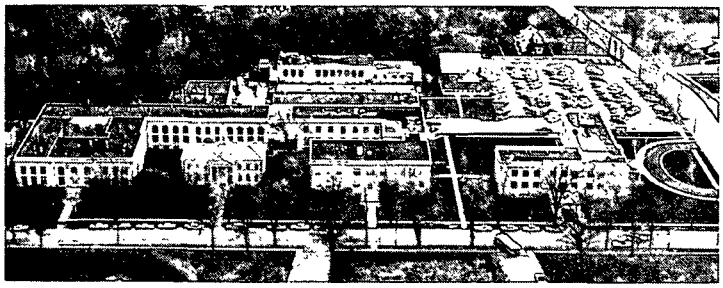

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

IPC TECHNICAL PAPER SERIES
NUMBER 216

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JANUARY, 1987

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Portions of this work will be used by TEH as partial fulfillment of the requirements for the Ph.D. degree at The Institute of Paper Chemistry

This paper is to be presented at the International Symposium on Wood and Pulping Chemistry in Paris, France on April 26-30, 1987

CELL WALL SULFUR DISTRIBUTION IN SULFONATED SOUTHERN PINE LATEWOOD: EFFECTS OF Na_2SO_3 CONCENTRATION AND REACTION TIME IN VAPOR PHASE COOKS

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ABSTRACT

The distribution of bound sulfur within the cell walls of sulfonated southern pine latewood chips has been experimentally investigated. The effects of reaction time and Na_2SO_3 concentration in the sulfonating liquor were studied in a 2 x 3 factorial experiment consisting of a series of vapor phase cooks. Sulfur distributions were determined by scanning transmission electron microscopy with energy dispersive spectrometry.

All treatments yielded a distribution characterized by a pronounced gradient of bound sulfur across the secondary wall. Sulfur counts decreased from a high value near the lumen to a minimum in the outer secondary wall and then increased toward a peak in the middle lamella.

INTRODUCTION

During the past decade, numerous workers have investigated sulfonation for the production of chemimechanical and chemithermomechanical pulps. They have found that sulfonation reduces refining energy and increases fiber flexibility and conformability. This results in a pulp which is stronger than the corresponding mechanical pulps and can serve as a partial replacement for kraft or other pulps in a wide variety of products.

On the fiber level, the degree of sulfonation of the various cell wall layers influences pulp properties. Wood chips in which the middle lamella lignin is softened by extensive sulfonation will tend to fracture in the middle lamella during fiberization. This results in fibers with a lignin-rich surface. Unsulfonated chips or chips with lower degrees of sulfonation tend to fracture in the outer secondary wall (1), leaving a carbohydrate-rich fiber surface with different bonding characteristics. Increased sulfonation of the secondary wall increases sheet density and strength through increased fiber wall flexibility and conformability. The distribution of sulfite across the secondary wall could also influence these properties. If the degree of sulfonation of the individual wall layers could be manipulated, pulp properties could be optimized for a variety of paper grades.

Recent years have seen increased interest in the use of electron microscopy to evaluate the distribution of bound sulfur across the cell wall. Scanning electron microscopy (SEM) with energy dispersive x-ray analysis (EDXA) (2) has been used to show that sulfur levels in the middle lamella are much higher than those in the secondary wall. However, the limited resolution of the SEM prevented a more detailed description. To obtain better resolution, Beatson, et al. (3) used transmission electron microscopy (TEM) with EDXA to evaluate cell wall sulfur distribution in sulfonated black spruce. The improved resolution allowed isolation of the cell corner and observation of the sulfur distribution across the secondary wall. These workers found a constant ratio of cell corner to secondary wall counts and a flat distribution across the secondary wall, no matter what the cooking conditions. All of Beatson's cooks were performed after long impregnation times at high liquor-to-wood ratios.

