

## Use of TOF-SIMS for the analysis of surface metals in H<sub>2</sub>O<sub>2</sub>-bleached lignocellulosic fibers\*

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**Abstract:** Oxidation of cellulose, caused by metal-catalyzed hydrogen peroxide decomposition, is one of the main potential reactions that can occur during the alkaline peroxide bleaching of pulp. This oxidation decreases the individual fiber strength and thus the sheet strength. The bleaching reaction should be controlled to limit cellulose degradation. The goal of this project was to characterize the fiber surface metal distribution using time-of-flight secondary ion mass spectrometry (TOF-SIMS) on laboratory-generated hydrogen peroxide-bleached pulps.

For this study, a single black spruce was chosen and kraft pulped. Peroxide bleaching was conducted via benchtop polyethylene bag bleaching in a temperature-controlled water-bath. The overall metals content was determined using inductively coupled plasma (ICP), whereas the surface metals were determined with TOF-SIMS. Many fundamental approaches to study metal identity and content in fibers have been undertaken, including ICP, electron spectroscopy for chemical analysis (ESCA), X-ray fluorescence, and UV–vis. None of these methods can provide the localized density distribution and metal-mapping ability that is available through TOF-SIMS. It has spectacular imaging capabilities that were exploited for evaluating metals on the fiber sheets used in this work.

The samples were subjected to other sheet and fiber testing. Tests conducted on select samples included brightness and viscosity. Factors in this experiment included metal addition, chelation, and peroxide charge.

### INTRODUCTION

The practice of pulp bleaching has undergone a paradigmatic shift in North America during the past several decades, mainly in response to environmental and societal pressures. The use of environmentally compatible bleaching chemicals based on oxygen, such as hydrogen peroxide, has grown to the point where the pulp and paper industry, as well as the textile industry, employ a combined total of approximately 300 K tons of hydrogen peroxide annually [1]. Hydrogen peroxide in particular is a potent, relatively inexpensive oxidant that chemically degrades chromophoric components in pulps and textiles very efficiently to generate by-products that have very low color, no AOX content, low chemical oxygen demand (COD), and excellent solubility. The generation of the active species for alkaline peroxide bleaching can be seen in reaction 1.



The peroxide anion can then react with an *o*-quinone or a conjugated carbonyl structure via a Michael addition or undergo a Dakin reaction with lignin structures. These reactions generally do not remove the lignin, but just remove conjugation and thus color. This can lead to higher pulp yields.

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However, despite its attractive bleaching and economic incentives, it suffers from the drawback of undergoing rapid disproportionation in the presence of transition-metal ions such as iron, copper, and manganese. The disproportionation reaction is very rapid and exothermic; it can be described by reaction 2 using iron as a typical metal reductant [2].



The two most important implications of reaction 2 are the inefficient consumption of hydrogen peroxide and the production of the highly reactive hydroxyl radical. Hydroxyl radical has the ability to severely damage the integrity of the carbohydrates that constitute the pulp as well as lead to Fenton-type reactions leading to other radical species [3].

This degradation is important, as it can lead to decreases in fiber and thus paper sheet strength as it is governed by the Page equation below (eq. 3) [4].

$$\frac{1}{T} = \frac{9}{8 \cdot Z} + \frac{3 \cdot w_f}{\tau_b \cdot l_f \cdot \text{RBA}} \quad (3)$$

$T$  = tensile strength

$Z$  = zero span strength

$w_f$  = fiber width

$\tau_b$  = breaking force of bond over bond area

$l_f$  = fiber length

RBA = relative bonded area

As the strength of the fiber decreases, if all other factors are held constant, the tensile strength of the paper sheet will decrease. Most industrial papers are considered well bonded, and thus the sheet strength is strongly correlated with fiber strength [4].

In all technical operations that use hydrogen peroxide, maximum bleaching performance requires activation of the peroxide and protection of the pulp. Although hydrogen peroxide bleaching is activated under alkaline conditions, protection of the pulp requires a metals management program. A chelation stage is typically installed prior to a peroxide (P) stage to bind deleterious transition metals, although some mills add  $\text{MgSO}_4$ , silicates, or chelants directly to a P stage to act as pulp protectors. The brightness response of pulps from hydrogen peroxide bleaching is a function of controlling the decomposition reactions arising from metal-induced disproportionation reactions to maximize availability of the oxidant.

