extremely reactive, lack optical absorption and appear in low concentrations during bleaching of pulp. The reactive hydroxyl radicals can abstract hydrogen atoms from most organic compounds and thus yield a great variety of products. By offering a probe that gives rise to a unique product, the hydroxyl radicals can indirectly be detected and their activity measured.

Since hydroxyl radicals are extremely reactive, they react almost at the site of their formation. The estimated half-life of a hydroxyl radical is within nanoseconds (Dreosti 1991; Roots and Okada 1975) and they will thus react in the immediate area of their formation. This has been suggested to be within five to ten molecular diameters by researchers working with DNA (Cadenas 1995). To be detected, the probe has to be
present in the surroundings in high enough concentration. The probe thus has to be a water-soluble low molar mass compound that gives rise to a unique product. Isopropyl alcohol (IPA, i.e. 2-propanol) was the best choice. IPA was shown to be inert to the other reagents and conditions prevailing during the bleaching. To avoid that the probe change the bleaching conditions the concentration used had to be kept low, but still high enough to catch enough of hydroxyl radicals. The small size and structural similarity with water, a boiling point close to the temperature of the simulated bleaching stage, makes the probability as high as possible that IPA can be present in the vicinity of where the radical formation takes place, i.e. both in the solid pulp phase and in the bleaching liquor. However, the hydroxyl radical method will most efficiently mirror the radical activity in the larger bleaching liquor phase. Anyway, the hydroxyl radical determinations will in some way reflect the overall hydroxyl radical activity during peroxide bleaching of the studied pulp.

Local sites of hydroxyl radical forming catalysts in the pulp may cause detrimental cleavages of the carbohydrate polymers causing depolymerisation and a lower pulp viscosity. The quantification of hydroxyl radical activity during a bleaching experiment may not show the actual negative effect on the solid pulp. Since it has to be considered that the hydroxyl radical activity determined by the probe, i.e. acetone formation, may exaggerate the activity in the liquid phase.

A starting point for the project was to apply the determination of hydroxyl radical activities to mill pulps collected from different TCF bleaching positions at a mill producing softwood kraft pulp and measure how they responded towards P-stage conditions. The aim was to measure hydroxyl radical activity and compare with the results from classical bleaching evaluations. The kinetics of hydroxyl radical formation and loss of viscosity from the different pulps, removal of catalytic metal ions in Q- or A-stages, addition of stabilizing magnesium ions and manganese in different forms that influenced the accessibility were also included in the study.
4 Method for radical determination

Hydroxyl radicals react with “everything”. Hydrogen atoms in organic compounds are then abstracted by the radical, forming a water molecule. When isopropyl alcohol (IPA) interacts with a hydroxyl radical an organic radical is formed that will react further to form acetone as the unique product.

A lot of techniques to measure radicals have been reported and included in an overview report by Laine (2000). Some methods do not work in alkaline media, for instance the method based on chemiluminescence (Backa et al. 1997). The method based on acetone formation was concluded to be the method of choice for hydroxyl radical determination and has been described and reported (Nilvebrant and Björklund-Jansson, 2003).

4.1 Pulp consistency

All bleaching experiments, where volatile acetone was quantified, were performed in a tightly shut glass vial at a pulp consistency of 2.5 % (250 mg pulp samples). Acetone escaped experiments made in polyethylene bags. A reason for the low pulp consistency was that evolution of gas during peroxide bleaching was occasionally extensive from some pulps. If the pulp concentration was too high in the small-scale experiments, the pulp sometimes separated in the glass vials used and made the bleaching inhomogeneous. At 2.5 % pulp consistency the problem was overcome. Bleaching experiments in polyethylene bags were also performed using the same conditions in parallel larger scale lab bleaching experiments at 10 % pulp consistency, where viscosity, ISO-brightness, end-pH and residual hydrogen peroxide were measured. The potential differences caused by the pulp concentrations were investigated.

4.2 Radical determination from wet or dry pulp

All standard laboratory bleaching experiments were made on never dried pulp, i.e., the dry content was about 30 % and the samples were stored in a refrigerator.

Dried pulp was generally used in the small-scale glass vial experiments. The amount of fibres was critical for a high reproducibility. A dry pulp was then more easily handled and stored.

A separate set of experiments was made to investigate if the measurements of hydroxyl radical activity differed if the samples that were peroxide bleached were made out of dried or never dried pulps. The wet and dried samples were P-bleached with and without Mg-addition, in triplicates, and the results showed no significant difference in the hydroxyl radical activity.
4.3 Reproducibility in hydroxyl radical determination

The repeatability in the quantification of acetone by head-space GC/MS was very high. The more important overall reproducibility, i.e., the amount of acetone formed in a repeated experiment starting from weighing of pulp, additions of chemicals and bleaching followed by acetone determinations was estimated. The quantification of hydroxyl radical activity in a pulp sample was done in triplicate experiments on each pulp sample. The reproducibility in the acetone quantification has been calculated by comparing the individual determinations for each sample and the standard deviation for the normalized values was found to be 0.135 (CV = 13.5 %). The calculation is based on 86 individual experiments and obvious outliers have been excluded, for instance a leaking sample vial. However, inhomogeneities in the small (250 mg) pulp samples introduced some uncertainty.

After the reproducibility of acetone quantification was estimated, we experienced that if the determinations by GC/MS were performed over a long period of time we needed to recalibrate the instrument. Thus, a series of three solutions of known acetone concentrations was analysed in connection with each series of bleaching experiments. That is, the later experiments are associated with an external standard calibration curve for each series of experiments.

The use of very small pulp samples when the formation of acetone was to be determined (250 mg) revealed that the transition metal ions may be unevenly distributed in the pulp. Significantly higher values were occasionally observed in one of the three samples (triplicates). This occurred seldom, in less than 4 % of the samples used for determination of the reproducibility. That the very high values occasionally found was due to inhomogeneity between the triplicate samples and not due to a variation in the determination of acetone was checked in four of these samples. The quantification of acetone was repeated and the more than 100 % higher values were confirmed. The explanation for the very high formation of hydroxyl radicals occasionally seen may be due to an uneven distribution in the pulp of catalysts that degrade hydrogen peroxide. Further, unevenly distributed organic contaminants, may be oxidized and consume hydrogen peroxide which could be an explanation to the less frequently seen divergent lower formation of hydroxyl radicals in some samples. However, generally all the triplicate samples were within the repeatability limit of 13.5 %, showing that the pulp samples were generally quite homogenous.

4.4 Units for the determined hydroxyl radical activity

The absolute amount of hydroxyl radicals generated in the bleaching experiment cannot be determined; it is only the fraction that reacts with the probe that is quantified. Instead the absolute amount of acetone, given in mg/l, was used to report hydroxyl radical activity in most experiments. However, in some of the initial experiments arbitrary units were used. These values are also quantitative and give the relative activity between the pulps in a set of bleaching experiments.
4.5 Limitations of the hydroxyl radical determination

Hydroxyl radicals are among the most reactive and short-lived species that exist. Thus, the site where the radical is formed is close to the site of its reaction. Limitation connected with the soluble probe method is discussed elsewhere (General discussion of the soluble probe method for hydroxyl radical activity determination, See 7.1).

The small sample size is another limitation, since only 250 mg dry pulp is used for a bleaching experiment. When the amount of transition metal ions is very low, the distribution of the catalyst may not always be homogeneous.

There are also some limitations and differences between the experimental techniques used for determination of hydroxyl radicals and of the other bleaching resultants (viscosity, end-pH, residual peroxide and brightness). It was concluded that water soluble low molar mass IPA was the best choice as a probe for hydroxyl radical determination. The decision to use IPA and to quantify acetone made bleaching in polyethylene bags impossible since acetone was then lost. Thus P-bleaching experiments were made in the classical way at 10 % pulp consistency to determine brightness, viscosity, end-pH and residual peroxide. In parallel, the same pulp was bleached on a smaller scale in gas-proof glass vials. The bleaching conditions were the same, except that homogenization during the bleaching by kneading could not be done in the head-space vials. Instead, the samples for acetone determination were homogenized in a heated ultra-sound water bath during the bleaching. The small-scale experiments further had to be performed at a lower pulp consistency, 2.5 %. This made start and end-pH more constant in the experiments made in vials than in those made in polyethylene bags, where a pH-change more easily could be observed.
5 Experimental

5.1 Pulp samples

Softwood kraft pulps (65/35 spruce/pine; about 35% saw mill chips) were collected at five different positions from one mill using a TCF bleaching sequence. The softwood kraft pulp was oxygen delignified in a two stage (OO) and further bleached in Q(OP)(PaaQ)(PO)-bleaching sequence to 89% ISO-brightness.

The charge of EDTA in the mill was 0.9 kg/ton in the first complexing stage and 1.0 kg in the second. The charge of peroxide was 6 kg/ton in the first peroxide stage and 28 kg in the second. In the first complexing stage 0.4 kg/ton of MgSO_4 was added and 0.5 kg/ton into the second, the (PaaQ)-stage.

The pulp samples were well-washed at the mill laboratory with de-ionized water and characterized at STFI-Packforsk with respect to kappa number, viscosity, ISO-brightness and metal ion content.

Table 1. Kappa number, viscosity and ISO-brightness for mill pulp samples.

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Kappa No</th>
<th>Visc ml/g</th>
<th>ISO-brightness %</th>
</tr>
</thead>
<tbody>
<tr>
<td>OOQ</td>
<td>8.7</td>
<td>863</td>
<td>55</td>
</tr>
<tr>
<td>OOQ(OP)</td>
<td>6.3</td>
<td>802</td>
<td>71</td>
</tr>
<tr>
<td>OOQ(OP)(PaaQ)</td>
<td>5.1</td>
<td>801</td>
<td>73</td>
</tr>
<tr>
<td>OOQ(OP)(PaaQ)(PO)</td>
<td>3.1</td>
<td>668</td>
<td>89</td>
</tr>
</tbody>
</table>

Table 2. Metal ion content in mill pulp samples, mg/kg.

