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THE ACCOMMODATION OF WATER WITHIN PULP FIBRES

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Synopsis In the water-swollen state, water is the major component of the cell wall of a pulp fibre—its amount often exceeding that of the sum of the other components. How this amount of water is accommodated in the cell wall obviously has a great bearing on the structure of the solid phase and the properties of the wet fibre as a whole.

It is proposed that in the wall of the wood fibre, water is held in a micro-porous gel of hemicelluloses and lignin which is distributed as fine platelets within a cellulose skeleton consisting of much distorted lamellae. As the lignin and hemicelluloses are removed by pulping, the amount of water in the wall increases as water fully occupies the spaces previously shared with these components. The subsequent mechanical action of beating is visualised as causing the slit-like spaces occupied by water to progressively link up and the coarser lamella separations to enter the range of visibility by optical microscopy. The entry of additional water into the cell wall, as induced by pulping or mechanical action, is believed by its delaminating action to bring about plasticisation of the wood fibre, a necessary prerequisite to paper-making.

Introduction

THE process of converting wood to paper is carried out almost completely in water and the interactions of the fibres with water are of fundamental importance. However, it is only within the last ten years that we have known, with any degree of certainty, the very basic information of how much water is inside the cell wall and how the amount changes throughout the paper-making process. The information came from the introduction of a new method of investigation—'solute exclusion'. This tool, once applied, rapidly gave us not only the amount of water but also its distribution within pores of different sizes. Further, since the structure of a porous system is but a negative picture of the structure of the solid phase, the data also led to considerations

Under the chairmanship of Dr H. Corte

of the structure of the cell wall as a whole. It is therefore of some interest at this conference to review the major findings provided by solute exclusion and to see how they have fitted in with the concurrent and subsequent findings by the use of other techniques.

The solute exclusion technique

MOST methods for examining the structure of a porous system are applicable only to dry materials. In order to apply these methods to studying the water-swollen structure of cellulosic fibres, wet fibres have often been solvent-exchanged from water, through alcohol to a nonpolar solvent which was subsequently evaporated. This procedure was considered to remove the water while preserving the water-swollen structure and was used because direct evaporation of the water collapsed the structure completely.

Considerable work was done on such solvent-exchange-dried materials, particularly by nitrogen adsorption,[1–7] and the findings laid the foundation of our concept of the structure of the cell wall in the wet state.[5–7] However, it was found that, as a result of the solvent-exchange-drying procedure, the swollen structure of pulps was only partially preserved.[7] This led to a search for new methods of investigation—preferably ones in which the structure could be examined in the actual presence of water. Such a method came out of the work of Samuelson who for a number of years had been extending the 'nonsolvent water' experiments of earlier workers to ones where the molecule in solution had a high molecular weight. In 1964, he carried out experiments for the first time with macromolecules which were not also polyelectrolytes and suggested that the results, which were free of concentration dependence, formed the basis of a method for determining the pore size distribution in wet fibres.[8] This work which was carried out using cotton and polynosic fibres, was taken up by Stone and Scallan who modified the technique and applied it to wood and pulp fibres.[9–12]

In the solute exclusion method, a sample of wet pulp containing a known quantity of water is placed in an aqueous solution of macromolecules of known size and 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 but not as dilute as if it had complete access to all the water in the pulp. From the resultant change in the concentration, it is possible to calculate the amount of 'nonsolvent water' or as it has now become known 'inaccessible water'. The amount is reported on the basis of the volume, or more accurately the weight, per gram of dry fibre. It increases

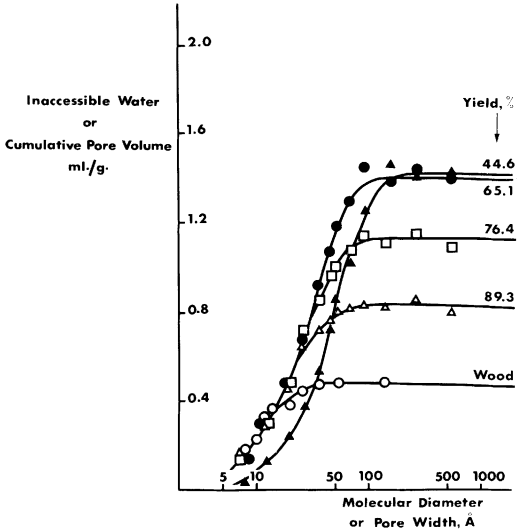

Fig. 1—Solute exclusion curves of sprucewood and kraft pulps prepared from the same wood[10]

with molecular diameter until a maximum is reached 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 (Fig. 1). For this work it was important that the macromolecules used were available in a range of narrow molecular weight fractions, were of known hydrodynamic diameter and, most important, did not in any way react with the surfaces of the fibres. The dextrans (supplemented by some simple sugars for low molecular weights) and polyethylene glycols were found suitable.

The amount of water inaccessible to a totally excluded macromolecule, i.e., as given by points on the plateau region of the solute exclusion curves, is the total amount of water within the cell wall expressed as a ratio of water to solid. It is thus identical by definition to what is known as the fibre saturation point. The results were unexpectedly high when first observed[9]—it had been believed for many years that the fibre saturation points for all woods and pulps were of the order of 0·3 g/g. However, agreement with the new values was obtained by an application of the pressure plate technique recently developed by Robertson.[13] This technique permits the measurement of equilibrium moisture contents of pulps at precisely controlled relative humidities between 99·00 and 99·99 per cent. Within this range of relative humidities

samples can be conditioned to a state where all the water has been removed from the coarser pores within a sample, e.g., lumina and inter-fibre pores, but is retained within the smaller pores such as exist within the cell wall.