The present work describes the brightness gains observed for a black spruce tree that has been separated into its constituent juvenile and mature pulp fibers. Remarkably, pronounced brightness differences have been obtained as a function of the metal distribution and process parameters used in the current study. Physical measurements including viscosity (indirect measure of cellulose degree of polymerization) have also been obtained to identify the degradation patterns and offer potential explanations or supporting evidence for the brightness differences. TOF-SIMS has been utilized to look at surface metals distribution and offer potential indirect measurement of the hydrogen peroxide decomposition.

## EXPERIMENTAL

### Black spruce pulp manufacture

A whole, defect-free black spruce tree approximately 40 years old was obtained courtesy of Consolidated Papers, Inc., in Wisconsin and was shipped to the Institute of Paper Science and Technology in Atlanta, Georgia for chipping at its industrial chipper. The tree sections were separated into juvenile and mature fiber sections by removing the top eight (8) feet of the tree (juvenile fiber) from the remainder. The sections were debarked by hand and split into cords for chipping. After chipping, all

chips were screened for undersized and oversized rejects; the accepts were 2–8 mm chip fractions that were shipped to Potlatch Company (Duluth, Minnesota). All pulp samples were maintained in a refrigerated environment, whereas all chips were kept in frozen storage.

### Bleaching and physical/chemical testing

All bleaching was done using Kapac polyethylene bags by adding the requisite chemicals (either 1.5% or 3% H<sub>2</sub>O<sub>2</sub>). NaOH (10%) was added to increase the pH to 11–12 and additives (EDTA, MgSO<sub>4</sub> each of the previous at 1% concentration relative to pulp mass, or 50 ppm iron) and all pulps had a consistency of 10%. The bags were heated to temperature (70 or 90 °C) in a hot bath for 60 min. Viscosity, brightness, <sup>31</sup>P, NMR and SEM data were collected for select samples on the appropriate instruments according to standard TAPPI and/or operational procedures as described in the results section. TOF-SIMS is described in greater detail due to its uniqueness.

### TOF-SIMS

Approximately 1 cm<sup>2</sup> pieces were cut from the center of the paper samples created from pulps using TAPPI standard methods. Each piece was mounted under a large mesh grid to facilitate charge compensation. TOF-SIMS conducted by analytical services of EVANS PHI, a member of the Evans Analytical Group. Details on the operation of this technique can be found in the conditions below and in the discussion.

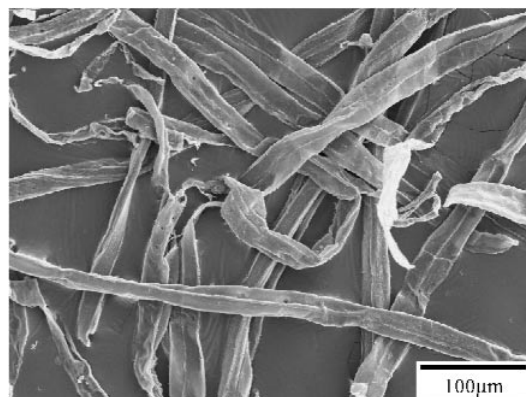
### Analytical conditions

Instrument	Physical Electronics TRIFT II
Primary ion beam	<sup>69</sup> Ga LMIG (bunched)
Primary beam potential	12 kV (+)
Primary ion current (DC)	2 nA
Nominal analysis region	150 × 150 μm
Charge neutralization (~20 eV)	Yes
Post acceleration	5 kV (+)
Masses blanked	No
Energy filter/contrast diaphragm	No/No

