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The Effect of Component Removal Upon the Porous Structure of the Cell Wall of Wood. II. Swelling in Water and the Fiber Saturation Point

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The fiber saturation point is defined as the amount of water contained within the water-saturated cell wall. Previous techniques for the determination of the fiber saturation point of wood and pulp fibers are criticized and it is suggested that the values of about 0.3 g/g frequently quoted in the literature are too low. Two entirely independent methods for finding the true fiber saturation point are presented and the results by both methods are in agreement. The fiber saturation point of air-dried and re-swollen black sprucewood was found to be 0.4 g/g rising to 1.2 g/g as the wood was pulped by the kraft process to progressively lower yields. A method of calculating the relative changes in water-swollen cell wall thickness from changes in the fiber saturation point is given, and the changes brought about by kraft pulping are calculated and discussed in terms of cell wall structure.

Keywords: Cell wall · Cell structure · Cell wall thickness · Data · Fibers · Saturation · Moisture content · Swelling · *Picea* · Softwoods

THE word "swelling" applied to an assemblage of fibers such as wood or wood pulp is very vague. The situation is best discussed with reference to a simple diagram such as Fig. 1, where three fibers are shown lying across one another to form a system in which water can be held in various ways. The walls of the fibers consist of a gel of carbohydrate and lignin that can take up water and thereby increase in volume after the manner of any gel material. Recent work (*1*) has indicated that in the dry state the walls are essentially nonporous and, hence, it follows that in the wet state the walls are swollen above their dry volume by an amount equal to the volume of water that they contain. This volume will be denoted V_c. The fiber walls enclose lumens, which will hold a certain volume of water V_L depending upon the morphology of the fibers and the state of lumen collapse. The external surfaces of fibers, particularly after beating, contain a "pile" of microfibrils that can entrap a volume of water V_F, and finally the interstices between a number of fibers form a capillary system that will hold a volume of water V_I.

Many of the methods used to measure the swelling of pulp fibers actually measure a composite of V_c, V_L, V_F, and V_I. The amount of each included in the quantity of water per gram of fiber depends not only upon the method used but also upon the experimental conditions adopted within the particular method. This is true of the permeability technique for measuring the swollen specific volume, the use of dilatometry for measuring swelling and the determination of the centrifugal water retention value. Consequently, when the total water held by the fiber system is found by these methods to have been increased by a given process, e.g., by beating, it is impossible to determine whether the increase was due to external fibrillation, cell wall swelling, or lumen expansion. It would be extremely useful in the analysis of beating to be able to make such a distinction.

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As part of a comprehensive and continuing study of the pore structure within the water-swollen cell wall of wood and pulp fibers (*1–4*),[1] it became important to have accurate information on the total amount of water that can be held by the wall; that is to say, the quantity V_c above. Upon examination of the literature, it soon became apparent that the measurement of V_c is by no means straightforward. Methods such as the ones mentioned above, which include water other than cell wall water, cannot be used. The direct approach of making microscopic measurements of cell wall dimensions in the wet and the dry state, although laborious and susceptible to error, has been applied to cotton and viscose (*6*) but has not yet been applied to wood pulp fibers. A method involving the determination of the amount of nonfreezing water at some temperature below 0°C exists (*7*), but the application of this method has been limited and the exact temperature to be employed is uncertain. The nonsolvent water technique using sodium thiosulfate as solute (*8*) is unsuitable because the molecule is both small and an electrolyte. (More will be said about this technique later.)

Our first approach to the solution of the problem was via the so-called "fiber saturation point" (FSP). This is a term introduced by Tiemann (*8*) in 1906 to describe the moisture content of wood when all the water from the gross capillary structure has been removed but no water has been removed from the cell walls. It is a term that has since been extended to other cellulosic fibers. The fiber saturation point is thus effectively V_c, and the term will be used throughout this paper to imply this. In the case of wood, the FSP has been obtained by plotting some property, such as mechanical strength, electrical conductivity, or heat of wetting, against moisture content as the sample is progressively dried, and observing the point of inflexion where water starts to leave the cell wall. The methods and results have been reviewed by Stamm (*9*), and values of about 0.3 g/g are found for many wood species. Another technique for measuring the fiber saturation point, and one that is applicable to all materials regardless of their physical form, is the measurement of the water sorbed by the material at various relative vapor pressures of water. The extrapolation of this water sorption isotherm from the highest relative vapor pressure readily obtainable by a saturated salt solution (0.95) to a relative vapor pressure of unity has been taken as the fiber saturation point (*10*). The results obtained by this method have also been reviewed by Stamm, and again values of about 0.3 g/g have been obtained, not only for wood but also for holocellulose, hemicellulose, lignin, and cotton and wood pulps of various yields, both beaten and unbeaten.