Using the hypothesis that the volume of water inaccessible to a given sized molecule equalled the volume of pores within the cell wall with widths below that of the molecule, the plots of inaccessible water against molecular size were regarded as cumulative distributions of pore volume with pore size. From each of these curves we may extract:

(i) a maximum pore size from the size of the molecule corresponding to the start of the plateau region,
(ii) an average, or more exactly, median pore size corresponding to that molecular size which is just excluded from half the total pore volume, and
(iii) an internal surface area which may be calculated by incremental analysis of the curve.[12]

Studies by solute exclusion

Wood

A TYPICAL solute exclusion curve for black sprucewood is the lower curve in Fig. 1. Similar curves for Sitka spruce[14] and white birch[15] have also been published. In general, wood itself has a considerably lower fibre saturation point than the pulps made from it and the median pore size is typically of the order of 10–12 Å.

The fibre saturation point as determined by solute exclusion varies from one sample of wood to another. Within a wood species the variation is not great and depends mainly on the previous history of drying. Thus, many determinations have been made at the Pulp and Paper Research Institute of Canada of black spruce and values were found to be consistently in the range of 0·40 to 0·50 g/g, the higher values being associated with wood that has never been dried and the lower values with wood that has been dried and rewetted. For Sitka spruce, values of 0·40 g/g for the never-dried wood and 0·31 g/g for the kiln-dried and reswollen wood have been reported.[16] Other woods upon which measurements of the fibre saturation point have been made by solute exclusion are Douglas fir,[17] slash pine,[18] sugar maple,[14] aspen,[14, 17] beech,[14] and white birch.[15] With one exception,[17] the values lie in the range 0·31 to 0·62 g/g and are on the average 50 per cent higher than those deduced by older and more suspect methods.[9] It has also been noted that earlywood has a slightly higher fibre saturation point than latewood[16, 17] and, in line with this, it has been suggested that the fibre saturation point decreases with increasing wood density.[17]

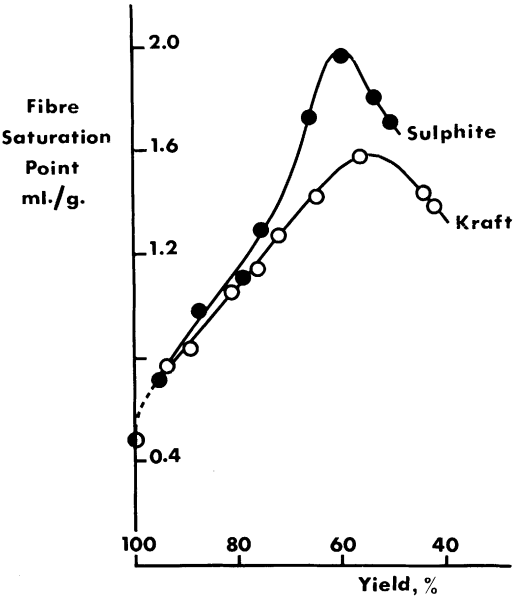

Fig. 2—The variation of the fibre saturation point with pulping yield for a number of pulps prepared from sprucewood[10]

Chemical pulping

Typical solute exclusion curves for pulp samples at different pulp yields are shown for the kraft process in Fig. 1. Similar curves have been obtained for sulphite pulps prepared from the same sample of sprucewood.[10]

As can be seen from the plateau regions of these curves, the fibre saturation point of wood rises considerably as a result of pulping (Fig. 2). However, an interesting calculation showed that the large increases in the amount of water within the cell wall that accompany pulping are not necessarily accompanied by similarly large increases in swelling (meaning a physical expansion of the wall).

The fibre saturation point is expressed as the amount of water in the cell wall per gram of solid material. However, a gram contains more fibres as the pulping yield is lowered. In order to judge whether swelling occurred, Stone and Scallan used the fibre saturation points to calculate the cell wall volume (solid plus water) of one gram of wood as it was cooked. The results could then be regarded as being proportional to the cell wall volume of a single wet fibre as a function of yield. The findings are shown in Fig. 3, from which it

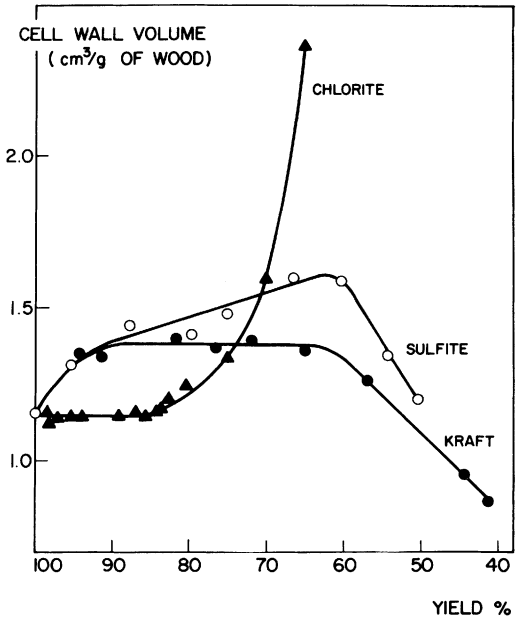

Fig. 3—The variation in the cell wall volume of one gram of wood as a function of yield when cell wall components are removed by sulphite pulping, kraft pulping, and sodium chlorite. The chlorite data[23] has been added to previously published pulping data[10]

can be seen that, during kraft pulping, swelling appears to be limited to a slight amount at the start of pulping. From 95 to 65 per cent yield the cell wall volume is constant and below 65 per cent yield the wet wall actually contracts. In sulphite pulping the behaviour is similar with the exception that the wall swells through the yield range 95 to 65 per cent and always remains more swollen than the kraft pulp. It has been speculated that this extra expansion of the sulphite pulp in the high yield range might be due to the introduction of hydrophilic sulphonic acid groups onto the lignin.[9]

