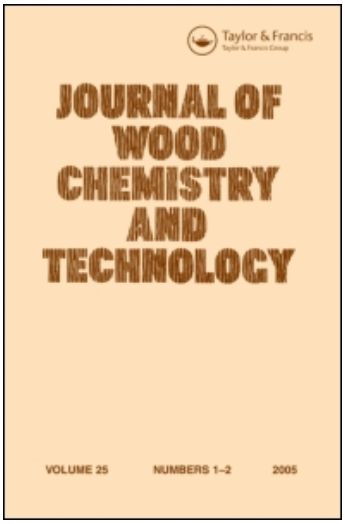

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The Distribution of Chlorine in Chlorinated Kraft Pulp Fibers from Spruce Wood as Determined by Tem-Edxa

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THE DISTRIBUTION OF CHLORINE IN CHLORINATED KRAFT PULP FIBERS FROM SPRUCE WOOD AS DETERMINED BY TEM-EDXA

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ABSTRACT

The chlorine contents in different morphological regions of chlorinated spruce kraft pulp fibers were determined by the TEM-EDXA technique. Observations were made before and after extraction with aqueous NaOH. The highest chlorine content was found in a spot in the cell corner primary wall. In the primary wall between the cell corners the chlorine content was lower than that at the cell corner but higher than that in the secondary wall. After the extraction stage, there was a low and approximately equal concentration of chlorine in all the morphological regions studied.

INTRODUCTION

We bleach our pulps with chlorine. It is an expensive and widely used process. Also the chlorolignins released in the extraction process may pose difficult problems environmentally. It is therefore important that we understand as far as possible the way in which chlorine reacts with the lignin in the pulp in order to modify and improve the process.

Although the topochemistry of pulping has been studied for many years,[1-5] there is little known about the topochemistry of bleaching.

Whereabouts in the fiber does the chlorine react with the lignin?

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From what region of the fiber is the chlorolignin extracted?

What is the distribution of chlorolignin in the fiber after chlorination and extraction?

The purpose of the present work was to seek answers to the questions above.

Kraft pulp fibers were chlorinated and the distribution of chlorine in the various morphological regions of the fiber was observed by transmission electron microscopy coupled with energy dispersion X-ray analysis (TEM-EDXA). The distribution of chlorine residual after alkaline extraction was also investigated. The methods used have been discussed in a previous report.[6]

EXPERIMENTAL

Small sticks (RxTxL = 0.1x0.1x1 cm) of black spruce earlywood were cooked in a bomb heated in an oil bath. The cooking conditions and the properties of the resulting pulp are listed in Table 1.

Some of the sticks were held in a small cage of stainless steel wire-mesh during the cook. In this way the shape of the original wood was retained. The sticks cooked in the wire-mesh cage were thoroughly washed and then chlorinated for 10 min according to the method described previously.[6] Some of the chlorinated pulp sticks were extracted with aqueous NaOH (5%) at 60°C for 10 min.

Table 1.

Cooking Conditions and the Properties of Pulp Produced

Effective alkali	31.0 $g.L^{-1}$ (Na_2O)
Sulphidity	30%
Liquor/Wood ratio	10:1
Temperature	150°C
Time	3 h
Pulp yield	52%
Kappa No.	50.8
Lignin content (Klason lignin)	7.7%

The chlorinated and extracted samples were dehydrated by freeze-drying, embedded in Vestopal W resin and cured at 70°C for 12 hours. This resin was found to be more suitable than methacrylate resin because of its stability in the electron beam. Like methacrylate, Vestopal W contains very little chlorine.

Sections of 200 nm thickness were cut with a diamond knife with an ultramicrotome and picked up on a carbon-coated collodion film over a 1.5 mm hole in a spectroscopically pure carbon grid.[7] The sections were then coated with carbon and analyzed by TEM-EDXA, according to the method described previously.[6] The spot size of the electron beam used was 200 nm. This was slightly larger than the width of the primary wall. Therefore some overlap occurred with the S_1 layer when primary wall measurements were made.

Because of the uncertainty in the degree of swelling of fibers after freeze-drying, the absolute values of the chlorine content are not given. Instead the chlorine content relative to that in the unextracted fiber wall was calculated. The mean deviation over four experiments was $\pm$ 20%.

For the preparation of electronmicrographs, some of the chlorinated fibers, before and after extraction with aqueous NaOH, were stained with 2% aqueous $KMnO_4$, embedded, sectioned and photographed by TEM.[8]

RESULTS AND DISCUSSION

The chlorine contents in the different morphological regions of the kraft pulp fibers are shown in Table 2. Data are given for the pulp both before and after extraction with aqueous NaOH. Before extraction the highest chlorine content was found in the cell corner primary wall (CCP). In the primary wall between cell corners (P), the chlorine content was lower than that in the CCP but higher than that in the secondary wall (S). Interestingly, the chlorine was found to be distributed uniformly in the S layer.

As we have seen here for chlorine, Wood and Goring[9] found the highest concentration of lignin to be in a spot in the cell corner

Table 2.

Chlorine Distribution in the Chlorinated Spruce Kraft Pulp Fiber Wall

Sample	Relative Chlorine Content		
	S	P	CCP
Chlorinated pulp	1	1.4	4.1
Chlorinated and extracted pulp	0.3	0.4	0.3

primary wall. Also, these authors noted that the lignin in the secondary wall was distributed uniformly as is the case with the chlorine.