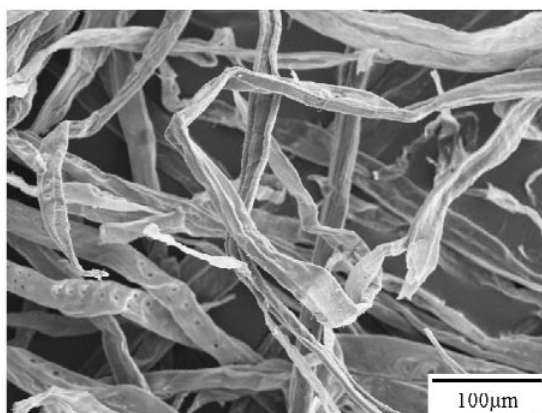
### DISCUSSION

Attempts were made to visualize the peroxide degradation of wood pulps through SEM microscopy, but this proved to be very difficult in a number of respects. In the preparation of the spruce pulps, care was taken to minimize physical damage to the chips in order to more greatly distinguish chemical from physical damage. Even with the extra levels of care, however, physical and possibly pulping degradations were present on the unbleached samples. It is difficult to always tell the difference between physical and chemical degradation. When looking at limited samples of bleached and unbleached pulps, even when bleached samples were “doped” with 50 ppm of iron to induce greater degradation, it was difficult to differentiate the level of degradations on the pulps through SEM. Through the study of the changes in viscosity converted to chain cuts seen later in Fig. 12, we know the samples were successfully degraded. Samples of cotton bleached with peroxide did show possible signs of degradation, but the spruce pulps, including a holocellulose pulp made from the same spruce wood, did not. Cotton was used as a reference as peroxide bleaching degradation successfully studied with SEM can be found in the literature [5]. The reason for the difference in the appearance of visible degradations between these

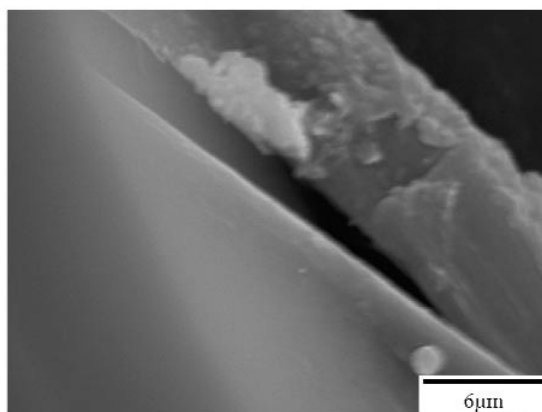
two lingo-cellulosic substrates is still not well understood. Sample micrographs can be seen in the following images, Figs. 1–3.



**Fig. 1** SEM of unbleached mature black spruce fibers.



**Fig. 2** SEM of bleached mature black spruce fibers.



**Fig. 3** SEM of bleached cotton with 50 ppm Fe.

To try to better understand the degradation on wood species a relatively new technique, TOF-SIMS, was employed. This is a powerful surface analysis technique that has begun to be used in pulp and paper, but also has numerous applications to other surface-orientated study including semiconductors [6–8]. TOF-SIMS also has the capability to display SEM style images that allow for location of compounds or elements on material surfaces. The use of TOF-SIMS for this application is described elsewhere [10]. TOF-SIMS is one of many surface analysis techniques that can be used to visualize surface groups or metals. The work of Barzyk *et al.* showed the use of a scanning electron microscopy-energy dispersive X-ray (SEM-EDS) technique to locate calcium bound to carboxylic acid groups across the fiber profile [9]. TOF-SIMS is advantageous in that it allows for the visualization of both molecular and elemental constituents [6]. Recent pulp and paper studies have included work by Kleen and others looking at the surface and bulk metals correlations as well as extractives content [11,12].

Through our work, it was found that the distribution of surface metals appeared to be different between peroxide-bleached and unbleached samples utilizing the imaging capabilities of TOF-SIMS that provide an SEM style image. A possible explanation for this distribution difference could be due to carbohydrate degradation as the end-groups remaining after degradation would be carboxylic groups. These carboxylic groups could bind the loose metals. Thus, the localizations of metals we see could actually be due to the localization of degradation and the corresponding available end-groups. It was originally hoped to use the carboxylic acid groups themselves to track the degradation, but the metals potentially bound to the acid allowed for better, although indirect viewing. There are several other pieces of evidence for this theory. When an unbleached sample is compared to a standard bleached sample and then to a sample “doped” with 50 ppm Fe, one can see an increase in localization of metals. TOF-SIMS images can be seen in Figs. 4–7.