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Ca (mg/kg)</th>
<th>Cu (mg/kg)</th>
<th>Fe (mg/kg)</th>
<th>K (mg/kg)</th>
<th>Mg (mg/kg)</th>
<th>Mn (mg/kg)</th>
<th>Mg/Mn mole ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>OO</td>
<td>1247</td>
<td>0.55</td>
<td>3.0</td>
<td>142</td>
<td>360</td>
<td>45.3</td>
<td>18</td>
</tr>
<tr>
<td>OOQ</td>
<td>285</td>
<td>0.84</td>
<td>2.1</td>
<td>28</td>
<td>118</td>
<td>0.7</td>
<td>381</td>
</tr>
<tr>
<td>OOQ(OP)</td>
<td>503</td>
<td>0.18</td>
<td>3.4</td>
<td>14.8</td>
<td>231</td>
<td>3.3</td>
<td>996</td>
</tr>
<tr>
<td>OOQ(OP)(PaaQ)</td>
<td>345</td>
<td>0.42</td>
<td>3.3</td>
<td>8.9</td>
<td>281</td>
<td>0.16</td>
<td>3968</td>
</tr>
<tr>
<td>OOQ(OP)(PaaQ)(PO)</td>
<td>402</td>
<td>0.32</td>
<td>4.0</td>
<td>14.8</td>
<td>215</td>
<td>3.4</td>
<td>143</td>
</tr>
</tbody>
</table>

5.2 Chemicals

Hydrogen peroxide, p.a 30%
Sodium hydroxide, Titrisol, 1 mol/l
Sulphuric acid Titrisol, 0.5 mol/l
Magnesium sulphate (MgSO_4 x 7 H_2O), p.a,
EDTA (Na2-EDTA) Titrisol, 0.1 mol/l (Merck)
DTPA (Titriplex V), p.a. (Merck)
Sodium acetate p.a.
Sodium carbonate, p.a.,
5.3 Standard laboratory P-stage bleaching

Standard P-stages were carried out at 10 % pulp consistency in sealed polyethylene bags that was intermittently kneaded during the bleaching. If magnesium was added it was made in the form of MgSO₄, and the P-stage was then denoted P*. The sodium hydroxide was added to the pulp and mixed by hand at room temperature. Finally hydrogen peroxide was added (20 kg/t), starting pH was adjusted by sodium hydroxide to 11.5 at room temperature and mixed with the pulp immediately before sealing and heating. De-ionized water was used throughout the experiments. The probe (IPA) was not added. Otherwise the bleaching conditions were the same as for the P-stages in small scale, cf. 5.4.

5.4 P-stage bleaching in small scale glass vials

The bleaching experiments where the formation of trace amounts of volatile acetone was to be determined were performed in septum sealed vials. All bleaching experiments when hydroxyl radical activity was determined were performed using 250 mg pulp, calculated as dry. Pure deionised and filtered water (MilliQ, Waters) was used to a final volume of 10 ml, which gave a pulp consistency of 2.5 %. Since the initial transition metal catalyzed formation of hydroxyl radicals is very fast, the vials had to be sealed immediately after the addition of H₂O₂. In the small scale experiments pH was set by sodium hydroxide higher than 11.5 before addition of hydrogen peroxide. After addition of the standardized charge of hydrogen peroxide (20 kg/t; 2 %) a starting pH of 11.5 at room temperature was obtained. The amount of sodium hydroxide needed was established in pretrials. The low pulp consistency made pH more stable than in the bleaching experiments made in plastic bags at 10 % pulp consistency. The probe isopropyl alcohol (IPA; 2-propanol) was initially added in a constant amount (5 %, 50 kg/ton calculated on dry pulp). The samples were heated in an ultrasonic bath at 80°C for 3 hours. The vials were then cooled and the acetone formed was analysed by Headspace GC-MS within 24 h.

The bleaching experiments in a series had to be made the same day and analysed within approximately 24 h. If the acetone containing samples were stored, even in a deep-freezer, some of the acetone may be lost.

Headspace GC-MS conditions:
The Head Space equipment used was a PE HS-40XL from Perker Elmer. The samples were preheated to 80°C just before sample withdrawal. An overpressure of 30 psi is built up in the whole system for 0.5 min. An injector needle holding the temperature 80°C then
B1 Hydroxyl radical formation during hydrogen peroxide bleaching

10 (53)

penetrates the rubber septum that shuts the glass vial and withdraws a sample of the gas phase above the pulp during 0.1 min.

The concentration of acetone was measured by using a HP 5890 gas chromatograph. The GC was equipped with a VF-23MS polar column (Varian), 30 m long and with an inner diameter of 0.25 mm. The film thickness inside the column was 0.25 μm. The injector temperature was 80°C and the final temperature 120°C. The oven temperature was kept at 35°C for 2 min followed by heating to 120°C with a heating rate of 10°C/min.

A higher signal could be obtained by measuring the fragment m/z 43, however in some samples a background signal at 43 appeared. Instead the molecular ion m/z 58 was used for quantification of acetone.

5.5 Pulp analysis

<table>
<thead>
<tr>
<th>Kappa number</th>
<th>SCAN-C 1:00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>SCAN-C 15:99</td>
</tr>
</tbody>
</table>

Metal ion analysis were made using ICP-AES. The samples were ashed at 575°C to remove all the organic material, and dissolved in hydrochloric acid before analysis, all according to a standard method used at STFI-Packforsk.
6 Results and discussion

The hydroxyl radicals are too unstable and short lived to be directly observed or quantified. A probe was therefore used to react with the radicals to form a unique product, acetone. After a bleaching stage, the amount of acetone formed was quantified as a result of the hydroxyl radical activity on the probe in the bleaching liquor.

6.1 Formation of radicals from different pulps

Initially the influence of pulp consistency on the standardized peroxide bleaching experiments had to be evaluated, since the peroxide bleaching experiments were made both at 10 % and at 2.5 % pulp consistency. No significant difference in viscosity and brightness could be seen, figure 1. However, the kinetic behavior differs between the experiments made in polyethylene bags and those made in small glass vials as shown by the hydrogen peroxide consumption in figure 2, due to the higher concentrations at 10 % conc.

![Graph showing viscosity vs. ISO-brightness for different pulp consistencies.](image)

Figure 1. Selectivity of P* bleaching (0.05 % Mg) of the OO and OOQ(OP)(PaaQ) pulps at different consistencies. The samples were bleached at different times, see also figures 6 and 7.
B1 Hydroxyl radical formation during hydrogen peroxide bleaching

12 (53)

![Graph](image)

*Figure 2. Consumption of hydrogen peroxide during P-bleaching of the OO and OOQ pulps, H₂O₂ charge 20 kg/t.*

Since the higher pulp consistence bleaching is performed at higher molar concentrations of the bleaching reagents, the kinetics of the peroxide bleaching is, as expected faster.

**6.1.1 Screening of the mill pulps**

Five industrial pulps that were obtained from a TCF bleaching sequence were screened for formation of hydroxyl radicals, *figure 3*. The aim was to get a foundation for how reliable the quantification of the hydroxyl radical activity was.
The OO pulp gave as expected the highest value for the hydroxyl radical activity. A much lower activity was obtained from the OOQ pulp and the other pulp aimed for a P-stage, the OOQ(OP)(PaaQ). To perform an additional P-stage on a pulp that had previously experienced industrial hydrogen peroxide bleaching conditions resulted in a relatively high detected hydroxyl radical activity.

Parallel bleaching experiments in polyethylene bags were made, where the effect of the standardized hydrogen peroxide bleaching stage on kappa number, viscosity and brightness were determined, table 3.

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Kappa No</th>
<th>Viscosity ml/g</th>
<th>ISO-Brightness %</th>
<th>Visc loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>OO</td>
<td>7.1</td>
<td>812</td>
<td>61.5</td>
<td>111</td>
</tr>
<tr>
<td>OOQ</td>
<td>5.8</td>
<td>829</td>
<td>76.0</td>
<td>34</td>
</tr>
<tr>
<td>OOQ(OP)</td>
<td>5.1</td>
<td>768</td>
<td>79.8</td>
<td>33</td>
</tr>
<tr>
<td>OOQ(OP)(PaaQ)</td>
<td>4.0</td>
<td>778</td>
<td>83.1</td>
<td>23</td>
</tr>
<tr>
<td>OOQ(OP)(PaaQ)(PO)</td>
<td>2.5</td>
<td>646</td>
<td>90.6</td>
<td>22</td>
</tr>
</tbody>
</table>

Table 3. Viscosity, kappa number and ISO-brightness after a laboratory P-stage on the mill pulps. Values before the P-stage are given in table 1. Only the pulp consistency differed from the experiments shown in figure 3 above.
6.2 Kinetics of hydroxyl radical formation during a P-stage

Results from the master thesis work by L-E Åkerlund (Åkerlund 2003) suggested the possibility of a lag-phase in the hydroxyl radical formation. This observation initiated a series of kinetic studies, where the possibility to avoid hydroxyl radicals in the initial 10-30 minutes of the P-stage was investigated. However, it can already here be concluded that no safe lag phase with respect to hydroxyl radical formation exist.

In order to confirm or reject the hypothesis, that an initial bleaching phase with almost no hydroxyl radical activity existed, three of the mill pulps, OO, OOQ and OOQ(OP)(PaaQ), were bleached in a standardized P-stage and hydroxyl radical formation was measured over time. The resulting hydroxyl radical activity reflected by the increased formation of acetone over time is illustrated in figure 4.

![Figure 4](image)

**Figure 4. Comparison between hydroxyl radical formation in a subsequent P*-stage for three pulp samples (OO, OOQ and OOQ(OP)(PaaQ)) as a function of time (20 kg/t; H2O2, 80 °C with 0.05 % Mg added, i.e. bleached P*).**

In this series of experiments the MS-instrument had a better detection limit than in previous determinations. Thus, a higher signal was obtain in this experiment and small amounts of acetone could be detected also in the initial time phase of the P-bleaching. The formation of hydroxyl radicals cease after about 90 min bleaching for the OO-pulp, indicating a complete consumption of the peroxide. This was confirmed by residual peroxide determinations. That is, no hydroxyl radicals are formed when the hydrogen peroxide was consumed. The pulps that were treated with complexing agents, OOQ and OOQ(OP)(PaaQ), gave rise to a much lower hydroxyl radical activity.

Too severe conditions in a final P-stage can cause unwanted loss of viscosity, when the purpose of the stage is focused towards brightness increase rather than delignification. In
these experiments the low boiling reaction product, acetone from IPA, limited the lab technique to lower reaction temperatures and an increased severity was instead simulated by a prolonged reaction time. The OOQ(OP)(PaaQ) pulp was P-bleached with the same conditions as in the previous kinetic experiments and the formation of acetone was quantified after 2, 5, 6 and 7 hours. No increased hydroxyl radical activity after prolonged bleaching could be seen. The formation of hydroxyl radicals became slower after 2 h bleaching time. This was not due to a complete consumption of hydrogen peroxide and could be referred to as a somewhat lower catalytic activity.