As a result of pulping the median pore size increases from 12 Å in sprucewood to almost 60 Å in the lowest yield pulp (Fig. 4). At any given yield, the sulphite pulps are observed to have a larger pore size than the kraft pulps in keeping with their higher degrees of swelling. At the time these observations were made, McNaughton and co-workers[18] had just published the molecular weights of lignin leaving the cell wall at various stages during kraft and sul-

phite pulping and the parallelism between the development of the average molecular weight of the lignin and the average pore size was remarkable (compare Figs. 4 and 5). Later, it was to be shown that an exact correspondence existed between the size of pores and the size of the lignin molecules, not only for the kraft and sulphite pulping, but also for chlorite delignification.[19] These observations have important implications for the interpretation of pulping reactions, however, for the present considerations, it can be said that the fact, that extracted lignin molecules have the sizes that they do, is a confirmation that the holes left behind in the cell wall are of at least the same size. The data on cell wall pore sizes in wood and pulp have also proved useful in interpreting the interactions of other macromolecular species with wood and pulp fibres, these include the cellulase enzyme,[14, 20] the polyamines[21] and the polyethyleneimines.[22]

In addition to its application to pulping studies, the solute exclusion technique has been used to study the removal of specific cell wall components. Ahlgren studied the removal of lignin from sprucewood by sodium chlorite.[23] He observed that the wet cell wall volume remained at the same level as in the wood down to 80 per cent yield (Fig. 3). Through the same yield range, the

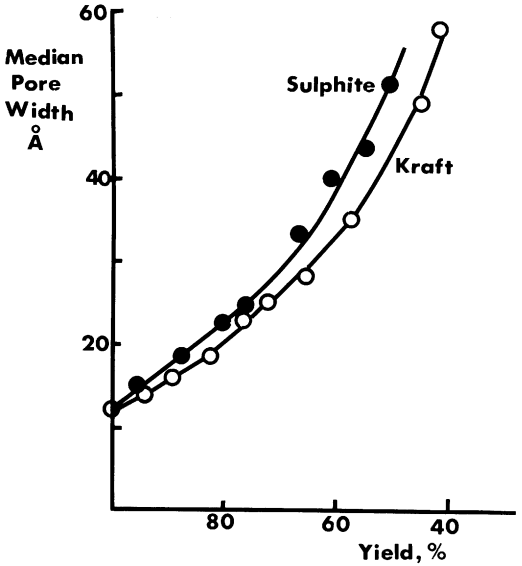

Fig. 4—The change of median pore width with yield for kraft and sulphite pulps prepared from black spruce[10]

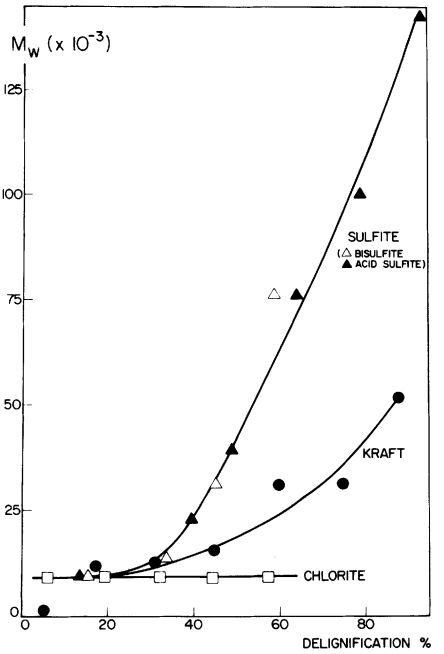

Fig. 5—The variation of the molecular weight of lignin with the yield at which it is removed from sprucewood by a continuous flow process. The chlorite data[19] was added later to earlier data on the pulping processes[18]

pores in the cell wall remained small and the lignin leaving the wall remained at a constant low molecular weight.[19] Since the chlorite reaction is specific for lignin during this yield range,[24] the wall was growing increasingly rich in hemicelluloses and yet no swelling (meaning physical expansion) was occurring. Taken below 80 per cent yield the wall swelled dramatically and the molecular weight of the extracted lignin increased. Notably, below 80 per cent yield the chlorite reaction is no longer lignin specific and hemicelluloses are also being removed.[24] These results appear to challenge the repeatedly expressed opinion that hydroxyl-rich, straight-chain hemicelluloses can be attributed with the ability to swell the cell wall, and that lignin, with its high degree of cross-linking, can be considered as acting as a restraining influence to swelling.[25] Ahlgren felt that the hemicelluloses somehow physically restricted the passage of high molecular weight lignin out of the wall and that

the lignin must therefore reside longer until further reaction reduced it to a suitable size. Following this theme, Kerr[15, 26] studied the delignification of white birchwood by sodium chlorite both before and after removal of the hemicelluloses by alkali. Whereas before the removal of the hemicellulose his observations were similar to Ahlgren's, after removal of hemicelluloses the molecular weights of the extracted lignin increased from the start of the reaction and the rate of delignification was more rapid.

Beating

The beating of pulp is a process where increasing the amount of water in intimate association with the fibre appears to be a major effect. Until the 1950's, the most commonly accepted theory for the enhanced strength of paper resulting from beating was that it was due to the raising and entanglement of fibrils raised on the fibre surface. The increased 'wetness' of the fibres resulting from beating was due to the retention of water by the fibril pile. However, the theory, which has its advocates to the present day, has one very serious shortcoming: it does not explain the large fraction of the increase in the tensile strength of paper which results from the first stages of beating during which little external fibrillation is evident.