This is most likely due to the fact that the Fe should cause more degradation of the peroxide into radicals and thus more damage to the carbohydrates leading to more end-groups and more metals localization. It is most likely that we were are looking at a surface degradation phenomenon through the TOF-SIMS, only a couple of molecules deep, that current microscopy experiments have been unable to detect.

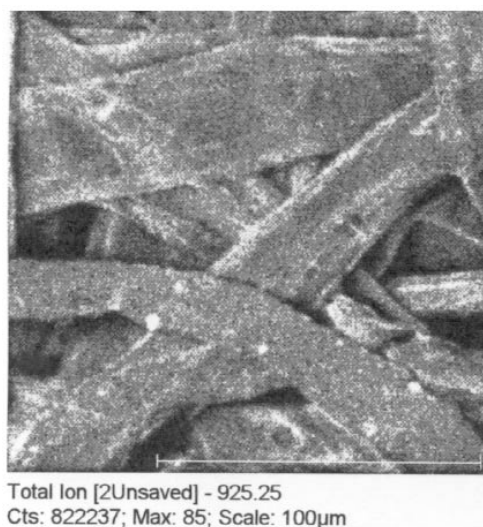
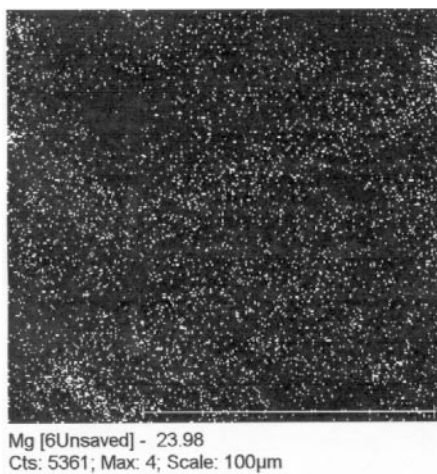
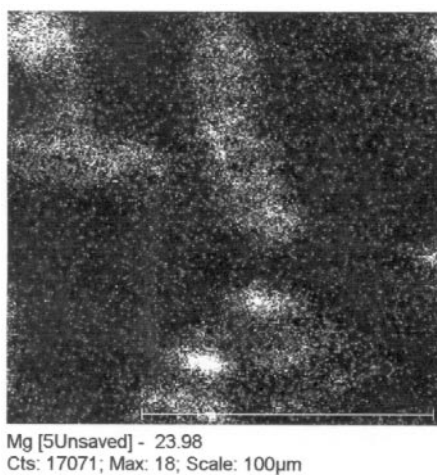


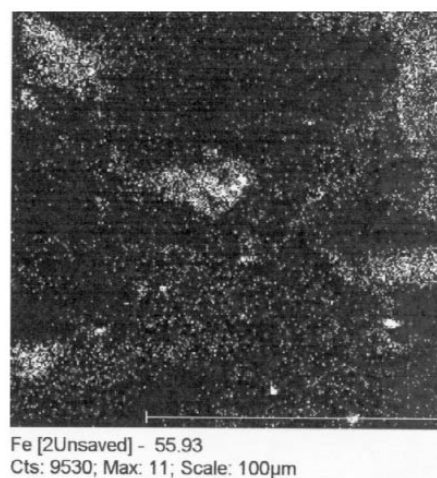
Fig. 4 TOF-SIMS total ion image of bleached mature fibers with 50 ppm Fe.



**Fig. 5** TOF-SIMS Mg image of unbleached mature fibers.



**Fig. 6** TOF-SIMS Mg image of bleached mature fibers.



**Fig. 7** TOF-SIMS Fe image of 50 ppm Fe "doped" bleached sample.

### Study of brightness before and after peroxide bleaching

One of the more surprising initial findings that stimulated this work in part was the unprecedented observation that strong brightness differences existed between juvenile and mature fibers after an oxygen delignification stage. Juvenile and mature handsheets obtained following a standard oxygen delignification run had a 3–5 ISO brightness difference relative to approximately the same starting brightness for both unbleached pulp samples. Not surprisingly, this difference manifested itself in hydrogen peroxide bleaching stages, though the differences were not as pronounced as observed for the oxygen delignification stage. Nonetheless, the results suggested that a chemical basis must exist for this brightness difference and subsequent peroxide-bleaching experiments were conducted. Based on extensive literature precedent, a strong basis for the bleaching differences lies in the metal ion identities and concentrations [13–20]. ICP was used to obtain the metal ion profile for the unbleached fibers, and the results are shown in Table 1.