![Graph showing hydroxyl radical activity and viscosity loss over bleaching time](image)

Figure 5. The formation of hydroxide radicals and viscosity loss (ml/g) for the OOQ-pulp in a subsequent peroxide stage.

The experiments on the kinetics of radical formation in figure 4 were complemented with lab-bleaching experiments of the corresponding pulp samples in polyethylene bags to follow the development of brightness and loss of viscosity. Bleaching was done for 30 min, 120 min and 300 minutes on the OO, OOQ and OOQ(OP)(PaaQ) pulps. Peroxide bleaching of the mill OOQ pulp exhibited an increase in hydroxyl radical formation and a lower viscosity with increased bleaching time, figure 5.

Similar trends were seen for the other pulps tested; OO and OOQ(OP)(PaaQ) (data are not enclosed). The hydroxyl radicals formed in a P-stage thus seems to correlate with loss of pulp viscosity. However, the relative decrease in viscosity during the P-stage differs between pulps. That is, the “viscosity loss/radical unit” seems to be less for pulps taken later in the bleaching sequence.

In the larger scale bleaching experiments, in polyethylene bags, on the OO pulp without any preceding chelating stage, the pulp had as expected consumed all the peroxide at the end of the bleaching. This was also indicated by an increase in the end-pH. Residual peroxide remained after 300 min when the chelated pulps, OOQ and OOQ(OP)(PaaQ), were bleached.
B1 Hydroxyl radical formation during hydrogen peroxide bleaching

16 (53)

The kinetic bleaching experiments on OO, OOQ and the OOQ(OP)(PaaQ) pulps revealed no surprises. Some examples of viscosity and ISO-brightness as a function of reaction time are shown in figures 6 to 8.

![ISO-brightness vs Reaction time](image1)

**Figure 6.** Brightness development for the OO-pulp P* bleaching made for comparison of pulp consistency.

![Viscosity vs Reaction time](image2)

**Figure 7.** Corresponding viscosity loss for the OO-pulp during P* bleaching.
6.3 Decomposition of H2O2 and high end-pH

It is well known that the self-decomposition of hydrogen peroxide in alkaline media into oxygen and water has an optimum around its pKa (11.6). The highest amount of acetone, i.e. the highest activity of hydroxyl radical formation was detected by the IPA probe at the pH closest to the pKa-value of H2O2. This was observed in a set of bleaching experiments where pH started from different levels. A standardized charge of 20 kg/t of H2O2 on pulp were used and starting-pH adjusted at room temperature to 12, 11.5, 11 and 10.5, respectively. At the pH 11.5 P-bleaching of the industrial OOQ pulp showed the highest hydroxyl radical activity, while both the higher and the lower pH-levels showed about ¼ of the activity table 4.

Table 4. P-bleaching of pulp sample OOQ

<table>
<thead>
<tr>
<th>Start-pH in P-stage</th>
<th>Hydroxyl radical activity (mg/l acetone)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5</td>
<td>6.4</td>
</tr>
<tr>
<td>11</td>
<td>4.9</td>
</tr>
<tr>
<td>11.5</td>
<td>24.1</td>
</tr>
<tr>
<td>12</td>
<td>6.8</td>
</tr>
</tbody>
</table>

The pH-optimum for self-decomposition of hydrogen peroxide seems to correspond with the highest hydroxyl radical activity detected by the soluble probe.

The starting-pH for a laboratory P-stage bleaching is usually higher than the end-pH. However, when all hydrogen peroxide is consumed in a non-optimal peroxide bleaching, end-pH was often higher than expected. A reason for this could be that the peroxide has
B1 Hydroxyl radical formation during hydrogen peroxide bleaching

been decomposed to hydroxyl radicals. The catalytic formation of hydroxyl radicals from hydrogen peroxide is accompanied by the formation of an equivalent of alkali, a hydroxide anion. The reaction is given below:

\[
\text{H}_2\text{O}_2 \xrightarrow{\text{Mn}^{n+}} \text{HO}^- + \text{HO}^\ominus + \text{Mn}^{(n+1)\ominus}
\]

This phenomenon has been observed for some of the peroxide bleaching experiments made in the standard polyethylene bag procedure. The bleaching experiments in glass vials were more dilute and pH was then kept more constant.

6.4 Catalytic metal ions

The metal ions able to catalytically decompose hydrogen peroxide, manganese (Mn), copper (Cu) and iron (Fe), can partly be removed from the pulp before the P-stage in a complexing Q-stage or by an acid treatment in an A-stage. These three transition metals were in this study determined together with calcium (Ca), potassium (K), sodium (Na) and magnesium (Mg).

The metal ion profiles for the mill pulps are given in table 2 under section 5.1. The highest levels of metal ions were, as expected, found in the OO-pulp. The metal ions in focus for obtaining good performance in a P-stage is Mn, since it is generally believed to be the most important factor for hydroxyl radical generation in a P-stage and Mg for its protective properties. High content of Mn enters the bleaching sequence together with the OO-pulp (45 mg/kg). The amount of Mn is efficiently reduced in the industrial Q-stage leaving only 0.7 mg/kg to enter the first peroxide bleaching stage. Before the second P-stage the level was even lower, 0.16 mg/kg. The content of Cu was always low, below 1 mg/kg, in the industrial pulps. Iron is difficult to remove, severe acidic conditions were needed (Table 5 below). The content of Fe was higher, between 2.1 and 4 mg/kg and almost constant over the process. There are reasons to believe that iron is present in a stable non-catalytic form i.e. as rust (Fe$_2$O$_3$).

6.4.1 Metal removal by different treatments

Removal of catalytic transition metal ions, particularly Mn, was also done in laboratory experiments. Starting from the OO-pulp different complexing agents and acidic conditions were tested. The complexing agents EDTA and DTPA were both efficient in removing Mn and simultaneously leave Ca and Mg ions (Table 5 contains all data from the laboratory metal-removal treatments). In addition, a new complexing agent, ethylenediamine di-O-hydroxyphenylacetic acid, (EDDHA) used in some fertilizers and suggested to trap and save the Vasa ship from catalytic iron ions could be of interest since it can be believed to function at higher pH or even during a P-stage. A similar compound, N,N-bis(2-hydroxybenzyl)ethylenediamine-N,N-diacectic acid (HBED), was commercially available and tested. It is a phenolic complexing agent known to be most active at high pH. The phenolic substituent can be assumed to make the complexing agent biodegradable. HBED was used in treatments at four different pH:s, a slight acidic (4.3), a neutral (6.6) and two alkaline
According to STFI-Packforsk's Confidentiality Policy this report is assigned category 2

B1 Hydroxyl radical formation during hydrogen peroxide bleaching

(9.0 and 11.0). The pKa-value of the phenolic group is probably above pH 10. Although, HBED only removed about half of the Mn from the OO-pulp, it also left more of the beneficial metal ions.

![Chemical structures](image)

**Figure 9.** Complexing agents that might work for trapping of transition metal ions at high pH (EDDHA and the tested HBED). (Additional chemical formulas are enclosed in the appendix: Complexing agent for metal ion removal.)

Acidic conditions set metal ions free and make it possible to remove them by water washing. However, acid cannot provide the selectivity of a complexing agent and both the detrimental transition metals and for instance the beneficial Mg-ions are removed. The content of Mn, Mg and Ca in the OO-pulp was reduced by 86, 89 and 88%, respectively in a standard laboratory A-stage (table 5). The A-stage again resulted in a higher hydroxyl radical activity during a subsequent P-stage, both when compared with the more efficient removal of Mn by EDTA or DTPA and with the less efficient HBED. Thus, a more thorough study on the acidic metal ion removing conditions was made.

The OO pulp was treated at different A-stage conditions. Treatments were made at room temperature, at 90°C and at more severe acidic conditions able to degrade hexenuronic acid. These different A-stages were performed both as single stages and as repeated laboratory treatments. Metal ion contents after complexing and acid treatments are collected in table 5. No difference in Mn content was obtained between an A-stage made at 20°C or at 90°C. Earlier shown by Bergnor-Gidnert 1999, figure 10. A repeated stage lowers the Mn content for both the low and the high temperature treatment. Even more acidic conditions removed the catalytic Mn down to 1.2 mg/kg in the single stage and to 0.4 mg/kg in the repeated hexenuronic acid degrading stage (95°C, pH 1.8, 3 h). These levels were even lower than those obtained after the complexing agent stages. However, the severe acidic conditions also removed most of the beneficial metal ions and acidic conditions at elevated temperatures are known to degrade hexA.
B1 Hydroxyl radical formation during hydrogen peroxide bleaching

![Graph showing Mn (mg/kg) vs. Final pH (25 °C) for different temperatures and stages.](image)

Figure 10. Removal of Mn metal ions. (Bergnor-Gidnert 1999).