In 1957, Emerton[25] proposed, in common with a number of previous authors, that it was the uptake of water within the cell wall that was important during beating, the imbibition being accompanied by internal fibrillation—a loosening of the fibre structure resulting in increased fibre plasticity. Emerton enlarged upon this viewpoint and proposed the form taken by internal fibrillation. In the early stages of beating, he believed the outer constricting layers of the fibre were disrupted and in part removed thus permitting the fibre to swell—a major result of which was the splitting of the cell wall into a series of co-axial lamellae. As beating proceeded, the lamellae would further subdivide into finer lamellae. The process of delamination, he saw as increasing the ability of fibres to deform plastically and to form extensive inter-fibre bonds upon water removal. Evidence given for the tendency of the wall to delaminate was mainly microscopic. For example, it had previously been pointed out that in highly beaten pulps there was a tendency for outer lamellae to peel away and that, what had often been taken as fibrils radiating from fibres viewed longitudinally, were in fact the folds and turned up edges of thin membranes.[27] Emerton suggested that some measure of the ability of a fibre to deform plastically would tell us all that we need to know about the progress of beating. However, he claimed that no entirely satisfactory method existed to do this nor was there an absolute method to measure the swelling of the cell wall.

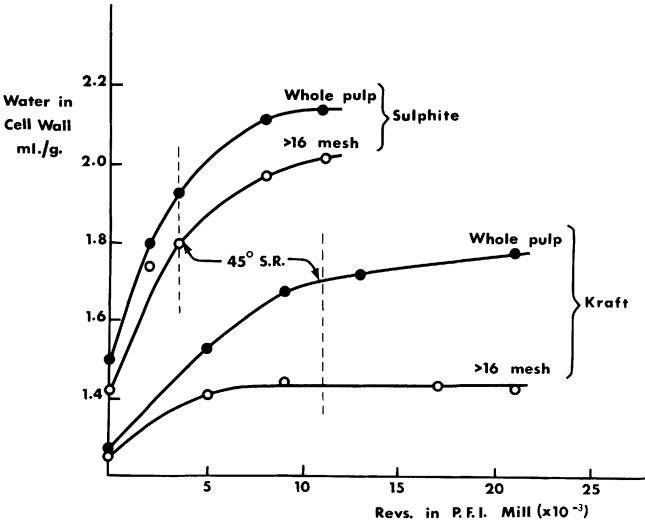

Fig. 6—The effect of beating upon the fibre saturation point of never-dried pulps commercially prepared from pine[11]

The solute exclusion technique provided the first absolute measure of swelling some ten years after Emerton's review, and confirmation that swelling accompanied beating came soon after.[11] As shown in Fig. 6 the amount of water in the cell wall (i.e., the fibre saturation point) increases appreciably during beating. It is significant that swelling increases most rapidly at the start of beating where strength development is most rapid and external fibrillation is a minor effect. The close relationship between swelling of a pulp and the strength of paper it will make is shown in Fig. 7.

The pulps shown in Fig. 6 in the 'never-dried' state are the same pulps shown in Fig. 7 but after drying and rewetting. It is evident from the different fibre saturation points at the start of beating that drying and rewetting results in a decrease in swelling. Examination of the complete solute exclusion curves reveals that the maximum and median pore sizes are also reduced (Fig. 8). Thus the reduced strength properties which are well known to result from drying can be attributed to a closing up of the cell wall structure, probably accompanied by an increase in internal bonding. This would result in less plastically deformable fibres capable of less extensive bonding. Beating on the other hand opens up the cell wall structure.

It has been speculated that the greater ease with which sulphite pulps beat is due to the fact that they have already been through a greater degree of

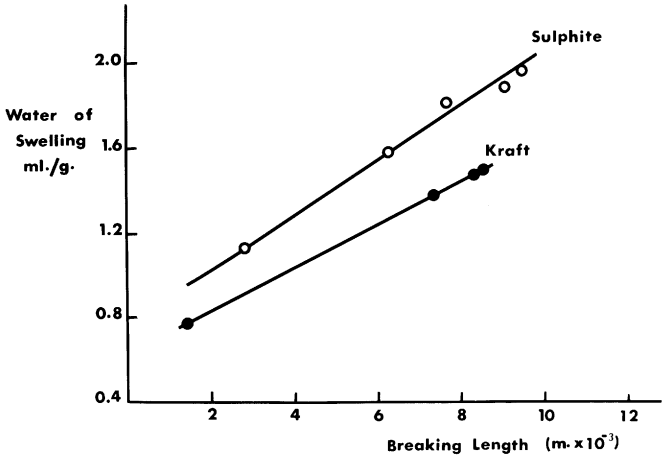

Fig. 7—The correlation between the fibre saturation point and the breaking length as the properties are changed by beating. The two pulps are the same as described in Fig. 6 but after conversion to dry lap and reslushing. Both measurements were made on the > 16 mesh Bauer–McNett fraction separated after beating[11]

swelling in the pulping process.[10, 11] The extra swelling of the sulphite pulp during pulping could thus be considered to be beneficial from the point of view of making a pulp which beats quickly and bonds extensively. On the other hand, the extra swelling could have also resulted in a breakage of so many pre-existing bonds in the cell wall, that it is responsible for the subsequent lower strength of sulphite fibres through a loss of cohesive strength. However, as has been said, these concepts are speculative. Certainly the swelling behaviour of kraft and sulphite pulps are very different but whether this is the cause or an effect of the primary difference between the two types remains to be shown.

Discussion of the data in terms of structure

THE results of solute exclusion determinations, in common with earlier data gathered by nitrogen adsorption indicate that the pores holding water in the cell wall are small and their surface area large. A basic structure composed of sheets of elementary fibrils separated by lamellar spaces of the same order of thickness as the elementary fibril appeared to satisfy the data. In wood, it was considered that a finely-porous lignin-hemicellulose gel filled the spaces between 'elementary lamellae' and that in pulp the spaces were fully occupied by water. Models built upon this concept showed the lamellae as completely

