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### SCIENTIFIC BASES OF WASTE PAPER TREATMENT

A theoretical analysis is provided of the influence of treatment processes on the papermaking properties of fibres resulting in some irreversible physicochemical changes. It is found that such processing operations as milling, wet pressing, drying and calendering exert an influence on the waste paper's ability to regenerate.

*Keywords*: wastepaper pulp, papermaking properties, hornification, swelling, defibering, shrinkage, ion exchange, osmotic pressure, surface tension, capillary phenomena, external and internal fibrillation.

#### Changes in Papermaking Properties of Wastepaper Pulp During Multiple Recycling

#### Fibre Swelling

Processing of fibrous raw materials is known to change their papermaking properties. It has been established that this change is associated with 'irreversible hornification', which is indirectly expressed in a reduced ability of fibres to swell during refining and conditioning of wastepaper before it is fed into the paper machine [14]. Processes like milling, wet pressing, drying and calendering influence the regeneration capacity of the paper. The deeper the processing, the poorer the properties of the processed paper. It has been established that reduced regeneration capacity can be attributed to decreased internal swelling of fibres. Milled pulp is characterised by greater internal delamination (fibrillation) than unmilled paper. It is noteworthy that the delamination disappears during drying and is never restored. The capacity of finely milled fibres to swell cannot be fully restored.

V.A. Kargin and G.L. Slonimsky believe that colloid swelling of pulp in water or alkaline solution is similar to the swelling of other polymers and may be represented as a result of the influence of differences in diffusion speed between small and big molecules.



Small water molecules quickly diffuse into the polymer, while big polymer molecules penetrate the space occupied by water very slowly, and these long and flexible molecules are capable of staying bonded and maintaining the body form similar to the original form, even if the amount of water diffused into the polymer is big [5].

Alkaline treatment contributes to the swelling of fibres as a result of ion exchange reactions [1, 14, 17]. Acid groups, such as polysaccharide carboxyl groups, dissociate within the fibre wall. Fibre swells intensively owing to osmotic pressure exerted by counter cations found in the solution (Donnan effect). Swelling level increases in the following row of cations:  $AI^{3+} < H^+ < Mg^{2+} < Ca^{2+} < Li^+ < Na^+$ . Where low-yield pulp is processed, the effect of osmotic pressure exerted by sodium ions appears unable to open up the horned surface of fibre wall without any mechanical impact of fibrillating milling.

Major factors that affect the speed of reagent diffusion into the fibre and, consequently, the swelling of pulp are the internal surface of the cellulose fibre which depends on the size and distribution of capillaries (pores) and changes in capillary size as a result of pulp treatments. Calculation of internal surface of the material and, more importantly, the assessment of changes in the internal surface of the material resulting from different impacts on pulp is an important supplementary method that helps in describing the pulp structure. Although pulp fibre is not a solid body, but has a complex fibrillary (capillary-porous, colloidal) structure filled with pores and capillaries of different sizes, most publications dedicated to pulp structure and reactivity do normally not take into account this factor and, more importantly, the changes in the internal surface of the pulp resulting from different treatments. The internal surface area calculated using one and the same method may change significantly depending on the pulp drying temperature. The higher the drying temperature, the smaller the surface area of the capillaries [6].

The swelling capacity of pulp may vary greatly depending on the pulping conditions, quality of the raw material and the chemical composition of the pulp. All other things being equal, increased pentosan content boosts the swelling capacity of pulp.

Swelling of fibres accelerates milling and, importantly, facilitates formation of fine and ultrafine fibrils of the fibre surface (external fibrillation), which further promote mutual binding of fibres. When pulp is soaked in water, they contact primarily through surface hydroxyl groups.

Water penetrates through intermicellary spaces and bonds to micellar surface hydroxyl groups making the fibres swell. Water does not penetrate micelles (which are ordered structures). As fibres swell, the bonds between micelles and microfibrils become weaker promoting the milling effect. Excessive swelling in the main part of the fibre is undesirable, as this makes it lose its integrity and reduces its strength [9].

Structurally ordered or, tentatively called, crystalline region of pulp and structurally disordered (amorphous) domain region behave differently after coming in contact with water. Amorphous pulp regions are more susceptible to water penetration and swelling. Consequently, when the external fibre surface opens up during milling, the milling process intensifies.