### Table 5. Metal ion content in OO pulp after different laboratory metal ion-removal treatments (mg/kg).

<table>
<thead>
<tr>
<th>Treatments on oxygen stage pulp (OO)</th>
<th>pH</th>
<th>Ca</th>
<th>Cu</th>
<th>Fe</th>
<th>K</th>
<th>Mg</th>
<th>Mn</th>
<th>Na</th>
<th>Mg/Mn mole ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>OO starting pulp</td>
<td></td>
<td>1247</td>
<td>0.55</td>
<td>3.0</td>
<td>142</td>
<td>360</td>
<td>45.3</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>EDTA</td>
<td>6.3</td>
<td>1017</td>
<td>0.47</td>
<td>1.4</td>
<td>56.0</td>
<td>330</td>
<td>2.4</td>
<td>n.a.</td>
<td>311</td>
</tr>
<tr>
<td>DTPA</td>
<td>5.9</td>
<td>953</td>
<td>0.14</td>
<td>0.73</td>
<td>21.3</td>
<td>259</td>
<td>0.97</td>
<td>n.a.</td>
<td>603</td>
</tr>
<tr>
<td>QQ</td>
<td>4.3</td>
<td>336</td>
<td>0.3</td>
<td>4</td>
<td>20.1</td>
<td>120</td>
<td>1.1</td>
<td>352</td>
<td>246</td>
</tr>
<tr>
<td>HBED</td>
<td>6.6</td>
<td>1134</td>
<td>0.38</td>
<td>5.7</td>
<td>115</td>
<td>301</td>
<td>13.5</td>
<td>n.a.</td>
<td>50</td>
</tr>
<tr>
<td>HBED</td>
<td>9.0</td>
<td>974</td>
<td>0.28</td>
<td>4.1</td>
<td>(281?)</td>
<td>215</td>
<td>19.7</td>
<td>n.a.</td>
<td>25</td>
</tr>
<tr>
<td>HBED</td>
<td>11</td>
<td>948</td>
<td>0.48</td>
<td>5.9</td>
<td>40.9</td>
<td>219</td>
<td>23.8</td>
<td>798</td>
<td>21</td>
</tr>
<tr>
<td>A-stage</td>
<td>2.5</td>
<td>151</td>
<td>0.28</td>
<td>2.6</td>
<td>7.9</td>
<td>41</td>
<td>6.2</td>
<td>n.a.</td>
<td>15</td>
</tr>
<tr>
<td>A (20°C)</td>
<td>2.5</td>
<td>188</td>
<td>0.63</td>
<td>3.9</td>
<td>15.7</td>
<td>46</td>
<td>7.1</td>
<td>34.5</td>
<td>15</td>
</tr>
<tr>
<td>AA (20°C)</td>
<td>2.5</td>
<td>86</td>
<td>0.49</td>
<td>3.8</td>
<td>12</td>
<td>19</td>
<td>3.2</td>
<td>15.8</td>
<td>13</td>
</tr>
<tr>
<td>A (90°C)</td>
<td>2.5</td>
<td>325</td>
<td>0.59</td>
<td>18.8</td>
<td>14</td>
<td>60</td>
<td>8.4</td>
<td>34.5</td>
<td>16</td>
</tr>
<tr>
<td>AA (90°C)</td>
<td>2.5</td>
<td>94</td>
<td>0.66</td>
<td>9.9</td>
<td>12.1</td>
<td>22</td>
<td>3.2</td>
<td>14.2</td>
<td>16</td>
</tr>
<tr>
<td>A (hexA)</td>
<td>1.8</td>
<td>40</td>
<td>1.1</td>
<td>0.7</td>
<td>5.0</td>
<td>10.3</td>
<td>1.2</td>
<td>10.9</td>
<td>19</td>
</tr>
<tr>
<td>AA (hexA)</td>
<td>1.8</td>
<td>12</td>
<td>0.7</td>
<td>1.1</td>
<td>7.0</td>
<td>2.3</td>
<td>0.4</td>
<td>5.8</td>
<td>13</td>
</tr>
</tbody>
</table>

n.a. = not analysed
6.4.2 Formation of radicals after metal ion removal with complexing agents

The differently treated pulp samples, with the aim to remove the catalytic metal ions, were then bleached in a standardized P-stage and the radical formation was measured, *figure 11*. Addition of Mg was done when the molar ratio Mg/Mn was below 30 (marked with *, that is after A, HBED pH 4.3 and pH 9). The HBED pH 11 treated pulp bleaching was performed both with and without Mg, with no differences in hydroxyl radical activities. OO and OOQ were both P and P* bleached.

![Figure 11](image-url)

*Figure 11. Hydroxyl radicals formed in a subsequent P-stage after different treatments of the mill oxygen stage pulp, which together with the mill Q-stage pulp were included for the purpose of comparison (*=Mg added).*

Significantly lower hydroxyl radical formation was obtained when the oxygen prebleached pulp was treated with EDTA or DTPA before the P-bleaching stage. Both the industrial Q-stage (EDTA) and the laboratory EDTA and DTPA treatments, as well as a repeated Q-stage (DTPA), efficiently reduced the amount of hydroxyl radicals detected.

The HBED treatment had a smaller effect both at neutral pH and when compared at more acidic or alkaline conditions. When used at the high pH of 11, HBED reduced the amount of hydroxyl radicals formed in the P-stage to half compared to the pulp P-bleached without a complexing stage.

Most bleaching experiments in figure 11 were also performed in polyethylene bags where the viscosity and brightness were measured, *figures 12 and 13*. Also an A-stage was included in the series. In agreement with earlier results (Åkerlund 2003), this pulp generated much more radicals than the pulps treated with complexing agents, although Mg was added in the P-stage.
B1 Hydroxyl radical formation during hydrogen peroxide bleaching

22 (53)

Figure 12. Mg was added in some P-stages (denoted *) in order to have a Mn/Mg mole ratio of > 30. In the figure also the relative hydrogen peroxide consumption in % are given (numbers above the bars). The (OO)-pulp was not P-bleached. "None"* represents a P*-stage on the (OO) pulp, i.e. without a previous Q-stage.

Figure 13. Mg was added in some P-stages (denoted * in the figure) in order to get a Mn/Mg mole ratio > 35. In the figure also the relative hydrogen peroxide consumption in % are given (figures above the bars). The (OO)-pulp was not P-bleached. “None”* represents a P-stage without a previous Q-stage, but with Mg-addition.
The EDTA and DTPA treatments resulted in the highest brightness after the standard P-stage. All treatments resulted in a loss of viscosity over the P-stage, however the differences were not big. No clear correlation between viscosity loss and hydroxyl radical activity in the P-stage could be seen.

6.4.3 Accessibility to catalytic metal ions

Not only the amount of catalytic metal ions but also how they are bonded influence their ability to generate hydroxyl radicals. The history of the pulp is thus important. A complexing stage removes catalytic metal ions and passivates them. A following P-stage have no effect on the content of catalysts, but increases the hydroxyl radical activity. This is illustrated in figure 14, where a big difference in hydroxyl radical activity during the first and second P-stage was shown for two pulps, even though the amount of manganese and iron was the same.

All mill pulps used in these experiments had a different origin than the mill pulps used in the other experiments reported.

Figure 14. Radical formation in the P-stage (underlined; no addition of Mg) for two different pulp samples. More radicals are formed in the second P-stage, even though the metal ion content was determined to be similar (mg/kg).

In another experiment, figure 15, an oxygen prebleached kraft pulp containing a lot of catalytic metal ions (65 mg/kg of Mn and 15 mg/kg Fe) gave a strong signal for the hydroxyl radical activity. A Q-stage removed most of the Mn and the hydroxyl activity in the standardized P-stage was less than halve (41 %). For instance a pulp with 10 mg/kg of Mn obtained after a Q-stage gave a lower hydroxyl radical activity in the standardized P-stage than pulps with less catalytic Mn present (6.8 or 6.5 mg/kg), which not were preceded by a complexing stage.
Figure 15. Relative hydroxyl radical activity (given in %) in a P-stage; the proceeding stage had a higher impact on radical formation than the content of catalytic metal ions.

Acid treatments that remove catalytic metal ions even more efficient, still gave a higher hydroxyl radical activity in a subsequent standard P-stage. The differences in P-stage hydroxyl radical activity after a Q and an A-stage may be explained. An efficient red-ox cycle for the metal ions is essential for the formation of a significant amount of hydroxyl radicals. A complexing agent like DTPA will trap the ions best when they are in their high oxidation stage (Mn$^{3+}$ better than Mn$^{2+}$), i.e. in the form that does not transform hydrogen peroxide to hydroxyl radicals. The A-stage may leave the residual catalysts in an activated, easily oxidized and reduced (by superoxide anions or via oxidation of organic material) state. Thus, a pulp prepared for a P-stage seems to be better off after a Q-stage than after an A-stage. Reduction of the catalytic metal ions may be the rate determining step for the generation of hydroxyl radicals. Thus, stabilization of transition metal ions may stop the chain reactions and be a way to minimize detrimental radical formation.

Accessibility of hydrogen peroxide to the catalytic metal ions is of great importance. The solid-solutions formed by added magnesium inactivates catalytic manganese. This concept was introduced by Lidén (1994) and is the subject of the thesis by Norberg (2003). When only the amount of transition metals is considered the conclusions made may be oversimplified. Iron may be present, but less active as rust. For instance, if manganese is added to pulp it can be oxidized to MnO$_2$ with quite different properties than Mn$^{2+}$ and Mn$^{3+}$ (Chirat and Lachenal 1994). Also the protective layer of magnesium carbonate on manganese carbonate is important for the accessibility of the catalytic metal ion towards hydrogen peroxide (Wiklund et al. 2001).
6.4.4 Activation of catalytic metal ions by acid treatments

The previously observed activation of pulps in an A-stage towards hydroxyl radical formation in a subsequent P-stage was confirmed by the results illustrated in figure 16.

![Figure 16](image1)

**Figure 16.** Increased hydroxyl radical activity was observed after different A-stage conditions (pH at room temperature was always 2.5) in a subsequent P* stage, compared to the OO and chelated OOQ pulp.

All acid treated pulps gave a higher hydroxyl radical activity compared to the OO pulp, although, the metal ion contents were much lower. The A-stage performed at room temperature reduced the Mn content in the pulp from 45 mg/kg in the OO-stage pulp to 7.1 mg/kg. But still the hydroxyl radical activity was higher. Double A-stages resulted in a halving of the Mn concentration to 3.2 mg/kg. But the hydroxyl radical activity remained high. An A-stage performed at 90°C was as efficient in removing metal ions (to 8.4 mg/kg) as the single A-stage at lower temperature. The same was valid for the repeated high temperature treated pulp, OOAA 90°C, yielding 3.2 mg/kg Mn. This was also the pulp that gave the highest hydroxyl radical activity during the subsequent P*-stage. The hydroxyl radical activity can not be directly linked to the content of catalytic metal ions. The Mn content in the OOQ pulp used for comparison was 1.0 mg/kg (the pulp metal contents are all listed in Table 5).

In the literature it is found that simple acid leaching is not very practical for reducing the metal ion content in the pulp. The metal ions in pulps are suggested to be mainly bound to uronic acid groups. Hexeneuronic acid groups are acidic and still ionized at a low pH. Such groups can efficiently trap catalytic metal ions like Mn in the pulp. An A-stage made at severe acidic conditions (pH adjusted to 1.8 at room temperature and treated at 95°C for 3 h) degrade HexA and lower the Mn content, figure 17. A single severe A-stage gave a content of 1.2 mg/kg and a repeated severe stage 0.4 mg/kg.
(Table 5). It has been shown that hydrolysis of hexenuronic acids groups will effectively remove metal ions (Vuorinen et al 1996).

