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FUNDAMENTAL AND PRACTICAL ASPECTS OF PAPER-MAKING WITH RECYCLED FIBRES

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Abstract

The basic mechanism for the development of an irreversible swelling hindrance is discussed. It is demonstrated that changes in cell wall structure caused by pulping, chemical modification and straining during drying influence the ability of fibres to reswell after drying.

The results indicate that structural alterations take place during the drying of a cell wall. It is suggested that the basic phenomenon is the irreversible closing of cell wall pores. This essentially leaves a fibre wall which is more resistant to the mechanical treatment which promotes swelling and more prone to fragmentisation and the production of fines.

Introduction and General Background

Recycled fibres are the primary raw material for paper production in continental Europe[1]. It is therefore not surprising that research is being performed in order to improve its papermaking properties. Considering the extreme importance of this raw material, it is rather more surprising that such small efforts have previously been made in this area. It is easy to identify the major performance limitations characteristic of the recycled fibres, both on the paper machine and in the final product, namely the poorer runnability and lower product strength potential compared with virgin fibres(2-6). However, one should also remember that the performance has to be balanced against price. And this important characteristic is lower for recycled than for virgin fibres. The concept of runnability includes several aspects, such as low drainage capacity or a high content of components that tend to precipitate and clog wires or other vital elements in the process. The latter aspect is of immense importance in many practical situations and has to be dealt with in various ways(7,8). The higher drainage resistance can be counteracted in various ways. A reduction in mechanical treatment reduces strength, however, and therefore the paper-maker has to seek a fine balance between runnability and the necessity to achieve adequate strength of the final product.

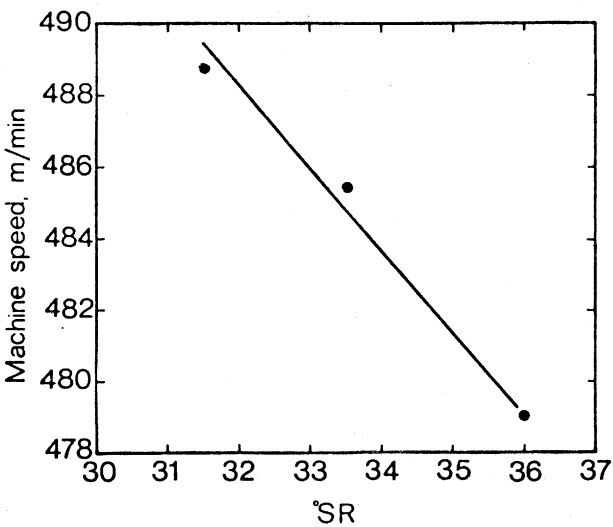


Fig 1—Machine speed versus drainage resistance of kraft pulp suspension containing 25% recycled fibres

In Fig. 1 this basic conflict is shown in an illustration of the effect on machine speed of increased beating of the recycled fibres. Due to the large scale of production in this case, a reduction in speed of 10 m/min may mean production losses of over 5,000 ton/year. This is clearly not acceptable and means that proper action must be taken to ensure maximum product capacity.

Several questions still remain to be answered with regard to the future usage of recycled fibres. A first is whether we can produce virgin fibres that are more suitable for secondary use. Another is concerned with the treatment of secondary fibres in the paper mill in order to improve their strength performance. A third is whether we can design equipment for, and recommend strategies of beating which to some extent counteract the development of drainage resistance in these fibres. The fundamental problem of why a fibre in its second life performs differently from a virgin fibre is closely linked to these practically and economically important questions.

In this review a series of studies performed at the Swedish Forest Products Research Laboratory (STFI) is summarised[9-15]. The experiments were carried out in order to explain and to shed some light on basic mechanisms taking place during the drying of virgin fibres and to comment on their practical implications. The work has been performed over a period of several years at STFI and includes both work done in the laboratory itself and trials carried out in different Swedish paper mills.

The fundamental question of why virgin fibres should behave differently from fibres which have once been dried is obviously related to what happens during the first drying and the consequent collapse of the cell wall. Evidently, as described in many previous papers[16,17], the swelling of the fibre is more or less destroyed in the first drying operation so that more mechanical action is necessary to reswell the fibre in its second use. This yields an undesirable amount of fines which increase the drainage resistance of the suspensions. The present discussion thus deals with the changes in the cell wall that take place during the drying of virgin fibres, and the importance of these changes with regard to developing beating resistance in the fibre wall. It should be emphasised that the results and the conclusions drawn from them refer only to chemical pulp.

It is suggested that the structure and chemical composition of the cell wall have a definite influence on its ability to reswell after the first drying. Furthermore, finer materials usually referred to as `crill´ or `fines´ play an important role, contributing to both the swelling potential and the drying resistance due to their high specific surface area. The reswelling of the fines is severely reduced by drying and the onset of swelling hindrances takes place at an earlier dryness level than for the cell wall. Moreover it is shown how pulps of different chemical composition behave with regard to reswelling after drying. The character of the cell wall was changed, in one set of experiments, by acetylation in a swelling and non-swelling medium, and, in another, by selective removal of cell wall components. With regard to the influence of drying, it is shown that both the drying temperature and the restraint during drying influence the reswelling.

The Cell Wall Structure and Swelling Behaviour

In order to understand the swelling behaviour of fibres, it is instructive to examine the morphological structure. The cell wall consists mainly of crystalline material characterised as microfibrils surrounded by matrix material. According to the model proposed by Kerr and Goring[18], the cell wall is characterised as a lamellar structure with microfibrils as reinforcing elements. These microfibrils are orientated in certain directions and are laid down in several layers in the cell wall. The amorphous material in between is mainly lignin and hemicelluloses[18,20]. This layered structure and division into crystalline and amorphous materials makes it easy, at least intuitively, to understand the response of the cell wall to mechanical treatment. There are essentially two ways in which the cell wall may react to mechanical treatment. Either it may fragmentise into shorter fibres or fibrils which are detached from the cell wall, or the whole cell wall may delaminate and develop yield cracks, whose dimensions may range from the molecular scale up to macrocracks separating the cell wall into layers. Moreover, in several investigations the existence of pores in the cell walls has been demonstrated. Their size and abundancy are altered by mechanical treatment and the mechanism of delignification. This has been discussed in a recent review by Ko[21].

The Swelling Behaviour of Fines and Fibres from Bleached and Unbleached Pulps

The emphasis in this paper on the reduction of swelling of once-dried fibres is based on the correlation between the swelling, measured as the water retention value (WRV) of the pulp, and the strength of the sheet. This relation holds over a given range independently of the composition of the pulp fractions present, as demonstrated in Figure 2[22-24].

