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THE CELLULOSE/WATER RELATIONSHIP

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Synopsis—This paper is a condensed survey of the interactions between water and cellulose materials. It is introduced by some general remarks about the interaction of water with solids, with special attention to hydrogen bonds, solutions and gels, then about the chemical and physical properties of cellulose fibres. The main discussion is devoted to the interaction of water below and above the saturation point, dimensional changes and restricted swelling, drying and hysteresis and, finally, the quantitative measurements of the absorbed water.

Introduction

THE cellulose/water relationship forms the very basis of papermaking. In the science and technology of the industry, the term is now generally used to include all the interactions that take place between water and not only cellulose, but also the other components that occur with it in papermaking fibres. These interactions can be reduced to a number of simple physicochemical processes, which either singly or in combination are to be found as basic mechanisms in almost all of the manufacturing steps in paper production and in many aspects of the behaviour of paper under use conditions.

The relevant processes to be treated in this paper are—

1. The reaction of water at fibre 'surfaces'.
2. Fibre swelling.
3. Interfibre and intrafibre bonding.

For each, it will be necessary to consider both increasing and decreasing water contents and, in some cases, water as both liquid and vapour.

The discussion will be introduced with some general remarks about the interaction of water with solids, with special attention to hydrogen bonds, solutions and gels. A short review will also be given of the chemical and physical properties of the cellulose fibres relevant to their interaction with water.

The present treatment of the subject is a survey covering a wide field. For more detailed studies, the interested reader is recommended to consult the following excellent sources—

Stamm, A. J., *Wood Chemistry*, ed. L. E. Wise and E. C. Jahn (Reinhold Publishing Corpn., New York, 1952), Part 2, Chap. 18

Howsmon, J. A., *Cellulose*, ed. E. Ott, H. M. Spurlin and M. W. Grafflin (Interscience Publishers Inc., New York, 1954), Part 1, Chap. IV: D

Barkas, W. W., *Mechanical Properties of Wood and Paper*, ed. R. Meredith (North Holland Publishing Co., Amsterdam, 1953), Chap. I–V

Browning, B. L., *The Chemistry of Wood* (Interscience Publishers Inc., New York, 1963), Chap. 9

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Interaction of water with solids

COMPARED with other liquids, water possesses unique properties such as high density, high viscosity, high surface tension, high specific heat and high latent heats of evaporation and fusion, all of which are the consequence of the strong bonds existing among its molecules.

Hydrogen bonds

In a free atom or ion the 'centre of gravity' of the positive charge in the nucleus and that of the negative charges of the electrons will always coincide. When the atoms are bonded together in molecules, however, some electrons are shared with neighbouring atoms, disturbing the electrostatic balance. Here, some different situations are of interest—

1. In homonuclear diatomic molecules (such as nitrogen, N_2) or heteronuclear ones with negligible ionic character (such as hydrogen iodide, HI and carbon monoxide, CO), the distribution of charge is symmetrical and the net result is a molecule with no dipole moment.
2. In some triatomic molecules such as carbon dioxide, CO_2 and carbon disulphide, CS_2, the bonds (C=O and C=S, respectively) involve an asymmetric charge distribution, but, owing to the symmetrical structure of the molecule (the bond angle O=C=O and S=C=S being 180° in each case), the charge distribution is also symmetrical and the molecule has no dipole moment.
3. If the molecule, however, is asymmetrical (which, for instance, is the case with triatomic molecules, when interatomic bonds are not co-linear), it will be a permanent dipole. Water is a typical example, the angle H—O—H being 104.5°.

Symmetrically charged molecules or ions may be polarised in an electric field, thus becoming induced dipoles. The electric field may be either a field between electrodes or the field surrounding an ion or a permanent dipole. Both permanent and induced dipole molecules will orient themselves in such electric fields and, in the case of ions or polar groups—in solution or in the solid phase—mobile dipole molecules will be mutually attracted, forming a layer of oriented molecules. Depending on the strength of the electric field and the nature of the attracted dipoles, it is supposed that such layers can be one molecule or several molecules thick. In the latter case, the attraction forces and degree of orientation decrease rapidly with increasing distance.

Being strong permanent dipoles, the molecules of liquid water attract each other and tend to arrange themselves by balancing out dipole moments. In the resulting structure, the hydrogen atoms lie in a position on or very close to a straight line between neighbouring oxygen atoms, forming a bond (the so-called hydrogen bond) between them. This orientation of the molecules, together with the hydrogen bonds between them, results in a dense structure with low mobility of the molecules and explains the characteristic physical properties of water such as high density, high viscosity, high surface tension, high specific heat and high latent heats of evaporation and fusion. It should be recalled that liquid water has a considerably higher density (1.000 at 4°C) than ice (0.917), showing that the molecules are more densely packed in water than in the well-ordered crystalline solid structure.

In general terms, a hydrogen bond is said to exist between a functional group A—H and an atom (or group of atoms) B in the same or a neighbouring molecule when there is—

1. Evidence of bond formation.
2. Evidence that this new bond linking AH—B specifically involves the hydrogen atom already bonded to A.

The tendency to form hydrogen bonds is strongest if the atoms A and B are two closely spaced electronegative atoms, usually oxygen, nitrogen, fluorine and, occasionally, chlorine. In the hydrogen bonds formed by water, the hydrogen atom is always in a position on or very close to one of the straight lines between neighbouring oxygen atoms. It is, however, always closer to one of the oxygen atoms than to the other. This indicates that, even if a hydrogen bond has been established between the hydrogen atom of one water molecule and the oxygen of another, this secondary bond is of less strength than the already established covalent bond. In accordance with this, the hydrogen bond is drawn as $R_1OH—OR_2$.

The strength of a bond can be measured by the energy required to rupture it or by the distance between the centres of the involved atoms. The regular

covalent bond, which binds the atoms of most molecules together, has an energy of 50–100 kcal/mole and an interatomic distance generally in the range 1–2 Å. The strength of the hydrogen bond varies, depending on the nature of the molecules involved. In FH—F^-, the energy is about 27 kcal/mole; but, in systems that involve oxygen, the energy is usually in the range 5–8 kcal/mole, corresponding to a distance of 2.5–2.9 Å between bonded oxygen atoms. In water, the distance between the H atom of one water molecule and the O atom of a neighbouring one is about 1.7 Å.

The extent of hydrogen bonding decreases in the sequence of phases solid → liquid → gas and increases with falling temperature.

Attractive forces can also exist between uncharged molecules without permanent dipoles. This type of binding (known as Van der Waals' forces) is weak and will usually have an energy of 2–4 kcal/mole at a distance of 3–5 Å. A characteristic of these bonds is that they rapidly decrease in strength when the distance l between the atoms involved increases, the energy being proportional to l^{-6}. In the case of electrostatic attraction—for instance, between ions—the energy is proportional to l^{-1}. Van der Waals' forces are therefore of little or no importance except in the case of very closely spaced atoms such as in the solid state. In crystalline high polymers such as in the 002 plane of cellulose, the total Van der Waals' force might be quite significant, owing to the well-ordered structure, the large area involved and a nearest distance between atoms of about 3.1 Å.

Hydrogen bonds are formed both within molecules and between molecules. From a papermaking point of view, the latter type is of greater importance. Hydrogen bonds are, as will be mentioned later, an important factor in keeping the cellulose molecules together in the crystalline microfibril; they are the means by which both liquid water and water vapour are bound to the hemicellulose-cellulose material of the fibre and they are formed within the cellulose material and between neighbouring fibres in close contact when wet fibres are dried. The active groups forming hydrogen bonds in cellulose and hemicellulose are primarily the hydroxyl groups, but carbonyl and carboxyl groups, if present, will also participate. Of these, the carbonyl groups form the strongest hydrogen bonds.

Solutions

When a substance M dissolves in a solvent S, forces of one kind or another are acting between M and S in such a way that the molecules M are wholly or partly covered by a layer of immobilised solvent molecules and thus move within the solvent as would a conglomerate of the solvent molecules themselves. The molecule M is said to be solvated by S. If the solvent is water, the molecules are said to be hydrated.