High-yield pulp is rich in hemicelluloses, which, one might think, should facilitate fibre swelling and promote strong interfibre bonds. However, high-yield pulp does not effectively swell all that much, as lignin prevents hemicelluloses from swelling and blocks formation of fine and ultrafine fibrils of the fibre surface. Hemicelluloses basically cover fibrils and act as a coupling agent providing a bond between lignin and microfibrils. Their chains are shorter than those of pulp and, as they swell, they may establish flexible cross bonds between adjacent fibres. The aforementioned lignin-hemicellulose gel prevents formation of hydrogen bonds between microfibrils during drying and maintains spaces between fibrils accessible to water. Low-yield pulp defibering reduces the amount of ligninhemicellulose gel facilitating establishment of irreversible hydrogen connections between microfibrils with the help of hydrogen bonds. In mechanical (wood) pulp defibering, this gel remains intact. That is why high-yield pulp is more difficult to mill than normal-yield pulp.

According to A. Scallan [20], lignin acts as a binder in the layered microfibril structure within a cell.

Pulp fibre swelling and hydration demonstrate an exothermic character, i.e., these processes are accompanied by heat release, which is why, as the temperature goes down, fibres are better fibrillated and the paper becomes tougher. The exothermicity of soaking pulp fibres in water and their swelling can be attributed to hydration of pulp functional groups, mainly hydroxyl. It is obvious that the more hydroxyl groups are affected by water, the more heat is released. Plasticity acquired by fibres when submerged in water can be assessed based on water swelling capacity. The more hemicelluloses there are in the fibre material, the more plastic it becomes when submerged in water.

In general, polymer swelling takes place in two stages. The first stage consists of a little fluid intake, heat release (swelling heat) and volume contraction. The volume of the swollen polymer is less than the total volume of the polymer and fluid taken in; volume contraction can be attributed to the small molecules of the solvent (water or alkali) that penetrate spaces between macromolecules contributing to tighter system packing. The fluid taken in at the first swelling stage (when heat is released) is spent on the solvation of polymer polar groups. Measurements show that a small amount of fluid (one mole per mole of polymer polar groups) is joined to the polymer with energetically strong bonds. Consequently, the solvation layer that covers macromolecules in the polymer solution is one molecule thick (monomolecular). This important fact was established during swelling heat measurements.

A lot of fluid is taken in at the second swelling stage but no heat is released. The fluid taken in is not bonded to polymer macromolecules but is diffusely absorbed by the porous structure of the fibre made up of microfibrils. Swelling and limited dissolution take place spontaneously [5].

### Fibre Drying and Hornification

The properties of pulp fibre are most affected during drying, which leads to some irreversible changes in fibre properties, namely loss of elasticity, hornification of fibre surface and increased fragility.

Paper is not just a capillary-porous material; it is a colloid material, so its drying is accompanied by irreversible colloid drying phenomena that affect the properties of the resulting material. These changes in properties during paper drying can be attributed, to a large extent, to the established irreversible changes in the wall structure of the fibres the paper is made from.

The physical nature of the irreversible changes that take place during drying is connected with the fact that, at first, the lumen and fibre pores contract, the tube-shaped fibre becomes ribbon-shaped, and then separate fibrils and small fibres are attached to the fibre outer surface. Finally, water is desorbed from the fibre walls, this having the greatest impact on the irreversibility of the properties of the dried plant fibre. It has been established that pores shrink to a certain extent even when pulp fibre is dried in mild conditions with the addition of wetting agents. Any other drying methods lead to irreversible and nearly complete disappearance of any pores smaller than 1 nm [9].

The internal and external fibrillations of the fibrous structure physically affect the ability of the fibres to adhere to one another. The internal fibrillation of the fibrous structure enhances the flexibility and papermaking properties of the fibre. Flexibility and toughness measurements may represent indirect methods for quantitative assessment of internal fibrillation of the fibrous structure of any specific fibre. In the examination [26] of semi-finished softwood products (thermomechanical pulp, chemithermomechanical pulp and fully milled and bleached kraft paper), the fibre was analysed after one and five treatments where samples were defibred and dehydrated on a chemical-free basis and paper sheets were then made and dried.