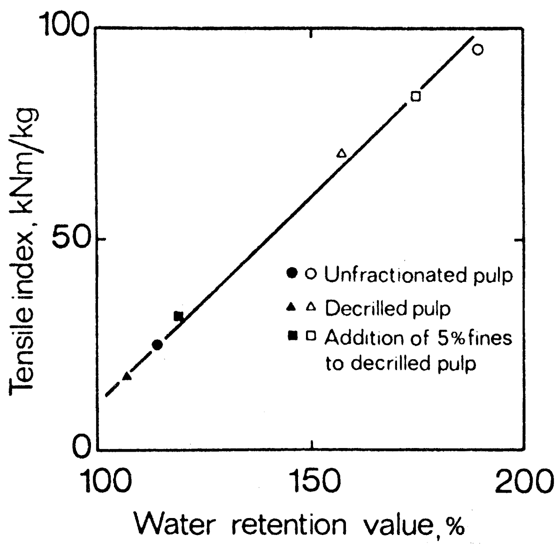


Fig 2—The relation between tensile index and WRV for handsheets made from unbeaten and beaten pulps containing fines or without fines
Symbol key: unbeaten = filled symbols,
beaten = unfilled symbols

It is implicit that any loss of swelling in either fines or the fibres will cause a decrease in strength. However, it is important to stress that the straight line dependence shown in Figure 2 is only a mathematical correlation and only valid for fibres and fines originating from the same pulp and within a limited range of fines addition.

The swelling of fines has in previous studies been established to be much higher than that of fibres. It is suggested that this should be ascribed to structural differences in material in the cell wall and material liberated from the cell wall. For bleached pulp it may be demonstrated that the finer material separated on a Celleco fractionator using a 100 mesh screen does not differ chemically from the cell wall material. The carbohydrate composition is shown for both dried and undried material in Table 1.

Carbohydrate content (% of total)	Primary fines (from unbeaten never-dried pulp)	Fines from beaten pulp			Coarse fraction from beaten pulp (never-dried)
		Never-dried	Once-dried	From beaten once-dried coarse fraction	
Arabinose	0.7	1.5	1.6	2.0	0.9
Xylose	9.9	14.5	15.0	14.2	9.7
Mannose	5.5	5.9	6.7	6.6	5.7
Galactose	0.5	0.66	1.1	0.6	-
Glucose	71.0	70.66	73.4	75.0	79.4
Rest (%)	12.4	6.9	2.2	1.6	4.1

Table 1
Chemical composition of fines and coarse fraction from bleached kraft pulp

In this context it should be noted that fines separated before and after beating are collected. The former are referred to as primary fines. With regard to the reswelling after drying, the scheme illustrated in Figure 3 was followed for both fines and fibres.

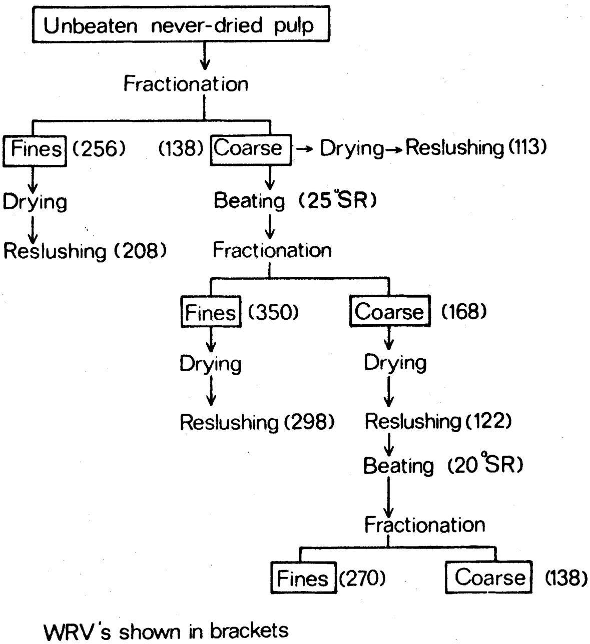
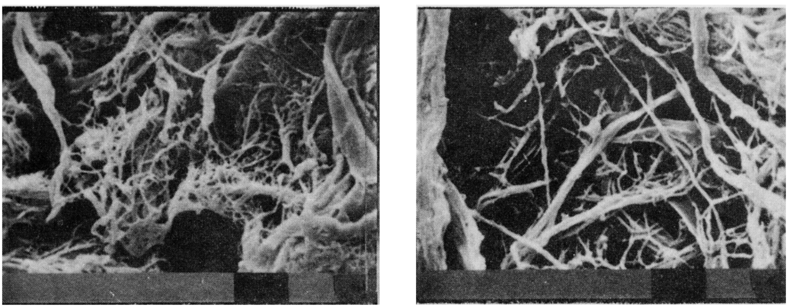


Fig 3—The experimental schedule for fractionation, beating, drying and reslushing

It is evident that the drying process reduces the swelling values of the fines. In particular, the high swelling value of the virgin fines obtained before beating is dramatically reduced. It is also found that the swelling value of fines obtained by beating a dried fibre is equal to the swelling value when reswelling dried virgin fines. This behaviour suggests that the swelling of the fines reflects the state of swelling in the cell wall. Moreover, it seems that the difference in swelling in the fines and the cell wall reflects the liberation from restrictive forces occurring in the laminated structure characterising the cell wall. It is well known that the breakdown of all connecting links in the cell wall, mainly holocellulose, gives rise to swelling values in the fibres close to those obtained for fines(25). It is also important to note that the degree of polymerisation (DP) is lower in fines than in the fibre (see Table 2).

This is a molecular feature with structural implications that represents a distinct difference between fines and fibres. It is not possible to state whether low molecular weight material has a tendency to accumulate in loosely attached material or whether the mechanical treatment leads to chain scission. Both hypotheses seem to be plausible. Moreover, drying does not change the DP.



a. b.

Fig 4—Micrographs of fines from bleached kraft pulp
(a) primary fines (b) fines obtained by beating

Table II Viscosity and WRV data for fines and coarse fractions of bleached kraft pulp

	Primary fines (fines from unbeaten pulp)		Fines from beaten pulp			Coarse fraction from unbeaten pulp		Coarse fraction from beaten pulp		
	Never-dried	Once-dried	Never-dried	Once-dried	From once-dried and beaten coarse fraction	Never-dried	Once-dried	Never-dried	Once dried	Once-dried and beaten
Water retention value (WRV) %	256	204	357	298	270	138	114	171	122	136
Viscosity (CED) cm^3/g	604	605	647	640	676	906	903	939	938	899
DP	861	863	928	918	974	1347	1343	1401	1400	1336

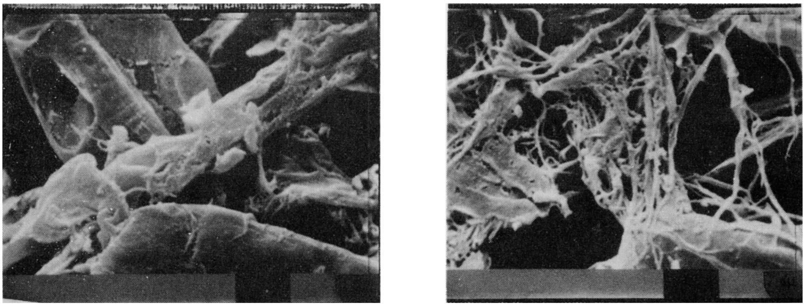
It is illustrated in the micrographs in Figs. 4(a) and 4(b) that both primary fines and fines obtained by beating are highly fibrillar materials.

A similar study was made on unbleached pulp, which shows that the chemical composition of primary fines differs widely from that of fines obtained by beating (Table 3).