Electrically charged units such as ions are readily hydrated, because the water molecules, being permanent dipoles, are oriented in the electrical field surrounding the ion and strongly attracted to it by electrostatic forces. In the case of small ions, the whole ion is covered by water molecules, mostly in several layers. Some large ions such as are derived from soap ($C_{17}H_{35}COO^-$ Na^+) are, however, only hydrated at the charged end and have a tendency, owing to the attractive forces between their unhydrated ends, to keep together in conglomerates. Many large molecules not normally soluble in water can be made so, however, by the introduction of ionic groups. In such a case, the state of solution depends upon the size of the molecules, the degree of dissociation of the ionic groups and the frequency of such groups along the molecules. Actual examples in the pulp and paper industry are—lignin sulphonic acid; alkali lignin in alkaline solution, in which case the phenolic hydroxyls are dissociated; acidic and basic dyestuffs, rosin size (the sodium salt of abietic acid); the sodium salts of carboxymethylcellulose and cellulose xanthate.

A substance can also be dissolved by water and its molecules hydrated because of the formation of hydrogen bonds between it and the water. Typical examples are alcohols and carbohydrates such as sugar. A prerequisite is that the substance in question contains electronegative groups such as —OH, —CHO, =CO, —COOH and —NH_2. In the case of large molecules, the content of such groups must be fairly high to ensure a continuous layer of bonded water around the molecule. In such cases, there might be several layers of oriented water around the molecule. Some examples are—starch, gamma-cellulose, polyvinyl alcohol and ethylhydroxyethyl cellulose.

Gels

Some molecules, both small and large, have a tendency to agglomerate to particles of such size that they scatter light, but still form solutions without sedimenting. The solution is called a sol and can be either lyophilic or lyophobic. In the case of a lyophilic sol, the solvent molecules are bound to the colloidal particles—that is, the particles are solvated. In the case of lyophobic sols, no such interaction between sol and dispersion medium takes place. If the solvent is water, the terms hydrophilic and hydrophobic sols are used. *Lyophilic* sols are readily dispersed in the medium and redispersible after coagulation; *lyophobic* sols disperse with difficulty, being unstable and not redispersible after coagulation. A *hydrophilic* colloid readily forms a solution in water; a *hydrophobic* colloid does so only with difficulty.

In a lyophilic sol, there might occur bonds of one kind or another between the colloidal particles to such an extent that the whole system of solvated particles and solvent forms a rigid body. Such systems are called gels and are

grouped as elastic or swelling gels and non-elastic or non-swelling gels. Well-known examples of the first type are agar-agar and gelatine; silica gel is of the non-swelling type.

The swelling shown by elastic gels as they take up solvent is a process that in its nature is the same as the solvation occurring when a molecule goes in solution. In the case of hydrophilic gels, the water is bonded by hydrogen bonds to hydroxyl groups or other electronegative groups or by electrostatic forces to ionic groups inside the gel.

Swelling can be unlimited or limited. In the first case, as long as more solvent is added, swelling proceeds continuously; the rigid structure of the gel is lost, the system becomes a sol and, finally, a molecularly dispersed solution. Rubber in benzene, cellulose acetate in acetone and agar-agar in water behave in this way. In the case of limited swelling, cross-linking bonds between the molecules restrict the expansion of the gel above a certain volume, despite the presence of an excess of solvent. In this state, the solvent within the gel can be regarded as a concentrated solution that is under an osmotic pressure balanced by the stresses in the cross-linked gel substance. Partly vulcanised rubber in benzene is an example of limited swelling. The swelling of a cellulose fibre is also restricted, as will be shown later.

An interesting case of limited swelling is a gel under stress. Certain amorphous high polymers are known to be soluble in suitable solvents if swelling and dissolution are allowed to take place when the polymer is in a stress-free condition. If stretched, however, the same high polymer becomes insoluble. The gel swells, but the swelling is limited. The stresses introduced are said to crystallise the structure partially (which means the formation of highly bonded areas) and to restrict the mobility of the macromolecules (which prevents them from solvating). A certain degree of mobility of the gel molecules seems to be a prerequisite for their going into solution.

When drying a swollen gel, the solvent molecules evaporate and their space is continuously filled by the neighbouring molecules by contraction of the solvent film. Because of their partial mobility, the high polymer molecules are drawn to each other, the net effect being that the gel shrinks. When the last solvent molecules between two gel molecules evaporate, bonds are formed between the latter and a solid body of appreciable mechanical strength can be formed. In the case of hydrophilic gels with water as solvent, these bonds are hydrogen bonds. Specially in the case of chain polymers, this kind of drying under shrinkage brings about a partial alignment of the gel molecules with each other and the building up of stresses within the solid body. Thus, a gel that has been dried under shrinkage is nothing but a gel under stress and will obey the laws of gels under tension. It seems to be worthwhile to keep this phenomenon in mind when dealing with the peculiar behaviour of dried

cellulose fibres on rewetting and when explaining the hysteresis of water vapour sorption isotherms.

Chemical and physical properties of cellulose fibres relevant to their interaction with water

THE chemical and physical natures of cellulose, hemicellulose and lignin were dealt with in detail at the 1957 Cambridge and the 1961 Oxford symposia. An outline of these aspects will now be given to provide a basis for understanding the behaviour of the fibre in contact with water or water vapour.

Native cellulose is built up from linear high polymer molecules of anhydro-*β-d*-glucopyranose having a chain length of 3 000–10 000 glucose units (1.5–5 μ). Being a monopolymer without branched molecules, cellulose occurs as a crystalline structure held together by covalent bonds in its length direction and by hydrogen bonds and Van der Waals' forces in the two planes at rightangles to the length direction. Despite the fact that both the hydrogen bonds and the Van der Waals' bonds are weak bonds, as already mentioned, the total forces holding the planes of the crystal together are strong as a result of the large surfaces and the regular structure. It should also be mentioned that native cellulose (cellulose I) has a denser structure than cellulose precipitated from solution (cellulose II).

In the native cells, cellulose forms the microfibrils, which have an unknown length and a width of 70–100 Å. So far as is known today, they consist predominantly of crystalline cellulose, but may also include regions of slightly disordered structure. The orientation of the microfibrils makes the fibre anisotropic. In wood fibres, the microfibrils of the secondary wall (S2), which makes up the main part of the fibre wall, run more or less parallel (15°) with the long axis of the fibre. In the outer layer of the secondary wall (S1), they form a helix around the fibre (65°) and, in the thin primary wall, a cross-layered structure.

Hemicellulose, on the other hand, is built up from different sugar monomers, the relative amounts of which vary with the wood species. The molecules are heteroglucans such as glucomannan, galactoglucomannan, arabinogalactan, glucuronoxylan and glucuronoarabinoxylan. Many of these are methylated and acetylated and some are branched. As a consequence of the irregular structure, the hemicellulose molecules are incapable of forming crystalline regions in the same way that cellulose does. Hemicellulose is of an amorphous nature and more or less ordered, hydrogen-bonded regions are supposed to exist only over small areas. Degree of polymerisation is 70–250. In the fibre, hemicellulose is located in the spaces between the microfibrils.

As a consequence of their chemical structures, cellulose and hemicellulose react in quite different ways towards both liquid water and water vapour.

With its dense and regular structure, crystalline cellulose is not penetrated by water: the native microfibrils therefore do not swell in water. Strong swelling agents such as 18 per cent sodium hydroxide solution, liquid ammonia, cuprammonium solution and quaternary ammonium bases are needed to open up the cellulose crystal. Water molecules bond only to the surface of the microfibrils and, possibly, to the disordered regions. As a further consequence of their crystalline structure, the microfibrils are relatively resistant to aqueous solutions of, for example, acids, oxidising agents and enzymes.

Being of an amorphous nature, the hemicellulose of the fibre is almost completely penetrated by water vapour and by water, both of which are taken up with swelling. It sorbs water both as vapour and as liquid. In general, its reactions with agents in aqueous solution in some respects resemble those of homogeneous systems. It will dissolve in swelling agents and, once isolated from the fibre, it is water soluble (for example, gamma-cellulose).

Lignin has a certain hydrophilic character, probably derived from its content of hydroxyl groups (1.15 per phenyl propane unit). It is a moot point whether lignin should be classed as hydrophobic or hydrophilic. Isolated Klason lignin, for instance, adsorbs water vapour, but does not swell appreciably in water. After sulphonation, however, it swells strongly.

In the fibre, lignin occurs in admixture with the hemicellulose, probably as a complex linked by covalent bonds.