It was established that almost all chemical (pulp) fibres were contracted to become flat as early as after the first cycle. Wall thickness was reduced in all fibres, although fibre roughness measurements showed no significant changes. It was found that, after multiple recirculation, the fibre wall became softer (i.e., the lumen area is reduced owing to softening of the wall material and internal fibrillation of the fibrous structure). This internal fibrillation of fibrous structure and progressive flattening (thickness adjustment) of the mechanical fibre cell material during this light (sensitive) treatment can be contractive and may be produced by fibre structure shrinkage during drying. Shrinkage forces produced by water surface tension may reach 100–1,000 atm when the size of the pores accessible to water in the amorphous microstructures of the cell wall is measured in millimicrons.

Crosswise contraction of fibres is ten times their lengthwise contraction. In low-yield pulp, for instance, these contractive forces produced at the final drying stage appear to prevent hydrogen bonds that were formed at fibre stretches earlier, during hornification, from opening. It is very likely that, when pulp fibre walls contract, compressive forces are transferred between them at their points of contact and so-called microcontractions are produced in the fibres [3].

Moisture acts as a plasticiser on plant fibres. Increased moisture content of paper suggests its increased plasticity so this paper can be easily compressed and smoothed when passed between calender rollers. If overdry paper is run through the calender, the sheets may break and the quality of the calendered paper will be poor: its smoothness, gloss and basis weight will be low. Paper with excessive moisture content should not be used in calendering either, as it might break or become darker in colour, the structure of the sheets might be destroyed, or glossed dark or transparent spots might appear on the paper surface. The latter becomes especially apparent is the paper was unevenly wetted before calendering and big drops of sprayed water fell on its surface.

Unlike chemical pulp, mechanical pulp, which is weaker, does not worsen its bonding potential and, what is more, even somewhat improves it during 1–6 treatment cycles.

According to contemporary beliefs, hornification takes place in the cell wall of wood fibre [20]. When fibre is dried, the delaminated parts of the fibre wall, i.e., pulp microfibrils, become bonded (Fig. 1); hydrogen bonds are formed between them, and microfibrils reorientate themselves and are adjusted. All this leads to formation of a close-ended structure.

When defibrillation occurs in water, the microstructure of the fibre cell wall remains more resistant to defibrillation, as some of the hydrogen bonds will not open. That is why secondary fibre is rougher and more fragile [12, 13].



Fig. 1. Changes in the fibre wall structure [25]: A–D – drying stages

According to some recent studies [19], hornification does not increase the crystallinity of pulp or the degree of ordering of hemicellulose in the fibre wall.

U. Weise and H. Paulapuro [26] thoroughly studied the fibre drying dynamics. They studied fibre cross sections in kraft pulp at different humidity using a laser scanning microscope, measured hornification and assessed the water retention capacity (Wasser-ruckhaltevermogens – WRV).

Irreversible hornification of fibres starts when the pulp reaches a concentration of 30–35% and continues until the concentration is 70–80%, depending on the freeness. Hornification does not immediately follow contraction, as the fibres contract most when dryness is above 80%. Diagrams 1 and 2 show schematically the changes in fibres at different drying stages.

Stage A represents wet kraft paper fibre before drying. Stage B is when, as a result of dehydration, the fibre wall matrix undergoes morphological changes, where the fibre concentration is circa 30%. Fibre wall lamellae (fibrils) are drawn closer to one another under the action of capillary forces. Throughout this stage, the cavity (space) in the fibril cross section might shrink. As the fibre dries further, the spaces between the fibrils keep shrinking and, by stage C, most cavities in the fibrous structure of the cell wall disappear altogether.



Fibres contract only at a right angle to fibril layers and fibre walls become thinner. At stage A, the wall width at fibre cross-section remains unchanged. By the end of drying at stage D, moisture removal takes place in the fine structure of the fibre wall, i.e., in its amorphous region. Kraft paper fibres contract evenly and considerably at the final drying stage, where the solid content exceeds 75–80%.

Fibre contraction at stage D can be reversed. Repeat wetting of Kraft paper fibres restores their initial form. Hornification takes place gradually, at stages B and C. Initial size values recorded during measurement of fresh fibre cross-sections cannot be ensured during repeat wetting of the sample. The space between the microfibrils in the layered structure of the cell wall becomes partly closed and the microfibrils remain partly inaccessible to water.

