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The Effect of Component Removal Upon the Porous Structure of the Cell Wall of Wood

Part III.   A Comparison between the Sulphite and Kraft Processes

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The swelling behaviour of the cell wall was examined as sprucewood was progressively cooked to lower yields by the sulphite and kraft processes. This was done by determination of the accessibility of the cell wall to water-soluble macromolecules of different sizes. These measurements allowed the calculation of the volume of the water-swollen wall and the distribution of water among pores of different sizes.

With respect to cell wall dimensions it was found that both pulping processes could be divided into two stages — from 100 to 60 per cent yield, and below 60 per cent yield. In the kraft process, the wet cell wall stayed constant in volume down to 60 per cent yield, solid material leaving the wall being exactly replaced by an equivalent volume of water. By contrast, during sulphite pulping over the same yield range the cell wall steadily swelled as components were removed. It is suggested that this swelling during the sulphite process causes such a disruption of the structure of the wall that sulphite fibres are henceforth weaker than the kraft. As the yield was lowered below 60 per cent, the cell walls of both sulphite and kraft fibres contracted. The sulphite fibres always contained more water than the kraft at a particular yield. Possible reasons for the various dimensional changes are suggested.

Within the cell wall, water was contained in pores whose average size increased as pulping proceeded — those in the sulphite fibres always being somewhat larger than in the kraft fibres at the same yield. Relations between the size of the pores and the sizes of molecules which may enter or leave the cell wall are discussed.

As far as chemical pulping is concerned the important function of water within the cell wall of wet wood fibres is as a transport medium for chemicals into, and cell wall components out of the wall. After pulping and fibrizing, the function of water in the cell wall is to confer flexibility to the fibres. These functions are well appreciated and yet quantitative data, both on the amount of water in the cell wall (of importance in the second case) and the distribution of water within the wall (of importance in the first case), have not yet been reliably obtained.