Although the value of 0.3 g/g has been widely quoted for many years, it has become increasingly apparent that it could not be correct. We first suspected this as a result of a study (*3*) of the drying of a bleached spruce sulfite pulp, in which, at various stages of the drying process,

[1] J. E. Stone and A. M. Scallan, unpublished work.

the water that remained was removed by solvent exchange (water to methanol, methanol to pentane) followed by evaporation of the final solvent. When the surface areas of the resulting aerogels were determined by nitrogen adsorption, it was found that the surface area of about 100 m^2/g remained constant down to a moisture content of 1.0 g/g, after which there was a progressive loss of surface down to complete dryness, when the surface area was less than 1 m^2/g. Since by far the greatest part of the 100 m^2/g is associated with surfaces within the cell wall (*3*), the onset of its disappearance during drying must coincide with the onset of water loss from inside the wall. This would therefore suggest an FSP of 1.0 g/g for the pulp studied, as opposed to the literature value of 0.3 g/g. Apart from the low value attributed to the fiber saturation point, we also question its constancy from material to material. As wood is first pulped and then beaten, considerable changes take place in physical properties; one might therefore expect changes in something as fundamental as the amount of water within the cell wall.

In order to clarify the situation, we decided to measure the fiber saturation point using two independent methods. The first method was the water sorption isotherm, which is one used by most previous authors. However, particular attention was paid to the measurement and interpretation of water sorption in the region of high relative vapor pressures. Neglect of this region proved to be the cause of error in most earlier investigations, as the following reasoning and later results will show.

When a water-saturated porous body is progressively equilibrated at a series of lower and lower partial pressures of water vapor, water will evaporate from the pores in order of decreasing size. The relationship between the radius of a pore and the relative vapor pressure at which the pore[2] loses its water is given by the Kelvin equation:

$$\log_e(p/p_0) = \frac{-2\gamma M}{rdRT} \qquad (1)$$

where

p/p_0 = relative vapor pressure
γ = surface tension of water
M = molecular weight of water
r = radius of curvature of the water surface, and also the radius of the capillaries if these are of circular cross section
d = density of water
R = gas constant
T = absolute temperature

If we now consider wood and pulp fibers, the majority of the capillaries fall into two size groups: the lumens and the cell wall pores. These differ in magnitude by a factor of at least 10 but probably more. The smallest lumens are about 5 μ in radius, whereas the largest cell wall pores must certainly be less than 1 μ and probably less than 0.1 μ in radius, considering that the cell wall itself is only a few microns thick. This suggests that there is likely to be a plateau or a point of inflexion in the desorption isotherm corresponding to the size gap between the final emptying of the lumens and the onset of the emptying of the cell wall pores. The moisture content at which this occurs would then be the fiber saturation point. Examination of Table I, in which the values of p/p_0 corresponding to various radii are given, suggests that this plateau or point of inflexion, if it exists, will be found below p/p_0 = 0.9999 and possibly above p/p_0 = 0.9900. Fortunately, there is now a method by which such high relative vapor pressures of water can be obtained quite readily, and this method, which employs a porous plate, has been adopted for the present study.

In view of the importance of having accurate data available on the swelling of cell wall substance, and the rather serious discrepancy between reported values and those that it was suspected might arise from the present study, it was felt desirable to employ a second and entirely independent method of measurement. The method chosen is based upon a modification of the nonsolvent water technique used by Samuelson to measure the total amount of water in swollen rayon fiber (*11*). In this method, a weighed quantity of fibers of known moisture content is placed in a known amount of a dilute aqueous solution of polymer, with the polymer molecules of such a size that they are too large to enter cell wall pores. From the change in concentration of the polymer solution brought about by the presence of the fibers, it is possible to calculate the amount of water taken up by the cell walls. This method of determining the fiber saturation point is superior to others in that the grosser structure of the sample is not involved, and also because the fibers are immersed in free water when the measurement is made and not partially dried as in most methods. Its limitation is that the concentration changes are usually quite small, and an accurate method of determining concentration must be available. It is also necessary to check that the polymer is chemically inert toward the fibers and is not physically or chemically adsorbed on the surface.