Hornification takes place when paper sheets reach the level of dryness typical of the press section of the paper machine. Hornification increases as freeness grows. The intensity of paper sheet drying increases fibre hornification, too [22]. According to U. Weise [24], there is "wet" hornification, where dryness exceeds 30–35%, which is described above, and "dry" hornification, i.e., additional hornification of fibres that takes place when a kraft paper sheet is dried at 105°C until it is 100% dry. In effect, the properties of hornified low-yield pulp often restore during fibrillating milling.

Different degrees of disposition toward hornification among different types of pulp become more apparent when compared to *WRVs*.

The main feature of the 'more moderate' mechanical fibre hornification described above is the ability of the fibre to retain water after drying (due to preservation of hemicellulose-lignin gel). Lower-yield pulp fibre does not have this ability.

### Paper Calendering

Research into how calendering affects the processing properties of wood pulp paper waste and wastepaper free from wood pulp have shown that the higher the degree of calendering, the greater the reduction in the breaking length of the samples obtained from pulp based on such paper. This effect can be attributed to reduced moisture retention and decreased fibre length. As the degree of calendering increases, the breaking length and the degree of pulp dehydration deteriorate. This effect can be observed with all initial freeness values, although it will be different for each of them. For example, the strength properties of paper made from low-freeness pulp deteriorate more than those of high-freeness paper. Moisture acts as a plasticiser on plant fibres.

Increased moisture content of paper suggests its increased plasticity so that the paper can be easily compressed and smoothed when passed between calender rollers.

One of the authors of this survey studied the effects of calendering of two-layer wallpaper on its porous structure [2]. The porosity of all pulp, as well as of the main and surface layers, was measured in samples.

The study was conducted using a KRM-1 device, with an  $\alpha$ -radiation and N<sub>1</sub> filter. Diffuse radiation was measured using a BDS-06 X-ray scintillation counter; the results were then printed on a digital printer. Paper samples of equal weight were fixed immovably and placed in an X-ray chamber exposed to vacuum treatment of up to  $10^{-1}$  kg/cm<sup>2</sup> to eliminate X-ray scattering by air particles.

Size of pores, mm	Number of pores $n \cdot 10^{16}$ in 1 m <sup>3</sup> of paper			
	Total weight of the sample	Main layer	Surface layer	
6.2	<u>59.50</u>	<u>69.50</u>	<u>46.70</u>	
	55.10	58.20	41.90	
10.8	<u>14.10</u>	<u>13.50</u>	12.80	
	13.50	12.90	12.50	
36.7	<u>1.43</u>	<u>1.20</u>	<u>1.62</u>	
	1.26	1.16	1.45	

Note. The numerator contains data for noncalendered paper, the denominator – for calendered paper.

X-ray diffraction measurements were performed within an angle interval of 5–80', with a scanning interval 2.5'. Background scattering was measured within the same interval. Corrections were made during calculation for absorption of radiation by the sample.

The table contains a comparison of equally-sized pores in different layers of samples. The comparison shows that there are fewer equally-sized pores in each layer of calendered paper than in noncalendered paper. The biggest difference was noticed with small pores. It was established that the surface layer in both samples contains fewer pores and calendering significantly reduces the number of small pores.

# Waste Paper Defibering

Chemical and Physical Processes

It is known that the active hydroxyl groups of fibre surface should be solvated with water molecules shown schematically as dipoles. As wet fibres are drawn closer to one another, bridge bonds are formed following the pattern shown in Fig. 3. As the fibres become drier, the middle

water molecule is removed, while the extreme ones are drawn closer to one another and active fibre groups become bonded again [9]. Water surface tension forces that make the paper shrink facilitate the mutual approaching of fibres as they are dried to remove water from capillaries (pores) in the sheet. Separate pulp chains come into close contact with one another, forming hydrogen bridge bonds, which is due to interaction between adjacent hydroxyl groups. The water bridge is then replaced with a hydrogen one (Fig. 4).

When dry paper is wetted, the water penetrates the pores in the paper sheet, pushing its way between the fibres and making

them swell. This breaks the strong hydrogen bridges (Fig. 2, A) and the fibres become bonded with loose water bridges (Fig. 2, B). Water acts as a lubricant, reducing the mutual friction between the fibres which also results in reduced mechanical strength of the paper when it is wetted.