In an earlier paper in this series [1], published values of the total water within the cell wall (the fibre saturation point) were criticized on the grounds that the values reported were too low. The true fibre saturation point was then determined for black-spruce wood and for the wood as components were progressively removed by the kraft process. The fibre saturation point was found to be 0.4 g./g. in the wood, rising steadily as components were removed to
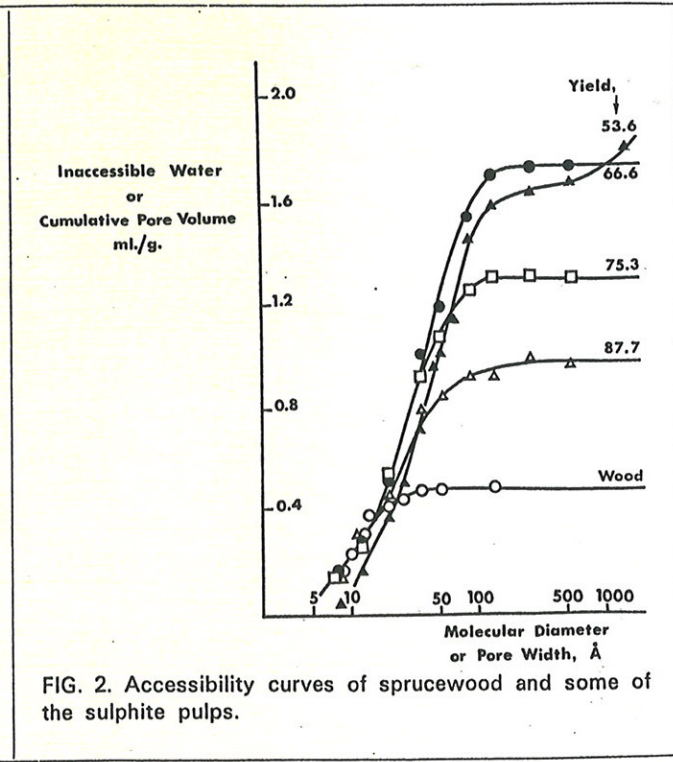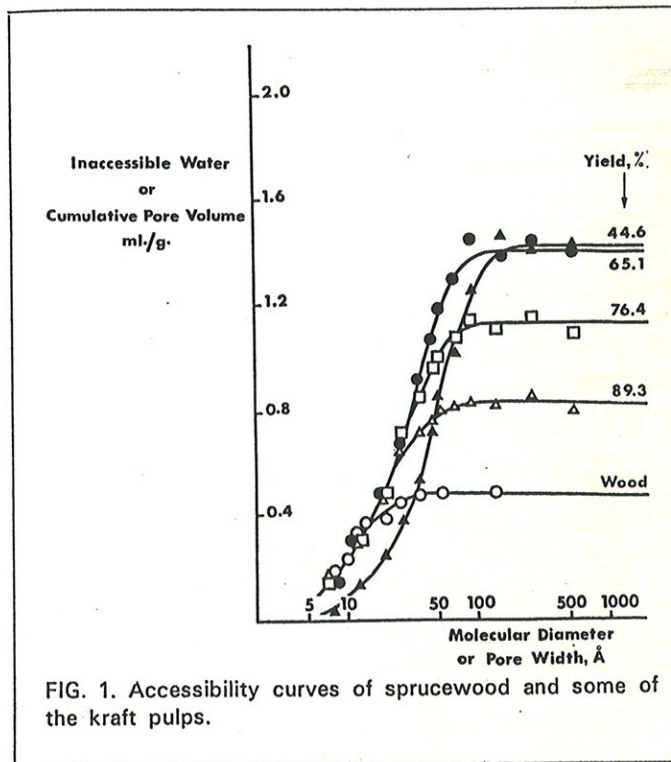
1.2 g./g. at the lowest yield (48.7 per cent). From these values, the volumetric changes in the water-swollen cell wall (which are largely reflected in changes in cell-wall thickness) were calculated. It was found that upon removing the first 5 per cent of material from the cell wall of the wood, there was a slight swelling. As the yield was lowered from 95 to 60 per cent there was no change in cell-wall thickness and then from 60 per cent down there was a steady shrinkage of the wall. These changes were discussed in terms of cell wall structure. It then became of interest to examine in the same way the changes brought about when wood is pulped by the sulphite process. This is done in the present paper, and interesting differences between the two pulps are brought to light.

In addition to increasing the breadth of the investigation by studying another pulping process, it has also been increased in depth by examining more closely the accommodation of water within the cell wall. It has been shown recently that in the dry state the wall is non-porous [2] and hence it follows that in the wet state the wall is swollen above its dry volume by an amount equal to the volume of water that it contains. This water must be distributed within the wall in spaces between the solid elements of the wall and, for the sake of definition, whether these spaces accommodate only one water molecule or a great many, they will be termed pores. The sizes of these pores are important since they must control the diameter of solute molecules which may enter them. These molecules may include those which constitute pulping and bleaching reagents, dyes, acetylating or other derivative-producing reagents, chemicals used as preservatives and dimensional stabilizers and also such biological reagents as the enzymes secreted by decay micro-organisms. Similarly, the sizes of the pores will control the sizes of molecules which may leave the interior of the wall. This is particularly important in pulping where particles of

lignin must be chemically detached from the very large cross-linked gel network that constitutes the lignin in wood and reduced to such a size that they are capable of finding an interconnecting pore system of sufficiently large diameter to reach the outside world. In the past, the study of pore sizes in cellulosic fibres has been largely confined to methods depending on solvent-exchange drying prior to measurement but this process recently has been found not to retain the water-swollen structure of the cell wall [1]. A technique for measuring pore sizes in the presence of water therefore became obligatory if reliable data were to be obtained, and in the present work the method adopted was based on the accessibility of the cell wall to molecules of various sizes in aqueous solution.