Carbohydrate content (% of total)	Primary fines (from unbeaten pulp)	Fines from beaten pulp	Coarse fraction from unbeaten pulp	Coarse fraction from unbeaten pulp
Arabinose	1.3	1.3	1.0	1.0
Xylose	7.4	4.1	6.6	5.2
Mannose	4.3	5.9	6.7	6.4
Galactose	1.2	1.3	0.1	0.7
Glucose	48.7	58.3	70.4	68.8
Acid soluble lignin (%)	0.4	0.2	0.2	0.2
Klason lignin (%)	32.0	25.7	13.0	11.3
Rest (%)	4.7	3.2	2	6.4

Table 3
Chemical composition of fines and coarse fraction from unbleached kraft pulp

The pulp was a never-dried kraft pulp with Kappa 66 and it can be seen that the primary fines contain more lignin than the other fractions. From the micrographs, Figs. 5(a) and 5(b) it is evident that the primary fines are of mixed origin with a high degree of non-fibrillar material. A close examination of the chemical composition of fines from kraft pulps has previously been carried out by Lindström and Nordmark[26].



a. b.

Fig 5—Micrographs of fines from unbleached kraft pulp
(a) primary fines (b) fines obtained by beating

To rule out the effect of chemical environment on swelling, the fines and fibres from the unbleached pulp were washed and neutralised according to the procedure suggested by Lindström and Nordmark[26]. However, the effect of drying on swelling was similar for washed and unwashed samples (Table 4). In the latter case measured swelling values for fines obtained by beating are higher. It is evident that there is a similar large reduction of the swelling values of the fines as was the case for bleached pulp. The swelling of fines obtained through beating is again drastically reduced by the drying process.

Moreover, it is seen that the DP-value is significantly lower in the fines fractions than in the fibres. The fines produced by beating have the lowest DP.

Table IV Viscosity and WRV data for fines and coarse fractions of unbleached kraft (K=66) pulp

	Primary fines (fines from unbeaten pulp)		Fines from beaten pulp		Coarse fraction from unbeaten pulp		Coarse fraction from beaten pulp	
	Never dried	Once-dried	Never dried	Once-dried	Never dried	Once-dried	Never dried	Once-dried
Water retention value (WRV) % (before washing)	314	215	722	309	158	128	182	154
Water retention value (WRV) % (after washing and buffering)	339	227	570	243	166	129	196	166
Viscosity (CED) cm^3/g	860	-	690		1303	-	1139	-
DP	1272	-	998		2013	-	1734	-

For both bleached and unbleached pulp the general behaviour of the fines and fibres after drying is similar. The virgin fines obtained by beating are by far the most highly swollen and they also lose about half of their swelling ability in the drying process. This must have a detrimental effect on the contribution of the fines to the strength potential of the pulp.

The reason for the high swelling of the fines compared with that of the cell wall material may be only partly understood from the differences in chemical composition, which are small for bleached and large for unbleached pulps. It seems, however, that the molecular parameter characteristic of fines is the low molecular weight. Previous work on the fines from bleached pulp has demonstrated that there are no drastic differences in crystallinity between fines and fibres[27]. The low DP may thus be assigned a structural significance in the sense of the fringe micellar model. Thus it could mean that interconnecting cellulose chains between crystalline zones are less abundant. The cohesiveness of the structure will become less and the crystalline regions more easily separable. It seems impossible to distinguish whether this breakdown takes place during mechanical treatment or whether these conditions exist in the wall due to localised chemical degradation. From the micrograph it is evident that the fines are a fibrillar material with a large variation in size. Evidently drying may change the geometric distribution by coalescence and irreversible agglomeration at all structural levels[28]. In the subsequent study, an attempt is made to establish at which dry content these phenomena start to occur.

The Effect of Dryness on Reswelling

The effect of dry content on reswelling was investigated in more detail in a study of the fines fraction screened from never-dried bleached kraft pulp with a 200 mesh Bauer McNett screen.

Fig. 6 shows how fibres (coarse) and fines obtained before and after beating reswell after being dried to certain dry solids contents. It is clear that never-dried primary fines have a lower WRV than fines obtained by beating never-dried fibres.

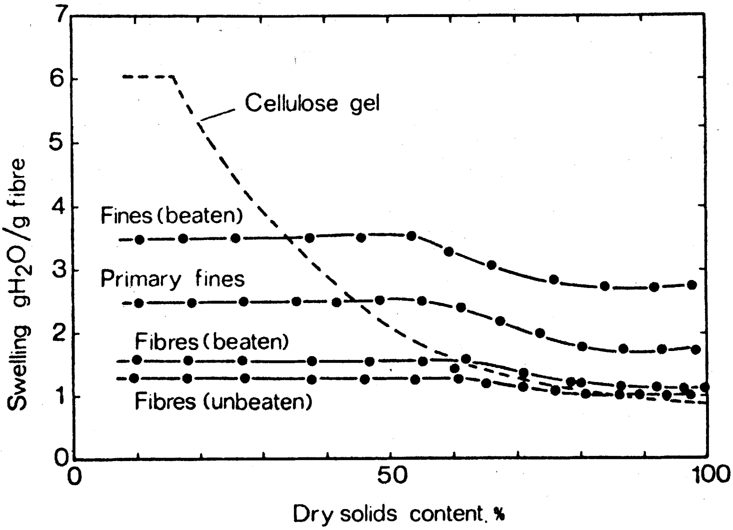


Fig 6—The effects of drying on reswellability of fines and fibres from bleached kraft pulp and cellulose cells

There is clearly a critical dry content to which the cellulosic material can be dried without experiencing any loss in water retention value.

Furthermore, this dry content is related to the level of initial swelling as reflected in the water retention value of the virgin material.

This diagram includes a master curve which reflects critical dryness when irreversible reswelling of cellulose gels takes place. The curve is obtained from the work of Westman[29], who suggested that this critical dryness represents the situation when pores are closed irreversibly. The cellulose gel should only be regarded as a model, but it seems that its curve coincides with that of the fibres at the dry content when the cell wall experiences an irreversible loss in swelling. The same behaviour is not evident for fines. Here it seems that the critical dryness at which irreversible swelling hindrances take place departs from the master curve for model gels. This is reasonable as the swelling in fines, measured as WRV, could not have the same structural meaning as for fibres which have a comparatively low specific surface. It seems more likely that the critical dryness level represents the concentration where irreversible coagulation phenomena take place. These may indeed lead to drastic changes in size distribution and in the number of accessible sites for the bonding of water molecules.

The Effect of Drying Restraint and Temperature

In Figure 7, it is shown that the WRV of dried fibres which

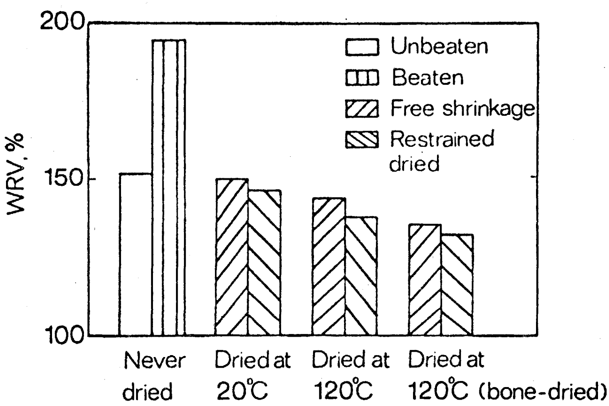


Fig 7—The effects of drying on the WRV

have been beaten in their virgin state is the same as that of the unbeaten virgin pulp. Apparently all the swelling gained in the beating of the fibres is lost as a result of drying, even when drying takes place at a low temperature. Higher drying temperatures further reduce the degree of swelling, but this effect is much smaller than that of the drying as such.