All peroxide bleaches of these fibers were conducted according to an algorithm that consisted of a hydrogen peroxide charge of 1.5 or 3.0%, a temperature of 70 or 90 °C, and the inclusion of three separate additives (EDTA, MgSO<sub>4</sub>, or 50 ppm Fe<sup>+2</sup>). The oxygen bleaching was conducted in a PARR Instruments pressure bomb at 10% solid pulp content, 2.5% w/w dry pulp of NaOH, and an O<sub>2</sub> pressure of 500 kPa. Since providing a list of all the data obtained would be too cumbersome for the scope of this paper, the most salient data to explain the trends of our work will be presented for discussion.

The brightness data provided some very intriguing trends between the juvenile and mature pulps. Even though the pulps began with similar brightness, metals content, and physical properties, the brightness after an oxygen or peroxide-bleaching stage was different. The starting fiber properties are shown in Table 2. The fiber quality, coarseness, and length data were obtained on an OpTest Equipment FQA (Fiber Quality Analyzer). Kappa is a measurement of lignin content (0.15 \* kappa = % lignin). Viscosity was measured with the CED method and brightness with the ISO method on random handsheets. Breaking length was measured on a random handsheet using the TAPPI standard zero-span tensile test.

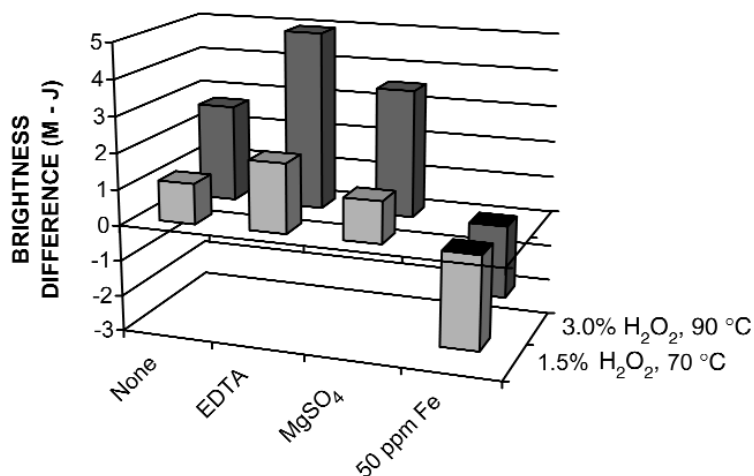
Figure 8 shows the brightness differences between a series of mature and juvenile peroxide samples plotted as a function of the conditions employed during the run.

**Table 1** Metals content, as measured by ICP, for juvenile and mature fibers.

Metal	Juvenile	Mature
Ba	24.2	25.0
Ca	1295.0	1290.0
Cu	19.8	19.6
Fe	32.7	19.0
Mg	189.0	170.0
Mn	191.0	150.0