Interaction of water with cellulose fibres

THREE types of water can be considered as taking part in the cellulose/water relationship—water of constitution, imbibed water and free water. As pointed out by Stamm, it is best to use the general term *imbibed water* for the water held by the fibre, as it is non-committal about the manner of take-up. The same holds more or less also for the term *sorbed water*, which is frequently used. In order to indicate whether the water has been taken up from the liquid phase or from the vapour phase, it has been suggested to make use of the prefix in such a way that **ab**sorption means liquid sorption and **ad**sorption vapour sorption. The terms will be used in this way in the present paper. In the literature, however, absorption and adsorption are often used without further qualification.

The line of demarcation between water of constitution and imbibed water is not very sharp. It may be defined as the condition corresponding to zero relative vapour pressure. Experimentally, zero relative vapour pressure can be approached only by heating at temperatures somewhat above 100°C, but at the same time the cellulose material runs the risk of decomposition. When dried under the conditions commonly used in the determination of moisture

content, the amount of bound water retained is probably less than 1 per cent. The transition between imbibed water and free water also is by no means sharp and is again to some extent a matter of definition. It will be discussed in more detail later.

The so-called *fibre saturation point* has to do with the transition between imbibed and free water. It is defined as the water content required to saturate the fibre walls completely without filling the lumen.

Interaction below saturation point

The effect of relative vapour pressure on the moisture taken up by cellulose fibres below their saturation point is illustrated by the sorption isotherms in Fig. 1. These isotherms have a characteristic sigmoid form; they refer to (*1*) desorption from the wet, never-dried state, (*2*) adsorption in moist atmosphere to the fibre saturation point and (*3*) desorption again. They illustrate the well-known hysteresis effect.

There are three main theories about the mechanism of water binding—the surface adsorption theory, the capillary condensation theory and the solid solution or gel swelling theory.

In the *surface adsorption* theory, the fibre is considered to have a large amount of internal surface, which contains active hydroxyl or other polar groups that can strongly bind water molecules through hydrogen bonds. The surfaces in question can be the surfaces of the cellulose microfibrils or surfaces around accessible voids and capillaries. The initial water sorbed is supposed to be distributed over the available surfaces in a monomolecular layer. In this way, the rapid increase in moisture regain at low vapour pressures and the straightening out of the adsorption isotherm at about 0.2 relative vapour pressure is explained. At higher relative humidities, the formation of multilayers is supposed to take place. It should be pointed out, however, that this theory does not explain the rapid increase in moisture content at high relative vapour pressure.

The *capillary condensation* theory is based on the fact that the vapour pressure of water in a capillary depends on the radius of the capillary and decreases with decreasing radius. As a consequence, the water of wet fibres will be retained in the capillaries at relative vapour pressures just below 1.0. It is supposed that water vapour from the surrounding air will also condense in an empty capillary system if the size of the capillaries corresponds to a vapour pressure lower than that of the moist air. In the case of cellulose fibres, such condensation might start at a relative vapour pressure of about 0.7 and the amount of water condensed will increase rapidly with higher vapour pressure. The lumen is a capillary of such size that, according to this theory, it should cause water to condense if the relative vapour pressure is

close to 1.0, but no observations have been reported that this is really the case. It could therefore be questioned if capillaries—and especially the larger ones—can be filled with water from the vapour phase or if they have to be filled by liquid water. If the latter alternative is the only possibility, the term *capillary condensed* water is misleading; but, as a capillary already filled with water can retain this water at relative vapour pressures below 1.0, a term like *capillary retained* water seems more appropriate.

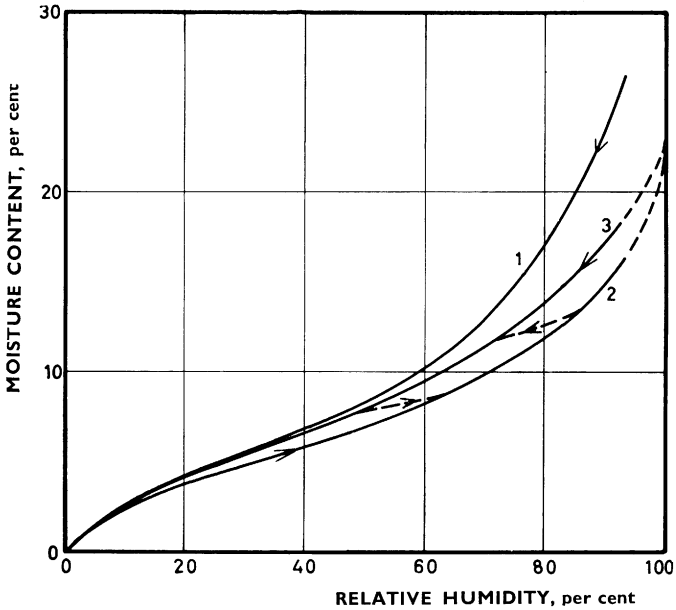

Fig. 1—Desorption and adsorption isotherms of a bleached sulphite pulp (Seborg, Simmonds & Baird[1])

According to the *swelling* theory, the adsorption takes place in the disordered regions of the cellulose material, where there are accessible hydroxyl groups capable of forming hydrogen bonds with water molecules. In wood fibres and especially in those of papermaking quality, the disordered regions are mainly located in the amorphous hemicellulose. The hemicellulose material thus behaves in the same way as has already been described for gels in general. According to this theory, the adsorption of water vapour over a wide range of relative humidities can be explained.

It should be pointed out that the two first-mentioned theories were presented by textile chemists in order to explain the adsorption of water by

cotton, which, if kier-boiled, contains very little material of a hemicellulose character, but very many capillaries. The last-mentioned theory was introduced later in order to explain the water take-up of substances like viscose rayon and cellulose film, which are rich in amorphous material, but with few or no capillaries.

Contrary to all earlier experience, Van den Akker and Hardacker have shown quite recently[2] that by the application of high pressure it is possible to squeeze liquid water out of a wood fibre at a moisture content in equilibrium with 69 per cent relative humidity at 22°C (about 8 per cent moisture regain). The water was sucked back into the fibre when the pressure was released. The pressure applied was up to 20 kgf/mm^2, with visible water droplets at 4 kgf/mm^2. This observation will undoubtedly influence the conventional thinking on the ways in which imbibed water is held by the fibre.

There is no reason to limit our view to one bonding mechanism for the uptake of water. Most likely, the sorption of water can be explained in many different ways. It should be kept in mind that the same type of sigmoid adsorption curve, which is considered to be typical for cellulose materials and which is the basis for the different speculations on the mechanism of water uptake, is obtained for a number of other substances of quite different nature such as wool, gelatine and sulphuric acid and that the general form of the isotherm is the same for all kinds of cellulose materials, regardless of whether they have an open structure with many light-scattering capillaries (wood, cotton, hot alkali refined woodpulp) or are optically dense (cellulose film, glassine) or whether they contain only cellulose or both cellulose and hemicellulose. Generally, it seems to be that the sorbed water mixes with the cellulose material on accessible sites, which might be surfaces of crystalline cellulose or fairly completely accessible amorphous regions.

The interest devoted to adsorption theories arises from the endeavour to have a better understanding of this important phenomenon and to be able to control those factors that are responsible for the swelling of pulp fibres in water and for the paper taking up water vapour. It should be pointed out, however, that thermodynamical observations like the adsorption-desorption isotherms, regardless of their characteristic form, can never explain the mechanism by which water molecules are bound to cellulose. For this purpose, experiments dealing with single molecules (for instance, labelled molecules) are needed.

There are two more aspects of the problem to be considered in this connection—the heat of sorption and the volume of the adsorbed water.

Water imbibition by a cellulose material is exothermic. Accordingly, the temperature coefficient of the sorption is negative; less water is adsorbed at

higher temperature and constant relative humidity. The evolution of heat when 1 gram of dry cellulose is fully moistened is called the *integral heat of sorption* and amounts to 10–25 cal/g according to the type of cellulose material (Table 1). The *differential heat of sorption* is the heat evolved when 1 gram of water is combined with or is extracted from a large quantity of the cellulose material. The differential heat of sorption varies with the moisture content of the material as shown in Fig. 2. The curve starts at a level of 280–300 cal/g water for dry material (which is very much the same for all kinds of cellulose material) and flattens out asymptotically to zero in the moisture range of 20–30 per cent (Table 2). The levelling-out point varies with the type of fibre and the moisture content at which the heat of sorption becomes zero corresponds to the fibre saturation point. Further water will be taken up without heat effects and is thus free water. When evaporating the sorbed water, the heat needed will be the sum of the average heat of vaporisation (585 cal/g) and the heat of sorption at the actual moisture content.