![Graph showing hydroxyl radical activity](image)

**Figure 17.** Increased hydroxyl radical activity was observed after different A-stage conditions in a subsequent P* stage, compared to the chelated OOQ pulp. “hexA” denotes A-stage treatment conditions to degrade HexA.

The conclusion is that an acidic treatment before a P*-stage increase the hydroxyl radical activity even when the content of catalytic Mn ions is very low. The increased activity is not due to a limited amount of Mg since 0.05 % Mg on pulp was added in all cases. Manganese is known to be present in pulp after alkaline treatments as an insoluble MnCO₃ precipitate with a protecting layer of MgCO₃ (Lidén and Öhman 1997, Lidén et al. 2001, Wiklund et al. 2001 and 2001b). Since carbonates are dissolved during acidic conditions, the different A-stage treatments remove the protecting layer on the potent catalyst. In this way the cyclic Fenton-reaction may be more pronounced in a subsequent P-stage.

### 6.5 Varied Mg-addition

Experiments were also made where the amount of the addition of Mg to the differently acid treated pulps was varied. All results are illustrated in *figure 18.*
A lower hydroxyl radical activity was surprisingly always obtained if no Mg was added to the acid treated samples, although the Mg/Mn ration was only 13 to 19 (Table 5). The only exceptions were for the pulp treated at repeated severe (HexA removing) acidic conditions, where a high addition of Mg gave lower hydroxyl radical activity. These two pulps not only had the lowest Mn but also the lowest overall metal ion content. Addition of 0.5 or 1.0 kg magnesium per ton pulp, then at alkaline pH the formed magnesium salts may have had a buffering effect. A more plausible explanation for the higher hydroxyl radical activity detected by the probe may be a replacement of Mn ions by the added Mg ions. Loosely bounded Mn ions in the solution can be expected to be more involved in redox-reactions in the liquor phase and this activity will generate hydroxyl radicals in solution. The short lifetime of hydroxyl radicals makes them then not detrimental to the pulp and more reactive with the IPA-probe, which also is present in the solution.

A positive effect on brightness of Mg addition was seen in the lab-bleaching of the OO-pulp in polyethylene bags, figure 19.

The consumption of hydrogen peroxide decreased when the metal ion content was reduced in the different A-stages, figure 20.
B1 Hydroxyl radical formation during hydrogen peroxide bleaching

Figure 19. (OO)-pulp. A-stage at pH 2.5, 23 °C. In the following P-stage 2 % H2O2 were charged and 90 °C, 180 min. The Mg-addition was varied at three levels, 0, 0.005 and 0.05 %. Within the bars the viscosities are given and above the bars the relative hydrogen peroxide consumption.

Figure 20. The consumption of hydrogen peroxide decreased as expected when the metal ion content was reduced in the different A-stages. (H2O2 charge was 2 %). The HexA removing conditions were more efficient in increasing brightness.
6.5.1 Importance of Q-treatment of acid activated pulps

The results above showed that an A-stage may be detrimental before a P-stage, with respect to hydroxyl radical activity. The importance of a preceding complexing stage after acid treatment before a subsequent P-stage has been previously been observed. The better viscosity and brightness in relation to consumed peroxide is illustrated in figure 21.

Figure 21. Left: A higher brightness at a given hydrogen peroxide consumption was obtained if the P* stage was made on a chelated pulp. Right: A better selectivity was obtained in the P* stage on pulp bleached at acidic D-stage conditions if well chelated.

Both acidic treatments and the use of complexing agents remove detrimental metal ions. However, the hydroxyl radical activity may be lower if the pulp entering the P-stage is chelated.

6.5.2 Addition of manganese ions in different forms before P-bleaching

Transition metal ions, like Mn, are removed from the pulp in a Q-stage. In this experiment some of the manganese ions were added back to the OOQ pulp before it was P-bleached. Their influence on the hydroxyl radical formation in the subsequent peroxide stage varied a lot depending on how the ions were trapped in the pulp.

More than 40 mg/kg Mn was removed in the industrial Q-stage (from 45 to less than 1) and in these experiments 20 mg/kg of manganese was added back in the form of manganese nitrate. The hypothesis was that added manganese ions will be partly inactivated by precipitation as oxides or hydroxides, after addition to pulp when the pH is made alkaline. Or that the manganese ions on the contrary will be able act as a catalyst for hydroxyl radical formation when they instead are trapped on the pulp as counter ions to insoluble fatty acid salts. A prerequisite for being catalytic and dangerous is that the manganese ions are able to change their oxidations state in a cyclic
B1 Hydroxyl radical formation during hydrogen peroxide bleaching

process. The hypothesis is that it may not be the amount of manganese but its form or surroundings that are decisive. This idea differs from the conclusions made by Chirat and Lachenal (1994), who has made a general conclusion that addition of Mn$^{2+}$ does not generate any hydroxyl radicals. Three experiment pulps were prepared and the resulting hydroxyl radical activities in a following P-stage are given in figure 22. The theoretical thoughts behind the additions are illustrated in the chemical drawings enclosed in the appendix: Addition of manganese ions.

1. OOQMn Addition of Mn(NO$_3$)$_2$ at neutral pH followed by an increase of pH to 12.0 at room temperature. The pulp was mixed for about half an hour at 10% pulp consistency before hydrogen peroxide (20 kg/ton) was added and heated at 90°C for 3h.

2. OOQMnF After addition of Mn(NO$_3$)$_2$ as in sample 1, the soluble sodium salt of a fatty acid (decanoic acid) was added in a small excess, the pulp pH was adjusted and P-bleached as above.

3. OOQFMn The fatty acid was added before the manganese, i.e. only the order of addition differed compared to the experiment above.

![Figure 22. Hydroxyl radicals formed in a subsequent P-stage after addition of manganese in three different ways to mill Q-stage pulp. The Mn was added as a solution of Mn(NO$_3$)$_2$ corresponding to 20 mg/kg pulp.](image)
When Mn ions were ion-exchanged into the carboxylic acid sites in the pulp, they could be inactivated by alkali induced precipitation of manganese hydroxide or air-oxidized to manganese ore. MnO₂ (Mn IV) is able to slowly degrade H₂O₂ to O₂ and H₂O without formation of hydroxyl radicals (OOQ Mn).

When instead the divalent Mn ions may have been “locked” at the carboxylic acid sites in the pulp by the addition of a fatty acid, an increased amount of hydroxyl radicals was formed (OOQ Mn F).

When Mn ions were added to the OOQ pulp when the soluble fatty acid salt (sodium decanoate) was added in advance, an insoluble manganese fatty acid salt was formed and precipitated onto the pulp surfaces. An extensive formation of hydroxyl radicals was observed in the following P-bleaching (OOQ F Mn).

When the OOQMn pulp was not washed before the P-bleaching – i.e. all of the added Mn was present in the pulp during bleaching. The Mn content of the OOQMnF and OOQFMn pulps were determined to 24.5 and 24.3 mg/kg, respectively, indicating that all of the added Mn (as soluble Mn(NO₃)₂) was trapped as insoluble fatty acid salts in the pulp. That is, the three pulps had the almost the same content of Mn, slightly more than 20 mg/kg.

In the small-scale experiments in glass vials all additions, bleaching experiments and hydroxyl radical determinations were made triplicates, all showing the same trends. Thus, these experiments show that not only the amount of catalytic metal ions in the pulp is important for the hydroxyl radical formation but the site and form, i.e. the oxidation state or counter ions, in which they appear is relevant.

For purposes of comparison, bleaching experiments in polyethylene bags were made on the three pulps with added Mn in different ways (OOQMn, OOQMnF and OOQFMn). In addition, a pulp was bleached where Mn was added in the same molar amount but as solid manganese ore, MnO₂. After the P-stage bleaching all pulp with added manganese had consumed all peroxide.
According to STFI-Packforsk’s Confidentiality Policy this report is assigned category 2

B1 Hydroxyl radical formation during hydrogen peroxide bleaching

ISO-brightness, %

Figure 23. All pulps with added manganese gave a lower brightness after the P-stage. Manganese ore, MnO₂ is brown and some is formed when the pulp is made alkaline.

Viscosity, ml/g

Figure 24. All additions of manganese reduced the pulp viscosity in the following P-stage.
The addition of manganese as MnO₂ resulted in a lower brightness after the P-stage, while the viscosity loss was minor. Mn²⁺ ions are easily oxidized to manganese ore, MnO₂, which is a brownish-black fine powder. All hydrogen peroxide was consumed and the end-pH was high after the polyethylene bag P-bleaching, which indicate a MnO₂ catalysed degradation. These results are in agreement with those reported by Chirat and Lachenal, however their conclusions could have been exaggerated.

The presence or formation of brown manganese ore did disturb the brightness determinations. An expected correlation with the determined high hydroxyl radical activity and the obtained pulp viscosity could not be found. The fatty acid-manganese salt formed in solution yielded a high signal from the soluble hydroxyl radical probe. On the other hand the formation in the pulp of insoluble inorganic precipitates gave a low signal from the soluble radical probe. However, a low pulp viscosity was obtained in both cases as a result of radicals generated close to the cellulose chains.

6.6 Scavengers for hydroxyl radicals

A hydroxyl radical is very reactive and it will react immediately with most organic compounds. To be able to scavenge the hydroxyl radicals something has to react faster with the radicals than the pulp. This is only possible if the hydroxyl radicals are formed outside of the pulp, in the surrounding solution.

6.6.1 Influence of magnesium additions to a P-stage

It is nowadays well known that magnesium in alkaline solutions do form a solid-solution that may trap detrimental catalytic manganese ions (Norberg 2003). The manganese ions are then prevented from readily changing its oxidation state between Mn²⁺ and Mn³⁺. To be able to control manganese ions the concentration of magnesium ions have to be high enough. The molar ratio between Mg and Mn has been suggested to be between 30 and 100. The loss of beneficial Mg in an A-stage can be compensated by addition of the metal ion to the bleaching stage or a selective removal by using EDTA (Basta et al. 1991).