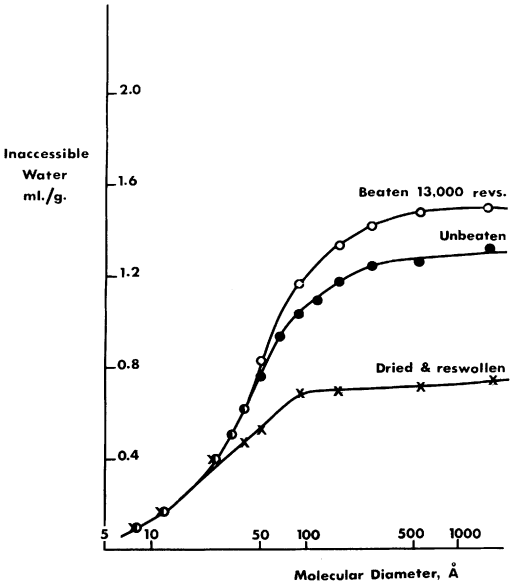

Fig. 8—The complete solute exclusion curves on the > 16 mesh fraction of the kraft pulp described in the previous two diagrams[11]

separated and perfectly concentric with the fibre axis.[6, 12] However, more recent considerations[26, 28] have lead to a modified view.[29] The basic structure is still essentially one of sheets of elementary fibrils but now it is suggested that areas of these are periodically displaced and bonded to adjacent sheets. As the development of the modification is relevant to an interpretation of the data in the last section, the following four paragraphs are taken almost verbatim from the original proposal.[29]

'To a first approximation, let us consider a low-yield pulp fibre to be comprised solely of cellulose microfibrils. Further, let us accept the postulates of Frey-Wyssling[30] as enlarged upon by Rånby[31] that the microfibrils are quadrilateral in cross section, and that the sides of these, which are oriented parallel to the cell wall, correspond to the hydroxyl-rich 101 planes of the crystal lattice. (Centola[32] has published evidence tending to favour preferred orientation of the 101 planes.)

A fibre wall dried from water has been shown to be essentially nonporous and to have a density close to that of the crystal lattice.[33, 34] It has also been shown that in this dry state, there are no hydroxyl groups which are not engaged in hydrogen bonding.[35] Therefore, it would appear that in the dried-from-water state, the microfibrils are bonded together in a close-packed array as shown in Fig. 9A.

Let us now consider the progressive swelling of this dry structure in water. Intrafibrillar swelling agents such as caustic soda of mercerising concentration, or certain amines, cause expansion of the crystal lattice mainly in the form of increased spacing of the 101 planes.[36] It would therefore seem reasonable to assume that water, although not an intrafibrillar swelling agent, but still a polar reagent capable of breaking and reforming hydrogen bonds, would also enter the more accessible of the 101 planes, which are the tangentially-oriented planes between the microfibrils. If this were so, then we might expect delamination of the wall upon swelling.

However, and this is the main concept of this hypothesis, let us suppose that the entry of water is not totally into the tangential spaces between microfibrils, but only preferentially so. This would mean that accompanying tangential cleavage would be a proportional cleavage of radially oriented bonds, although to a lesser degree. The result of this slight change in interpretation is a change in the appearance of the wall, particularly in the intermediate stages of swelling (Figs. 9B and 9C) where the wall in cross-section does not have the appearance of perfectly concentric lamellae. Nevertheless, with further swelling and the breakage of all tangential bonds, the wall does become concentrically delaminated (Fig. 9D).'

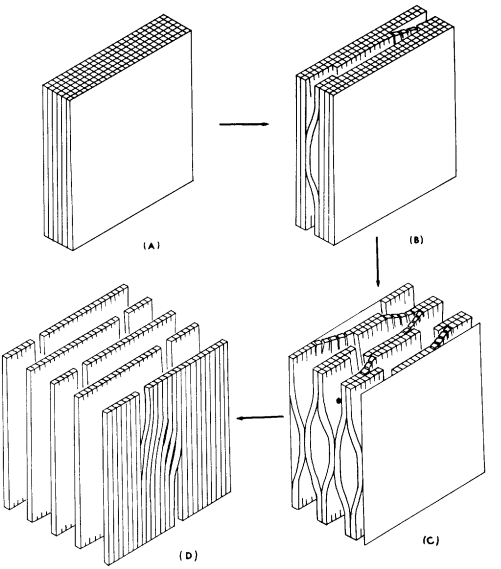

Fig. 9—The pattern of internal fibrillation of the cell wall with progressive swelling, as might be expected from the preferential cleavage of tangentially-oriented bonds. The sketch is of a small section of a wall with zero fibril angle[29]

This concept is not totally dependent upon the proposition that the elementary fibrils have different numbers of hydroxyl groups per unit area in the two directions. A weaker attachment in the radial direction would also result from a lower degree of alignment of the elementary fibrils due to a fibril angle change. From the work of Dunning we know that both the S_1 and S_3 layers are composed of at least a dozen finer layers of different microfibrillar orientation[37] and it is not unreasonable to assume that there are also subtle differences in orientation as we pass through the S_2. A further possibility is that hemicelluloses preferentially coat certain sides of the elementary fibrils.[26]

Let us now consider briefly how this model fits in with solute exclusion and other data.

