

Paper and Pulp

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1. Pulp

Wood and other lignocelluloses, such as straw or other annual plants consist of many different cell types in which cellulose, hemicelluloses, and lignin are the main chemical components. In the chemical digestion of lignocelluloses, lignin, which is embedded predominantly between the wood fibers as a binder and in the outer cell wall layers, and the hemicelluloses are largely dissolved out of the fiber matrix. The cohesion of the structural elements is lost in this process. The fibrous material obtained after digestion, consisting principally of cellulose, is called pulp.

The chemicals used in the digestion cannot quantitatively eliminate lignin from the wood matrix. In addition, unwanted, sometimes colored accompanying substances, called wood extractives, may remain in the cell walls. For most uses, the residual lignin and the extractives must be eliminated in a subsequent bleaching treatment. Moreover, partial or complete removal of hemicelluloses by bleaching and purification is required if the cellulose in the pulp is to be employed as raw material for chemical products.

Pulps that are used to make paper and board are called paper or chemical pulps, and those processed in the chemical industry are known

as dissolving pulps. Pulps are also classified according to the type of raw material used (softwood or long-fiber pulps, hardwood or short-fiber pulps, straw pulps, etc.) and the pulping process employed (e.g., kraft, sulfite, and soda pulps).

The pulping and bleaching processes must be adapted to the final use of the pulp. The digestion of the raw material and the bleaching of the pulp can be carried out with varying intensity, or the latter step can be completely omitted. Depending on the intensity of pulping, it is possible to differentiate between semichemical and high-yield pulps and between chemical pulps and dissolving pulps. Depending on the residual lignin content of chemical and dissolving pulps, a difference is also made between harder and softer pulp qualities. Semichemical and high-yield pulps can be used with or without bleaching, but chemical and dissolving pulps must usually be bleached. There are slightly bleached, partially bleached, and fully bleached qualities of pulp. Paper and board production is by far the dominant use; only about 5 % is processed in the chemical industry.

1.1. Raw Materials for Pulp

Apart from good availability and processibility, the distribution and morphology of the cell types and the chemical composition are important criteria for the suitability of lignocelluloses for pulp production. The proportion of fibrous elements with a favorable length-to-width ratio is crucial for the technological properties of the resultant pulps. The cellulose content as well as the amount of lignin and its structure determine the pulp yield and the conditions to be used for digestion. In particular, acid sulfite digestion, and also the further processing of pulp, can be adversely affected by accompanying substances, such as fats, waxes, phenolic components, or mineral inclusions. The average composition of important raw materials for pulp production is presented in Table 1. Note that considerable deviations in individual analytical data can be observed, depending on the method of analysis and especially on the sample of raw material used. However, the values given do exemplify the essential differences in the chemical composition of conifers (softwoods), deciduous woods (hardwoods), and annual plants.

The most important raw material for the production of pulp is wood, softwoods being preferred. However, hardwoods have gained increasing importance because, in comparison with softwoods, they have some interesting advantages for the production of pulp and paper (Table 2). Only 7–8 % of pulp production is based on annual plants, which are mainly employed when wood is not available [16].

The morphology of the lignocelluloses varies considerably (see also → Wood). Conifers have the most homogeneous structure. They consist to more than 90 % of tracheids with an average length of 3 mm and a width of 30–50 μm . These fiber cells have a length-to-width ratio > 100:1 and are ideally suited to papermaking. On the other hand, the parenchyma cells, which occur only in small amounts in conifers, have unfavorable technological properties. They are very small and have an unfavorable length-to-width ratio of ca. 3 : 1.

The structure of hardwoods is much more heterogeneous. The most important cell type are the libriform (or scleremchyma) fibers, which account for 40–60 % of the tissue of most deciduous trees. The average length of hardwood fibers

is usually less than 1 mm. The fiber width varies greatly, in the range 10–40 μm , depending on the type of wood. In addition, hardwoods contain vessels and, in comparison with conifers, a higher content of parenchyma cells. The vessels are very voluminous, with relatively thin, partially perforated walls and a low length-to-width ratio.

The cellular dimensions of annual plants are extremely variable. In comparison with wood, the cells are, in most cases, shorter and have thinner walls, and the parenchyma content is very high. A simplified survey of the cellular composition and morphology of various raw materials for pulp is presented in Figure 1 [17].