The technique used was introduced in a previous paper [1] — the solute exclusion technique: A sample of wet pulp containing a known quantity of water is placed in an aqueous solution of known concentration. The solute molecules then diffuse into all the water associated with the fibres with the exception of the water confined within pores of narrower widths than the diameter of the solute molecules. The solution thus becomes more dilute, and from the resultant change in concentration it is possible to calculate the amount of water inaccessible to the molecules used, or, in other words, the amount of water which does not contribute to the dilution. Based on a dry fibre weight of one gram, the amount of water so measured is termed "inaccessible water"*. It increases with molecular diameter until a maximum is reached

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*The term "non-solvent water" rather than "inaccessible water" has been used by many authors over a number of years and also by ourselves. We believe it to be inappropriate however, because although a small fraction of the water in cellulose gels may have lost its solvent properties due to its strong association with cellulose at the solid-liquid interface, the majority of the water is present as free liquid. We therefore suggest the term "inaccessible water" for water within the cell wall to which the solute molecules do not have access and the term "solute exclusion" to the technique for determining it.

FIG. 1. Accessibility curves of sprucewood and some of the kraft pulps.

FIG. 2. Accessibility curves of sprucewood and some of the sulphite pulps.

at the point where the solute molecules are completely excluded from the cell wall. Thereafter, the inaccessible water is independent of any further increase in molecular size. The plot of inaccessible water versus molecular diameter is thus effectively the cumulative pore volume versus pore size, and provides all the information required concerning the accommodation of water within the cell wall.

Experimental

Wood and Pulp Samples — The species of wood used for all experiments was black spruce (Picea mariana). Pulps of various yields were prepared by cooking longitudinal wafers of the air-dry wood for different lengths of time. The conditions used in the sulphite and kraft cooks have already been reported [3]. After cooking, the pulps were defibrized to some extent by a short treatment in a Waring blendor. They were then washed free of water-soluble material and stored in water at 5 deg. C. until required.

In a previous publication, it was suggested that the most appropriate 100-per-cent-yield sample would be green rather than dried wood [1]. Consequently, in the present work, the material used for the 100-per-cent-yield sample was wood meal obtained by drilling into the face of a disk which had been cut from a tree immediately after felling. Its initial moisture content was 0.5 g./g. based on the oven-dry weight.

Solute Molecules — A series of water-soluble solute molecules was required in a wide range of sizes so that their ability to penetrate the cell wall varied from having almost the same accessibility to the wall as water itself, to being totally excluded. It was also important that the molecules chosen did not react chemically or physically with the cell wall material. For this purpose the polysaccharide dextran commercially available from Pharmacia Ltd. in a number of different molecular weight fractions was chosen. Preliminary experiments showed that the experimental values for inaccessible water were independent of the concentration of the dextran solution, thus indicating the absence of sorption of dextrans onto the fibres. Further, it was found that the range of molecular diameters within each of the fractions was fairly narrow compared with the range of pore widths within the cell wall — an important requirement of the solute exclusion technique. As the dextran fractions were not available in very low molecular weights, they were supplemented with a number of low molecular weight sugars: stachyose (Mol. wt. 666), raffinose (504), maltose (342) and glucose (180).

Grotte [4] has reviewed evidence showing that dextran molecules with few cross-links, such as those from Pharmacia, behave in solution as hydrodynamic spheres whose diameters may be calculated from their diffusion coefficients by the Einstein-Stokes formula:

$$\text{Diameter} = \frac{RT}{3\pi\eta D N} \quad (1)$$

In this equation, R is the gas constant, T is the absolute temperature, η is the viscosity of water, N is Avogadro's Number and D is the diffusion coefficient. The diameters given in Table I were found by inter-

TABLE I — Properties of macromolecules.