It may be stated that values for the fiber saturation point have been obtained by the two techniques that are in excellent agreement with one another. They are, as suspected, substantially higher than the frequently reported value of 0.3 g/g. Because our primary interest was in the structure of the cell wall of wood and the way in which it changes during conversion to pulp, rather than in the FSP of a specific wood or pulp sample, it was decided to follow the change in FSP during the kraft pulping of sprucewood to a series of progressively lower yields. The results proved to be unexpected and unusually interesting.

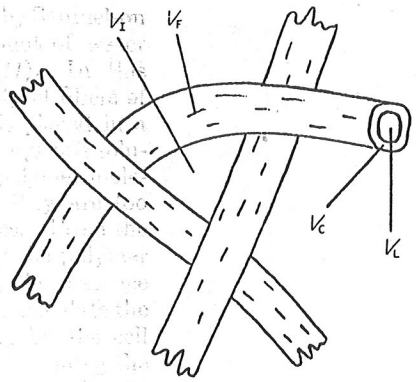

Fig. 1. Ways in which water may be held by fibers.

Table I. Calculations Based on the Kelvin Equation at 25°C

Relative vapor pressure of water, p/p_0	*Effective capillary radius, μ*
0.99999	106
0.9999	10.6
0.999	1.06
0.99	0.106
0.98	0.052
0.95	0.020
0.50	0.0015

EXPERIMENTAL

Preparation of Wood and Pulp Samples

The wood used was air-dried black spruce (*Picea mariana*) in the form of microtome cross sections 100-μ thick and 2 cm^2 in area. When examined as wood (100% yield), the sections were soaked in water for several weeks before use.

Samples of pulp were required also in the form of microtome sections, and these were prepared by subjecting wood microtome sections to a pulping procedure. In order to prevent disintegration during cooking and subsequent washing, the wood sections were placed individually between layers of cotton cloth. This method of cooking microtome sections has been described previously (*12*). The composition of the kraft liquor and the cooking conditions were also the same as reported previously (*12*). The yields and lignin contents are included in Table II. The cooked and washed sections were kept

[2] This is for a pore in a rigid material. Presumably, with a pore in a viscoelastic material like cellulose, which is nonporous (*1*) once it is completely dry, a drop in p/p_0 results in the pore losing some of its water and collapsing to the size in equilibrium with the new relative vapor pressure.

Table II. Fiber Saturation Point of Kraft Cooked Spruce

Sample	Yield, %	Lignin, %	Fiber saturation point, g/g: Pressure plate[a]	Fiber saturation point, g/g: Nonsolvent water
K0	100	27.0	0.40	0.42
K20	92.4	27.3	0.67	0.70
K35	89.0	27.6	0.74	(0.66)
K50	80.0	28.5	0.86	0.92
K65	77.8	28.2	0.94	0.94
K80	70.4	25.2	1.06	1.08
K95	61.6	19.3	1.16	1.22
K110	53.4	12.3	1.21	1.28
K125	48.7	6.5	1.14	1.21

[a] Water retention at p/p_0 = 0.9975 (50 psi).