The work described here was done to relate the cell wall sulfur distribution in southern pine latewood to sulfonation conditions. The effects of Na_2SO_3 concentration and cooking time were investigated at a low liquor-to-wood ratio (vapor-phase cooks), in an effort to find conditions that would result in different cell wall sulfur distributions.

EXPERIMENTAL

Extracted and air-dried latewood chips were impregnated with sodium sulfite solution, drained, and rapidly heated with steam to 134 degrees C. After a specified time, the chips were cooled, exhaustively washed, dried, and impregnated with Spurr resin. Transverse 250 nm sections were prepared and mounted on 200 mesh ultrahigh-transmission nickel grids. Scanning transmission electron microscopy with energy dispersive spectrometry (STEM-EDS) was used to obtain linescans that consisted of measurements at 64 points, or pixels, across the double cell wall, from lumen to lumen. The measurement taken at each point was the number of sulfur counts detected from the K_α sulfur peak (a range of 2.18-2.44 kev in the x-ray spectrum), minus the background. The STEM used was a Jeol JEM 100-CX with an ASID4D scanning unit; it was equipped with a liquid nitrogen cooled anticontamination trap to minimize specimen damage and

mass loss. The EDS system was a Tracor Northern TN-2000.

In anticipation of a large natural variation in sulfur content in various regions of the wood chip, the experiment was designed to quantify the hierarchy of variances in the data. This was necessary to allow rigorous statistical tests of significance of the effects of the main experimental variables, Na_2SO_3 concentration and time at maximum temperature. These two variables were arranged in a 3 x 2 factorial design. For each of the resulting six treatments, two chips were examined, and within each chip, double walls at three different locations were scanned. These were chosen to be at specified points across the thickness of the chip (along the radial axis of the wood source); one at the chip center, one near an outside face, and one at an intermediate point. Duplicate (adjacent) scans were made in each double wall, giving a total of 12 scans per treatment.

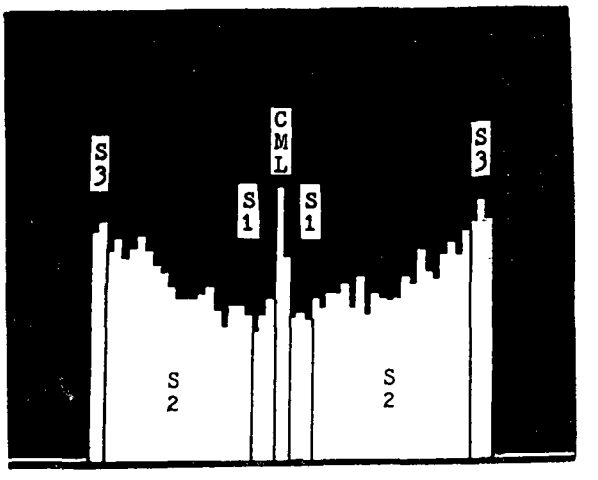
RESULTS

Yield and sulfur content data are shown in Table 1. Very little wood material was lost during the cooks, which suggests that delignification could not have had a major influence on sulfur distribution. As expected, higher Na_2SO_3 charges yield a higher sulfur content. Time at temperature had a smaller effect.

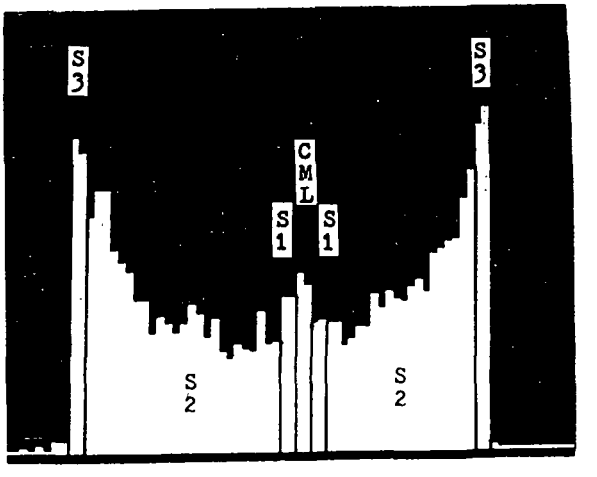
Time at Max. Temp., Min	Na_2SO_3 Concentration, g/L liquor	Yield, % o.d. wood	Sulfur Content, % o.d. treated wood
20	60	98.9	0.41
20	130	98.7	0.53
20	200	98.5	0.70
40	60	99.0	0.40
40	130	98.8	0.59
40	200	98.5	0.71