TABLE 1—FIBRE SATURATION POINT AND INTEGRAL HEAT OF SORPTION FOR DIFFERENT CELLULOSE MATERIALS (COMPILED BY STAMM)

Material	*Saturation point, g water/100 g oven-dry solids*	*Heat of sorption, cal/g*
Standard cotton	17	10
Sulphite pulps	25–28	13–15
Holocellulose	16	28
Wood	28–33	17–20
Mercerised cotton	40	18
Viscose rayon	38–42	20–25

The value 300 cal/g for the heat of sorption at zero moisture content corresponds to 5.4 kcal/mole of water, a value which shows that the initial water is held with bonds that correspond in strength to hydrogen bonds of the type OH—O, thus strongly supporting the hydrogen bond theory.

About the initially sorbed water, the observation has been made that there is less reduction in free energy during the process of adsorption than corresponds to the heat effect, involving a *reduction in entropy*. This means that the water molecules are bound to the cellulose material in a more or less oriented manner (Fig. 2).

It should be observed from Fig. 2 that both the bonding energy and the reduction in entropy level out gradually, showing that the transition from highly bonded water to free water is not sharp, but quite continuous.

When dealing with the nature of the sorbed water and the mechanism of

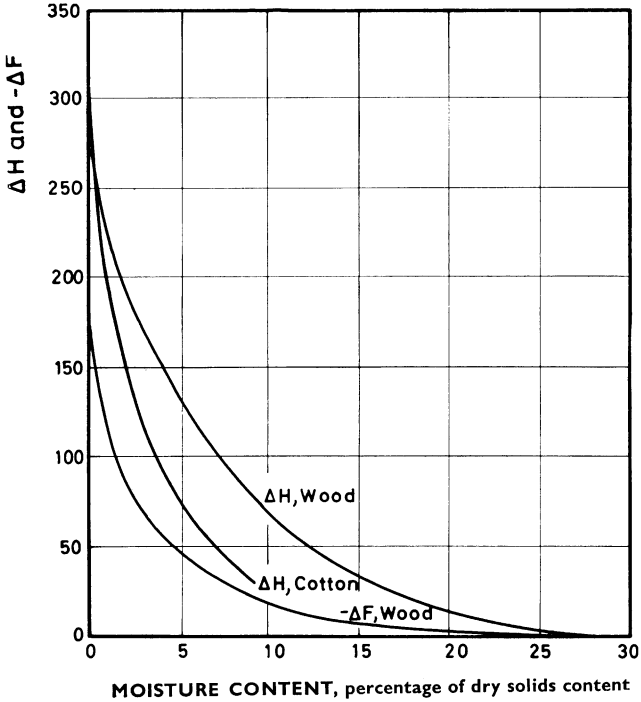

Fig. 2—Differential heat of sorption (ΔH) and free energy changes (− ΔF) as a function of moisture content (Stamm)

bonding, great interest has also been devoted to its specific volume. Measurements of the specific volume of cellulose materials are usually made by displacement methods. Today, helium is considered to be the best displacing medium, because it is not adsorbed. It is supposed also to penetrate the voids

TABLE 2—EFFECT OF PULPING CONDITIONS ON THE CELLULOSE/WATER RELATIONSHIP PROPERTIES

Type of pulp	*Yield, per cent*	*Gamma-cellulose, per cent*	*Pento-san, per cent*	*Breaking length, km*	*Acces-sibility, per cent*	*Moisture regain (65% rh), per cent*	*Amount of 'bound water', g water/g cellulose*	
							−10°C	$Na_2S_2O_3$
Chlorite holocellulose	67.9	38.9	8.2	—	34.8	9.34	0.36	0.82
Strong sulphite	49.5	12.6	4.6	6.5	16.8	7.32	0.33	0.32
Soft sulphite	46.5	8.8	3.7	4.7	13.9	6.91	0.31	0.21
Dissolving grade sulphite pulp	44.6	6.9	2.6	3.7	10.6	6.58	0.30	0.16
Above pulp hot alkali refined	33.4	2.1	0.2	1.7	7.3	6.30	0.28	0.02

between unbonded chains of the amorphous regions. Calculated from the difference in specific volume values obtained in water and in helium, the average density of the adsorbed water up to the fibre-saturation point is 1.033 for cotton, with the initially adsorbed water having a density of about 1.10. The conclusion usually drawn is that the sorbed water is highly packed. It could also be said that water, despite the system being heterogeneous, mixes with the accessible parts of cellulose material in the same way as with alcohol or sulphuric acid, processes that (as is well known) take place with contraction.

Interaction above saturation point

So far, the present discussion has mainly been concerned with the adsorption of water from the vapour phase. Appreciably more water is taken up when the fibres are wetted by liquid water. What really happens when the fibres are dipped in water seems not to have been thoroughly studied. Wood at the fibre saturation point (about 30 per cent moisture) takes up three times the amount of water when soaked in water; this is accompanied by further swelling, but without generation of heat. In the case of pulps, the collapsed lumen is observed to be opened and filled with water; probably, large capillaries inside the cell wall behave in the same way, as they would not have been filled with water from the vapour phase condensation, as discussed earlier. In this process, the surface tension forces of the water and the hydrophilic nature of the cellulose material will be of importance. When drying the wet fibre at a relative vapour pressure close to 1.0, this capillary-held water will not evaporate, owing to the depressed vapour pressure at the meniscus—it is 'capillary-retained'.

In the case of wet fibres, the transition between bound water and free water is almost impossible to define and it seems to be of no practical meaning to do so. Most likely, there are large amounts of water having a slightly depressed vapour pressure (0.98–0.999) and the transition from bound to free water will be quite continuous.

As is well known, completely dry fibres wetten slowly when soaked in water. If the fibre is moist, wetting proceeds more rapidly and this effect has been observed to take place up to a moisture content of about 4.5 per cent.

Liquid water is not only bound to the cellulose material inside the fibre wall, but also to some extent to the surface of the fibre. The amount of such externally held water will increase rapidly when the fibre wall is broken down by mechanical action (beating), forming wall fragments and fibrils.

When wet fibres are pressed together in such a way that the wet units come in close contact, they form a relatively strong structure. This phenomenon has not been studied closely. It seems likely that the cellulose surfaces are not

brought in direct contact with each other, but that neighbouring surfaces share the same layer of bound water and that this layer, because of its organised structure and hydrogen bonds, is capable of transferring rather strong forces without breaking. In such a layer, the water molecules in the centre will be the least bound and oriented, therefore the most mobile. If enough water is present, the centre will consist of free water of no special orientation or extra strength. With decreasing water content, however, the layers of oriented water will merge into each other and form a stronger bridge. This immobilisation of the fibre surface water and the development of mechanical strength is of interest to the papermaker both from a drainage and wet web strength point of view. In which way the bonding capacity of such water is determined by fibre properties is not known. Most likely, factors such as the amount of external surfaces, fibrillation, fibre flexibility and the amount and nature of the surface hemicelluloses are of importance.

To this kind of interfibre attraction should also be added the effect of water surface tension forces. There are three phases in the wet web—fibres, water and air. The water will thus form menisci against the air phase and the surface tension in these menisci will contribute to press the fibres against each other and to give mechanical strength to the wet web.

Restricted swelling

The swollen cellulose fibre is an example of restricted swelling. As pointed out earlier, hemicellulose is water soluble if once extracted from the fibre with the help of swelling agents. As no dissolution takes place when soaking the fibre in water, the swelling must be restricted in one way or another. Possible swelling restricting elements could be—

1. The primary wall, which, because of its cross-layered fibrillar structure, is isotropic from a mechanical point of view.
2. The fibrillar spiral of the outer layer of the secondary wall S1. It is known from balloon-swelling in chemical agents that the fibrillar spiral of S1 causes the 'nodes' and that complete swelling takes place only after the S1 spiral has been ruptured.
3. Irregularly oriented microfibrils crossing the parallel structure of S2.
4. Cross-linking bonds within the hemicellulose gel such as (postulated) chemical bonds between hemicellulose molecules, well-ordered highly hydrogen-bonded areas and crossing molecules.
5. If lignin is present, covalent lignin-hemicellulose bonds.