Essentially this is in accordance with previous findings of Stone and Scallan[(18)]. These authors also noted that subsequent beating restored the swellability of fibres dried at lower temperatures. However, after the fibres had been dried at higher temperatures it was not possible to restore the swelling to the original value, even after prolonged beating. This indicates that the development of swelling restrictions is made permanent by the establishment of irreversible bonding and hornification in the cell wall when drying is performed at elevated temperatures[(30)].

If the swelling hindrances were related to the accessibility to water of the hydrophilic wood polymers, it would be expected that the development of such hindrances would be accompanied by a corresponding reduction in moisture regain at a given relative humidity. Table 5 presents moisture sorption data for fibres

Drying condition	Moisture regain g/g at relative humidities			
	32%	52%	73%	85%
20°C	5.2	6.9	9.7	11.8
120°C Dried to 95% solids	5.3	6.9	9.7	11.8
120°C Bone dried	5.3	6.5	9.3	11.5

Table 5
Moisture regain data for samples reconditioned after submission to different drying conditions.

dried under various drying conditions and then reconditioned. It is seen that the moisture regain is not influenced by the drying temperature, except for bone-drying which leads to a small reduction in moisture regain. This is in line with the suggestion that such treatment may lead to thermal breakdown of the carbohydrate chain. Studies by Teder, Back et al.[30,31] have discussed the chemical reactions that may occur when cellulosic materials are subjected to high temperatures.

The application of restraint during drying leads to somewhat lower swelling than is shown by fibres obtained from a freely dried sheet. Apparently the hindrances to swelling are influenced by the state of deformation in the cell wall during the preceding drying.

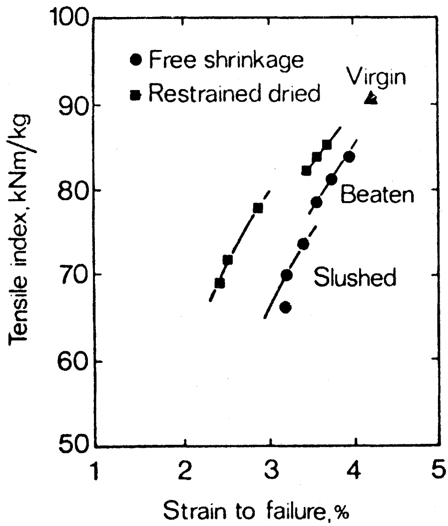


Fig 8—Tensile index versus strain to failure for sheets made from unbleached kraft pulp dried under different drying condition

In this context it should be noted that fibres which have been once-dried under a given degree of restraint display a memory of the drying conditions. As seen in Figure 8, sheets made from bleached fibres dried freely show a larger strain at the same strength than do sheets made from fibres once-dried under restraint. The effects are to some extent erased by beating.

The same diagram is shown for unbleached fibres (Fig. 9). However, the difference between freely dried fibres and fibres dried under restraint is smaller than for bleached fibres. However, fibres which have been over-dried display lower strength values and high strain values. In this case it seems that the over-drying makes permanent the effect of free drying.

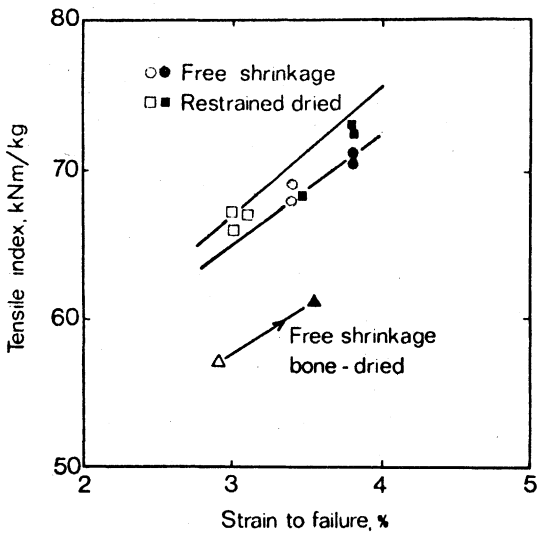


Fig 9—Tensile index versus strain to failure for sheets made from unbleached kraft pulp dried under different drying condition
Key: unfilled symbols = reslushed; filled symbols = beaten

However, for milder drying conditions there are no large shifts between fibres which have been freely dried and those which have been dried under restraint in their previous life. These results illustrate that pulps which are dried under restraint and pulps which are dried freely will behave differently. In practice this is experienced as a major difference between sheet-dried and flash-dried pulp. The latter gives a final product which has the character of a freely dried pulp. Figure 10 compares the properties of papers made from flash-dried and from sheet-dried pulp. The same original pulp was used and only the drying conditions were varied. Beating may be used to reduce the difference between the two pulps with regard to the properties in the final product.

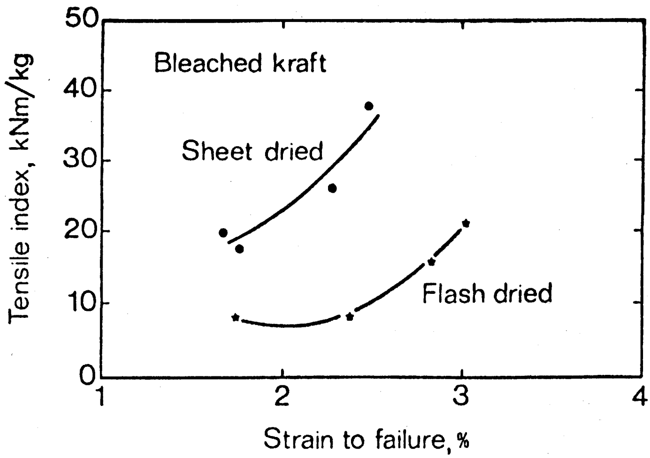


Fig 10—Tensile index versus strain to failure for sheet made from sheet-dried and flash-dried bleached kraft pulp

From the laboratory study it is evident that the effects may be expected to become more severe if the effects of free drying are made permanent by over-drying. To prevent over-drying in flash-drying all free fibres should by-pass the high heat zones. In rebuilding flash-dryers this precaution should be taken into account; this has been done in some installations for the production of flash-dried pulp(32).

Structural Aspects of Reswelling of the Cell Wall

Evidently irreversible changes in the swelling hindrances start to occur above a critical solids content and are influenced by the state of deformation during drying. This focusses interest on the nature of the swelling of the cell wall. In the literature[33,34] it is suggested that water is active in swelling through the following mechanisms:

1) equilibration of the partial free energy of free water and of water interacting with the wood polymers,

2) displacement of morphological units to form pores of different sizes.