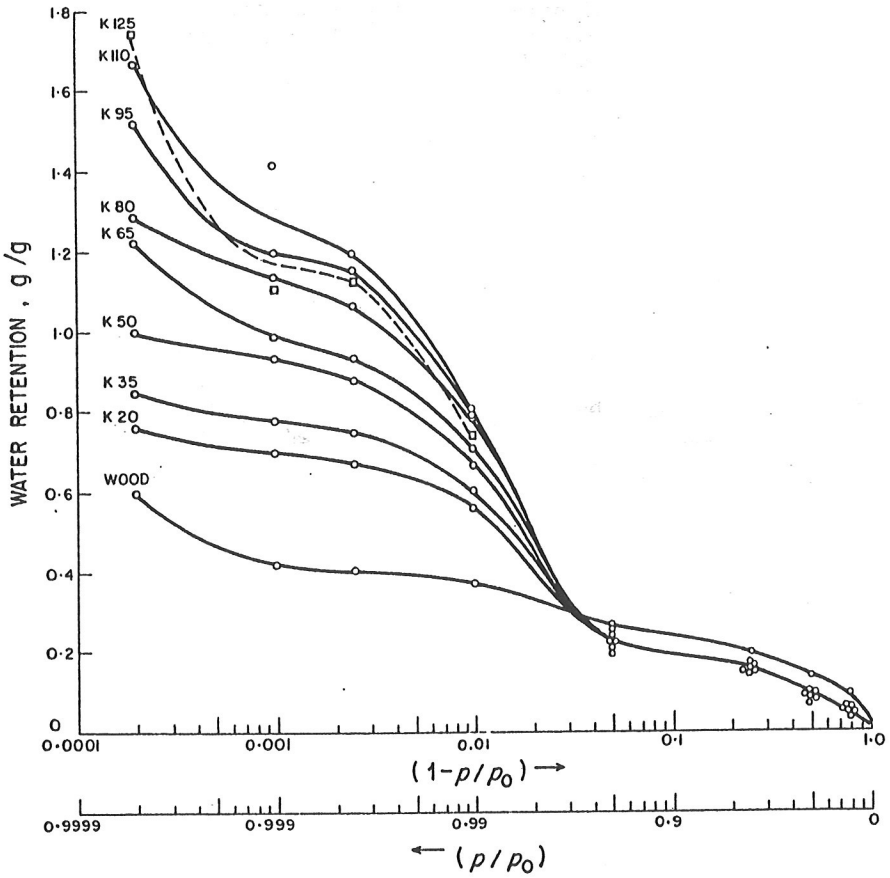

Fig. 2. Water desorption isotherms of wood and kraft cooked microtome cross sections.

immersed in water between the layers of cotton cloth until they were used.

In the nonsolvent water experiments, either microtome sections or ordinary pulp fibers were used because the physical shape of the sample was immaterial.

Fiber Saturation Point from the Desorption Isotherm

The water retained by samples upon desorption to relative vapor pressures in the 0.9999–0.9900 range was determined by the porous plate technique developed for soil moisture studies. This method was first used in studies of pulp fibers by Barkas (*12*) and, more recently, has been used extensively by Robertson (*13*). The procedure consists of placing a wet sample of the material to be tested upon a wet porous ceramic plate[3] and applying a gas pressure above the sample. The gas pressure tends to force the water from the sample through the plate, and is opposed by the surface tension forces of the water within the capillaries of the sample. Where the surface tension force is less than the gas pressure, i.e., in the larger capillaries, the water is forced out of the sample; where the surface tension forces are higher than the gas pressure, i.e., in the smaller capillaries, the water remains within the sample. The relationship between the applied pressure P and the critical radius r is given by

$$P = \frac{2\gamma}{r} \qquad (2)$$

Once equilibrium has been reached, all pores larger than the critical radius calculated from Eq. (2) for a particular pressure will be free of water, and the relative vapor pressure of the gas above the sample will be that calculated from a substitution of the critical radius into Eq. (1). The time to reach equilibrium is usually a matter of days, after which time the pressure is released.

In order to provide as simple and as unambiguous a capillary system as possible, and thereby to increase the chance of obtaining an easily interpretable isotherm, fiber samples in the form of microtomed cross sections were used. Such sections contain no large amount of interfiber pores and the lumens are fully accessible to the receding menisci, which are the bottlenecks represented by the pits eliminated. For each point on the desorption isotherm, duplicate samples, each consisting of ten microtome sections held between the two strips of cotton cloth in which they were cooked, were placed upon the pressure plate. The gas pressure was then applied and the samples were left for at least a week. It had previously been found that the presence of the cotton cloth did not affect the equilibrium moisture content of the samples; however, it did make the sections easier to handle and better contact was made with the plate. Once equilibrium was reached, the pressure was released, the upper strips of cloth were removed from the samples, and the samples were rapidly transferred to weighing bottles and weighed wet and oven dry to give their moisture contents. Sets of samples were treated at 4, 20, 50, and 200 psi, giving four points for each pulp, corresponding to relative vapor pressures of 0.9998, 0.9990, 0.9975, and 0.9900.

In order to measure the amount of water held by a sample at relative vapor pressures below 0.95 (0.95, 0.75, 0.44, and 0.22 were actually used), a sample in the form of one or two very wet microtome sections was placed in the pan of a Cahn recording electro microbalance mounted within a desiccator. The atmosphere within the desiccator was adjusted to p/p_0 = 0.95 by placing within the desiccator a vessel containing a saturated solution of potassium nitrate. When the recorder showed that the sample had reached a constant weight (usually in at least 24 hr), the weight was noted and the saturated solution of potassium nitrate was quickly replaced by one of sodium chloride. The procedure was repeated with salt solutions of lower and lower relative vapor pressures, and eventually the dry weight of the sample was determined by replacing the

[3] The actual apparatus used the "15 Bar Ceramic Plate Extractor, Cat. No. 1500," produced by the Soil Moisture Equipment Co., Santa Barbara, Calif.

last salt solution by phosphorus pentoxide. The moisture content at each relative vapor pressure was then calculated and the isotherm plotted.