As swelling proceeds, some of the structural bonding elements come under load and an equilibrium is set up between the tension in these and the osmotic swelling pressure. In the water-saturated fibre, one must therefore always reckon with a considerable inner swelling pressure, balanced by the outer

layer of the fibre, the internal fibril structure and the resistant hydrogen bonds or lignin bonds in the hemicellulose gel. It would be reasonable to assume that this swelling pressure in the case of lignin-free pulps would increase with the hemicellulose content of the fibre.

During mechanical treatment, the action on the fibre is concentrated on those elements that restrict swelling and are already under a tension, which in many cases will be close to their breaking load. As these break, further swelling takes place until a new equilibrium is established between the swelling pressure and the new group of structural elements, which now comes under tension.

Cross-linking within the cellulose material can be achieved artificially, for instance, by treatment with formaldehyde under acid conditions. Ether bridges are supposed to be formed between the molecules of the amorphous regions. This is a technique used to increase the wet resistance of viscose rayon and it is also known that woodpulp after such treatment becomes free and difficult to beat and that the solubility in 18 per cent sodium hydroxide solution (gamma-cellulose) decreases markedly. The paper formed is weak, bulky and opaque. All these observations indicate that swelling has been further restricted because of the introduced cross-linking with chemical bonds.

Quantitative measurements of the absorbed water

Many attempts have been made to measure the amount of bound water of papermaking fibres in water suspension. As is clear from the earlier discussion, it is impossible to define the amount of bound water in a wet pulp and the values obtained by different methods depend as a result on actual experimental conditions. Figures for bound water should therefore be handled with the greatest caution and should be used only for comparison of pulps of the same type. Among suggested methods the following may be mentioned—

1. Water retained after centrifuging under standard conditions. The value obtained (WRV) depends on the centrifugal force used and the centrifuging time.
2. Water permeability; measurement of the viscous flow. The results are given as *effective fibre volume* and *specific surface*.
3. Treatment with a salt solution (such as thiosulphate) and calculating a postulated separation into a salt-containing fraction of free water and a salt-free fraction of bound water. The result depends on the salt concentration.
4. Determination of the latent heat of fusion of a frozen wet sample and calculating the amount of postulated frozen and unfrozen water. The result depends on the freezing temperature.

It should be mentioned, too, that the fibre saturation point and the total heat of sorption (Table 1) and the moisture regain at a certain relative humidity can be used for a given kind of fibre to indicate the amount of water taken up when soaking in liquid water.

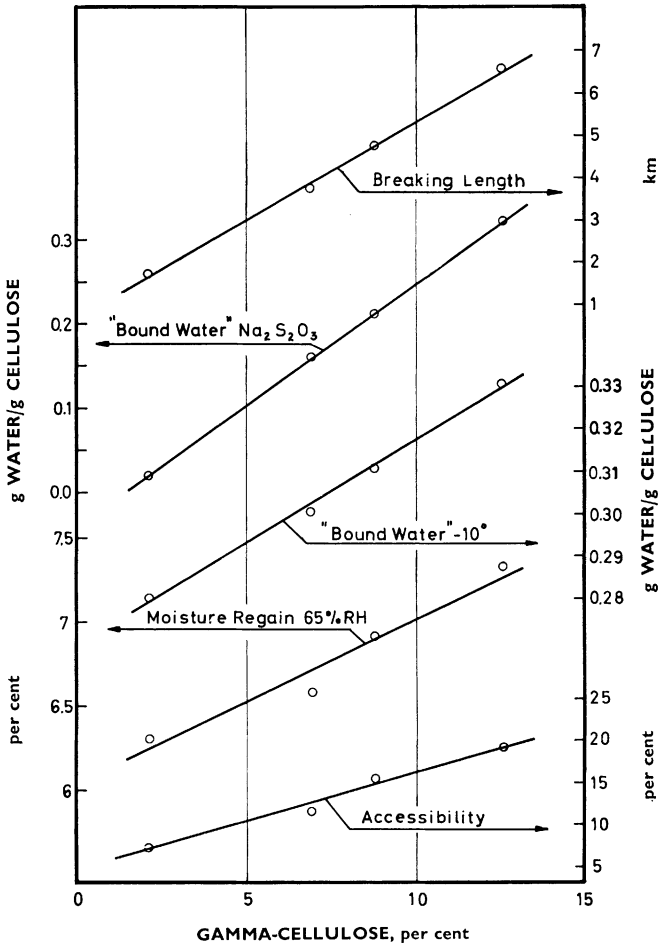

Fig. 3—Cellulose/water relationship properties as a function of the gamma-cellulose content of the pulp (same pulps as in Table 2)

The methods mentioned have been used to determine how processing conditions and the quality of the pulp influence its uptake of water. Some examples will be given here.

Drying decreases the water retention value; a slush sulphite woodpulp with WRV 160 changed its WRV to 104–112, depending on the way of drying.[3] When soaking a sulphite pulp in water, the WRV increased from 127 after 2 h soaking time to 146 after 2 days and 169 after 25 days.[3] Sulphonation of a semi-chemical pulp increased the WRV from 115 to 175, which is considered to be partly a consequence of the introduced hydrophilic sulphonic acid groups.[4] The delignification of a strong sulphite woodpulp with sodium chlorite increased its WRV from 157 to 173.[3]

It seems to be generally accepted today that the hemicellulose content of the fibre, under otherwise comparable conditions, is the main factor controlling its relationship to water. To illustrate this, Table 2 has been compiled. A chlorite holocellulose pulp and three bleached sulphite pulps of different yields have been prepared from the same lot of spruce wood. The rayon pulp has been hot alkali refined, by which treatment its hemicellulose content was markedly decreased. The five pulps thus cover the yield range 68–33 per cent. The hemicellulose content is indicated by the amount of gamma-cellulose and the amount of accessible material as measured with the Nickerson hydrolysis method. Pentosan values are also included. The interaction with water is described by moisture regain values at 65 per cent rh and bound water determined by both the freezing method at $-10°C$ and the thiosulphate method (2 per cent solution). For comparison, the breaking length of the unbeaten pulp is also included.

The correlation among these properties for the sulphite pulps is shown in Fig. 3, in which the gamma-cellulose content, being considered to be a fairly accurate estimation of the amount of hemicellulose, has been put on the abscissa. As can be seen, the data used to describe the interaction with water correlate well with the gamma-cellulose content, which strongly supports the concept that, for a given kind of fibre, the amount of hemicellulose is the major factor controlling the interaction of a pulp with water. The reader's attention is drawn also to Table 1, which shows that the saturation point and the heat of sorption are related to the hemicellulose content of the cellulose material.

Drying

When analysing the mechanism of drying, a distinction should be made between the macro-behaviour of the fibre assemblage and the processes occurring at a micro-level within the fibre wall and in the bonding material in the areas of interfibre contact.

As has already been discussed, the fibres in the wet web are held together by rather strong forces in the connecting system of water. This is a combined effect of surface tension and the forces in thin water films; the thinner the

films, the stronger the forces. As a consequence, the fibres are drawn or pressed against each other. When drying starts, first the free water and later on the surface bound water evaporate and, in order to fill the space of the evaporated water, the fibres are drawn together. This mechanism of sheet consolidation based on the action of surface tension was suggested by Campbell in 1932 and is today known as the Campbell effect. He calculated the compressing forces to be of the order of 6 kgf/cm^2 in the case of fibres and appreciably higher if fibrils are also present.

The first phase of drying ends when the water content of the fibre passes the saturation point. Up to this point, only the web has been consolidated and, if dried on the papermachine, the contraction of the web has almost completely taken place in the *z*-direction of the sheet. This consolidation will be favoured if the fibres are made flexible by beating and if the open voids between the fibres are filled with fibre fragments and fibrils—free or anchored at the fibre surface—thus increasing the amount of surfaces in close contact with each other.

When passing the saturation point, the imbibed water starts to evaporate and the fibre shrinks. In this phase of drying, movable units such as separated microfibrils and hemicellulose molecules align themselves partly to each other. With some exaggeration, it could be said that the consolidation taking place between the fibres during the first phase of drying proceeds at the molecular level in the second phase. Referring to what has already been said about the drying of gels in general, it needs only to be stated here that, at the end of drying, hydrogen bonds are formed wherever cellulose and hemicellulose molecules are brought into close enough contact. This happens all over within the fibre wall, as well as in the combined surface material of two crossing fibres. In the latter case, a paper bond has been formed.