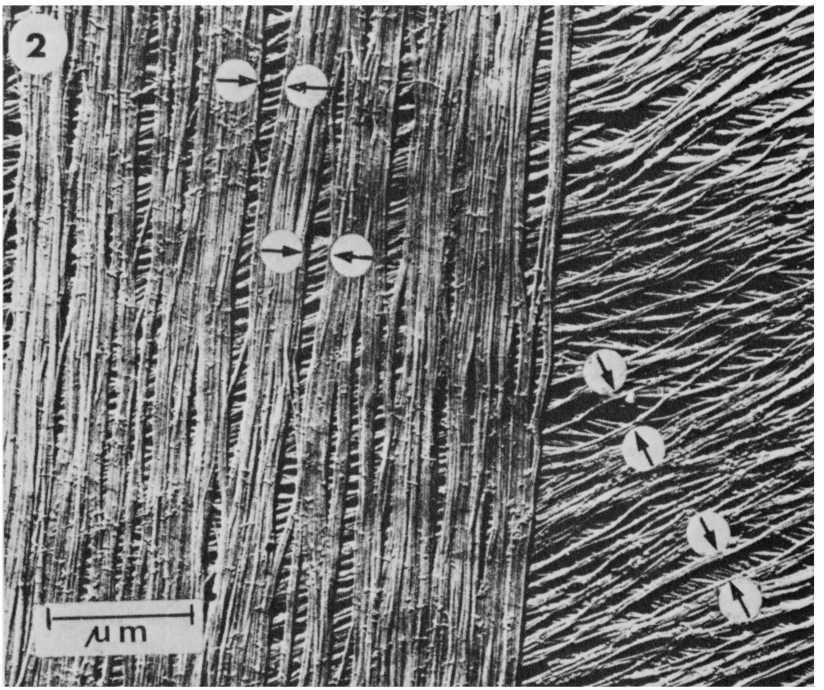

Fig. 10—One of a number of micrographs published by Boyd and Foster[41] and variously attributed to A. Frey-Wyssling and R. D. Preston. This one of an inner wall of *Cladophora prolifera* shows clearly the type of 'lenticular opening' within lamellae which are suggested as common amongst plant cell walls

Wood

To obtain a structure for wood which is compatible with much current data, it is only necessary to suppose that at the time of lignification the cellulose was in, or forced into, a state of swelling as shown in Fig. 9C. Lignin would then take the form of tangentially oriented platelets within the cellulose structure of much distorted lamellae. Such a structure could easily be taken as a random distribution of lignin amongst cellulose fibrils as was reported by Heyn when first examining the ultrastructural distribution of lignin in wood sections.[38] However, more recent work by Kerr and Goring[39] using essentially the same techniques have provided support for almost exactly the model proposed here.

The honeycomb structure represented by Fig. 9C has other advantages as a model for the structure of the cell wall of wood over the idealised concentric lamella model. The small but finite number of radial pores provides room for a small amount of tangential movement to accompany the predominately radially-oriented contraction and expansion of the wall observed during drying and swelling treatments.[40] They also provide a pathway for the movement of reagents into the cell wall and, during pulping, a pathway for the rather large lignin fragments out of the wall. The presence of radial linkages in the wall, while the wall is in an intermediate state of swelling, provides the wall with cohesive strength which could persist after the removal of lignin and hemicellulose by pulping.

More recently Boyd and Foster[41] have presented microscopic evidence for structures such as those discussed but for the tangential aspect of cell walls (Fig. 10). They suggest that microfibrils are laid down parallel and close together. However, as a result of later expansion of the wall during growth, the microfibrils bend somewhat forming 'a trellis-like configuration in which lenticular openings appear between still bonded positions'.

The pulping process

The removal of lignin and hemicellulose during pulping results in a progressive increase in average pore size, however, the changes in wet cell wall volume are comparatively small. It would therefore appear that to a large extent the increase in pore size is the result of water occupying fully the spaces previously occupied by the lignin–hemicellulose gel.

Down to 65 per cent yield, the constancy of cell wall volume occurring during kraft pulping would indicate little disturbance of the cellulose skeleton, but in sulphite pulping some expansion of the wall is apparent and it is possible that in order for the latter to occur, there is some loss of bonding between elementary lamellae.

Below 65 per cent yield, in both sulphite and kraft pulping the cell wall appears to contract and it is possible that with the removal of interstitial material, the lamellae start to aggregate and move towards a structure such as 9B. Part of the loss of volume during this yield range could be the complete loss of middle lamella material which has been shown to be preferentially attacked at this stage of cooking.[42]

Stöckmann[43] has made measurements by optical microscopy of the wet cell wall dimensions in the cross-sectional faces of blocks cooked by the kraft process to different yields. Fibre saturation points calculated from these measurements agree very well with those measured by solute exclusion. The actual dimensional changes, however, vary subtly from those deduced by the latter method. Stöckmann reported that the net movement, as a result of cooking, was a small reduction in the outer perimeter of the fibre and maintenance of the volume of water achieved by an increase in wall thickness, the movement being towards the lumen.

Drying and beating

Used in conjunction with the concepts of Emerton, the model readily yields an interpretation of drying and beating. If we suppose that following pulping the cell wall is in a state of swelling between structure B and C in Fig. 9 as discussed above, then drying will result in a movement to structure A and beating a movement towards structure D.

In rewetting dry fibres, it has been observed that the fibre saturation point is less than that of the never-dried state and the pores smaller (Fig. 8). This situation fits Fig. 9B and we must assume that it results from the failure to re-open of some of the bonds formed during drying. The tensile strength of paper made from dried and rewetted pulp is well known to be less than that of paper made from 'never-dried' pulp. This, too, is in keeping with a higher degree of internal bonding within the rewetted pulp and consequently a lower plasticity of the fibres.

With the beating of rewetted fibres, the fibre saturation point may be brought equal to and then made to exceed that of the never-dried pulp. The sizes of the pores increase proportionally and it can be assumed that the wall structure passes towards the stage represented by Fig. 9D.

For beating or excessive swelling induced by chemical means, the model suggests complete and uniform tangential delamination. An interesting alternate possibility comes from the work of Boyd and Foster.[41] Breakage of one bond within the structure would result in an increasing stress on neighbouring bonds which would result in the propagation and widening of the opening. Such 'cracks' could, once initiated in a few places between radially

adjacent lamellae grow in preference to further debonding of the elementary lamellae. The cracks could, but need not necessarily, encircle the wall.

The introduction of the concept of gross delamination in addition to a finer structure to the cross-sectional and longitudinal aspects of the wall could explain the discrepancies between the results of microscopy and physico-chemical measurements. The data from solute exclusion[12] and previous data by nitrogen adsorption[5, 6] have demonstrated that the pores within the wet cell wall are quite small and that the cell wall has a very high surface area. This information would indicate that the structural elements within the wall are extremely fine. Optical microscopy on wet samples has, on the other hand, only ever revealed a small number of rather thick, widely spaced lamellae.