The Fiber Saturation Point by the Nonsolvent Water Technique

Recent work has shown that the water-soluble molecules of dextran 110[4] are so large that they cannot enter the cell wall pores of kraft cooked black spruce (*5*). If very wet fibers are immersed in a dilute aqueous solution of this material, the water associated with the fibers over and above the fiber saturation point will dilute the solution, whereas the water within the cell wall will not. Thus, if δ_s is the fiber saturation point in grams of water per gram of dry fiber, and if the wet fibers consist of p grams of dry fibers associated with q grams of water, the presence of the wet fibers will dilute the solution by $q - p\delta_s$ grams of water. If c_i is the initial concentration of the solution in grams of solute per gram of solution, w grams of this solution added to the fibers will have a final concentration given by:

$$c_f = \frac{w}{w + (q - \delta_s p)} c_i \qquad (3)$$

or, rearranging

$$\delta_s = \frac{w + q}{p}\left[1 - \left(\frac{w}{w + q}\right)\left(\frac{c_i}{c_f}\right)\right] \qquad (4)$$

Hence, by measuring the change in concentration of a known weight of polymer solution brought about by a known weight of fibers of known moisture content, the fiber saturation point may be calculated.

The procedure followed was very simple. Into a small weighing bottle was placed 1.0 g of wet pulp or microtome sections from a batch of previously determined moisture content. To this was added just sufficient 1% dextran 110 solution to cover the sample (3.5–5.0 g). The mixture was then allowed to stand for 1–3 days with periodic shaking, after which 1 ml of solution was withdrawn with a syringe and injected into the narrow bored 10-cm cell of a Zeiss photoelectric precision polarimeter reading to 0.005°. Previous experiments had shown that the optical rotation was proportional to the concentration of the dextran 110, and, hence, the ratio of the rotation of the stock solution to that of the solution taken from the sample after standing was taken as equal to c_i/c_f. The wavelength used was 436 nm, because of the higher sensitivity at this lower wavelength than at the more conventional wavelength of 578 nm. For each pulp, δ_s was determined at least in duplicate, and the average values are recorded in Table II.

[4] Dextran 110 has a mol. wt. of 110,000 and was obtained from Pharmacia, Uppsala, Sweden.

RESULTS

The complete desorption isotherms for spruce and eight pulps of different yields are shown in Fig. 2. The method of plotting the data requires some explanation. If isotherms are plotted against p/p_0 on a linear scale, the points at high relative vapor pressures are extremely congested, and there is a strong temptation to extrapolate the isotherm to $p/p_0 = 1$, which, as stated earlier, is misleading. A suitable method of plotting the data is to plot water retention against the function $(1 - p/p_0)$ on a logarithmic scale (*14*). The values of p/p_0 corresponding to each value of $1 - p/p_0$ may then be denoted on an extra abscissa.

It can be seen in Fig. 2, that there are indeed inflexions in the isotherms as predicted on theoretical grounds. The inflexions are not very marked in certain cases, but, taken collectively, they can be considered real enough to justify the belief that they represent the fiber saturation points. There is little to choose between readings at $p/p_0 = 0.9999$ and 0.9975, and so, in order to obtain some numerical values for the fiber saturation points, the values of water retention at $p/p_0 = 0.9975$ have been taken somewhat arbitrarily as the fiber saturation points. The values are recorded in Table II. Very strong support for relating these inflexions to the fiber saturation points is provided by the nonsolvent data also recorded in Table II. Here it can be seen that the amount of water inaccessible to dextran 110, which may be taken to be the amount of water contained within the cell wall, is virtually identical with the volume of water associated with the fibers at $p/p_0 = 0.9975$.

Returning to Fig. 1, it is readily apparent from an examination of the isotherms why other investigations have obtained lower values for the fiber saturation point using the water desorption isotherms with data obtained at partial pressures of 0.95 and below. Extrapolation of the isotherms from 0.95 either to 1.00 in a linear plot or to 0.999 in a logarithmic plot will necessarily give low values for the fiber saturation point, because the step in the isotherm above 0.96 is bypassed. Also, because the isotherms for all the pulps regardless of yield follow a very similar path below $p/p_0 = 0.95$, an extrapolation from this value gives a single fiber saturation point for all pulps. It is only by actually measuring the water contents in regions of high partial pressure that valid values can be obtained.

The results in Table II are plotted in Fig. 3, and it is clear that the fiber saturation point is strongly affected by pulping in that it generally increases with decreasing yield. At all yields, the values are much higher than the 0.3 g/g that has been widely quoted. The value of 0.4 g/g for wood has been confirmed recently by others examining Sitka spruce by the nonsolvent water technique (*15*). Values of over 1.0 g/g for low yield pulps have been suggested by Robertson (*15*), although in his work the measurement of water retention at high relative vapor pressures was made on fiber pads. Therefore, because of the presence of interfiber pores in these samples (largely absent in the microtome sections used in the present work), the exact fiber saturation point was somewhat uncertain.