As was pointed out earlier, the drying of a swollen gel is accompanied by shrinkage. With its complicated fibrillar structure, the fibre cannot shrink freely and, owing to its interlocked position in the paper web, it cannot move or rotate. Hence, stresses are built up in the fibre wall as a result of drying; the microfibrils will be under tension or compression, as will also be the interfibrillar cementing hemicellulose material. This is referred to as dried-in stresses, the amount of which undoubtedly controls quite a number of the mechanical and physical properties of the paper.

The transition between the first and second phase of drying as outlined here, is not sharp when drying paper, board and pulp sheets. In technical drying, the surface of the sheet will always dry faster than the centre and the surface thus will change to the second phase while the centre is still in the first, resulting in irregular drying. Certain papers show 'skin' effects[5] and the irreversible hornification of pulps shows up even at an average dry

solids content of 60–65 per cent, whereas the fibre saturation point is about 75 per cent. If, however, drying is performed slowly by bringing all fibres to the same dry solids content, step by step, the two postulated phases of drying can be separated, as is shown in Fig. 4. In this case, the opacity of a sheet made from the semi-dried pulp has been used as a tool to follow the irreversible effects of drying. For the actual pulp (a strong sulphite pulp), the transition between the first and the second phase is about 75 per cent dry solids content, which fits well with the fibre saturation point that could be expected for this type of pulp.

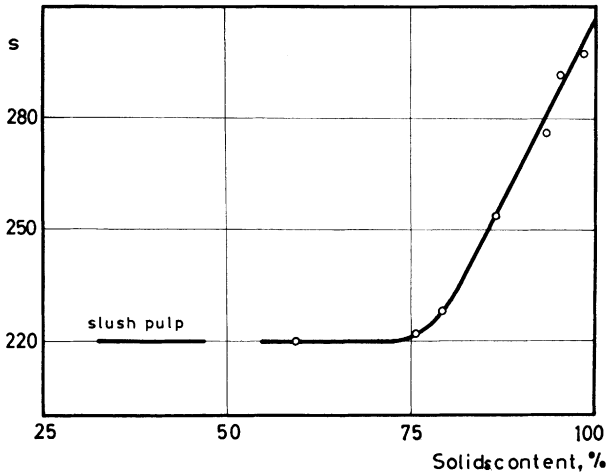

Fig. 4—Effect of drying on opacity—a never-dried strong sulphite pulp was dried to equilibrium in atmospheres of different humidities

When dealing with the transition between the first and second phase, it should also be mentioned that at the end of the first phase, when the free water has been evaporated, the water films in the fibre-to-fibre bonds are extremely thin and consist of bound water. The paper has an appreciable strength (despite the fact that it is still wet) and the fibres are firmly fixed to each other. When fibre shrinkage starts in the second phase, the fibres will not slip in the bonded area and the shrinkage in the cross-direction of one fibre will stretch the segments of the partner fibre in their length direction. Again, dried-in stresses are built up in the paper.

The paper web contracts as soon as the water between the fibres begins to evaporate. In order to avoid this contraction, the paper must be stressed. The

tension required to balance the force of shrinkage can be taken as an indication of the tension forces acting in the contracting water system of the web. Fig. 5 shows how these forces are very low below a solids content of 40 per cent and then increase rapidly in the range 60–80 per cent.

The strength of the wet web sheet at different dry solids contents is also illustrated in Fig. 5. As can be seen, the tensile strength is low at solids contents below 60 per cent, then increases rapidly and uniformly.

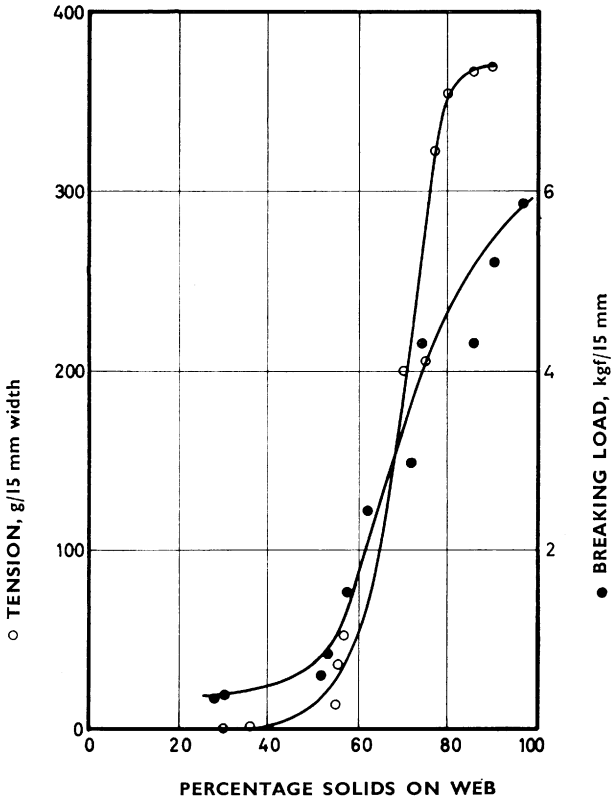

Fig. 5—Course of drying for an unbleached sulphite pulp—tension required to prevent shrinkage ○ and development of tensile strength ● (Lyne & Gallay[6])

Hysteresis

For a given cellulose fibre sample, the moisture sorption at a given relative vapour pressure is greater when the fibre is brought to equilibrium from the wet state or a higher relative vapour pressure than when the fibre is brought

to equilibrium from the dry state or a lower relative vapour pressure. This phenomenon is known as hysteresis and is shown in Fig. 1. The curve 2, starting with a completely dry sample and ending at the saturation point, is called the standard adsorption isotherm; curve 3, correspondingly, the standard desorption isotherm. Experimentally, the relative vapour pressures very close to 1.0 are impossible to obtain. So long as adsorption or desorption starts at either the dry point or the saturation point, respectively, repeated adsorption and desorption will, as a first approximation, give the same hysteresis loop bound by curves 2 and 3. At any point within this loop, equilibrium between the fibres and water vapour may be established by interrupted adsorption followed by desorption or vice versa, as indicated by the dotted lines in Fig. 1. Consequently, the moisture content of cellulose material in equilibrium with moist air is not given solely by the relative vapour pressure in the atmosphere, but depends also on the history of the sample, a fact that is important to keep in mind when dealing with the moisture content of paper and specifically when conditioning paper to an exact moisture content.

The ratio of the adsorption to the desorption values is essentially constant at all relative vapour pressures, except at the ends of the loops. It is about 0.85 and varies only slightly for different cellulose materials (wood, cotton, sulphite woodpulp).

No generally accepted explanation yet exists for the hysteresis phenomenon. Reference is often made to the following mechanism.[7]

When dry cellulose comes into equilibrium with atmospheres of increasing relative vapour pressure, molecules of water are adsorbed and cause swelling of the (hemicellulose) network. The swelling breaks secondary bonds between the molecules of the network and causes the number of hydroxyl groups capable of acting as strong sorption sites to increase with increasing relative vapour pressure. If desorption is now allowed to occur, the network tends to contract. This contraction is delayed, however, by the persistence of bound water on the new sorption centres formed on adsorption. Therefore, a higher moisture content occurs at a given relative vapour pressure on desorption.

The hysteresis effect can also be explained on the same basis as the earlier mentioned restricted swelling of gels under tension. During desorption, the network, which has been in a swollen state, is relatively stress-free. On drying and shrinkage, partly or completely, stresses are built up in the fibre both on a micro-level in the hemicellulose areas and on a macro-level in the fibrillar structure of the fibre wall. During adsorption, the dried fibre will therefore be under extra stress and, at any given relative vapour pressure, the swelling will be more restricted than for the corresponding fibre undergoing desorption.

As is well known, never-dried cellulose materials are more swollen than corresponding samples after drying and rewetting in water. This holds for green wood, fresh cotton taken directly from the boll, slush pulp and the rayon filament after spinning and washing. The desorption isotherm of the never-dried sample is included in Fig. 1 and, as can be seen, the amount of retained water is higher than at standard desorption. This effect of drying is by its nature similar to the mechanism underlying desorption-adsorption hysteresis. It should therefore be explained in the same way. In particular, the explanation based on partly stress-free swelling in the wet state and pronounced limited swelling, owing to dried-in stresses in the dry state, seems to be well applicable.