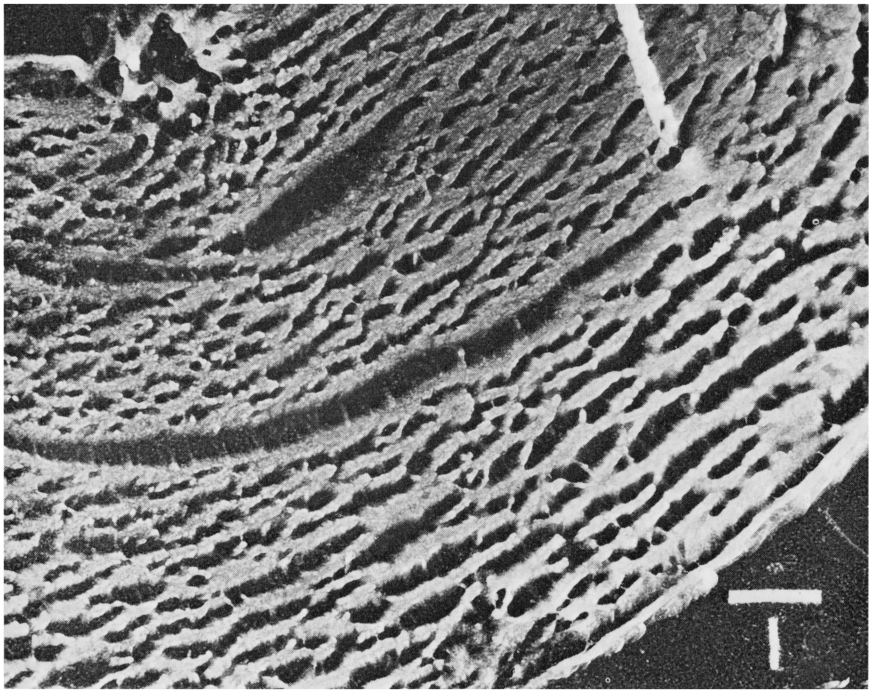

Fig. 11—An electron micrograph of a cross-section of a spruce sulphite fibre prepared after solvent-exchange of the fibre from water to a mixture of butyl and methyl methacrylates, followed by polymerisation. After sectioning, the polymer was washed out and the section metal shadowed. Inset 1 μm. Micrograph by G. M. A. Aberson[5]

However, it is important to note that these lamellae are only observed after the use of powerful swelling agents[44] or after beating.[45, 46]

The application of electron microscopy to pulp fibres in cross-section to reveal the wet structure is much more suspect than that of light microscopy because of the number of suspect stages in sample preparation, i.e., solvent exchange from water to monomer, polymerisation and sectioning. Methacrylate embedding is particularly suspect as causing swelling over and above the natural state of the fibre.[47] Nevertheless, micrographs such as that in Fig. 11 show clearly that the wall is capable of delaminating in the manner suggested.

References

1. Haselton, W. R., *Tappi*, 1955, **38** (12), 716–723
2. Merchant, M. V., *Tappi*, 1957, **40** (9), 771–781
3. Thode, E. F., Swanson, J. W. and Belcher, J. J., *J. Phys. Chem.*, 1958, **62** (9), 1036–1039
4. Sommers, R. A., *Tappi*, 1963, **46** (9), 562–569
5. Stone, J. E. and Scallan, A. M., *Pulp Paper Mag. Can.*, 1965, **66** (8), 407–414
6. Stone, J. E. and Scallan, A. M., *J. Polym. Sci.:* Part C, 1965, **11**, 13–25
7. Stone, J. E. and Scallan, A. M., In *Consolidation of the Paper Web*, F. Bolam, Ed., Tech. Sect. Brit. Paper and Board Makers' Assn., London, Vol. 1, 1965, 145–174
8. Aggebrant, L. G. and Samuelson, O., *J. Appl. Polym. Sci.*, 1964, **8** (6), 2801–2812
9. Stone, J. E. and Scallan, A. M., *Tappi*, 1967, **50** (10), 496–501
10. Stone, J. E. and Scallan, A. M., *Pulp Pap. Mag. Can.*, 1968, **69** (6), 288–293
11. Stone, J. E., Scallan, A. M. and Abrahamson, B., *Svensk Papperstidn.*, 1968, **71** (19), 687–694
12. Stone, J. E. and Scallan, A. M., *Cellulose Chem. and Technol.*, 1968, **2** (3), 343–358
13. Robertson, A. A., *Tappi*, 1965, **48** (10), 568–573
14. Tarkow, H. and Feist, W. C., In *Cellulases and Their Applications*, Ed. Gould, R. F., Amer. Chem. Soc. publication, Advances in Chemistry Series, No. 95, 1969, 197–218
15. Kerr, A. J. and Goring, D. A. I., *Can. J. Chem.*, 1975, **53** (6), 952–959
16. Tarkow, H. and Feist, W. C., *Forest Prod. J.*, 1967, **17** (10), 65–68
17. Ahlgren, P. A., Wood, J. R. and Goring, D. A. I., *Wood Sci. and Technol.*, 1972, **6** (2), 81–84
18. McNaughton, J. G., Yean, W. Q. and Goring, D. A. I., *Tappi*, 1967, **50** (11), 548–553
19. Ahlgren, P. A., Yean, W. Q. and Goring, D. A. I., *Tappi*, 1971, **54** (5), 737–740
20. Stone, J. E., Scallan, A. M., Donefer, E. and Ahlgren, E., In *Cellulases and Their Applications*, Ed. Gould, R. F., Amer. Chem. Soc. publication, Advances in Chemistry Series, No. 95, 1969, 219–241