After a while, moisture that comes in contact with the surface of sized paper passes through the interfibre pores and overcomes the hydrophobic barriers of residue particles of rosin or another size to emerge on the other side of the sheet.

The fibre surfaces accessible to moisture are not equal in terms of wetting.



Fig. 3 Diagram of interfibre bridge bonds based on water dipoles: 1 - water dipoles, 2 first fibre, 3 - second fibre.



Fig. 4. Diagram of bridge bonds between parallel pulp chains: a – chains joined by lateral bonds using hydrogen bridges in dry fibre, b – chains joined by water molecules using water bridges in wet fibre

Outer surfaces covered with hydrophobic size residue absorb water worse than fibre pores and potential internal fluid passages that can be accessed by size particles to a limited extent. Consequently, the moisture that comes in contact with at least some part of the fibre surface penetrates the pores in the fibre walls and further permeates through the internal moisture-conducting passageways of the fibres in accordance with the capillary soaking law at a speed that, in hard-sized paper, by far exceeds the velocity of fluid flow in capillaries and pores formed by the outer surfaces of the fibres.

Even so, the paper infiltration rate depends on factors other than the size of the internal moisture-conducting passageways and their degree of wetting. First of all, we should mention the contact area of fibres (an increase in this area facilitates the transfer of moisture between fibres) and the degree of hydrophobicity of fibre surface (as this degree increases, the anticapillary properties of the interfibre spaces become more prominent).

In unsized or semi-sized paper and when wetting fluid (e.g., SAS) is applied, it will flow through the interfibre and intrafibrous passageways. The infiltration rate will depend on the size of the interfibre pores.

The duration of fluid action on paper and the initial degree of hydrophobicity of the surface of the interfibre pores are thus the factors that determine the soaking mechanisms and the absorption capacity of sized paper. According to the present-day idea of moisture paths in wetted paper, the negative influence of calendering on paper sizing degree may be explained by paper consolidation where closer contacts are established between fibres, thus intensifying interfibre moisture passage.

The physics of capillary phenomena inform that the fluid velocity in the capillary system where the hydrostatic pressure is zero can be defined by the following expression

 $dl/dt = r\sigma \cos\theta / 400\eta l$ ,

where l is fluid penetration depth, cm,

t is fluid penetration time, s,

r is capillary radius, cm,

 $\sigma$  is surface tension, N/m,

 $\theta$  is contact angle of wetting, degrees,

 $\eta$  is fluid viscosity, Pa·s.

This formula may be used for paper sheet structure only with a certain degree of approximation as the formula has been developed for a system where capillaries are equally-sized.

# Hydrodynamic Conditions at Waste Paper Deflaking

According to O.A. Terentiev, in a running pulper 1 (Fig. 5), rotor 2 is like a centrifugal pump (or a screw) that transfers to the defiberised pulp the energy that makes the fluid in the pulper vat move in a spiral-like trajectory. The pulp spirals upwards near the walls of the pulper vat,

going back to the rotor in the centre over the same trajectory. A vortex is formed as a result of this on free pulp surface 5.



Engine

Двигатель

If the wall of the pulper vat has vertical rails, the vortex is more prominent as the vertical component of the velocity dominates in the flow.

Experimental sounding of the flow in the pulper vat [8] was used to obtain the velocity structure on the meridional plane of the pulper vat. Fig. 5, sections I and II, show diagrams 3 describing the qualitative aspect of velocity distribution. There is a transition zone between upward and downward streams (local vortex zone 4) where the velocity is low or uneven.

Рисунок				
Рис. 5. Схема потока в	Fig. 5. Diagram of the flow on			
меридиональной плоскости	the meridional plane of the pulper			
ванны гидроразбивателя	vat			

This area is like a solid border between flows. The only difference is that its structural components have to undergo continuous changes: the surrounding flows snatch out some parts of the pulp and replace them with other parts all the time. The material is thus smoothly deflaked in the pulper vat and this area does not accumulate undeflaked material. There is a theory that a local vortex area imitating the fluid wall has been created allowing movement on to creation of a construction diagram for the pulper vat (Fig. 5). The power that is supplied to the rotor is spent on transferring kinetic energy to the fluid in the pulper vat and on material deflaking.