Table 1. Yield and sulfur content data.

The general shape of the double-wall linescan histograms was basically the same for all treatments. As shown in Fig. 1, there was a pronounced sulfur gradient across the secondary wall with higher sulfur levels toward the lumen and lower levels toward the middle lamella. The extent of this gradient varied from very sharp to, in some cases, almost flat. There was also a pronounced peak in the compound middle lamella, presumably due to the higher lignin concentration there and high sulfur levels at the cell corners. There were no net sulfur counts from the lumen, an observation which validates the background subtraction technique employed.



a)



b)

Figure 1. Typical (a) and extreme (b) examples of net sulfur count histograms from double-wall linescans. a) Histograms from a 40 minute cook with 130 g/L Na_2SO_3. b) Histogram from a 20 minute cook with 200 g/L Na_2SO_3.

Table 2 summarizes the data by recording the mean sulfur counts at selected points in the double wall for all treatments. Average secondary wall sulfur counts increased with increasing sulfur concentrations and, at high sulfite concentration, with time. The same appeared to be true of the cell corner data, but in this case missing data precluded a rigorous test of significance of the time effect.

The gradient across the secondary wall can be partially described as the ratio of the maximum (A) near the lumen to the minimum (B) near the middle lamella. To deal with the experimental variation in the data and to simplify the task of defining A and B, the secondary wall

data were smoothed using stepwise polynomial regression. Most of the regression curves could be smoothed by polynomials of order 3 or less, such as those shown in Fig. 2, but others required higher order polynomials.

Time, min	Na_2SO_3 Concentration, g/L liquor	Net Sulfur Counts[a] A	B	CC	A/B	CC/B	S
20	60	288	188	530	1.65	2.97	225
20	130	393	262	773	1.49	2.89	304
20	200	672	398	1177	1.70	3.01	474
40	60	270	185	537	1.59	3.18	212
40	130	433	277	799	1.68	2.84	343
40	200	913	640	1733	1.42	3.08	722
Mean ± 95% conf. int.:					1.59 ± 0.15	2.98 ± 0.22	

[a]A = maximum near lumen; B = minimum in S2; CC = cell corner; S = mean secondary wall (S_2 + S_3)

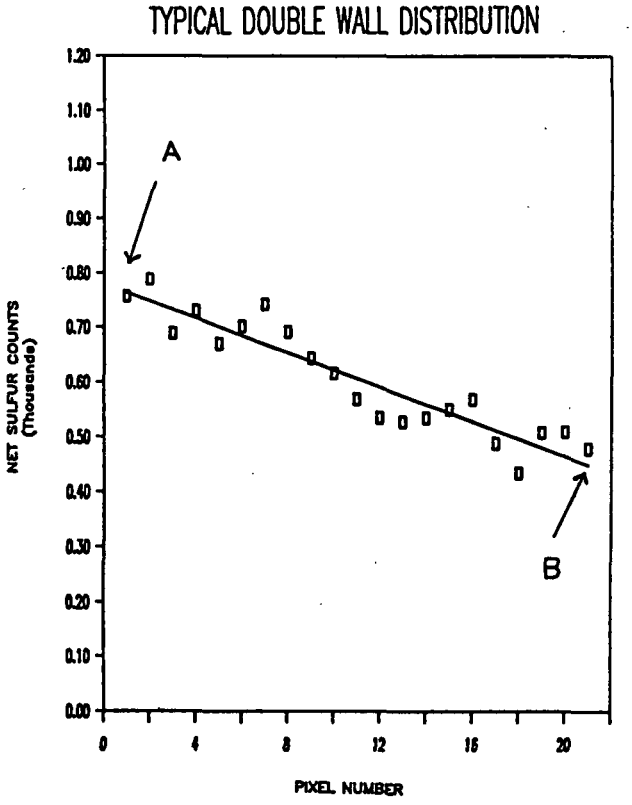
Table 2. Treatment means for various parameters used to describe the degree of sulfonation of different cell wall layers.