The lower the amount of transition metals, especially manganese, the better the bleaching response will be. However, even very low levels of manganese may be detrimental for the pulp. The addition of magnesium to the P-stage may outbalance their negative effect. An explanation could be in which form the catalytic metal ions are present. During pulping, bleaching and complexing stages most of the detrimental metal ions are removed from the pulp. A continuous rearrangement of the metal ions to sites that offer a more stable configuration occurs. Carboxylic acid groups are the most obvious sites for positively charged metal ions like manganese. In alkaline pH most of the manganese will end-up as insoluble manganese carbonate (MnCO₃). A molar ratio between the amount of magnesium and manganese above 5 or up to 30 has been reported to stabilize the catalytic Mn-ions (Lidén 1994; Devenyns and Plumet 1994). A high enough magnesium/manganese concentration ratio in the P-stages is known to be able to form so-called solid-solutions that may prevent manganese ions from acting in a
According to STFI-Packforsk's Confidentiality Policy this report is assigned category 2

B1 Hydroxyl radical formation during hydrogen peroxide bleaching

34 (53)

catalytic manner. Also the formation of magnesium carbonate as a protecting layer on manganese carbonate has been presented (Wiklund 2001, 2001b).

Magnesium ions can only appear in one oxidized state, as Mg\(^{2+}\) ions. That is they can not take part in metal ion catalysed reactions. Manganese belongs to the so-called transition metals and can appear in many oxidation stages, +2, +3, +4 and +7. The Mn\(^{2+}\) can readily be oxidized by H\(_2\)O\(_2\) to Mn\(^{3+}\). The Mn\(^{3+}\) ion is an oxidant that has been suggested to be able to oxidize organic substrates. For example, carbonyl functions can be introduced into cellulose, as a consequence the cellulose chain will be cleaved and viscosity lost under alkaline conditions. As a result of the Mn\(^{3+}\) induced oxidation the reduced Mn\(^{2+}\) reappear. Thus, two types of detrimental reactions may occur; formally illustrated below. If these reactions occur in a P-stage hydroxyl radicals will be formed in a chain reaction.

\[
\begin{align*}
\text{Mn}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Mn}^{3+} + \text{HO}^* \\
\text{Mn}^{3+} + \text{cellulose} & \rightarrow \text{Mn}^{2+} + \text{oxidized cellulose}
\end{align*}
\]

In a solid-solution formed by magnesium ions at high pH, a Mg\(^{2+}\) ion can be replaced by a Mn\(^{2+}\) ion since they have a similar radius. Since only Mn\(^{2+}\) ion fits in the solid solution, due to its oxidation stage it is prevented from changing its oxidation state to Mn\(^{3+}\). In this way, the catalytic effect of manganese is stopped by the addition of magnesium.

The possibility has to be considered that addition of magnesium sulfate will form a buffering hydroxide at high pH-values. However, a brief calculation on the used charge of 0.05 % Mg gave that pH would be only marginally lower in the P-stage when hydroxyl radicals were measured at a pulp consistency of 2.5 %.

6.6.2 Radical formation with and without additional magnesium

In the mill MgSO\(_4\) was added at two positions to secure a sufficient molar ratio between Mg and Mn. All industrial pulps collected from different fiberline positions, except the oxygen stage pulp, thus had a sufficient content of magnesium (Table 2). Even so, all five mill pulps were also lab-bleached in a P-stage with an addition of 0.05 % MgSO\(_4\) on pulp and the differences in hydroxyl radical formation were determined.

The differences were small and just above the limits of significance for the analytical method used. Addition of magnesium to the OO pulp did not influence the formation of hydroxyl radicals in a following P-stage. The observed hydroxyl radical activity was somewhat lower after addition of Mg on the pulps taken further down the bleaching sequence, i.e. OOQ, OOQ(OP), OOQ(OP)(PaaQ). The results of these repeated P-bleaching experiments are enclosed in Appendix: Additions of magnesium. The overall conclusion must be that no significant differences were observed in the hydroxyl radical activities for the mill pulps at the standardized bleaching conditions used.

However, a prolonged bleaching where the time at 80ºC was more than doubled for the OOQ(OP)(PaaQ) pulp, showed a significant difference in hydroxyl radical activity.
Surprisingly a high hydroxyl radical activity was observed at long bleaching times when the standard addition of Mg (0.05 %) was excluded. This was in spite of the fact that the OOQ(OP)(PaaQ) pulp had a high Mg to Mn ratio.

The importance of additional Mg was confirmed in a time-extended peroxide bleaching of the OOQ(OP)(PaaQ) pulp made in larger scale bleachings in polyethylene bags (figures 26, 27, 28). A big positive impact on the pulp viscosity was then observed. A small difference was also seen in the consumption of hydrogen peroxide. However, no significant difference in brightness was seen in contrast to the much lower viscosity and higher hydroxyl radical activity that was found when no Mg was added. The positive effect of Mg on hydroxyl radical activity and viscosity may follow a different mechanism than stabilization of Mn. The content of catalytic Mn was very low with 0.16 mg/kg and the Mg content 281 mg/kg, yielding a Mg/Mn ration of 4000, even before the extra addition of magnesium.
B1 Hydroxyl radical formation during hydrogen peroxide bleaching

36 (53)

Figure 26. Extended peroxide bleaching versus viscosity on the OOQ(OP)(PaaQ) pulp without and with addition of 0.05 % Mg.

Figure 27. Brightness increase during the extended peroxide bleaching of the OOQ(OP)(PaaQ) pulp, without and with addition of 0.05 % Mg.
According to STFI-Packforsk's Confidentiality Policy this report is assigned category 2

B1 Hydroxyl radical formation during hydrogen peroxide bleaching

6.6.3 Displacement of manganese by magnesium

Some of the results obtained in the project indicate that an increased hydroxyl radical activity may be detected in the bleaching liquor after the addition of magnesium. If the amount of magnesium ions is too low to form a stabilizing solid-solution, instead a higher activity was observed, than the expected lower.

Another possibility for interaction between manganese and magnesium ions is that both can act as counter ions to negatively charged carboxylic acids. If Mg$^{2+}$ ions are present in a large excess they may stoichiometrically displace other cations. It is for instance well known that Mg$^{2+}$ does replace Ca$^{2+}$ in oxalate. In this way magnesium ions may turn more of the manganese ions into solution, where they may act more efficient as a catalyst for hydrogen peroxide decomposition. An increased hydroxyl radical activity in solution is also easily detected by the soluble probe.

Acid conditions dissolve metal ions, for example MnCO$_3$, and simultaneously protonate the charged carboxylic acids that previously trapped the metal ions as counter ions. Thus an A-stage releases and make it possible to wash away metal ions. However, some carboxylic acids present in pulps are very acidic and stays ionized even at acidic conditions. For instance oxalic acid with its two carboxylic acid groups is ionized down to very low pH. Its pKa-values are 4.19 and 1.23, which means that half of the most acidic group in oxalic acid remains charged at pH 1.2. Some carbohydrate derived acids also remain charged at low pH, for instance isosaccharinic, 4-O-methyl-uronic and hexeneuronic acid with pKa-values around 3.5. It is possible to believe that a divalent Mn$^{2+}$ ion previously trapped via both of its charges only loses one of the linkages towards the pulp in an A-stage. Some of the catalytic trace metal ions can then not be washed away. We suggest that the remaining Mn$^{2+}$ ions can be more reactive as a catalyst for degradation of hydrogen peroxide into hydroxyl radicals after an A-stage.
The surrounding of the catalytic metal ion is changed from being very well located and thus satisfied between two charged groups that form a stable complex around the transition metal, to a less stable position.

A displacement of trace amounts of Mn$^{2+}$ ions by Mg$^{2+}$ ions in the solution may facilitate a locally increased formation of hydroxyl radicals. The soluble probe will pick up such an activity. However, such an increased hydroxyl radical activity will have no effect on pulp and its viscosity.

6.6.4 Influence of carry-over in P-stage

Some experiments were made to compare the “clean” lab-bleaching experiments with conditions prevailing in an industrial bleaching sequence. Addition of filtrate COD, NaOAc and Na$_2$CO$_3$ were done to the standardized P-stage. A “dirty” final PO-stage filtrate was used instead of pure water in a series of lab-bleaching experiments both in polyethylene bags and in vials for hydroxyl radical determinations. Thus a P-stage filtrate was added to the standardized P-stage performed on the OO and on the OOQ(OP)(PaaQ) pulps. The water added was partly replaced by a fresh OP-stage filtrate, the charge was based on analysis data of a lab and an industrial P-stage filtrate. The hydrogen peroxide charge was compensated for the residual peroxide and the added filtrate corresponded with 0.65 % (6.5 kg COD/t).

The possibilities to transform the reactive hydroxyl radical to a less reactive and thus more selective radical, the carbonate anion radical (CO$_3^{2-}$) were investigated. Acetic acid was added as a model for the COD and a substitute for the complex mixture in a filtrate. We have reasons to believe that the extremely reactive radicals that will react with the IPA probe also may react with added acetate or carbonate. To get a quantifiable amount of acetone 5 % of IPA was always present in the vial-bleaching experiments. This corresponded to 50 mg/g pulp or 0.832 mmol. The same molar amount of carbonate or acetate was added. The added probe will now have an added competitor for the radicals.
and a lower signal could then be expected, theoretically a bisected signal from acetone will then be obtained. Additional data are found in Appendix: Additions to the P-stage.

**Figure 30.** (OO)-pulp (a), (OO)Q(OP)(PaaQ)-pulp (b), 20 kg/t \( \text{H}_2\text{O}_2 \), no Mg-addition except for the “Mg-case”. Observe that in the mill Mg was also added in the (PaaQ)-stage.

**Figure 31.** (OO)-pulp (a), (OO)Q(OP)(PaaQ)-pulp (b), 20 kg/t \( \text{H}_2\text{O}_2 \). No Mg-addition except for the “Mg-case”.