Thus the hindrance to reswelling after drying of a never-dried cell wall is related to a change in one or both of these functions. The degree of swelling due to establishing a thermodynamic equilibrium between the water and water interacting with the wood polymers is controlled by parameters such as pH, ionic strength, and degree of ionisation of the wood polymers. These phenomena have been studied in detail by Lindström[35] and Westman[29] for model systems.

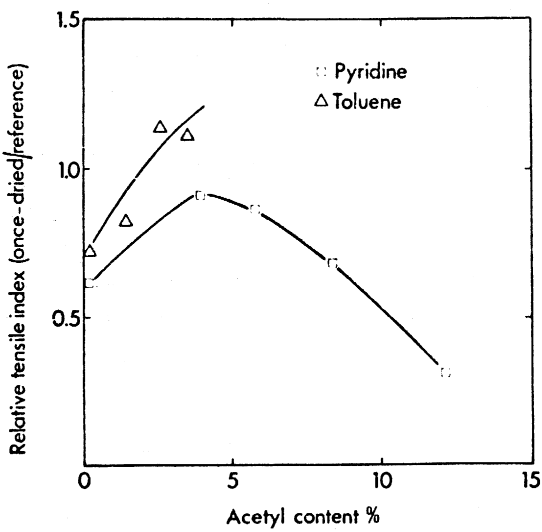


Fig 11—Relative tensile index as a function of acetyl content

Swelling due to the existence of holes is a phenomenon into which thermodynamics offers no insight. It has to be explained by assumptions concerning the structural features.

Obviously, mechanisms regulated by thermodynamics are reversible. However, for swelling controlled by the existence of pores or voids it is easy to envisage irreversible behaviour. In previous studies it has also been suggested that the pores do display irreversible closing during drying, while the interaction between water and wood polymers is relatively undisturbed. In a study(15) carried out on bleached fibres which have been acetylated in a swelling medium (pyridine) or a non swelling medium (toluene), the reswelling after drying was improved by esterification of hydroxyl groups. Firstly, this means that the closing of the structure is dependent on the presence of the hydroxyl groups. Secondly, as the effects are similar in both acetylation media (of which one does not permit esterification in the bulk phase) the locking mechanism must be ascribed to phenomena on surfaces. Figure 11 shows that the strength recovery is analogous to that shown by virgin unesterified fibres and at low acetyl contents increases with degree of acetylation in both toluene and pyridine. This result is in agreement with the concept that the irreversible swelling hindrance is related to the physical voids in the cell wall structure.

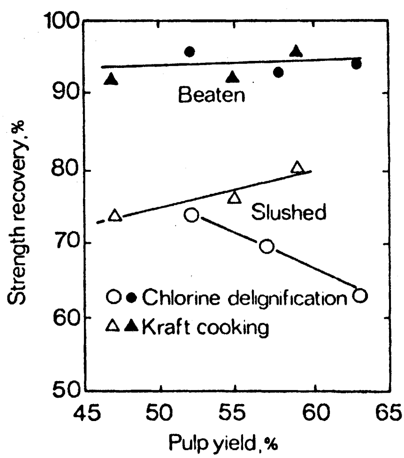


Fig 12—The strength recovery of handsheets made from pulps delignificated by chlorine treatment or by kraft cooking plotted against pulp yield. (Beating refers to 4000 rev. PFI.)

In contrast to the relatively simple modifications of the cell wall obtained by esterification, major changes may be introduced by different processes and extents of delignification. Figure 12 shows the behaviour of pulp fibres which have been reswollen and made into sheets after prior drying. The strength recovery is plotted versus yield and ordinary kraft pulping is compared with kraft fibres which have been selectively delignified with Cl_2. The procedure is described in detail in a previous paper[10].

As seen, slushing of the dried fibres gives a level of swelling whose development with yield differs for the two types of pulp: thus the selectively dilignified pulp shows less reduction in swelling with decreasing yield while the opposite is the case for the kraft pulp. The interpretation of the behaviour may be formulated in terms of the structure of the cell wall for the two types of fibres. Selective lignin degradation should lead to a lamellar structure which is easily reswollen by mild mechanical treatment following slushing. The lower the yield, the higher the degree of lamellation, which should enhance reswelling and strength recovery. In kraft pulping, the breakdown of the matrix polymers is more irregular and the closure of the cell wall is made more permanent as the yield is diminished. These tendencies are only identifiable at a mild mechanical treatment level and beating erases effectively the influence of yield on the strength recovery.

The Effect of pH

In a separate study by Lindström and Carlsson[36] it has been found that pH during drying has an efect on reswelling. Thus they have demonstrated that the reswelling measured as WRV depends on the pH of drying in the same way as WRV depends on pH for virgin pulp. It should be pointed out that in these measurements the WRV measurement was made at a reference pH value. These effects only occur for unbleached pulp, not for bleached pulp. It seems reasonable to assume that the basic mechanism must be related to the ionisation and salt formation of the ionisable groups in the lignin. Moreover, in this work it has been shown that the pH of reslushing has a definite influence on reswelling. These findings are in good agreement with practical studies in which the strength of corrugated waste was followed versus pH in the defibration operation.

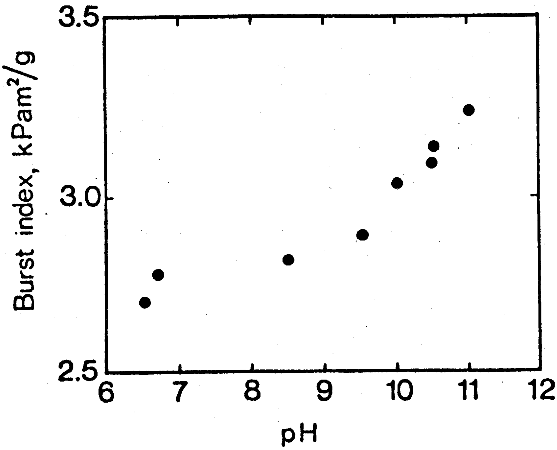


Fig 13a—Burst index versus pH of the suspension during refining of the recycled corrugated board

Figure 13(a) shows the development of burst strength versus pH. This may be compared with a laboratory study of Lindström and Carlsson(36) where changes in WRV of once-dried kraft pulp due to pH during reslushing is followed, (Figure 13(b)). Empirical studies have shown that the correlation between burst and WRV is linear.

An increase in the strength of the recycled material used for liner-board production is extremely important, as it permits a reduction in the amount of virgin material required. Thus the practice of defibration under highly alkaline conditions should be striven for. In this specific study it was found that the strength value of the final product was a linear combination of the strengths of the recycled material and virgin pulp. Running at a specified burst strength meant that the mill could reduce the amount of virgin kraft when the pulping of the recycled material was carried out at higher pH.