Analysis of variance (AOV) of the A/B ratio data showed that double walls differed significantly in this respect, but in no systematic fashion. There was no significant chip-to-chip variation and there was no significant effect of either Na_2SO_3 concentration or cooking time on the A/B ratio. The confidence interval for the mean A/B ratio lies well above 1.0, showing that the secondary wall gradient exists, beyond any reasonable doubt.

The results from the CC/B ratio AOV are generally the same as those from the A/B ratio AOV. There was no significant Na_2SO_3 concentration effect, but, again, there was substantial random wall-to-wall variability.

DISCUSSION

All sulfonation treatments investigated resulted in a pronounced gradient of bound sulfur concentration across the latewood secondary wall, in addition to the middle lamella peak previously observed by Beatson et al. in spruce. Sulfur concentrations decreased continuously from the S3 layer to a point at or near the S1, before increasing toward a maximum in the middle lamella (Fig. 1 and 2, Table 2). The reason for the existence of this gradient has not yet been determined, though studies toward that end are in progress. Possibilities include gradients in lignin concentration or reactivity, or limitations on diffusion of sulfite into the cell wall from the lumen.



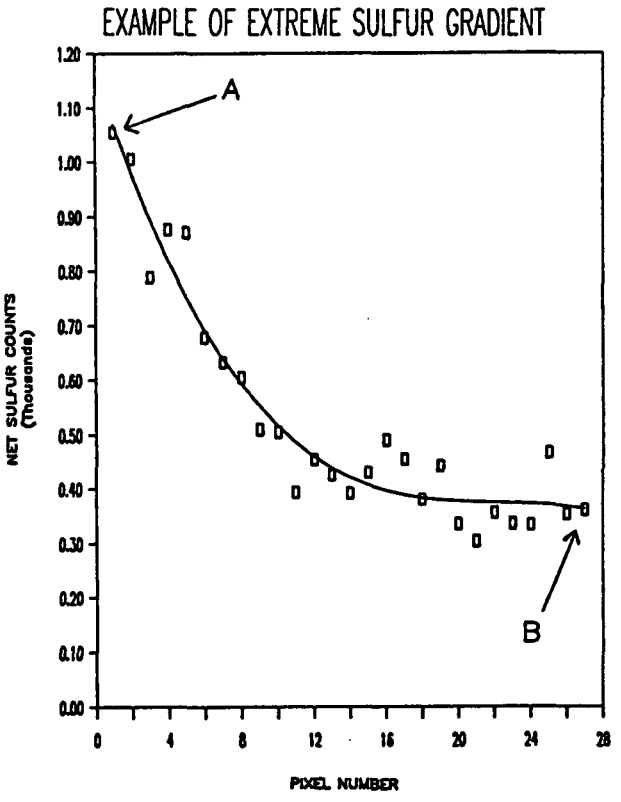


Figure 2. Smoothed linescan data for single secondary walls (S2 + S3); a) From the wall on the left in Fig. 1a; b) From the wall on the left in Fig. 1b.