This effect goes under the name *irreversible hornification*, the degree of which depends on the kind of pulp and the degree and way of drying. The strength properties of sheets made from unbeaten, slush and dried pulps, respectively, are quite different, but after proper beating of the dried pulp the properties of the sheet can be brought very close to that of the slush pulp.[8] The effect of beating in this special case seems therefore to be to break the bonds formed by drying, thus releasing the stresses that restrict swelling. In general, the main effect of beating might be to break those bonds in the fibre—they may be native or formed in the pulping process—that restrict swelling.[9] It could also be said that, from a beating point of view, the effect of drying and hornification is the same as moving the pulp backwards along the beating curve into an extrapolated region beyond the unbeaten slush pulp.[8]

The dimensional changes as well as other changes in the properties of the fibre taking place as a consequence of adsorption and desorption also show hysteresis loop has the same general form and characteristics as that for moisture regain.

Dimensional changes

Both wetting with liquid water and imbibition of water vapour are accompanied by changes in the dimensions of the fibre—that is, the fibre swells. This swelling is markedly anisotropic. Because the main part of the non-swelling microfibrils (those of the secondary wall S2) are oriented roughly parallel to the fibre axis and since the swelling material is the amorphous hemicellulose between the microfibrils, the dimensional changes will take place at rightangles to the fibre length. When S2 and the fibre become thicker, the periphery of the fibril spiral of S1 increases and this causes the fibre, if free to move, to rotate around its own axis. The expanded periphery of S1 will also tend to shorten the fibre and, on drying, the reverse effects should occur. A small extension (0.1–0.4 per cent) of the fibre during drying has been reported by Jentzen,[10] who found its magnitude to be independent of

drying load and related to fibril spiral angle. According to earlier investigations, woodpulp fibres elongate by about 1 per cent when wetted, as do cotton fibres.

In width, woodpulp fibres appear to undergo 20–25 per cent shrinkage when dried from the water-saturated condition to 0.25 relative vapour pressure.[11] The extent of this shrinkage increases with beating degree. On rewetting the dried fibres, only about 70 per cent of the shrinkage is recovered (Fig. 6).

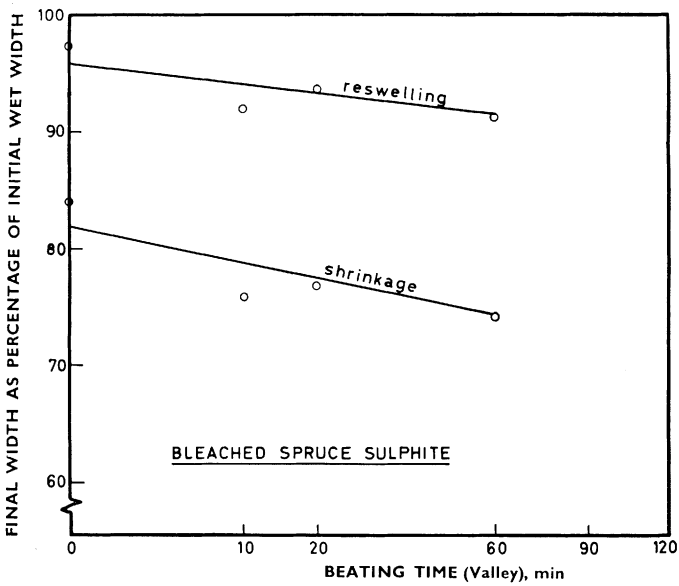

Fig. 6—Changes in width of bleached spruce sulphite fibres on drying and subsequent reswelling in water (Page & Tydeman[11])

Because of the considerable scatter between the shrinkage results for individual fibres, it was concluded that factors additional to removal of thermodynamically bound water are responsible for shrinkage. Those suggested were loss of capillary water with collapse of capillaries and the possible rearrangement of the internal structure arising from the tensions operating.

Simultaneous measurements of the width changes and water contents of never-dried pulp fibres through a desorption-absorption cycle[12] have shown that at very high relative vapour pressure large changes in moisture content can occur without proportionate width change. One conclusion from this

study was that the dimensions of fibres in water and in equilibrium with air of 0.95 relative vapour pressure are not appreciably different.

Attention should also be drawn to the irregular way in which the fibre changes its cross-sectional area when dried. This is a consequence of the relatively thin fibre wall and the roughly square—not circular—fibre cross-section. When the lumen water evaporates, contraction takes place predominantly in one direction, whereby two opposite fibre walls are brought in close contact and the other two are folded: the fibre is said to collapse. Typical features of collapsing were shown by Jayme & Hunger at the 1961 Oxford symposium. Fibres with thin secondary walls such as springwood tracheids and low density hardwood fibres collapse to ribbons, whereas the thick-wall fibres (summerwood, dense hardwoods) keep their native form better. In paper, the fibres generally collapse in the *z*-direction of the sheet.

Conclusion

THE MAIN purpose of this paper has been to present a unified picture of the more important practical and theoretical aspects of the cellulose/water relationship. The paper technologist will find, however, that not all the cellulose/water interactions important in practice have been included; nevertheless, it is felt that simple analysis of these in terms of the basic mechanisms described—hydrogen bonding, solvation and swelling—will lead to a satisfactory interpretation.

The paper has highlighted certain areas in which our scientific knowledge of the relationship is deficient. Two particular areas of importance that require further exploration are the nature of the forces that seem to exist between cellulose surfaces separated by several molecules of water (which is of great significance in the understanding of wet web strength) and the changes that occur in the nature and distribution of the water in fibres as they are first removed from liquid water and allowed to come to equilibrium at very high relative humidities and vice versa.

The tradition in this field of paper science has been to approach many of these relationships from the thermodynamic point of view. This has led to useful understanding up to a point, but it would appear that the return from further effort along these lines may be less rewarding than a change to a more mechanistic approach that involves, for example, tracer experiments, rate studies and particularly more extensive direct microscopical observation.

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Transcription of Discussion

Discussion

Chairman—To open the discussion, I would like to return for a while to the more fundamental concepts that Giertz referred to. During this week, we shall be discussing in many different ways how water leaves the cellulose phase. We could ponder this afternoon a little about the way that water is bonded in the fibrous phase and consider the components in the fibre that are responsible for the adsorption of the water. What I am going to present is a continuation of my discussion at the Oxford symposium in 1961—the question of the accessibility not just of the cellulose, but of the holocellulose fibres and the wood structure.

The report brought out last time is now largely presented in two papers in *Tappi*, together with co-authors from Syracuse. This work has been continued during the last three years in Stockholm together with Prof. Erik Forslind and the invited researchers Dr Hanna Rizk (from Egypt), Ralph Noe (from U.S.A.) and Harry Peacock (from England).

You may recall from our earlier work that we found a distinct difference in the water (hydroxyl group) accessibility of hardwood and softwood represented by spruce and birch: about 50 per cent for birchwood against 60 per cent for spruce. Why? In the *Tappi* papers, we indicated one possible reason to be that the hemicellulose in hardwood (birch) is partly acetylated, giving internal hydrogen bonds between the acetyl groups and adjacent hydroxyl groups that would be strong enough to resist the deuterium and tritium exchange reactions, yet the resulting inaccessibility would not be enough to explain the total effect.

Supported by a grant from the Pioneering Research Committee, Appleton, we have applied NMR measurements to this problem. Wide line NMR measurements cannot distinguish between protons in the water phase and protons in the cellulose phase. The difference between the two phases is small in this respect and related to the carbon atoms, which do not interfere so much in NMR work on the protons in the hydroxyl groups.

First, a few words on the background to NMR measurements. With the specimen in a strong magnetic field, the proton spins are oriented and will absorb energy from a high frequency beam at resonance. If the protons are

undisturbed (free protons), they give a sharp resonance line (a narrow absorption band). If, however, the protons are disturbed, for example, by other protons or by restrictions in their motion, they will give a broad band—a broader and more extended band, the more disturbed (or coupled) the protons are. We have run our measurements on holocellulose specimens from birch and spruce woods that have retained the wood structure undisrupted. Delignification of the wood is a very tedious operation, which was performed by using the peracetic acid method. At different degrees of drying, the holocellulose specimens give resonance curves that always contain a narrow band superimposed on a broad band, referring to protons that move freely and have restricted motion, respectively. The separation of the narrow and the broad band in the resonance curves is a rather intricate matter that has to be performed by computers with certain assumptions about the shape of each band. The interesting point is that there is a distinct difference between the hemicellulose in spruce and birch holocelluloses. Careful drying and deuteration of the birch holocellulose can completely remove the narrow band and give a residual broad band that is not unaffected by the removal of the narrow band. This indicates a distinct and rather large fraction of strongly hydrogen-bonded structure. This narrow band removal by drying and deuteration cannot be performed in spruce: some part of the narrow band will always remain, indicating either residual water or some rather freely vibrating protons, which cannot be strongly hydrogen-bonded.