DISCUSSION

The primary purpose of this study was to learn a little more about the interior of the cell wall of water-swollen fibers as lignin and hemicellulose are removed from within it. We recently studied these changes by the N_2 adsorption technique, which showed that the surface area and pore volume increase rapidly as material is removed from sprucewood and reaches a maximum at about 70% yield and drops as the yield is reduced to 50% (*2*). The investigation reported here has shown that the total amount of water in the cell wall increases several fold over this same range of pulp yield; therefore, it is now possible to put together these two sets of data and discuss their meaning in terms of structure.

The first thing that must be appreciated is that as wood is pulped to lower and lower yields, the average weight of a single fiber decreases, so that a gram of pulp contains more and more fibers. For structural studies it is necessary to examine how the quantity of water associated with a fixed number of fibers, rather than with 1 g of pulp, varies with yield. To do this, the fiber saturation point can be multiplied by the yield, and the quantity of water thus obtained is that associated with N fibers, where N is the number of fibers in 1 g of wood. The result is shown in Fig. 4(a). The change in the volume of the solid materials of 1 g of wood can also be calculated as it is pulped: it is 0.667 cm^3 at the start [the reciprocal of dry cell wall density, i.e., 1.5 g/cm^3 (*1*)] and drops to half this value at 50% yield. This change is depicted in Fig. 4(b). Since the water-swollen cell wall is comprised only of solid material plus water, it follows that by adding Fig. 4(a) and Fig. 4(b) we obtain the upper curve in Fig. 4(c), which is the variation with yield in the total cell wall volume of the fibers in 1 g of wood.

Figure 4(c) refers to the volumetric changes in the cell wall of N fibers. Obviously, the volumetric changes in the cell wall of a single fiber follow the same pattern on a reduced scale. How are these volumetric changes reflected in changes in the dimensions of the fiber? It is well known that a fiber stays ap-

Table III.

Yield, %	Total pore volume,[a] FSP in ml/g	Macro-pore volume,[b] ml/g	Micro-pore volume,[c] ml/g
100	0.41	0.01	0.40
92.4	0.68	0.04	0.64
89.0	0.70	0.08	0.62
80.0	0.89	0.27	0.62
77.8	0.94	0.33	0.61
70.4	1.07	0.54	0.53
61.6	1.19	0.63	0.56
53.4	1.24	0.55	0.69
48.7	1.17	0.57	0.60

[a] Average of pressure plate and nonsolvent water data Table II.
[b] As measured by nitrogen adsorption (2) with graphical interpolation to permit comparison at the same yield.
[c] The difference between columns 2 and 3.

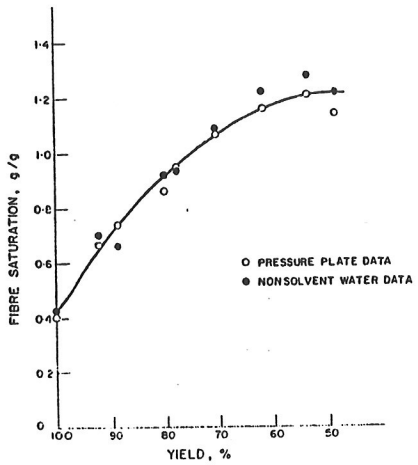

Fig. 3. Fiber saturation point of kraft cooked pulps.

proximately the same length throughout the pulping process; therefore, these volumetric changes must be due to changes in cross-sectional area. There are two possible ways this may occur; The first is a change in the diameter of the fiber, and the second is a change in the thickness of the cell wall. Microscopic observations made by us on microtome cross sections revealed that any changes in the cell wall brought about either by drying or by pulping were (where detectable) seen as changes in cell wall thickness. Changes in diameter to account for the same amount of volumetric change would have been readily observed, but they were not. We must therefore conclude that any volumetric changes shown in Fig. 4(c) are to a good approximation directly proportional to changes in thickness of the water-swollen cell wall.