**Table 2** Physical properties of juvenile and mature fibers.

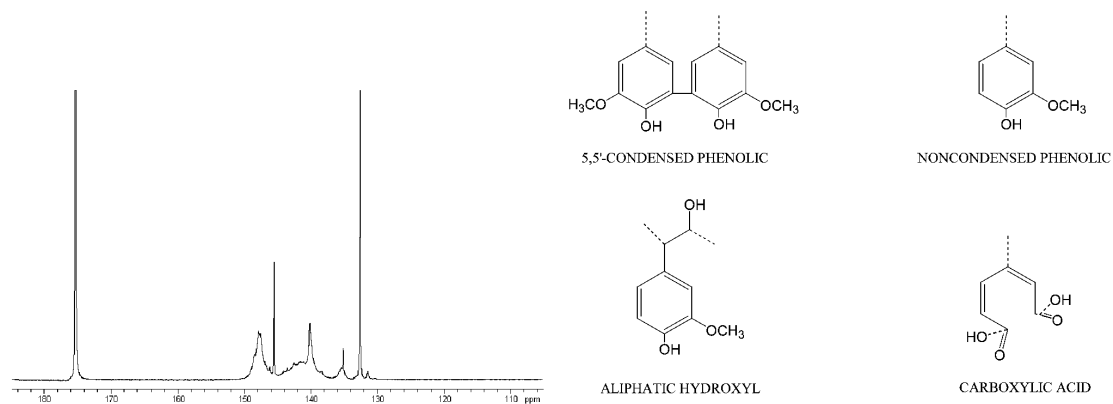
Sample	Brightness	Freeness	Breaking length	Viscosity	Length	Coarseness
Units	ISO	mL	km	cP	mm	mg/m
Juvenile	36.82	710	13.66	24.89	2.227	0.127
Mature	36.48	710	15.38	22.96	2.367	0.139



**Fig. 8** ISO brightness difference between juvenile and mature wood for peroxide bleaching.

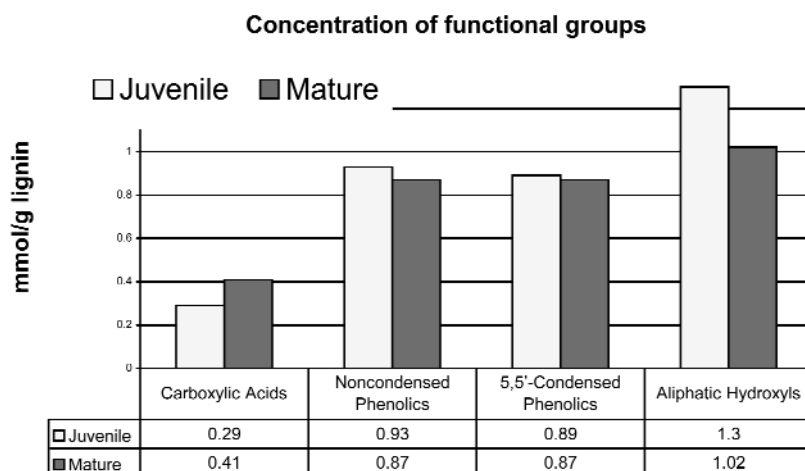
The addition of iron (iron II chloride) caused the pulps to diminish their brightness, but the attenuation among the pulps was reproducible and varied in the same manner despite the fact that the fibers were from the same tree. These results show that varying the bleaching conditions can vary the brightness difference between the juvenile and mature fibers.

These differences could in part be due to lignin differences. NMR was run on juvenile and mature samples. All spectroscopic NMR data was obtained on a 400 MHz field Bruker NMR spectrometer employing <sup>31</sup>P NMR sample preparation and spectral collection parameters that have been previously published [21]. The NMR data are based on distinct structural features of lignin that are classified as the carboxylic acids (typically a result of severe ring oxidation), 5,5'-condensed phenolics, noncondensed phenolics, and aliphatic hydroxyls. The concentrations of these structural units are quantified relative to an internal standard and are accurate for the sample of lignin under interrogation. Since our yields for residual lignin isolation are on the order of 50–70%, we do not make absolute statements about the lignin nature, but past work bears out the general usefulness and legitimacy of this method [22–24]. Figure 9 shows a typical <sup>31</sup>P NMR spectrum of the residual lignin isolated from juvenile spruce pulp and selected example structures from lignin.