Macromolecule		Molecular weight, M_w	$\frac{M_w}{M_n}$	Molecular diameter in solution, Å
Glucose		180	1.0	8
Maltose		342	1.0	10
Raffinose		504	1.0	12
Stachyose		666	1.0	14
Dextran	1.4	1400	1.3	20
	2.6	2600	1.3	26
	5.4	5400	1.3	36
	8.8	8800	1.4	45
	10	11.200	2.0	51
	20	21,800	1.5	68
	40	39,800	1.5	90
	100	100,500	1.6	140
	500	420,000	2.7	270
	2,000	2×10^6	—	560
	24,000	24×10^6	—	1600

polation of the diffusion data given by Granath [5] for a similar series of dextran fractions and that given by Longsworth [6] for the sugars.

Solute Exclusion Technique — The pulp under investigation was first washed with distilled water until free of all water soluble material, i.e. until the refractive index of the washings matched that of the distilled water. A 5-g. sample of the wet pulp representing about 1 g. dry weight was then weighed into a small bottle. To this was added about 12 g. of a 2-per-cent stock solution of a solute molecule. The bottle was then tightly stoppered and was allowed to stand for two days with periodic vigorous shaking. After this time about 1 ml. of solution was withdrawn with a syringe containing a Millipore filter and injected into one of the twin cells of a Rayleigh interference refractometer (Hilger Watts model M154). The solution was then compared with distilled water in the other cell. The reading given by the instrument being proportional to the concentration of the solution, it was divided into the reading obtained when the original stock solution was compared with water to give the ratio of the initial to the final concentration of the solution used in the experiment (c_i/c_f). After this was done, the pulp sample was washed free of solution, filtered, dried at 105 deg. C. and weighed to obtain the dry weight. The amount of water inaccessible to the solute molecule was then calculated according to the formula [1]:

$$\delta = \frac{w+q}{p}\left[1 - \frac{w}{w+q} \times \frac{c_i}{c_f}\right]$$

where δ = inaccessible water in grams per gram of dry pulp

p = dry weight of sample

q = weight of water in sample

w = weight of solution of solute molecules

c_i = initial concentration of solution of solute mol.

c_f = final concentration of solution after addition of wet pulp

Results

Typical plots of inaccessible water versus molecular size are given for kraft and sulphite samples in Figs. 1 and 2, respectively. As indicated earlier the inaccessible water increased with increasing diameter of the solute molecule until a maximum was reached

at the point where the molecule was completely excluded from the cell wall. Thereafter no further increase in molecular diameter had any effect on the value of inaccessible water and the plateau formed is the so-called "fibre saturation point". The fibre saturation point and various other deductions which may be made concerning the distribution of the water amongst pores of different sizes are best considered separately.

Fibre Saturation Point and Cell Wall Swelling — The fibre saturation point or total amount of water within the swollen cell wall is also the total pore volume

and is equal to the inaccessible water found with a totally excluded molecule. In general, all molecules larger than dextran 110 (diameter 140 Å) were excluded and the values of inaccessible water with this and larger molecules have been averaged to give the fibre saturation point. In the case of the low-yield sulphite pulps, an example of which is given in Fig. 2, a point of inflexion rather than a plateau was reached with the large molecules. This has been observed before, particularly in beaten low-yield pulps [7], and it is thought to be a result of this pulp having fibrillated surfaces, the fibrils prevent-
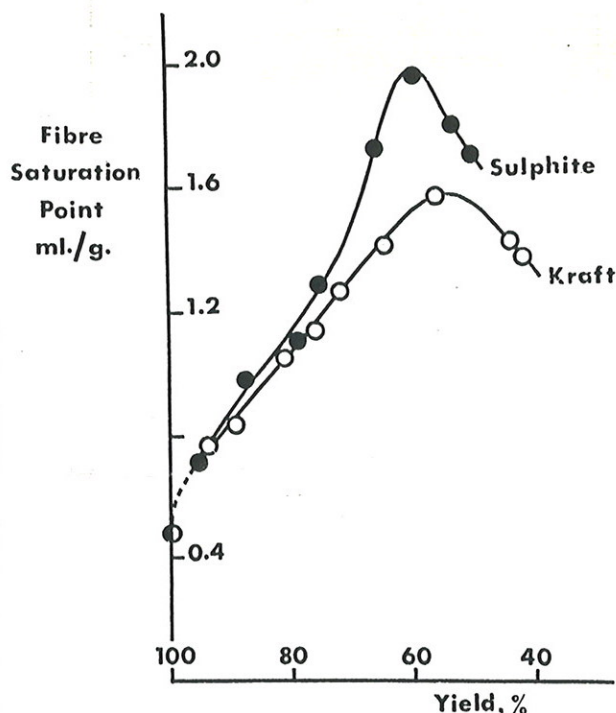