The results from the standard lab-bleaching with additions showed that for the OO-pulp all peroxide had been used/degraded, while the OO(OP)(PaaQ) pulp had used about 50 % of the charge and 90 % in case of carbonate addition. No negative effects on brightness were observed except for addition of carbonate, a form of alkali. The effects on viscosity was absent for the more delignifying peroxide bleaching of the OO-pulp, maybe somewhat higher after the addition of Mg or carbonate. This same minor increase for Mg occurred on the OOQ(OP)(PaaQ)-pulp. However, all other additions had a significant negative effect on the more chromophore eliminating P-stage. The registered hydroxyl radical activities after the additions of soluble components; bleaching filtrate, carbonate or acetate the signal for hydroxyl radical formation was very low. This can be interpreted as a successful competition with the IPA probe resulting in less formation of acetone. The expected huge hydroxyl radical activity...
According to STFI-Packforsk's Confidentiality Policy this report is assigned category 2

B1 Hydroxyl radical formation during hydrogen peroxide bleaching

40 (53)

released by the transition metal containing OO pulp resulted in a low amount of acetone formed. The same amount of acetone was obtained if the same molar amount of carbonate or acetate was added. The additions scavenged the hydroxyl radicals, that is prevented them from reacting with the probe. The P-filtrate performed even better, resulting in a acetone formation measured as 7.1 mg/l compared to 10.9 and 10.6, respectively. The OOQ(OP)(PaaQ) pulp also resulted in very low acetone formation, 8.2 for the filtrate and 4.7 for carbonate, compared to about 17 when no additions were made. Raw data are listed in All experiments on pulps where hydroxyl radical activity was determined were made on the same amount of pulp, at the same pulp consistency and with the same concentration of probe. By keeping these conditions constant and performing a standardized P-bleaching stage different pulps and treatments of pulps can be evaluated.

Some additional non-published data from experiments made in connection with the master thesis work by L-E Åkerlund can be used to help evaluating the results from the experiments where additions were made of filtrate, carbonate and acetate. A low pulp consistency gave the highest amounts of acetone formed from the 5 % addition of IPA probe. In these experiments the hydroxyl radicals were not generated by a P-stage bleaching, instead they were “synthetically” generated from PON (peroxynitrite). The radical precursor, PON, is stable in the alkaline water phase and decomposes when pH is made acidic. Thus, the hydroxyl radicals were generated homogeneously in the water phase when pH was changed. The pulp was present as solid insoluble fibres, thus, they do compete but not efficiently with the dissolved probe. If the pulp consistency was lower than 5 % the amount of acetone formed from the reaction of hydroxyl radicals and the probe was almost constant from a specific addition of PON, which was quantitatively decomposed to hydroxyl radicals. The amount of pulp was varied to yield varying pulp consistencies of 20, 10, 5, 2.5, 1.25, 0.67 and 0.33 %. At 10 % pulp consistency the yield of acetone was significantly lower and at 20 % much lower. That is, at a high concentration of pulp the reactions with the soluble probe began to be driven out of competition. These experiments make it possible to conclude that the hydroxyl radicals formed homogeneously in solution are mainly trapped by the dissolved probe instead of reacting with the solid fibres present, as long as the pulp consistency is low. This should not be confused with the case when the radicals are formed during a P-stage by catalytic metal ions that are not homogenously distributed in the water solution.

If instead of pulp fibres a soluble polymer (PEG 4000) was added in corresponding concentrations [pulp consistencies] the scavenging of the homogenously formed hydroxyl radicals were much higher. Low amounts of polymers , homogenously present in the solution together drastically reduced the amount of acetone formed. The conclusion is that a soluble compound competes efficiently with the IPA probe. The graphs with the results from the experiments are enclosed in Appendix: Synthetic hydroxyl radical generation from peroxynitrite.

In a bleaching situation on pulps the hydroxyl radicals are generated from the positions where the catalytic metal ions are situated. For chemical pulps the most probable
positions are in the solid fibre phase. Now we can make the conclusion that it is not possible to compare different additions to the water solution, or bleaching filtrates in experiments where pulps are P-bleached, when the hydroxyl radical activity is to be determined by a soluble probe.

6.7 Sequential peroxide stages

A series of P-bleaching experiments were done on pulps that had been treated in a sequence of repeated P and Q-stages. However, the hydroxyl radical activities were too low to be quantified. That is, when the OOQ pulp was further lab bleached under the conditions of the standard P-stage and followed by one or more new Q-stages before the standard P-stage. All values for the acetone formation were very low and some values were too low to be reliable. Some of the raw data is enclosed in the appendix: Additions of magnesium. As a consequence, no lab-bleaching experiments in polyethylene bags for the purpose of comparison were made.
7 General discussion of conclusions

7.1 General discussion

Chain cleavages and loss of pulp viscosity is most often caused by either an attack by a hydroxyl radical or an acid catalysed hydrolysis. If an acid catalysis is the reason, then a proton is needed for attack on an oxygen linkage and simultaneously activate the glucosidic bond before it is hydrolysed by water. Protons, hydroxonium ions or the solvated hydroxonium complexes are relatively stable and the catalyst may penetrate into the pulp and attack the cellulose chains.

On the other hand, the lifetime, and thus the distance, that a hydroxyl radical may survive or travel is very short, nanoseconds and nanometres are discussed. Accordingly, the hydroxyl radical must be formed close to the polymer chain to be able to initiate cleavage of the cellulose. It can react with a water molecule forming a new hydroxyl radical, but also with all other organic compounds carrying hydrogen atoms. The hydroxyl radical will abstract any hydrogen leading to the formation of a less reactive intermediate.

How relevant is then a soluble probe method for hydroxyl radical activity determination? The use of a small soluble probe makes it possible to trap hydroxyl radicals formed in the vicinity of the cellulose polymer. However, only a fraction of the probe will be present close to the cellulose chain in the fibre wall during the short moment when the hydroxyl radical is active. The probe molecules present in the surrounding bleaching liquor will more frequent and hydroxyl radicals formed will then more easily find a probe molecule. Thus, the amount of acetone formed will reflect the overall hydroxyl radical activity. Anyway, a stable pulp with a low amount of catalytic metal ions will be mirrored by a low acetone formation, while an unstable pulp with a lot of or activated metal ions will be mirrored by a high acetone formation.

In controlled experiments the method can be used to yield quantitative numbers, which may be used for comparisons. However, in a mill situation differing amounts of dissolved material in the process liquor will compete with the IPA probe molecule for the hydroxyl radicals. The measured hydroxyl radical activity will be lower when dissolved components compete for the radicals. Fewer will find and react with the probe, yielding a misleadingly low hydroxyl radical activity.

7.2 Concluding discussion

Hydroxyl radical formation during peroxide bleaching has been claimed both theoretically and by experiments. Many of these could however be questioned, now the formation of hydroxyl radicals during P-bleaching conditions has been confirmed. Quantitative determination of hydroxyl radical activity in a P-stage is possible by the use of the IPA probe. Comparisons between different pre-treatments of a pulp can be
done by the addition of the same amount of probe at the same pulp consistency in a standardized peroxide lab-bleaching stage. The amount of acetone formed is a measure of the hydroxyl radical activity and it opens a possibility to measure the response or catalytic effect of the pulp towards the hydrogen peroxide present.

Hydroxyl radicals are formed by metal ion catalysed cleavage of hydrogen peroxide when and where the two reactants meet. If this happens in a homogenous solution the small and soluble IPA probe will have a good possibility to trap a fraction of the hydroxyl radicals and give an estimation of their activity in the sample. However, if the catalytic metal ions are present in the solid phase, that is in the fibre wall, on pulp surfaces or on fines, a lower response from the probe is expected. Active catalytic metal ions trapped deep in the fibre wall will decompose the entering hydrogen peroxide to hydroxyl radicals. This formation close to the polymeric cellulose may be most detrimental, since the hydroxyl radicals will react close to where they were formed. In such a case the concentration of pulp will be much higher than the concentration of IPA and a low amount of acetone will be formed. A low hydroxyl radical activity will then be observed, though the damage of the pulp quality may be high.

The hydroxyl radical activity during a P-stage performed in the laboratory on a pulp taken at different positions in the TCF bleaching sequence could be quantified. As expected, the pulps aimed for an industrial peroxide-stage, the OOQ and the OOQ(OP)(PaaQ) pulps, responded with a low formation of acetone. Thus, both pulps had obtained a good metal ion profile with a low amount of transition metals and a high Mg/Mn ration.

Hydroxyl radicals are suggested to result in a lower pulp viscosity. This has previously been shown by artificially generated radicals via gamma irradiation or via decomposition of peroxynitrite. The generation of hydroxyl radicals from hydrogen peroxide in a P-stage has now been confirmed during authentic conditions. A correlation between hydroxyl radical activity and loss of viscosity in a lab P-stage has also been shown. The formation of hydroxyl radicals accumulated over time in a P-stage, indicating a continuous generation. A lag phase with very low hydroxyl radical activity in the initial phase of a P-bleaching was initially observed, however it was out ruled.

A higher end-pH than the starting-pH may indicate a complete loss of residual peroxide and an extensive hydroxyl radical formation. An increasing pH in the P-stage may be used as an indication of high hydroxyl radical activity. Since transition metal ion catalysed decomposition of hydrogen peroxide to a hydroxyl radical is accompanied with the formation of an equivalent of hydroxide ions. The rising pH may be an applicable tool, which could signal if a pulp does not behave well in a P-stage.
8 Summarized conclusions

- Hydroxyl radical activities can be quantified during a standardised P-stage.
- The mill pulps aimed for a peroxide bleaching stage showed low hydroxyl radical activities in the P-stage.
- An initial lag-phase with low radical activity does not exist.
- Acetone accumulates in a P-stage over time, when IPA is present as a hydroxyl radical probe.
- When all hydrogen peroxide is consumed, the formation of new hydroxyl radicals ceases.
- The loss in pulp viscosity can be correlated with hydroxyl radical activity.
  - However, it was not possible to find a general correlation that made it possible to compare different pulps.
  - Catalytic metal ions located in the fibre close to cellulose will influence viscosity more than catalysts present of the surface of fibres and fines.
  - The amount of measured hydroxyl radicals detected by the probe was increased with increased accessibility to the metal ions.
  - The response from the probe was also affected by the presence of dissolved organic material, leading to competing reactions in the bleaching solution.
- An increased end-pH in relation to the starting-pH, may indicate a high hydroxyl radical activity and a complete consumption of peroxide.
- The complexing agents EDTA and DTPA efficiently reduced hydroxyl radical activity. The phenolic HBED complexing agent also removed metal ions, decreased radicals and increased brightness, however less efficiently.
- Control of manganese is a key to hydroxyl radical formation. However, not only the amount is critical but in which form or oxidation state it appears.
- All tested A-stage conditions increased hydroxyl radical formation in a subsequent P-stage.
  - The metal ions are solubilized by acid. However, the smaller amount of residual ions is left in a non-stabilised, more catalytically active form.
- Pulps that have been acid-treated yield a lower hydroxyl radical activity in a P-stage if the remaining metal ions are inactivated using a complexing agent.
- An extra addition of magnesium to the standardized P-stage had no significant effects on hydroxyl radical formation on any of the pulps obtained from the industrial bleaching sequence.
- A positive response from additional magnesium was observed when the pulp aimed for final bleaching (OOQ(OP)(PaaQ) was P-bleached with a prolonged reaction time, 7 h. Both a lower viscosity and a lower hydroxyl radical activity were achieved when 0.05 % MgSO₄ was added.
• Additions, for instance of a bleaching filtrate, had a negative effect on viscosity. However, the hydroxyl radical activity could then not be correctly quantified by the probe.
  o Hydroxyl radical formation during hydrogen peroxide bleaching can only be monitored in pure systems under controlled conditions.