Figure 1 shows the transmission electronmicrographs of permanganate stained cross-sections of chlorinated spruce kraft pulp fibers before and after the extraction with aqueous NaOH. Before the extraction, lignin-rich areas are revealed as darker zones because permanganate is an electron-dense stain which is specific for lignin.[8] The CCP is darker than the P which is, in turn, darker than the S. Similar behavior in spruce kraft pulp has been observed by Parham.[4] However, after the extraction, most of the residual lignin was removed so that no dark areas were observed in the layers of the fiber wall. Thus the lignin distributions illustrated by the electronmicrographs in Figure 1 parallel the chlorine distribution shown in Table 2.

From Table 2 it is apparent that, after extraction, the chlorine contents of the three morphological regions were low and essentially equal. If we assume that in all regions, the lignin contains the same proportion of chlorine, the result means that the lignin contents are equal in CCP, P and S after extraction. The highly concentrated spot of lignin in the cell corner primary wall has disappeared. The ease with which the chlorinated lignin in the primary wall at the cell corner is extracted parallels the behavior of lignin in wood where it was observed that after chlorination and during extraction the relative rate of removal of cell corner middle lamella lignin was faster than that of secondary wall lignin.[6]

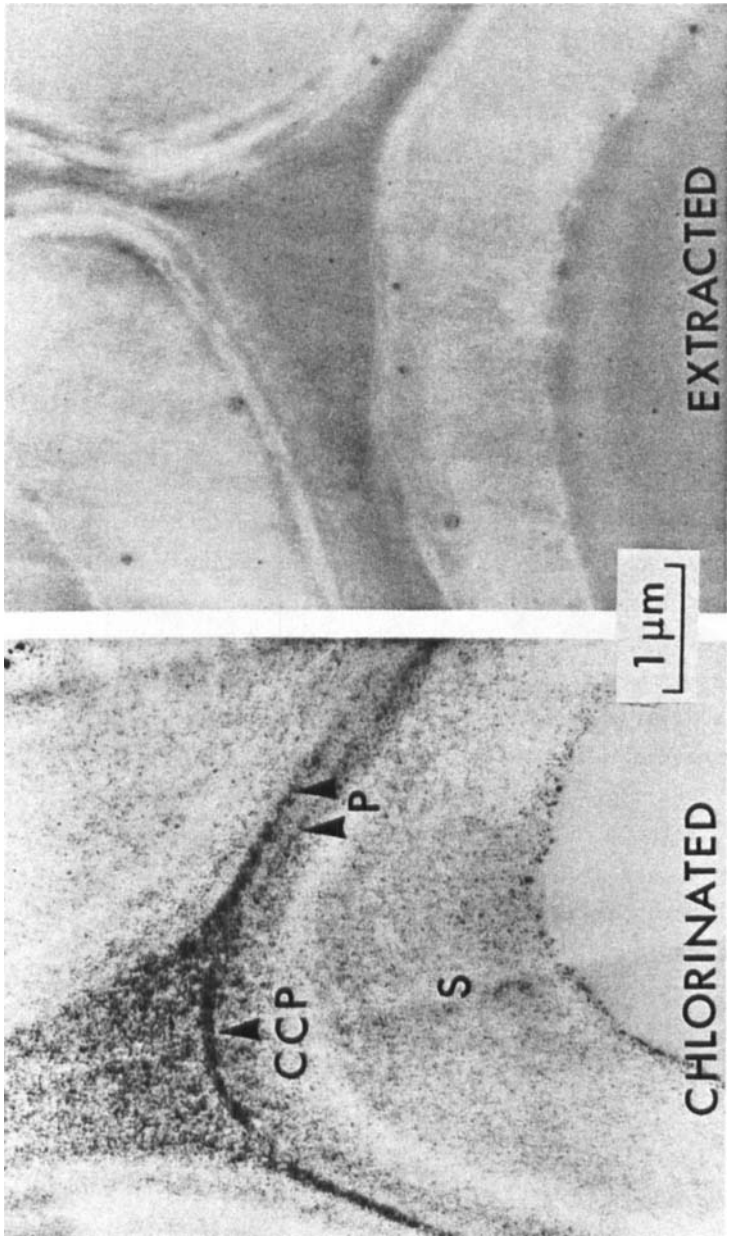

Figure 1. Chlorinated spruce kraft pulp fibers before and after extraction with aqueous NaOH. Stained with 2% $KMnO_4$.

It should be noted that the kappa number of the pulp used (50.8) was somewhat higher than customary values for bleachable grade pulps. The reason for using the higher kappa number was to have enough lignin in the fiber for accurate measurement. Even under these conditions the reproducibility was only fair. However it is unlikely that the chemical and morphological properties of the residual lignin will change much between a kappa number of 50 and, say, 30, a typical industry value. Thus, the conclusions drawn from the results obtained are probably valid for commercial unbleached pulps.

CONCLUDING REMARKS

The results show that the topochemical distribution of the chlorine in chlorinated kraft pulp fibers is similar to that of the lignin. The highest concentration is found in the cell corner primary wall with lower concentrations in the primary wall between cell corners and the secondary wall. However, after extraction with aqueous NaOH, most of the chlorine residual in the cell corner is removed and the chlorine content is low and approximately equal in all the morphological regions. The first chlorination and extraction stages, therefore, seem to be a leveller in reducing the lignin concentrations to a low value in all regions of the fiber. In a previous paper[9] it was speculated that the higher concentrations of lignin in the primary wall of unbleached fibers at high kappa number could affect fiber fibrillation and fiber stiffness and hence the properties of the paper made from such fibers. The present work shows that after the first stages of chlorination and extraction, the "sheath" effect would be negligible. It would then be expected that the small, evenly distributed concentration of lignin would contribute mainly to the color of the fibers and would not have much effect on their papermaking properties.

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