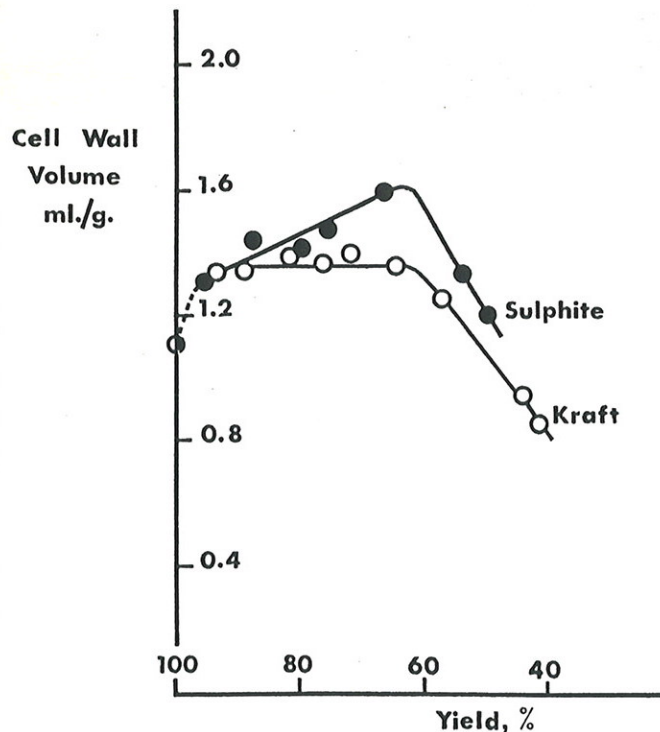FIG. 3. Variation of fibre saturation point with yield.

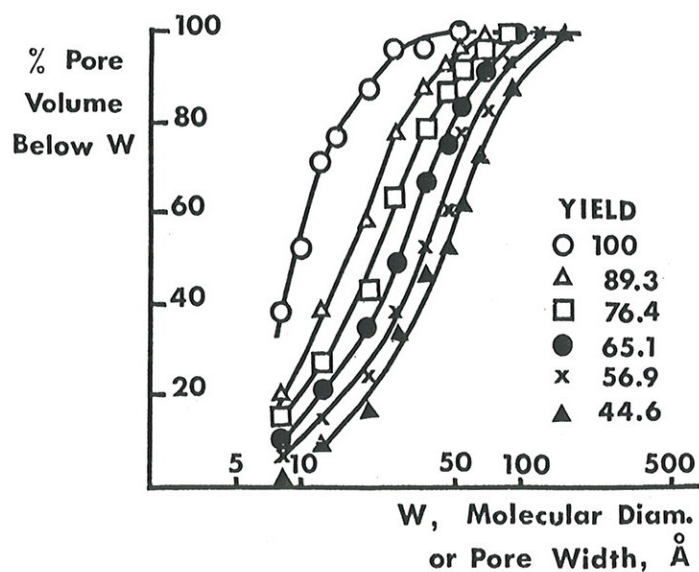FIG. 4. Variation of cell wall volume with yield.