The distribution of lignin across the cell wall has received considerable attention. In loblolly pine, studies based on lignin skeletonizing and bromination followed by x-ray analysis have indicated a uniform lignin distribution across the S2 layer and higher levels in the S3

(4-7). In an effort to quantify this difference, Saka and co-workers (6,7) found the ratio of S3 to S2 levels to be about 1.4, although the interpretation of the results of both the bromination and skeletonizing techniques has been questioned (4,8). A higher lignin level in the S3 could account for much of the difference in sulfur counts between the S3 and the minimum near the S1. However, the S3 includes only the first few pixels in the linescan and, as exemplified by the data in Fig. 1 and 2, a gradual decline that extended well beyond the S3 layer was usually observed. If the sulfur distributions were entirely the result of the lignin distributions recorded in the literature, there would be a sulfur peak in the S3, an abrupt drop in counts at the S3-S2 interface, and a flat distribution across the S2.

A second plausible explanation for the existence of the observed sulfur gradients might be the presence of a similar gradient in lignin reactivity. Although the existence of such a gradient has not been demonstrated, there is evidence of differences in phenolic hydroxyl content between the secondary wall and middle lamella in spruce (9-11), the ratio being in the range of 1.5 to 2.0 in favor of the secondary wall. Similar differences could conceivably exist within the secondary wall of pine, but there is as yet no evidence for them.

Limitations on the rate of diffusion of the sulfonating reagent into the cell wall from the lumen are the third possible explanation of the observed gradients, and perhaps the most likely. Although intrafiber diffusion is not believed to be a controlling factor in pulping to low yields (12,13), its importance in high-yield pulping is not yet well understood. It is hypothesized that sulfite ion in the liquor, which permeates the cell wall at the outset, is consumed fastest in the region of the double wall that contains the highest concentration of lignin - the middle lamella. The resulting gradient of sulfite ion concentration causes inward diffusion from the liquor contained in the lumen, which serves as a reservoir. Continued sulfite ion consumption in the middle lamella and nearby regions preserves the gradient, resulting in a higher average concentration of sulfonating reagent in the part of the S2 near the lumen than in the part near the middle lamella. This, in turn, results in a greater degree of sulfonation in the former region.

This hypothesis is consistent with the observations recorded in Table 2, inasmuch as, at the higher Na_2SO_3 concentrations the sulfur contents of all morphological regions increase with increasing cooking time. At lower concentrations chemical depletion slows diffusion and reaction rate to such an extent that the increase upon prolonged cooking is not evident. In both cases, it is possible that electrostatic effects associated with interactions between the negatively charged sulfonic acid groups introduced into the lignin and the negatively charged diffusing sulfonating species contribute to a progressive decrease in diffusivity as the reaction proceeds.

It is notable that increases in either time or liquor concentration increase the net sulfur counts in all morphological regions (Table 2). As a result, the shape of the sulfur distribution, as indicated by the A/B and CC/B data, is not affected by changes in these variables.

CONCLUSIONS

Sulfonation of loblolly pine latewood in "vapor-phase" cooks results in a nonuniform distribution of bound sulfur across the double cell wall. The distribution is characterized by a steady decrease in sulfur content from the S3 layer to a region in the S2 near the middle lamella as well as by a peak in the middle lamella and high values at the cell corners. The shape of the distribution is not affected by changing the reaction time at 134 degrees C from 20 minutes to 40 minutes, or by changing the concentration of Na_2SO_3 in the liquor of the "vapor-phase" cook from 60 to 200 g/L. Changing either variable does, however, change the absolute values of the sulfur concentrations in the various morphological regions.

The observed distribution is consistent with a hypothesis involving rapid consumption of chemical in the middle lamella region, and a persistence of the resulting concentration gradient as a result of the slowness of diffusion of sulfonating reagent from the liquor in the lumen.

ACKNOWLEDGMENTS

We thank John D. Litvay and William J. Whitsitt for valuable discussions.

Portions of this work will be used by T.E.H. as partial fulfillment of the requirements for the Ph.D. degree at The Institute of Paper Chemistry.

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