8.1 Further work

There is an interest to measure hydroxyl radicals also in an oxygen stage. However, experimental problems exist with the overpressure needed to simulate an industrial O-stage bleaching and in the subsequent quantification of the volatile acetone formed. Even though these problems may be overcome the relevance of the quantitative hydroxyl radical determinations in an O-stage can be questioned.

The technique could be utilized to check if a specific treatment of an industrial pulp results in a different hydroxyl radical activity. It can also be used for comparing the effects of different pre-treatments.

Optimal addition of magnesium may also be a possibility to investigate by determination of the hydroxyl radical activity.
9 References


Cadenas, E. In DNA and free radicals; Ed. Ahmad, S., Ellis Horwood, Chichester, UK, 244 (1995).


10 Appendixes

10.1 Appendix: Reproducibility and accuracy

Reproducibility and accuracy of normalized determinations of acetone from peroxide bleaching experiments are discussed below. All the accounted results regarding hydroxyl radical activity from the bleaching experiments have been performed in triplicates. Only the individual samples taken over time in the kinetic experiment series were duplicates. The repeatability in the quantification of acetone by head-space GC/MS was very high. The more important overall reproducibility, that is the amount of acetone formed in a repeated experiment starting from weighing of pulp, additions of chemicals and bleaching followed by acetone determinations were high. The reproducibility in the acetone quantification as a measure for hydroxyl radical activity have been calculated by comparing the individual determinations for each sample and the standard deviation for the normalized values was found to be 0.135 (CV = 13.5 %). The calculation is based on 86 individual experiments and obvious outliers have been excluded, for instance a leaking sample vial.

After the reproducibility of acetone determination was estimated, we experienced that if the determinations by GC/MS were performed over a long period of time we needed to recalibrate the instrument, since he setting for the multipliers had been changed. This is not a problem when the usual use of internal standards is applied. However, in this investigation an internal standard could not be used, because it is reactive towards the hydroxyl radicals aimed to be quantified. Thus, a series of three solutions of known acetone concentrations were determined in connection with each series of bleaching experiments to be analysed for acetone. That is, the later experiments are associated with an external calibration curve for each series of experiments.

A reservation has to be made. After the reproducibility of the method based on quantification of acetone had been done, only obvious outliers and mistakes were left out when the results were collected. That is, pulp samples were not always excluded when the spreading was statistically too wide especially when very low signals were obtained.

10.2 Appendix: Additions of magnesium

Formation of hydroxyl radicals (arbitrary units) in a standardized P-stage made on mill pulps compared to the formation of hydroxyl radicals on the same pulps after addition of magnesium salt.
According to STFI-Packforsk’s Confidentiality Policy this report is assigned category 2

B1 Hydroxyl radical formation during hydrogen peroxide bleaching

49 (53)

<table>
<thead>
<tr>
<th>Addition of magnesium to industrial pulps</th>
<th>With addition of 0.05 % MgSO₄ (raw data)</th>
<th>Remaining hydroxyl radical activity with Mg (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp</td>
<td>No MgSO₄ addition (raw data)</td>
<td></td>
</tr>
<tr>
<td>OO</td>
<td>0.329</td>
<td>100 %</td>
</tr>
<tr>
<td>OOQ</td>
<td>0.145</td>
<td>96 %</td>
</tr>
<tr>
<td>OOQ(OP)</td>
<td>0.273</td>
<td>82 %</td>
</tr>
<tr>
<td>OOQ(OP)(PaaQ)</td>
<td>0.254</td>
<td>70 %</td>
</tr>
<tr>
<td>OOQ(OP)(PaaQ)(PO)</td>
<td>0.274</td>
<td>82 %</td>
</tr>
</tbody>
</table>

Previous experiment that was replaced by the one given above

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Raw data (mg/l acetone)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OOQ</td>
<td>0.1254</td>
</tr>
<tr>
<td>OOQ(OP)</td>
<td>0.1160</td>
</tr>
</tbody>
</table>

Extended P-bleaching of the OOQ(OP)(PaaQ) pulp with and without addition of Mg showed a big difference.

<table>
<thead>
<tr>
<th>Hydroxyl radical activity (mg/l acetone)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OOQ(OP)(PaaQ) 120 min + MgSO₄ 0.05%</td>
</tr>
<tr>
<td>OOQ(OP)(PaaQ) 300 min + MgSO₄ 0.05%</td>
</tr>
<tr>
<td>OOQ(OP)(PaaQ) 360 min + MgSO₄ 0.05%</td>
</tr>
<tr>
<td>OOQ(OP)(PaaQ) 420 min + MgSO₄ 0.05%</td>
</tr>
</tbody>
</table>

Generally the signals related to hydroxyl radical activities were low in all experiments where repeated and sequential standardized P-stage bleachings were made. Since the absolute amount of acetone formed were too low, the results could not be used to draw significant conclusions. However, some trends were seen after different additions of magnesium and the data are collected in the following table.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ac</th>
<th>Raw data</th>
</tr>
</thead>
<tbody>
<tr>
<td>22-2 PQ (050831a)</td>
<td>4.6</td>
<td>0.031860</td>
</tr>
<tr>
<td>22-2 PQ (050831a) + MgSO₄ 0.005%</td>
<td>3.7</td>
<td>0.025333</td>
</tr>
<tr>
<td>22-2 PQ (050831a) + MgSO₄ 0.05%</td>
<td>5.5</td>
<td>0.037983</td>
</tr>
<tr>
<td>22-2 PQ (050831a) + MgSO₄ 0.1%</td>
<td>8.0</td>
<td>0.055060</td>
</tr>
<tr>
<td>21-2 PQP (050831b)</td>
<td>5.6</td>
<td>0.038857</td>
</tr>
<tr>
<td>21-2 PQP (050831b) + MgSO₄ 0.005%</td>
<td>5.2</td>
<td>0.035623</td>
</tr>
<tr>
<td>21-2 PQP (050831b) + MgSO₄ 0.05%</td>
<td>6.7</td>
<td>0.046077</td>
</tr>
<tr>
<td>21-2 PQP (050831b) + MgSO₄ 0.1%</td>
<td>8.0</td>
<td>0.055247</td>
</tr>
</tbody>
</table>
B1 Hydroxyl radical formation during hydrogen peroxide bleaching

50 (53)

10.3 Appendix: Additions to the P-stage.

Addition of COD, carbonate and acetate to the P-stage (PO)-stage filtrate, charge 0,65 % COD

NaAc: 0,0682 g/g
Na₂CO₃: 0,0882 g/g

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hydroxyl radical activity (mg/l acetone)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OO P-filtrat</td>
<td>7,1</td>
</tr>
<tr>
<td>OO karbonat</td>
<td>10,9</td>
</tr>
<tr>
<td>OO HOAc</td>
<td>10,6</td>
</tr>
<tr>
<td>OOQ(OP)(PaaQ) P-filtrat</td>
<td>8,2</td>
</tr>
<tr>
<td>OOQ(OP)(PaaQ) karbonat</td>
<td>4,7</td>
</tr>
<tr>
<td>OOQ(OP)(PaaQ) HOAc</td>
<td>failed</td>
</tr>
</tbody>
</table>

10.4 Appendix: Synthetic hydroxyl radical generation from peroxynitrite.

Relative comparisons of the hydroxyl radical activity detected by the soluble IPA probe were made using an insoluble (pulp) and a soluble (PEG) polymer at increasing concentrations. At a low pulp consistency, below 5 % (2.5 % was used in the experiments), the signal obtained from the reaction with the probe was not strongly dependant on the solid pulp present. At higher pulp consistencies the signal was four to five times lower. Even very low concentrations of a soluble polymer drastically reduced the signal from the IPA probe.
The signal for hydroxyl radical activity in the bleaching experiments was not significantly scavenged if the pulp consistency was kept low.

A soluble polymer added in the same concentrations as pulp (see the figure above) scavenged the probe at very low concentrations.
10.5 **Appendix: Complexing agents for metal ion removal**

Chemical structure of the complexing agents EDTA and DTPA used in pulp mills to remove transition metal ions.

Complexing agents that might work for trapping of transition metal ions at high pH (EDDHMA, EDDHA and the tested HBED).

10.6 **Appendix: Addition of manganese ions.**

The theoretical thoughts behind the experiments when Mn was added to a pulp are illustrated in the chemical drawing below.

**OOQ-pulp** A Q-stage traps and removes Mn and leave the pulp in Na-form.

**OOQMn-pulp** Addition of the Mn followed by formation of inorganic Mn compounds before P-bleaching.
pulp OOQ

\[
\begin{align*}
\text{addition of} & \quad 20 \text{ mg Mn / kg pulp} \\
\end{align*}
\]

\begin{align*}
\text{Mn(NO}_3\text{)}_2 & \quad \text{Fatty acid salt (sodium palmitate, } C_{15}\text{COO}^- \text{ Na}^+ \text{)} \\
\text{OOQMnF-pulp} & \quad \text{Addition of the Mn followed by trapping of Mn in the pulp before P-bleaching.}
\end{align*}

pulp OOQ

\[
\begin{align*}
\text{addition of} & \quad 20 \text{ mg Mn / kg pulp} \\
\text{Mn(NO}_3\text{)}_2 & \quad \text{Fatty acid salt (sodium palmitate, } C_{15}\text{COO}^- \text{ Na}^+ \text{)} \\
\end{align*}
\]

\begin{align*}
\text{OOQFMn-pulp} & \quad \text{Addition of the Mn in the presence of a fatty acid salt, i.e. trapping of Mn on the pulp before P-bleaching.}
\end{align*}