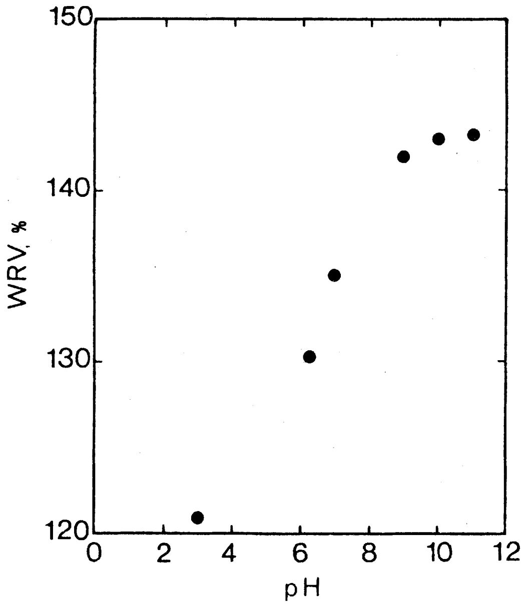


Fig 13b—WRV versus pH during reslushing of 53% yield unbleached kraft pulp (Lindstrom and Carlsson)

Discussion

Why do the pores not open up again when the fibre is rewetted after drying? Apparently the increase in swelling induced by beating is more or less revoked by the drying process. If it is accepted that structural pores are more susceptible to irreversible closure, there must be a process that locks the surfaces together. Moreover, the locking mechanism must be efficient enough to erase the `memory´ of the previous pore. Obviously a pore which represents a physical discontinuity in the cell wall must contitute an excellent position for the creation of very high surface tension forces which will pull the surfaces together during drying. No doubt the conditions for creating an adhesive bond are extremely good. In the work of Stone and Scallan[17], it is in fact suggested that the forces may lead to a plastic flow mechanism in the interface. In this case it is likely that considerable strain-hardening may take place and promote the healing of cracks.

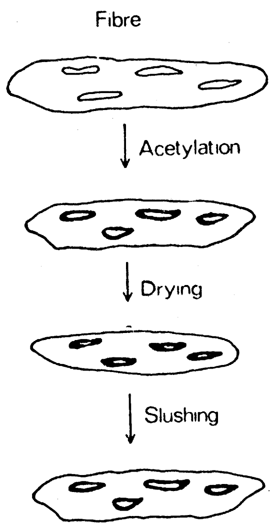


Fig 14—A schematic description of changes in fibre wall due to acetylation, drying and slushing. It is suggested that acetylation creates a hydrophobic lining (darker zones) on the surfaces of the pores

In recent studies[21] it has also been suggested that the irreversible closing of the interior surfaces is due to the same mechanism as is found in irreversible coagulation, ie hydrophobic bonding or secondary bonding due to van der Waals type attraction forces.

Whatever the mechanism, the previous void, reflecting a weak position in the cell wall, is welded together. This results in a more brittle material, in which the tendency to delaminate will be less pronounced than for virgin fibre, reducing the number of weak spots. The experiments on the recycling of acetylated fibres confirm this model. It is suggested that acetylation of virgin pulp leaves a hydrophobic lining on the surfaces of the pores accessible to acetylation in toluene. Thus these are made permanent and may not be healed by drying, as illustrated in the model in Fig. 14. The fibre retains its re-swelling ability and properties may be recovered to a greater extent after drying.

As illustrated in the model in Fig. 15, the fines obtained in beating consist to a large extent of fibrils which are strongly coupled to each other by the bonding mechanism that takes place during drying. Thus, when once more liberated they do not have the same ability to reswell as fines from virgin fibres and they contribute more to the specific surface area of suspension than to the swelling potential. In a sense they start to behave more like fillers with less effect on the strength and more on the drainage properties.

Also, the effect on re-swelling of straining during drying must be explained by a structural phenomenon. Thus high drying stresses promote the closing of the pores and the establishment of permanent adhesive bonds. Obviously freely dried fibres remember somewhat more of their original structure.

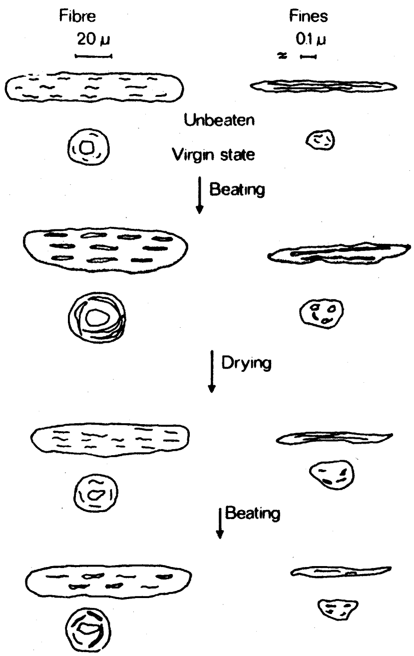


Fig 15—A schematic description of structural changes in the fibre wall and fines due to beating, drying and rebeating

By virtue of this model it may be understood that it is thought to be important to create delamination in the cell wall and that this tendency to delamination is reduced by the drying operation. Thus, a smaller number of weak points is present in the cell wall of secondary fibres than in that of virgin fibres. Thus greater shearing action on the cell wall is needed in order to produce delamination. It seems reasonable that high consistency refining should be used instead of only low consistency treatment. The latter may be efficient for virgin pulp which delaminates easily but it may be insufficient for recycled fibres which demand a high degree of cell wall deformation in order to deform and fail in the delaminating mode instead of fragmentising into finer material.

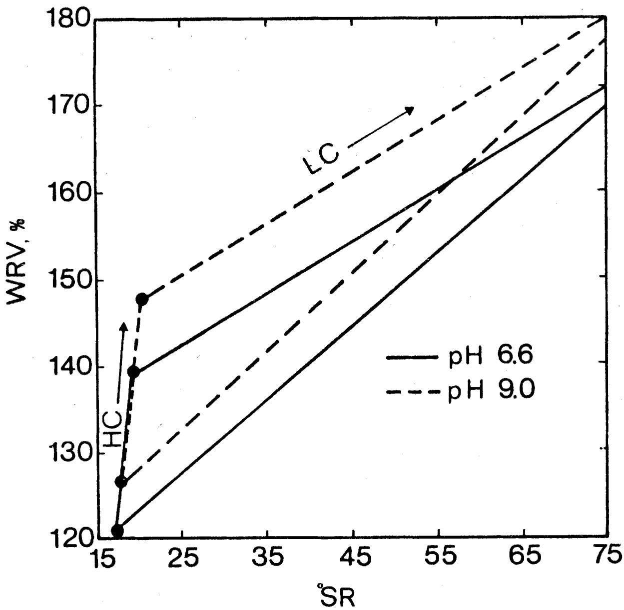
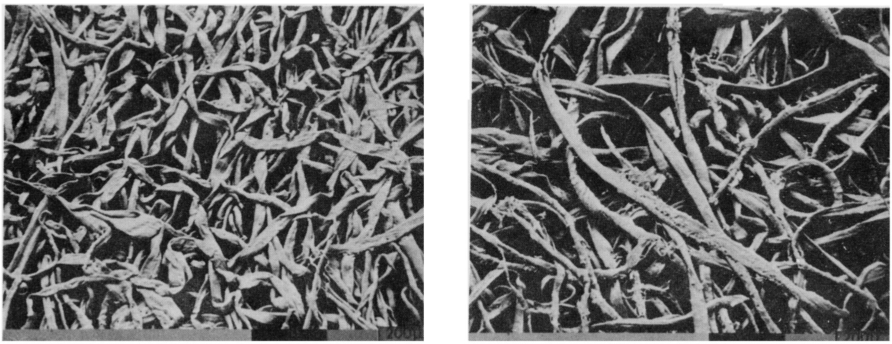


Fig 16—WRV versus °SR for high (HC) and low (LC) consistency defibration and refining systems

Fig. 16 gives a general diagram summarising a series of experiments performed with high-consistency (HC) and low-consistency (LC) refining commercial recycled corrugated board. The high consistency defibration combined with a low consistency beating system manages to give the pulp a higher specific WRV at a lower drainage resistance than the low consistency system where the defibration steps were performed in low consistency refiners.