To express the results succinctly, these three years of research have shown that hardwood is indeed a hard wood and softwood is soft wood, though it goes deeper than that. It means we have distinctive differences in the type of bonding between the cellulose framework and the hemicellulose in softwood and hardwood, respectively. The hydrogen bonding in hardwood holocellulose seems to be considerably stronger than in softwood holocellulose.

I have asked Dr Leopold to speak about some recent, unpublished work by him and his students that has appeared as a short summary in the last issue of *Polymer Previews*.

Dr B. Leopold—Giertz mentioned that crystallised cellulose is not easily penetrated by water. On the other hand, hemicellulose is very prone to attract water and may consequently have a great effect on the interaction between water and cellulose. Our work may be of some value in this connection, because it throws further light on the differences between various wood components in this respect.

The background to this is that we made use of the well-known fact that if a polymer is subjected to strong mechanical action, the molecular weight is reduced. Furthermore, it has been shown that this effect can be attributed to

direct transfer of mechanical energy to covalent bonds. This in turn means that the mechanical behaviour or the mechanical condition of the polymer is the main factor that governs the rate of degradation under mechanical action; in other words, if the polymer is able to distribute the mechanical energy very widely, there is a small reduction in molecular weight. On the other hand, if the mechanical energy is concentrated only at certain points, a very quick drop in molecular weight results.

This means that mechanical degradation can be used in a roundabout way to determine how plastic the polymer is. This is not new: it has been used on polystyrene and other polymers. Our use of it was to find what factors affect the plasticity of cellulose in water. We know, of course, that water is the plasticiser, so to speak, but perhaps there are factors that facilitate the plasticisation by water. We prepared for our study wood specimens containing different amounts of wood components such as lignin and various hemicelluloses, then subjected them to strong mechanical action, using a vibratory ball mill and finally measured after certain lapses of time the drop in molecular weight of the cellulose.

There were expected effects, but some were unexpected. Firstly, the rate of degradation was different, depending on the nature of the suspending medium. If this medium is water, a certain degradation rate is observed; if it is methanol, the rate is roughly doubled; if benzene, the rate increases to something like ten times as much. This supports the idea that plasticisation is the most important factor governing the rate of mechanical degradation.

I shall discuss the effect of two different components—lignin and hemicellulose. One would expect the presence of lignin to restrict the plasticity of cellulose because of its three-dimensional nature, also because of its lower ability to accept water than certain other components. Indeed, the rate of degradation in the presence of lignin is of the order of three times that of cellulose alone. What about the effect of hemicellulose? It is difficult experimentally to study this, because it is very hard to obtain specimens that contain nothing but xylan and little glucomannan or vice versa. By preparing many specimens of varying composition, we were able roughly to separate the effects of xylan and glucomannan: their differences in effect are so large that they must be real. If the amount of xylan is varied, there is virtually no effect at all on degradation rate, but the rate falls to about one third of that for pure cellulose when it is related to glucomannan content.

Thus, the only component in the wood that facilitates the plasticisation of cellulose by water is glucomannan. Xylan does not show this effect, despite the fact that it is just as hydrophilic as glucomannan. We have attempted to explain this by saying that the glucomannan and the cellulose are the two components most closely associated in the fibre; in other words, the glucomannan

is, if not co-crystallised, at least located in space close to the cellulose and its hydrophilic properties can therefore come into play in facilitating the entry of water into the fibre. Xylan is located in a more peripheral position, so it will not attract water into the cellulose and affect its plasticity.

Dr J. A. Van den Akker—There has been a great deal of interest in the effect to which Giertz refers on page 69 and, at this symposium, Parker has informally introduced a thermodynamical consideration. In view of this interest and of the importance of the effect to our knowledge of the cellulose/water relationship, Giertz has suggested that I come to the blackboard for a brief discussion of the experiment. The expression of water from an air-dry fibre was observed by Hardacker of the Institute's Physics Section during the experimentation with the first model of the compacted fibre dimension apparatus (description of the second model of the CFDA will soon be published). The CFDA, which is placed on the stage of a microscope, permits the operator to observe a fibre that is mechanically compacted between a pair of transparent anvils. Fortunately, Hardacker's preliminary experimentation with the CFDA was done in an unconditioned laboratory during humid summer weather, because the effect would have been missed at 50 per cent rh. Experiments with several pulps in a variable-humidity room showed that expression of water occurred only when the relative humidity was above 65–70 per cent; the perimeter of the expressed water was irregular and it was estimated that the volume of the water between the perimeter and the edge of the fibre was several per cent of the volume of the compacted fibre when the compacting stress was in the neighbourhood of 10–15 kg/mm^2 and the relative humidity was about 70 per cent.

The result is not inconsistent with data that we presented then*—for example, a steady load of 7 450 lb/in^2 on a water-soaked, never-dried button of spruce sulphite pulp expressed water to an equilibrium moisture content as low as 19.6 per cent (*dry* basis). This included the water in the interfibre voids. The desorption isotherm for that pulp shows that this moisture content corresponds to equilibrium of the uncompacted material at a relative humidity of about 83 per cent. If allowance could be made for the interfibre void water, the equilibrium relative humidity would be found at a still lower level. The results of both series of experiments have suggested to us that the pulp fibre wall is a spongy system of interconnected voids. According to the Kelvin equation,† Hardacker observed the expression of water from voids in which the miniscus radii were not larger than about 30 Å.

* *Tappi*, 1959, **42** (4), 340–344

† See, for example, Barkas, W. W., *Mechanical Properties of Wood and Paper*, Ed. R. Meredith (North-Holland Publishing Co., Amsterdam; Interscience, New York, 1953)

Discussion

Mr J. R. Parker—The observation by Hardacker and Van den Akker that liquid water can be squeezed out of wood fibres does not prove that the fibres contain liquid water under normal pressures. The minimum possible pressure at which liquid water could be expressed from any material containing moisture in equilibrium with an atmosphere of given percentage relative humidity can be determined from thermodynamic principles by comparing the work required to expel a small quantity of liquid by a reversible isothermal comparison cycle with that required to extract and liquefy a corresponding volume of vapour. The minimum pressure would depend upon the partial volume of the water within the moist material. If the partial volume were 1.00 cm^3/g, the minimum pressure would correspond to the values of P tabulated in Table 1 of the paper by Robertson (page 92). For a relative vapour pressure of 0.70, P is almost 5.0 kgf/mm^2. The actual pressure necessary to squeeze out water would be more than this, because of irreversibility and the rigidity of the material. The pressure of 10 kgf/mm^2 observed by Hardacker is therefore consistent with thermodynamic theory, it is not the result of some peculiarity of cellulose.

Dr H. K. Corte—I would like to refer to Giertz' statement (page 67) that the theory of multi-layer adsorption does not explain the rapid increase in moisture content at higher relative humidities. The contrary is true. It was precisely this phenomenon that prompted Brunauer, Emmett & Teller to extend the original Langmuir adsorption theory to cover the formation of several layers. The BET theory describes the complete adsorption isotherm of water vapour on cellulose, if the maximum number of layers is taken to be six. This was pointed out at the first Cambridge symposium (*Fundamentals of Papermaking Fibres*, page 31). A practical consequence is that one needs to know the moisture content at only two relative humidities in order to draw the whole isotherm.

Chairman—Before closing this discussion, I would like to comment on the interpretation of Leopold's data. I prefer to interpret it that the hemicellulose (largely xylan) plus water has no protective effect on the hardwood cellulose, maybe because it 'crystallises' or regularly associates with cellulose. The softwood hemicellulose (largely glucomannan), on the other hand, is more loosely hydrogen-bonded and more intimately associated with water according to the NMR data. Leopold's results have also shown these hemicelluloses in fact to have a plasticising effect. This would be in line with our recent NMR data. I would like to read the whole paper, however, before I comment further.