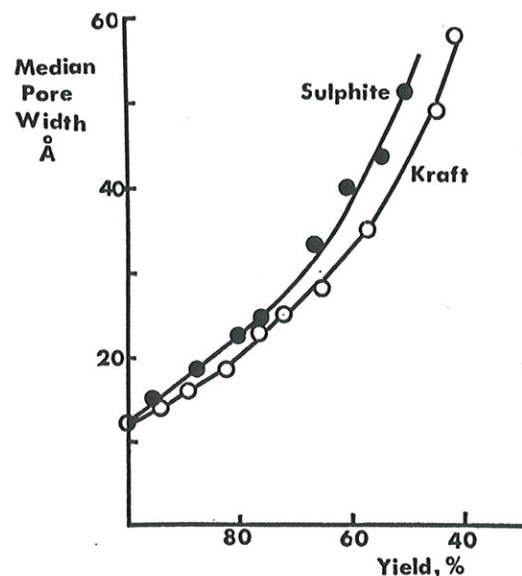FIG. 5. Normalized accessibility curves of the kraft pulps.

FIG. 6. Variation of median pore width with yield.

ing the close approach of the largest molecules. In these cases the fibre saturation point has been defined as the amount of water inaccessible to dextran 2000 (diameter 560 Å).

In Fig. 3 the fibre saturation points have been plotted against pulp yield. It is seen that at all yields the sulphite pulps held more water than the kraft. In both processes, the fibre saturation point increased from 0.48 ml./g. for never-dried wood to a maximum at 60 per cent yield of 1.6 ml./g. for kraft and 2.0 ml./g. for sulphite. Below about 60 per cent yield the fibre saturation point decreased.

It does not follow when we are dealing with pulps of different yield that if the fibre saturation point increases the cell wall necessarily swells. The fibre saturation point is based on one gram of dry pulp and this quantity will contain an increasing number of fibres as the yield is progressively lowered. To judge whether swelling occurs, by which we mean an increase in cell wall volume, the volume of solid material plus water in a fixed number of fibres must be compared. This may be done by considering how the volume of solid plus water associated with one gram of wood changes as it is pulped. To do this, the fibre saturation point is multiplied by the yield and to this value is added the specific volume of the solid material (0.667 cc./g. the reciprocal of the dry cell wall density) multiplied by the yield. This quantity may be considered to be directly proportional to the thickness of the cell wall [1].

The total cell wall volume thus obtained is plotted against yield in Fig. 4. As shown in the previous publication [1], the kraft-cooked cell wall initially swelled slightly, was then constant in volume from 95 to 60 per cent yield and thereafter contracted. (As the present results were determined on a new series of pulps, they provide confirmation of the earlier findings.) In contrast to the kraft-cooked fibres the sulphite-cooked cell wall, although it showed approximately the same initial swelling and final contraction, showed a steady swelling in the 95 to 60 per cent yield range. Speculation on the causes and effects of this interesting difference will be made in the discussion.

Range of Pore Size — All samples examined revealed a certain amount of water inaccessible to the smallest molecules employed — glucose. It must therefore be concluded that the width of the smallest pores that accommodate water within the swollen cell wall are below the diameter of glucose (8 Å).

The upper size limit of the pores was found from the point at which the accessibility curves such as those in Figs. 1 and 2 level out. In wood, the maximum pore width was only 36Å. However, it increased with pulping, being about 90 Å down to 65 per cent yield for the kraft process and 140 Å for lower yields. Sulphite pulp showed a more drastic change in maximum pore width with yield; down to 75 per cent yield the maximum pore size was 140 Å, at 66 per cent yield, 270 Å, and below 66 per cent yield, 560 Å.

Pore Size Distribution and Median Pore Size — If, for a series of pulp yields, inaccessible water is plotted against pore size, the changing distribution of pores that these plots represent is not easily seen due to their different fibre saturation points. The change in distribution is most clearly seen if the curves are normalized as shown in Fig. 5, which is drawn for the kraft pulps. As wood is pulped to progressively lower yields, the distribution broadens and the aver-

age pore size moves steadily to higher values. The same general picture exists with the sulphite pulps.