21. Allan, G. G. and Reif, W. M., *Svensk Papperstidn.*, 1971, **74** (18), 563–570
22. Allan, G. G. and Reif, W. M., *Svensk Papperstidn.*, 1971, **74** (2), 25–31
23. Ahlgren, P. A., *Chlorite Delignification of Spruce Wood*, Ph. D. Thesis. McGill University, Montreal, 1970
24. Ahlgren, P. A. and Goring, D. A. I., *Can. J. Chem.*, 1971, **49** (8), 1272–1275
25. Emerton, H. W., *Fundamentals of the Beating Process*, Marshall Press, London, 1957
26. Kerr, A. J., *Physico-chemical Mechanisms of Delignification*, Ph.D. Thesis. McGill University, Montreal, 1974
27. Ambross, K., Emerton, H. W. and Watts, J., *Proc. Tech. Sect. Brit. Paper and Board Makers Assn.*, 1954, **35** (3), 487–506
28. Scallan, A. M. and Green, H. V., *Wood and Fiber*, 1975, **7** (3), 226–233
29. Scallan, A. M., *Wood Sci.*, 1974, **6** (3), 266–271
30. Frey-Wyssling, A., *Science*, 1954, **119** (3081), 80–82
31. Rånby, B. G., In *Fundamentals of Papermaking Fibres*, Ed. Bolam, F., Tech. Sect. Brit. Paper and Board Makers' Assn., Kenley, England, 1958, 55–82
32. Centola, C., *Das Papier*, 1955, **9** (23/24), 588–592
33. Stone, J. E., Scallan, A. M. and Aberson, G. M. A., *Pulp Pap. Mag. Can.*, 1966, **67** (5), 263–268
34. Stayton, C. L. and Hart, C. A., *Forest Prod. J.*, 1965, **15** (10), 435–440
35. Ellis, J. W. and Bath, J., *J. Amer. Chem. Soc.*, 1940, **62** (10), 2859–2861
36. Davis, W. E., Barry, A. J., Peterson, F. C. and King, A. J., *J. Am. Chem. Soc.*, 1943, **65** (7), 1294–1299
37. Dunning, C. E., *Tappi*, 1969, **52** (7), 1326–1335
38. Heyn, A. J. N., *J. Ultrastruct. Res.*, 1969, **26** (1–2), 52–68
39. Kerr, A. J. and Goring, D. A. I., *Cellulose Chem. Technol.*, 1975, **9**, 563–573
40. Stamm, A. J. and Smith, W. E., *Wood Sci. and Technol.*, 1969, **3** (4), 301–323
41. Boyd, J. D. and Foster, R. C., *Can. J. Bot.*, 1975, **53** (23), 2687–2701
42. Proctor, A. R., Yean, W. Q. and Goring, D. A. I., *Pulp Paper Mag. Can.*, 1967, **68** (9), 445–453
43. Stöckmann, V. E., *Tappi*, 1971, **54** (12), 2038–2045
44. Roelofsen, P. A., *The Plant Cell Wall*, Gebrüder Borntraeger, Berlin Nicolasse, 1959
45. McIntosh, D. C., *Tappi*, 1967, **50** (10), 482–488
46. Page, D. H. and De Grâce, J. H., *Tappi*, 1967, 50 (10), 489–495
47. Dlugosz, J., *Polymer*, 1965, **6** (8), 427–436

Discussion

Dr H. Corte Anticipating the next contribution I would like to make just one comment. You have molecules of different sizes in water and this solution surrounds the fibres. The essence of the method is that molecules of different sizes can penetrate crevices of different dimensions. You assume that all these molecules stay dissolved and are not adsorbed onto the cellulose surfaces. In the next contribution we will hear that gas molecules of a much lower molecular weight are considered to be adsorbed on the walls of the fibres and do not penetrate the interiors of the fibres at all. This seems a little contradictory.

Scallan I don't think this is contradictory. For this technique, we deliberately chose molecules which were not adsorbed and we tested this before we even started. The molecules we used were also carbohydrates, namely, detran fractions and simple sugars. Derek Gray, however, is using molecules which are adsorbed only on the surface of his moist fibres.

Prof. B. K. Steenberg The concertina model being used by you as a model of delamination caused by beating is certainly interesting. But the concertina breaks in tension. Beating is supposed to be mainly in the compression mode.

Scallan When I said that delamination would occur during beating, I was referring to the gross fissures as observed by optical microscopy. These are not visible before beating or mechanical action or severe swelling. I am not sure, however, that the large ones are the ones that are important. There is the development of paper strength during pulping and the increase in the fibre saturation point which is very similar to that reported for beating, and it may be there is a fine lamella structure which is playing a part, here.

Steenberg So your explanation of the lamella doesn't necessarily require a mechanical action, it is just the swelling itself that makes the delamination.

Scallan I think the swelling itself can cause delamination.

Under the chairmanship of Dr H. Corte

Steenberg I agree. But you also say that you can explain beating, meaning, as far as I understand, that this delamination can go further when mechanical action is carried out on the system and of course the concertina model shows how you can do that and even get break. I am in a position to explain the model that can do this under the conditions. I just wanted to ask whether you had found one. The interesting thing is that if you have a system of cylinders, parallel organised, tightly packed, and then exert shear on this package and you will find that there is a stress rotation around the circular rods. So, they are stressed in rotation while you do the shear and this obviously gives you the necessary forces for delamination, so I think you are perfectly right, I have only helped you to give a mechanism which in shear action can produce delamination.

Scallan I don't have much to add, all we really did was to enlarge on Emerton's interpretation. I don't think we know everything about beating yet, though.

Steenberg But your paper states that swelling increases with delamination and that delamination is there and I think you are completely right. I only assisted you by giving a mechanical explanation, which you haven't done with concertina or the Australians haven't done with the concertina because it is compression.

Prof. R. H. Marchessault I gathered that you said that more tangential rather than radial breaks would explain the delamination. From the model I would have said that it was the other way round. More radial breakage than tangential breakage.

Scallan I mean tangentially orientated breaks, caused by radial forces.