Waste paper deflaking (defibering) and pulp movement should be treated as two sides of the same process. The most active deflaking elements are the rotor and the rails on the pulper vat body, i.e., those parts that exert mechanical stress on the deflaked paper. Yet their effectiveness depends on the pulp velocity, the angle of impact formed by the paper hitting the rotor blades and rails, as well as on the frequency of repetition of the active elements' impact on the same particles of deflaked material. The last factor becomes more prominent when circulation in the pulper vat takes place mainly on the vertical (or meridional) plane as the share of low-efficiency energy spent on horizontal movement decreases in this case. The velocity gradient, in turn, has a beneficial influence on deflaking, but one may reasonably assume that this influence will be less effective than the mechanical impact of the elements described above.

Analysis of the above prompts the conclusion that efficient work of the pulper vat rests on both the pulp flow dynamics of the pulper vat and the breaking capacity of its active mechanical elements.

If we assume that the loss of energy resulting from mechanical impact on the deflaked material may be corrected to equivalent hydraulic loss, the power consumed by the rotor may rightfully be calculated using the hydraulic method. The calculations were based on the energy balance of the flow in the pulper vat.



It was accepted that the flow in the pulper vat formed a closed circuit built on the basis of the above idea of the process physics.

If we assume that there is fluid wall 2, the flow will be split into three segments forming a closed circuit (Fig. 6). Segment I is the rotor area. Here, the material is deflaked as a result of collision with the blades and the flow receives energy from the rotor and starts moving in a circuit.

Рисунок			
Круг	Fig. 6. Circuit		
	<mark>Рис</mark> Круг		

Segment II is the upward stream area (from the exit edges of the rotor blades up to the upper fluid surface elevation  $Z_0$  in the pulper vat). This segment can be characterised by well-developed diffusion. Here, one can install rails to orientate the flow to the meridional plane and exercise additional mechanical impact on the deflaked material. This segment is characterised by the highest initial flow energy, by well-developed diffuser hydraulic losses and shock losses, if rails are installed. Segment III is the downward stream area (from the upper fluid surface elevation up to the exit edges of the rotor blades). Here, the fluid affected by the residual pressure, gravity and suction force of the rotor rushes back to the rotor and the circuit closes. A vortex is formed on the free surface.

Recommendations given in the literature on how to calculate the power consumed by the pulper rotor are summed up in the following formula [4]

$$\mathbf{N}_p = \zeta \,\rho \,n^3 \,D^5$$

where  $N_{\rm p}$  is rotor power, W,

 $\zeta$  is trial coefficient,

 $\rho$  is pulp density, kg/m<sup>3</sup>,

*n* is rotor speed,  $s^{-1}$ ,

D is the biggest diameter of the circle of the exit edges of the rotor blades, m.

The defibering force applied in the pulper should be sufficient to break the structure of waste paper sheets and separate associated foreign materials (e.g., a laminated layer) without destroying them. The impeller (rotor), which rotates at a linear velocity of 12–20 m/s (the measurement is provided for the blade point furthest from the rotor centre), provides the force needed to transform paper into pulp. It should be noted that an increase in the number of rotations of the rotor boosts (in cubic dependence) power intake. In addition, the ram effect produced by the impeller impedes unloading of the pulper.

In order to ensure efficient deflaking, one has to adjust the geometric characteristics of the pulper vat, impeller, rails and the linear velocity. The diameter of the sieve openings in the pulper vat is adjusted based on the availability or absence of equipment ensuring efficient final paper deflaking in the process scheme.

The shive content of the pulp varies between 15% and 40%, depending on the defibering ability of the waste paper.

Popular drum pulpers (rotational velocity -100-120 m/min, diameter -2.5-4.0 m, length - up to 30 m) are used to defibre low wet-strength paper. They are used most often to process old newspapers and magazines with deinking. The moisture-resistant components of the paper mix cannot be defibred and are discarded as waste [10].

### Final Defibering

Disk screens (turboseparators) are similar to pulpers in terms of both geometric characteristics and hydrodynamic performance. As the sorting disk has smaller openings and the rate of energy delivery in these comparatively small-sized machines is higher, their defibering performance is also higher and these machines are more energy-efficient than pulpers.