**Fig. 9** <sup>31</sup>P NMR of extracted mature pulp lignin and common lignin structures.



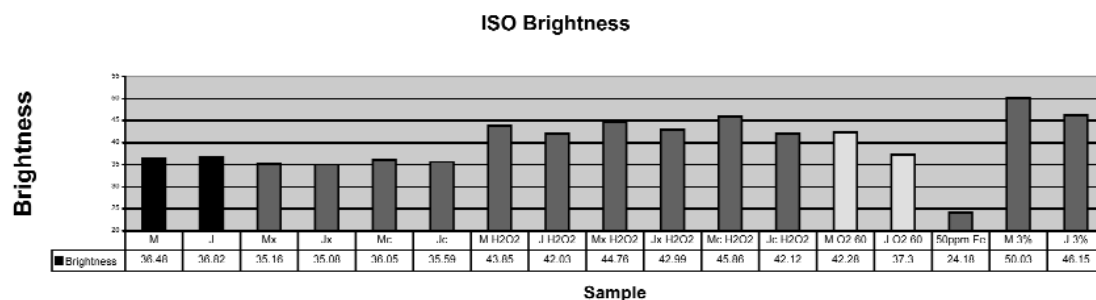


**Fig. 10** Measured amounts of lignin structural groups for juvenile and mature lignin samples.

Figure 10 shows a comparison between the lignin extracted from juvenile and mature fibers. Although the differences are small, the differences in carboxylic content could lead to differing ease and amounts of bound metals and differences in aliphatic content could affect bleachability.

Attempts were also made to eliminate extractives (fatty acids, resins, waxes) and differences in metals distribution as potential causes. For this, an acetone extraction and a chelation reaction were conducted on both the juvenile and mature fibers. Both of these procedures did not eliminate the brightening difference between juvenile and mature fiber or drastically change the starting brightness. The results of these studies, as well as a comparison to the standard 1.5% peroxide bleach, a 3% peroxide bleach, and an oxygen bleach, can be found in Figure 11. In this figure, M and J stand for juvenile and mature respectively with all bleaches at 1.5% peroxide charge with the exception of the 3% reactions (the subscripts x and c stand for extracted and chelated, respectively).

The importance of this data is that as the ratio of juvenile to mature wood is changed for a given bleaching reaction the brightness will be affected. This will translate to a change in final product quality or changes in the bleaching reaction to compensate, which could lead to increased cost and variability. As “old-growth” timber becomes less available, it will be replaced with faster-growing or younger trees with a greater juvenile wood character. These results point to important implications of this change.



**Fig. 11** ISO brightness comparison of juvenile and mature bleached and unbleached samples where c and x stand for chelated and acetone extracted respectively.

### Study of degradation before and after peroxide bleaching

The physical properties of the pulps were also tested by using standard CED viscosity measurements to evaluate degradation during the brightening reactions. All viscosity information was converted to the appropriate DP (degree of polymerization), which was compared to the original DP ( $DP_0$ ) to yield a chain scission count ( $[1/DP - 1/DP_0]DP_0$ ) that reflects the integrity of the cellulose chains. The larger numbers are indicative of greater chain damage. Figure 12 illustrates the degradation in the fibers as a function of selected conditions for juvenile and mature wood.

The physical damage was principally measured by CED viscosity, using zero-span and fiber quality as supporting evidence. All spruce pulps were damaged to some extent during the course of the bleaching. The lignin levels were not reduced, and the SEM/TOF-SIMS studies show that fiber damage is more of a surface phenomenon than those seen in textiles. The clear ramification of this finding is the diffuse nature of the carbohydrate damage in pulps that translates to cellulose chain scission and a decrease in the tensile fiber strength.

For the juvenile fibers, the most obvious damage was incurred with the iron doping. Chain scissions of up to 0.29 (not shown) were obtained as compared to 0.03 under "mild" conditions (low temperature and hydrogen peroxide charge) with no doping. As can be seen in Fig. 3, the effect of increasing bleach concentration and temperature induces further damage, but the damage is not precipitous with iron doping. The underlying factor contributing to this response may be the nature of the pulp. In juvenile tree sections, there is a greater abundance of tension wood that is more difficult to pulp or bleach due to the higher levels of lignin. The lignin may act to react more efficiently with radicals or other deleterious substances, thus "protecting" the pulp. The influence of additives such as EDTA and  $MgSO_4$  was not apparent until more forcing conditions (high temperature and high hydrogen peroxide charge) were used, in which case the chain scission was reduced by up to 50%. The manganese ion was probably redox-stabilized by inclusion in an isomorphous magnesium complex, and EDTA was able to effectively compete for copper and manganese in solution. Despite the efficacy of the above additives, degradation is still a concern since iron is known to undergo self-hydrolysis, chelate very strongly, and is thus very difficult to completely remove, allowing it to engage in Fenton-type reactions that lead to the compromise of the pulp physical properties.