This corresponds with an earlier study(11) on a different raw material. The results thus indicate that a HC- system produces less fines and more fibre wall swelling than the LC-systems in reaching a specific water retention value. This behaviour conforms with the model proposed in the fundamental study. This effect is similar to that observed by increasing pH. The increase in WRV agrees well with the results of laboratory studies(36).



a. b

Fig 17—Micrographs of high consistency treatment of virgin and recycled fibres
(a) virgin fibres (b) recycled fibres

The difference between HC-treatment of virgin and recycled fibres is illustrated in the micrograph (Fig. 17). As seen, the virgin fibres became highly curled in a HC treatment while the recycled fibres tend to become more swollen than curled(37). As a matter of fact recycled fibres after HC treatment have the appearance of virgin unbeaten fibres.

With regard to the runnability of the pulp on the paper-machine, it is to be expected that the drastic increase in fines content with low consistency treatment should influence parameters such as drainage after the press section and steam consumption per tonne of dry product. In a mill trial(13), the results of which are shown in figure 18, this has been shown to be the case. As seen the steam consumption decreases markedly as the degree of high consistency treatment increases, while the dryness after the third press increases. The high amount of fines obtained through LC treatment effectively hinders drainage and steam permeation in the dryer. These trials indicate the strong sensitivity of running conditions and paper properties to the strategy of the beating and mechanical treatment of secondary pulp.

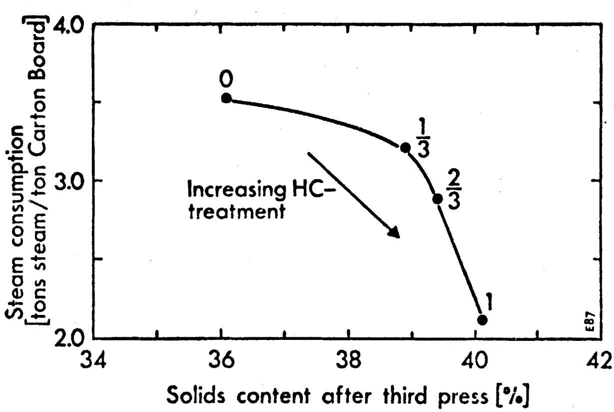


Fig 18—The specific steam consumption is plotted against solids after the third press. The solids content after the press increases with increasing HC-treatment

Final Remarks

Opening up the cell wall of a once-dried fibre is a much more complex problem than it is for a virgin fibre. Since secondary fibres now constitute half the raw material of the European paper industry, it is more than ever necessary to develop beating equipment or other treatment specially designed for such fibres.

In our studies, no panacea has been found, but the understanding reached should constitute the basis for the development of strength vitamins for secondary fibres.

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Discussion

Discussion following papers presented by Dr. D.W. Clayton and Mr.A. de Ruvo

Mr. A.de Ruvo, STFI, Sweden

I want to ask Dr. Clayton about the mechanical properties. What is known about what it is that is really happening in the cell wall that gives rise to the different mechanical properties of pulps? You indicated that there are now methods of improving the properties of soda-AQ pulps to the level of those of kraft pulps. This I find very interesting.

Dr. D.W. Clayton, Paprican

I would like to give you a complete answer, but am afraid I can't. Some of the early work, as you may know, was done with rather large proportions of ethylene diamine (EDA) mixed with the wood because we were trying to develop a method of accelerating delignification. With up to 40% EDA added to the wood we obtained a delignification rate in soda pulping equal to that in kraft. This was an interesting technical result, but was not commercially viable. However, the tear factor at a given tensile value for soda pulp made with this proportion of EDA was extremely high, ranging up to 130, which is very high indeed. We were intrigued by this result, but I am afraid failed to discover a reason for it.

Mr. A. de Ruvo

Unfortunately, I can see our ending up in the usual situation. We notice various changes, but understand so very little of what is happening in the cell wall that we cannot relate them to the quantities we know to be associated with the mechanical properties of paper.

Dr. D.W. Clayton

I don´t agree with you. We need to know the answers to these observations. Above all, we need to know just why it is that AQ, while being chemically equivalent to sulphite in its lignin removal, nevertheless reduces strength and gives us lower tear values at given tensile. Presumably there is some degrading action on the polysaccharide caused by the oxidative power of the AQ, but in that case how is it prevented by the presence of sulphite in kraft pulping? The strengths of kraft and kraft-AQ pulps are identical.

Prof. H.W. Giertz, University of Trondheim, Norway

I would like to make a historical remark. You showed how Isbell´s work is the basis for our understanding of peeling. But I must point out that the first studies of peeling were not designed to increase the yields of kraft pulping, rather the aim was to decrease the yield when producing acetate, high alpha pulps. The whole business of peeling has been explained by a group at Billerud.

A recent Ph.D thesis presented to the University of Trondheim deals with the question of AQ treated kraft pulps. The author was surprised at the very high tear to tensile ratios, and on investigating the fibres found them to be curled by the AQ process. We believe this curling could account for the very high tear strengths found in these pulps. This work was published some months ago in Norsk Skogindustri(1). (The only paper I have found that might be referred to deals with soda-oxygen pulps: this is the reference given - ed.)

Dr. D.Abson, Weyerhaeuser Technology Center, USA

I wonder just how relevant it is to rely so heavily on handsheet properties, such as tear index, when evaluating a new pulping process like soda-anthraquinone. The paper-maker, after all, will be much more interested in its process-related properties, dewatering behaviour or wet strength, which will affect its performance on the paper machine.

A point that should influence our evaluation of soda-AQ pulps, and which may even outweigh the disadvantages of reduced tear strength, is the possibility of simplifying the conversion of sodium carbonate to sodium hydroxide in a sulphur free system. This gives significant benefits in capital and operating costs, and I would be interested to hear your comments.

Dr. D.W. Clayton

Yes, the use of soda-AQ does allow the possibility of direct causticisation, which may considerably reduce costs. It all comes down to a question of economics, whether the product being made needs the better mechanical and optical properties. For some mills strength may be the dominant issue.

On the question of comparing strengths, I quite agree with you. The only reason for my using the tear tensile ratio is its being a very quick and simple method of indicating differences. A detailed comparison would, of course, involve the determination of full beating curves, and measurement of optical properties. My intention was to obtain quick comparisons between different pulps.

Mr. D.G.N. Stirling, Wiggins Teape, UK

Mr. de Ruvo mentioned the effects of temperature and constraint during drying on pulp strength, but I am not certain whether market pulp at 10% air dry would count in your terminology as once-dried or not. Do pulp mills take any steps to limit the damage caused by drying? Are the figures you showed for the differences between sheeted and flash-dried pulps representative of normal flash-dried pulps, where some over-drying can be expected, or are they representative of pulps for which special care has been taken?