In order to complete paper or broke defibering, after processing in the pulper, the paper pulp is treated using hydrodynamic shock machines. A deflaker equipped with a  $3,000-4,000 \text{ min}^{-1}$  velocity rotor is one of these. The rotor–stator gap is permanent (0.5–2.0 mm).

The operating efficiency of these machines during final defibering may be changed, depending on the size of the pulp shives, their concentration and the content of coarsely dispersed waste. Ideally, the defibering degree should make at least 95% once treatment is completed. From one to four material passes through the deflaker, is considered economical, depending on pulp type and purpose. Specific energy consumption in this case constitutes 25–40 kWh/t.

## The Mechanisms of the Action on Secondary Fibres during Pulp Milling

A. Kriebel and R. Sigl [17] have theoretically analysed possible changes in fibre properties throughout the pulp treatment process (Fig. 7). These changes might include fibre shortening and external and internal fibrillation of the fibrous structure, leading to fibre plastification, release of fines and increased swelling capacity. All impacts (processes) listed on the right-hand side of the picture, apart from fibre shortening, which reduces strength, enhance the papermaking properties of the pulp.

#### Milling-Related Processes

The main purpose of milling is to prepare the pulp fibre surface for formation of interfibre bonds in the paper sheet.



Fig. 7. Possible impacts on fibres during pulp treatment

Two types of phenomenon occur simultaneously during milling: a) purely mechanical impact produced by milling elements on plant fibres whereby their shape and size are changed, b) colloid and chemical impact expressed in fibre hydration. The term 'hydration' is understood to mean colloid and chemical phenomena that start with swelling of the hydrophilic plant fibres (which increases during the milling process) and are accompanied by fibrillation of their cell walls, release of fines and an increase in the external fibre surface where water absorbing OH<sup>-</sup> groups are exposed [5]. This creates conditions where fibres can become bonded to one another, forming a strong sheet structure.

Unmilled fibre can swell 20%–30% crosswise, milled fibre – to double their diameter. Fibre milling is associated with external and internal fibrillation.

External fibrillation is accompanied by an increase in the external surface of the fibres and an increased number of water-absorbing hydroxyl groups on their surface. The specific surface of fully swelled fibre is 200 times larger than that of dry fibre. The fibres themselves become slack and water can easily access the interfibre spaces. In internal fibrillation, fibrils are not released; the fibres remain as strong as ever, only they become more flexible and softer as a result of swelling of the hemicelluloses, which can be found mainly in interfibre spaces.

It is obviously easier for surface tension forces in the paper sheet capillaries to move and draw closer the fine fibrils than the non-fibrillated source fibre. This is the primary contributor to increased shrinking and dense structure of paper made from fibrillated fibre.

Fibre fibrillation during milling is thus important not just in order to facilitate the mechanical interweaving of fibres and fibrils, but also to create a denser and, consequently, stronger sheet as a result of the impact of surface tension forces. One should bear in mind that fibrillation leads to an increase in the developed surface of fibres where hydroxyl groups that were previously hiding in the deep emerge. The hydrogen bonds between fibres are established in these groups. Fibrillation boosts the number of contacts between fibres, thereby enhancing sheet strength.

Milled pulp is more layered internally than unmilled pulp and this layering disappears during drying and is never restored during further deflaking.

## **Process Factors**

# The Effect of Temperature

Cellulose fibre swelling and hydration are known to be exothermic, i.e., they are accompanied by heat release [5]. Consequently, as temperature goes down, the ability of fibre to become bonded with water and swell in it increases. A rule of thumb states that milling is performed faster and easier in cold water in winter than in summer. Under these conditions, fibres are easier to fibrillate and the paper is stronger. If milling is performed at high temperatures, fibres fail to swell sufficiently and do not achieve the necessary flexibility level, are poorly fibrillated and become easy to chop crosswise. Paper made from this fibre is porous and has low mechanical strength.

There is no contradiction in the fact that the heating of semi-chemical hardwood and softwood pulp and waste resulting from groundwood pulp fine screening during milling is beneficial. It enhances the mechanical strength of milled pulp and reduces the power consumption associated with milling.

The plastifying action of lignin and hemicelluloses at high temperatures that facilitates milling takes precedence over the swelling of the pulp component of the fibre [9].