In order to give a value to the average pore size we have taken the median, that is, the pore size at which one half of the pore volume is contained in larger pores and one half in smaller pores. In Fig. 6 the median pore size for both kraft and sulphite pulps is plotted against yield. At all yields the average pore size in the sulphite pulps was larger than in the kraft. Both pulps showed a steady increase in pore size with decreasing yield. The median pore size continued to increase below 60 per cent yield even though the wall as a whole was contracting.

Discussion

The Swelling of the Cell Wall — Evidence has been reviewed [3] that during the maturing of the wood cell wall during growth, the initially strain-free wall composed primarily of cellulose and hemicellulose is expanded by the introduction of lignin, displacing the carbohydrate matrix and causing the formation of built-in stresses. Pulping may then be visualized as a reversal of this process; removal of the lignin and hemicellulose allowing the cell wall to contract to the strain-free state that it had before maturation. This would explain the contraction of the cell wall which occurs in both processes as the yield drops below 60 per cent.

The most interesting difference between the kraft and the sulphite fibres brought to light in this work is their different swelling behaviour during pulping
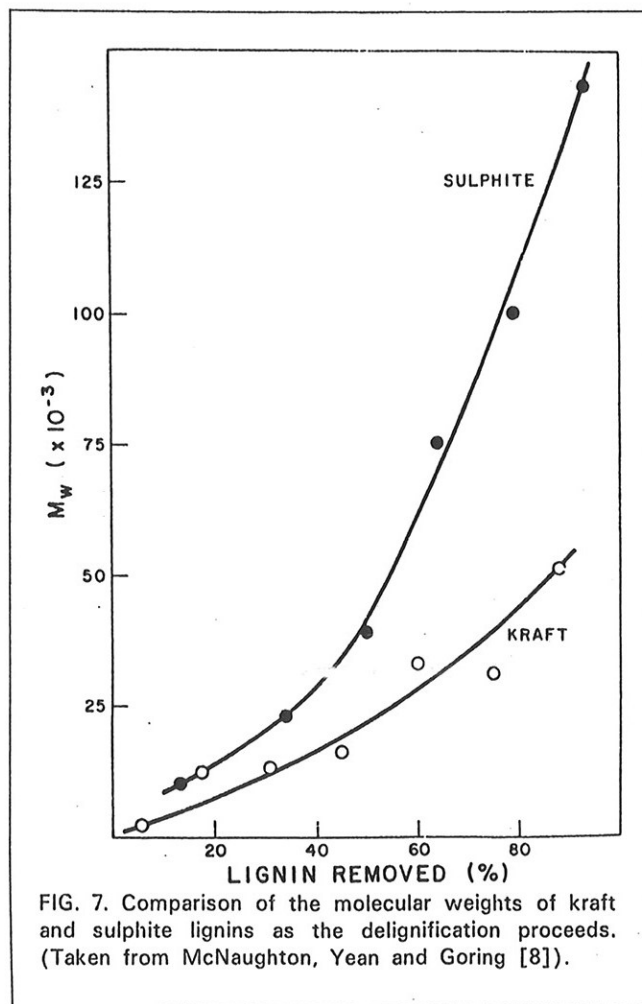

FIG. 7. Comparison of the molecular weights of kraft and sulphite lignins as the delignification proceeds. (Taken from McNaughton, Yean and Goring [8]).

at yields above 60 per cent. Our explanation for this difference is based on the assignment of separate roles for hemicellulose and lignin in promoting and inhibiting swelling. Hemicellulose molecules with their large affinity for water are considered to be present in the water-swollen cell wall as compressed springs. The lignin, on the other hand, being a three-dimensional cross-linked polymer distributed throughout the system, may be considered as a matrix of tie-rods locking the cell wall of wood in its strained configuration. In both the kraft and suphite processes, at a given yield, the pulps have a roughly comparable composition and therefore the intermediate swelling behaviour of the sulphite cannot be attributed to, say, a higher hemicellulose content. It is suggested that, in the kraft process, lignin and hemicellulose are removed together, the lignin which remains being sufficient to maintain the wall in its strained state. In the sulphite process, however, besides removing lignin, the liquor reacts with the remainder, breaking chains and forming an insoluble sulphonic acid. The destruction of the cross-linking function of the lignin allows the hemicellulose to swell the cell wall. An alternative explanation would be that the swelling of sulphite fibres is due to the formation and swelling within the carbohydrate system of the polyelectrolyte gel represented by lignin sulphonic acid. However, we have found that the complete removal of lignin from spruce wood with sodium chlorite solution leads to a swelling which is similar to that obtained during sulphite pulping, demonstrating that hemicellulose alone, when unrestricted by lignin, is capable of producing the observed effect.