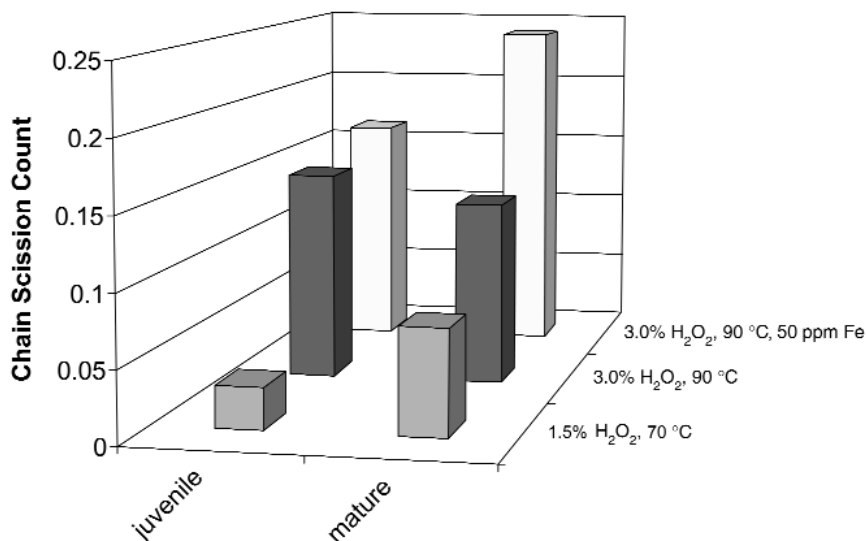


Fig. 12 Comparison of degradation between juvenile and mature fibers for peroxide bleaching.

The mature spruce pulp has a very similar response to the juvenile pulp as shown in Fig. 12, but under iron doping, it has approximately a two-fold drop in the scission count. Not too surprisingly, neither  $\text{MgSO}_4$  nor EDTA are as effective as evidenced in the juvenile pulp for controlling viscosity. As indicated earlier, the mature pulp has a much higher level of acids that tend to promote enhanced chelation of iron. Interestingly, from a TOF-SIMS surface profile, iron ions tend to agglomerate in scattered pockets upon doping. Since it is known that the self-hydrolysis of iron disfavors EDTA trapping, the response of the mature pulp was expected, undergoing a serious loss in pulp integrity after increasing the iron content by a factor of almost three-fold. What is most surprising is that  $\text{MgSO}_4$  was not as effective for pulp protection as witnessed in the juvenile pulp.

The juvenile and mature fibers found in spruce pulp display different chemical responses arising from structural differences in their residual lignins. Their ability to chelate iron ions varies and can easily be gleaned from the brightness data obtained from the “doped” samples. The physical degradation of the spruce pulp fibers is also a function of the ease or difficulty associated with chelating detrimental metal ion species such as iron or copper. Commercial sheets typically exhibit failure due to defects in individual fibers instead of relative bonded area, and thus fiber degradation associated with bleaching should be minimized.

## SUMMARY

Most metals appear heterogeneously distributed on fiber surface of bleached samples, but more homogeneous on unbleached samples. Concentrations of metals may be due to carboxyl end-groups remaining from bleaching-induced degradation of cellulose. The physical and chemical characteristics of juvenile and mature fibers obtained from the same black spruce tree (*Picea mariana*) have been investigated before and after hydrogen peroxide bleaching to evaluate the observed differences in their individual brightness response after hydrogen peroxide bleaching. Mature fibers, in general, after either hydrogen peroxide bleaching or oxygen delignification display a greater propensity to brighten, but also tend to degrade at a faster rate than the juvenile fibers. This result may be a function of the differing metal distribution found in the fibers and in turn may be a direct consequence of the lignin structural characteristics and metal affinity for the fiber surface. These differences will become more important as the use of old-growth timber in the paper industry is replaced with faster-growing trees and younger with a higher juvenile wood content.

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