It can be seen that, as the first few percent of wood substance are removed, there is a small but significant rise in cell wall thickness. This may be a general phenomenon or it may be because the wood used for the initial point on the curve had been dried before these experiments, and the simple soaking in water

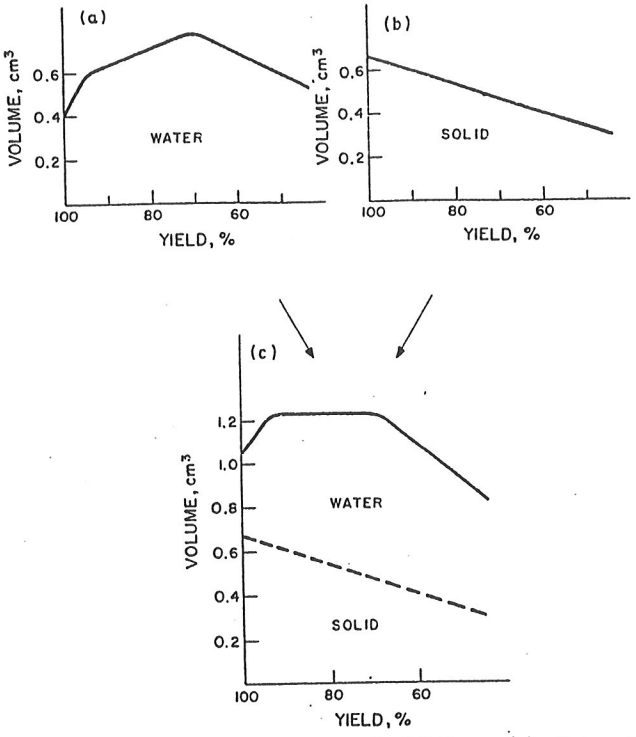

Fig. 4(a). Volume of water in the cell walls of N fibers. (b). Volume of solid in the cell walls of N fibers. (c). Total volume of the cell walls of N fibers.

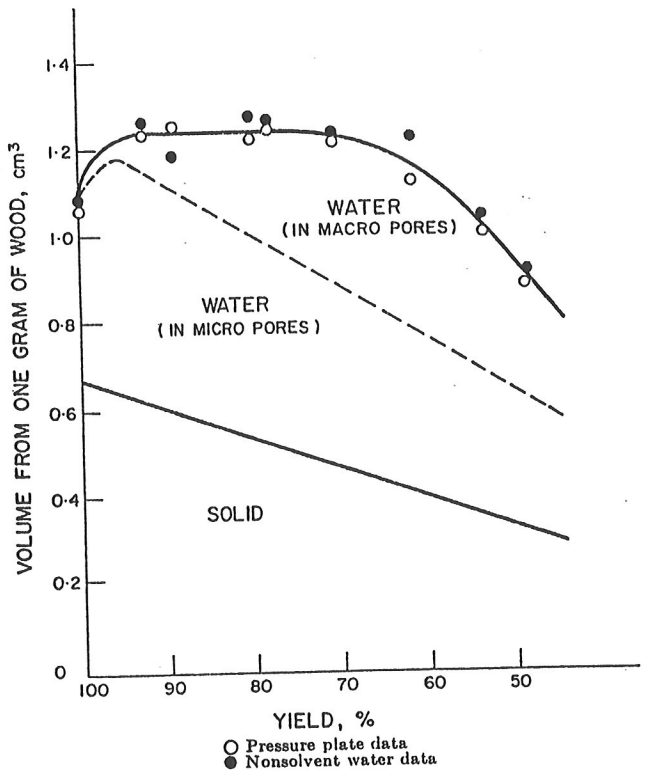

Fig. 5. Volumetric changes brought about by pulping 1 g black spruce by the Ural V process.

at room temperature that it had received before test was not sufficient to swell the wood to its never-dried state. The samples at lower yields had all received some treatment with warm pulping liquor, which could have returned the cell wall to its original dimensions. It is a matter that needs further study.

The most interesting feature of Fig. 4(c) is the constancy of cell wall thickness from 95% down to 70% yield, which implies that, as solid material is removed from the cell wall, the space previously occupied by the material fills with water, with the volume of the pores created equal to the volume of solid material removed. Below 70% yield, the situation changes and we are no longer dealing

with a porous body of fixed external dimensions being eroded away from inside; instead, the porous body starts to shrink.