Mr. A. de Ruvo

In answer to your second question, we simply sampled a flash-dried pulp while simultaneously making sheets from it. Thus my figures should be representative of normal flash-dried pulp, though they are only a check on the first part of the curve.

They refer only to slushing, which gives of course, very low strength values. A little beating would greatly improve these values, possibly increasing the tensile index to 6 or 7. It is known that the effects of beating on a commercial sample are very small, and this is borne out by the results here. Over-drying can indeed be a problem, and while we were carrying out these experiments we had the idea that it is the free fibres that are most likely to over-dry, and so by rejecting them from the first cycle we could avoid the problem. This concept is patented and in use in two Swedish mills.

In answer to your first question, the critical moisture content is around 30%, so that a 10% moisture content pulp would, in my view, be over-dry. We would like to devise a way of maintaining the full strength in market pulps, but it is a matter of economics.

Mr. P. Howarth, UMIST, UK

Mr. de Ruvo's figure 6 shows how the onset of permanent drying induced fibre damage varies with solids content. We reported at the last symposium on some similar work using the enzyme technique. We entirely agree that when the fibre to water ratio reaches 1:1 damage begins, and we believe this to be a very important result for practical paper-making. If the sheet breaks on the machine and the broke can be removed at a high enough moisture content then the fibre will not be degraded.

We find that air-drying is about the most severe treatment that fibres can be given: an air-dried handsheet is subject to more permanent fibre degradation than paper made on a machine and dried to similar moisture content. The rapid, high temperature drying to which paper is subjected on the machine is far less damaging than slow air-drying.

Mr. de Ruvo

You are suggesting that there is a significant effect of the time-scale of the drying, so that fibres don't notice the rapid changes introduced by the paper machine.

Our studies didn't cover this, but I could well understand how the paper machine might introduce transients, particularly in moisture gradients. It is well known, for example, that Yankee dried board is initially much drier on one side than on the other.

A more profound description of the drying process would need to take into account time dependent phenomena. Since there is a locking phenomenon involved, it is likely that both plastic flow and creep are significant.

Prof. H.W. Giertz

I want to remark on our understanding of the influence of drying on the fibre. Firstly, it must be kept in mind that, as has been pointed out, a fibre always exhibits restricted swelling. Secondly, as was discussed at the 1965 symposium, high molecular weight polymers which can undergo swelling and then go into solution exhibit reduced solubility when subjected to stress. This result I think is very relevant to understanding the mechanisms occurring during drying.

As the fibres dry they shrink and the hemicellulose between the microfibrils comes under stress. This gives rise to the well-documented dried-in stresses. Your results show how paper dried under tension is more difficult to re-slush, and I wonder if it is the presence of the gel system with all the dried-in stresses which is responsible for this. Such secondary fibres would swell less than new ones, and require more mechanical action to achieve the same degree of swelling.

Mr. A. de Ruvo

While I agree with what you say, I am afraid we didn't investigate this. What we wanted to show was that fibres remember the stress histories they experienced during drying. You are referring to a slightly different phenomenon which I can't comment on at this time.

Prof. K.I.Ebeling, Helsinki University of Technology, Finland

In your figure 10 you showed that `sheet dried´ bleached kraft has a higher tensile strength at failure than `flash dried´ kraft pulp. You mentioned that this was due to the differences in drying tensions. Could it also be an effect of `high consistency refining´? The screw press which is always used in conjunction with the flash-drying process, is actually performing some mild high consistency refining.

Mr. A. de Ruvo

In our experimental rig we had only a normal cylinder press before the flash drier. I would not expect this to produce the same sort of refining action that you suggest may occur in a screw press.

Dr. M.B.Lyne, Paprican

Your paper dealt primarily with the strength aspects of recycled fibres, although your title referred to more general practical considerations. Have you therefore considered the behaviour of other parameters, for example the dynamic wetting? This is of course of great important in coating and litho printing.

Mr. A. de Ruvo

As I have said before, the range of our investigations was limited. To date, we have looked at ways of improving the strength of papers made from recycled fibre. Next, which we have already begun, we shall look at de-inking, and this will include some investigations of the dynamic wetting problem you mentioned.

Dr. M.B. Lyne

In your opinion, is it the presence of impurities or the effects of drying on fibre porosity that is responsible for the reduction in rewettability of recycled fibres?

Mr. A. de Ruvo

The ways in which raw material has to be treated in order to remove impurities have a great effect, not only on the rewettability but also on all the mechanical properties.

Mr. P.T. Herdman, Wiggins Teape, UK

Going back for a moment to Mr. Howarth's comment, it occurs to me that if the handsheets were dried on discs or in frames following the normal practice, then they would be subjected to very severe drying restraint. Could it be that it is this restraint rather than the time-dependent phenomena suggested that has the dominant effect? This would agree with the data presented in figure 8 of your paper.

Mr. A. de Ruvo

That is quite possible. I was merely making a suggestion, and what you are saying is of course, quite relevant.

Mr. P. Howarth

In our experiments we used both restrained and unrestrained sheets, and as a result are able to say that time is an important parameter. The whole hour that is takes to air-dry a handsheet clearly causes more permanent damage to the fibres than the rapid drying process on the paper machine. Indeed, we have seen that changing the temperature profile on the machine can also affect the extent of fibre damage.

Dr. D. Wahren, IPC

The density of the sheet is much affected by machine drying. Because the drier felt holds the sheet in constant contact with the cylinder, much larger densities are achieved on the machine than in handsheets. Could this density difference be contributing to the results observed by Mr. Howarth? We have conducted also experiments in which paper has been dried under constant z-direction pressure to different densities, and have found that this way we can obtain considerably improved tensile strengths, similar to those found in press-dried paper.

Dr. B.Jordan, Paprican

Could you elaborate more on the connection between drying and curling? We have seen in our experiments differences in curlation between dried and never-dried pulps, though there is definitely some hysteresis present. Dried fibres can be curled, though not as much as never-dried.

Mr. A. De Ruvo

We have shown very dramatically that once-dried fibres do not curl as much as virgin fibres. I ascribe this difference to the major changes in the cell wall that drying causes. Virgin fibre is very much more flexible because of the laminated construction of its cell walls.

Prof. B. Steenberg, R.I.T., Sweden

(Written comment received after the end of the symposium.)

The authors state (page) that it has been suggested that water is active in swelling by "... the equilibration of the partial free energy of free water and of water interacting with the wood polymers", but also as an alternative that "... water is active because of the existence of holes in the fibers." They state that the latter condition "...is a phenomenon into which the laws of thermodynamics offers no insight." They offer the explanation that "...obviously mechanisms regulated by thermodynamics are reversible".

Thermodynamics certainly deals with irreversible mechanisms, as evidenced by the treatment of the Carnot cycle, and by the Third Law.

Thermodynamics, however, is normally applied to macroscopic systems, where the fluctuating extensive variables can be represented by their mean values. In so called small systems, involving for instance, bubbles, drops, pores, or polydisperse systems the thermodynamic variables have probability distributions which can no longer be represented by single values. Second and higher order moments must be included(1).

As long as only bulk properties are measured it is impossible to distinguish a thermodynamic approach using appropriate distribution functions from a concept based on the distribution of so called `holes´.

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