The different swelling behaviour of the cell wall during kraft and sulphite pulping may well be responsible for the different mechanical properties of fibres which are isolated by the two processes. It is very well known that sulphite pulps beat more rapidly than kraft, i.e. they fibrillate, break up into fibre fragments and develop their maximum strength more quickly, and, in a recent study [7], it was shown that the walls of kraft fibres do not continue to swell after the first few minutes of beating whereas sulphite fibre walls continue to swell throughout the beating period. It seems reasonable to conclude that this poorer cohesion within the wall of wet sulphite fibres is a direct consequence of the swelling and internal disruption which took place during pulping. The lower dry strength of sulphite fibres may have a similar origin — an internal disruption of the wall during pulping so that, upon drying, a less perfect packing of the microfibrils occurs, leading to poorer dry cohesion.

If, indeed, the swelling of the fibres in the first stages of sulphite pulping is responsible for their subsequent lower strength, then in order to produce stronger fibres by the sulphite process an attempt should be made to reduce or eliminate the swelling. Experiments along this line are in progress.

Accessibility of the Cell Wall — It has been shown that in the cell wall of wood itself there is a narrow distribution of very small pores and that as the wood is pulped to progressively lower yields the distribution broadens and the average pore size becomes steadily larger. Down to 60 per cent yield this is consistent with the observation that the cell wall is either constant in volume or swelling while the solid content in steadily diminishing. Thus, it is to be expected that as solid elements are removed from the cell wall, the distances between the remaining ones, i.e. the pore size, will get greater. Below 60 per cent yield there is an apparent anomaly — the cell wall is contracting and yet the pores are increasing in size. However, this may be the result of many smaller pores linking up to form a few large pores as the material separating them is dissolved away. Calculation shows that this could result in the average pore size rising even during contraction of the total system.

An immediate conclusion which can be drawn from the pore size distribution curves (Fig. 5) is that there is a limit to the size of molecules or other particles which may readily enter or leave the water-swollen cell wall. At any yield there will be very little hindrance to the entry of small molecules or ions such as those in cooking liquor. However, there is a definite limit, which will depend upon yield, to the size of macromolecules which can disentangle themselves from and diffuse out of the wall during the cooking process. We would therefore expect that during the first stages of cooking, while the pores are small, only small molecules may leave the wall. As the cook proceeds the small pores originally present may be visualized as linking up to form larger pores through which large molecules may pass. That the molecular weight of extracted lignin increases as the cook proceeds has been shown by McNaughton, Yean and Goring [8], and there is a close correspondence between their variation of molecular weight with yield (Fig. 7) and our variation of median pore size with yield (Fig. 6). They also showed that at a given yield the molecular weight of lignin extracted by the sulphite process is higher than that extracted by the kraft process.

The accessibility of the cell wall of wood and the changes which take place during pulping might be expected to have important implications for any process which involves a chemical or physical interaction between solute molecules and the cell wall. For example, the attack upon wood by wood rotting microorganisms will be affected by the accessibility of the wall to various enzymes secreted by the micro-organism. The dimensional stabilization of wood by bulking with polyethylene glycols or other polymers requires the movement of a reagent into the spaces between cell wall components. In the case of delignified wood, dyeing, the preparation of cellulose derivatives, graft polymerisation and numerous other reactions are clearly situations where cell wall accessibility may be important.

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