#### The Impact of Hydrodynamic Conditions

Hydrodynamic impact basically translates into the fibre suspension hitting the milling elements and walls of the milling machine. This impact supplements the mechanical impact on the fibre. Fibres also rub against one another and against the milling elements and walls of the milling equipment.

Increased rotational velocity of the rotor plate is due to an increased fibre fibrillation effect and reduced shortening, where total power consumption associated with milling slightly increases and the performance coefficient of the milling machine is decreased. At the same time, an increase in the rotational velocity of the rotor, along with an increase in pulp concentration, enhances its circulation and fibre swelling, makes the fibre flexible and soft, and strengthens interfibre bonds in ready-made paper.

If narrow blades are available, they can be installed abundantly on the milling elements. An increased number of knives improves the efficiency of milling machines and enhances the combing impact of blades on pulp fibre. It has been established that, in milling machines equipped with comparatively narrow blades, one may obtain wet long-fibre pulp, provided the specific pressure is moderate and the pulp is diluted to a medium degree.

## Pulp Milling Considerations

Secondary fibres of mechanical pulp have their own bonding potential, which may be increased. For instance, the thickness of the wall of a long-fibred fraction is reduced during refining pulp milling performed at high concentrations. Some fibrils are likely to lose the external layer of the fibre cell wall [16, 17, 20]. This effect is more prominent in the compacted layers of late wood fibre than in loose-textured early wood.

Waste paper supplied to the paper mill after defibering in the pulper has the form of a suspension consisting of fibres of different lengths. The milling of this pulp that is heterogeneous in terms of fibre length and composition inevitably leads to the well-known and unnecessary shortening of an already short-fibred fraction, which might cause a deterioration in the properties of the paper. It is, therefore, preferable to perform the milling very carefully, at a comparatively low specific pressure, which, in turn, might entail negative phenomena: insufficient development of a long-fibred fraction, increased milling time and power consumption.

Yet the possibility of undesirable shortening of short fibre cannot be ruled out. These considerations earlier led us to the conclusion that it is advisable to mill different fractions separately [16].

The benefit of separate milling of long-fibred fractions of paper subjected to discolouration has not been confirmed [23]. Separate treatment of long-fibred fraction required more power, while the fibre strength differed insignificantly from that of the paper sheet made from pulp milled without fractionation.

# Conclusions

1. Of all papermaking processes, drying has the biggest impact on fibre properties, changing them irreversibly. Changes in fibre properties are associated with the phenomenon of 'irreversible hornification', which is indirectly expressed in a reduce ability of the fibres to swell during refining and conditioning of wastepaper before it is fed into the paper machine. The physical nature of the irreversible changes in the fibre properties that take place during drying is connected with the fact that, as drying starts, the internal channel (lumen) and fibre pores contract. The tube-shaped fibre becomes ribbon-shaped and water is desorbed from the fibre walls, which has the biggest impact on the irreversibility of the properties of dried plant fibre.

2. Irreversible hornification of fibres starts when pulp reaches a concentration of 30–35% and continues until the concentration is 70–80%, depending on the freeness. Hornification does not immediately follow contraction, as the fibres contract most when dryness is above 80%.

3. Alkaline treatment contributes to swelling of the fibres as a result of ion exchange reactions under osmotic pressure. The major factor that affects the speed of reagent diffusion into the fibre and, consequently, swelling of the pulp is the internal surface of cellulose fibre, which depends on the size and distribution of capillaries (pores) and changes in capillary size as a result of pulp treatments.

4. Unlike chemical pulp, mechanical pulp, which is weaker, does not worsen its bonding potential and, what is more, even somewhat improves it during 1–6 treatment cycles. The main feature of the 'more moderate' mechanical fibre hornification described above is the ability of fibre to retain water after drying (owing to the preservation of hemicellulose-lignin gel).

5. Processes like milling, wet pressing, drying and calendering influence the regeneration capacity of the paper and the deeper the processing, the poorer the properties of the processed paper.

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# D.A. Dulkin, L.A. Yuzhaninova, V.G. Mironova, V.A. Spiridonov Scientific Bases of Waste Paper Treatment

A theoretical analysis is provided of the influence of treatment processes on papermaking properties of fibres resulting in some irreversible physicochemical changes. It is found that such processing operations as milling, wet pressing, drying and calendering exert an influence on the waste paper's ability to regenerate.