Before this discussion is continued, it is necessary to introduce the data derived from the first part of this study (*2*). In that work, the volume of pores within the cell wall was measured by nitrogen adsorption and by mercury intrusion on a series of kraft pulps prepared under similar conditions to those reported in the present work. Since these techniques cannot be applied in the presence of water, the pulps were solvent-exchange-dried from the never-dried state before the determinations. This procedure is commonly thought to remove the water from the cell wall while retaining its water-swollen structure. If this is the case, the pore volume after solvent exchange should be equal to the volume of water that the cell wall contained. In Table III the pore volumes obtained in the first part of this work (*2*) are compared with the volumes of water within the cell wall found in the present work, and it is seen that the pore volumes, as measured by nitrogen adsorption after solvent-exchange drying, are considerably lower. The comparison confirms our recent suspicions of the inadequacy of solvent-exchange drying for preserving exactly the swollen cell wall structure (*4*). In this paper we suggested that only a fraction of the pores in the water-swollen cell wall were retained after solvent-exchange drying, and these were termed macro-reticular pores in the belief that they were larger in size than those collapsed by the procedure (the micro-reticular pores). More recent work confirms their relative sizes (*5*). Let us therefore examine the collected data with these ideas in mind; i.e., that the fiber saturation point (in ml/g) represents the total pore volume, that the pore volume found after solvent exchange represents the volume of larger pores, and that the difference between these two volumes represents the volume of smaller pores.

In Table III it is seen that the micro-reticular pore volume per gram of pulp is fairly independent of yield throughout the kraft cook (apart from wood, but this anomaly has been discussed before). This constancy is interesting but misleading and a better understanding is obtained if the micro-reticular pore volume is multiplied by yield. When this is done the micro-reticular pore volume per fixed number of fibers decreases as the cook proceeds. In Fig. 5 the water in the cell wall has been subdivided into that contained within macro-reticular pores and that contained within micro-reticular pores. From this diagram it is clear that to a first approximation the water within the cell wall of wood fibers is contained wholly within small or micro-reticular pores. As the wood is pulped, larger or macro-reticular pores are progressively created not only at the expense of a volume of solid material but also at the expense of the micro-porous system. This latter concept might be visualized as small pores combining to form larger pores as the solid material separating them is eroded away.

It is possible to link the physical changes outlined above to what is known about the chemistry of pulping. Pulping consists essentially of the dissolution of lignin and hemicellulose, and, since these materials are in an amorphous disordered state, it seems reasonable to suggest that the micro-reticular pore system is to be identified with spaces within the water-swollen lignin-hemicellulose macromolecular network. The disordered portion of the cellulose network (*ca.* 30% of the cellulose) should also contribute to the micro-reticular pore system.

Applying this reasoning to the multilamella model for the cell wall described earlier (*3*), the following situation can be hypothesized. In wood the cell wall is composed of many layers concentric with the cell axis. These layers or lamellas are alternately cellulose-rich and lignin-hemicellulose-rich. In the cellulose-rich layers, the cellulose is in the form of microfibrils and the microfibrils are arranged in the form of sheets. During the early stages of pulping, down to 70% yield, the layers of lignin hemicellulose dissolve away, which reduces the amount of material containing micro-reticular pores and leaves the cellulose-rich layers intact with macro-reticular pores between them. During what may be termed the second phase of pulping, from 70% yield down, the cross-linking effect of the lignin is progressively removed, the cellulose network is released, and, being released, it is able to move. This it does in such a way that the spaces between lamellas start to close up, macro-reticular pore volume is lost, and the cell wall shrinks. As to why the cellulose should move in such a manner that shrinkage is caused as soon as the restrictions placed upon it by the cross-linking of lignin are removed, it can be hypothesized that during the growth of the cell wall, the intussusception of lignin and hemicellulose imposes a strain upon the system, which expands the cellulose network so that the removal of these materials permits the reversion of the cellulose to its strain-free state in which the total volume of the system is smaller.

The usefulness and significance of classifying pores into macro-reticular and micro-reticular may well be questioned in view of the artificial and arbitrary nature of the solvent exchange procedure used for making the division, and the fact that this procedure causes considerable shrinkage, pore loss, and undoubtedly many structural changes within the cell wall. We recognize this, and believe that structural studies of water-swollen fibers should always be performed, if possible, while the fibers are still saturated with water. Our most recent studies, to be published shortly, have been based on this belief and have shown that there is a continuous distribution of pore sizes in water-swollen cellulose, ranging from virtually zero up to several hundred angstroms. Our reasons for including data in this paper that were obtained on solvent exchange dried fibers, and for using the terms macro-reticular and micro-reticular are: (1) to show that solvent exchange drying does *not* preserve the total pore volume; (2) to link the present data with earlier work that used solvent drying for studying water-swollen fibers; (3) because solvent exchange is used for certain important techniques, particularly electron microscopy; (4) because, in a porous body containing a wide distribution of pore sizes, any procedure that will separate the pores into two categories, depending upon their response to some particular treatment, becomes a useful tool for obtaining additional information about the system.

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