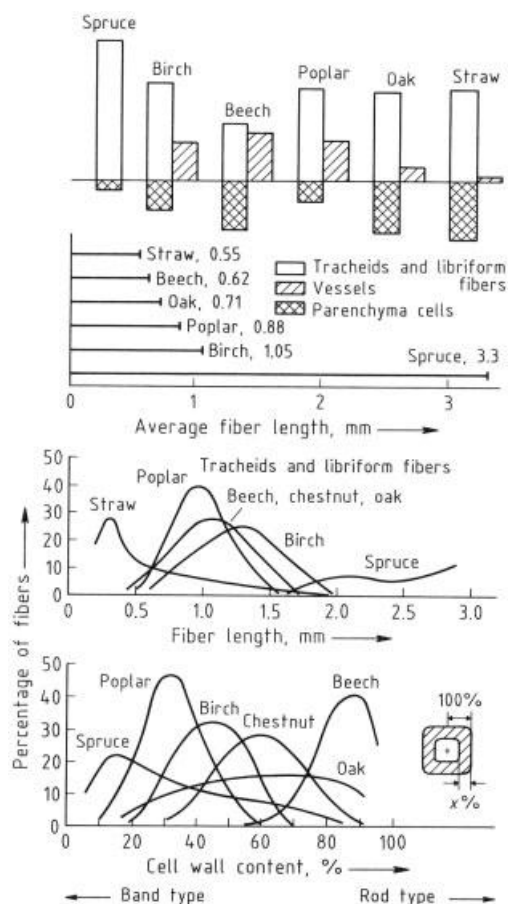


Figure 1. Composition and morphology of various pulp raw materials

In the pulp and paper industry, a morphologically correct differentiation of cell types is not

Table 1. Chemical composition of important raw materials for pulp production

Common name	Scientific name	Cellulose, %	Hemi-cellulose, %	Pentosan, %	Lignin, %	Ethanol/benzene extract, %	Ash, %	Silica, %
Scots pine	<i>Pinus sylvestris</i>	44	26	9	28	4	0.4	
European spruce	<i>Picea abies</i>	43	27	9	29	2	0.4	
Douglas fir	<i>Pseudotsuga menziesii</i>	47	22	7	30	5	0.3	
Silver fir	<i>Abies alba</i>	43	27	11	29		0.5	
Silver birch	<i>Betula verrucosa</i>	46	36	25	19	2	0.3	
European birch	<i>Fagus sylvatica</i>	45	35	22	22	2	0.3	
Trembling aspen	<i>Populus tremuloides</i>	50	31	17	18	4	0.3	
Blue gum	<i>Eucalyptus globulus</i>	47	27	17	26	1.5	0.3	
Wheat straw	<i>Tritium vulgare</i>	38	36	28	19	4	5	3.5
Rice straw	<i>Oryza sativa</i>	32	36	25	12	4	16	12
Sugarcane bagasse	<i>Saccharinum officinarum</i>	38	36	27	21	3	2	1.5
Bamboo	<i>Dendrocalamus strictus</i>	35	32	18	26	5	3.5	2.5

Table 2. Advantages of softwoods and hardwoods for pulping and papermaking

	Softwoods	Hardwoods
Wood production	usually higher productivity	in some cases extremely high productivity (e.g., eucalyptus, poplar), higher stock stability
Wood	more uniform raw material, especially better stem formation, easier to debark, longer fibers, higher yields in acidic cooking	higher specific weight (e.g., eucalyptus, beech, birch) → lower transport cost → higher digester capacity → higher pulp output lower lignin content → easier to pulp → less energy and chemicals consumption higher yields in alkaline cooking
Pulp	better wet web strength, better drainage properties	requires less beating energy, rapid strength development during beating, better bleachability → fewer bleaching stages → lower chemical demand → less pollution (chlorine-free bleaching possible)
Paper	high strength properties, especially tear strength, better runability	better sheet formation (higher content of hemicelluloses), usually smoother surface, higher bulk, higher opacity → better printability

made. All cells are designated as fibers. The suitability of cells for papermaking depends essentially on the length-to-width ratio and the ratio of twice the radial cell-wall thickness to the lumen diameter. The latter is important for the flexibility or stiffness of a structural element. In this respect, considerable differences can be observed within the same cell type due to the seasonal growth rhythms and to the formation of specific cell structures because of special stresses in certain tissue regions. At the start of the growth period, cells having a large diameter and thin walls (springwood) are formed, while at the end of the vegetation period, thick-walled cells are

produced (summerwood). Compressive and tensile stresses can also result in the formation of especially thick-walled cells that are capable of absorbing these stresses. The increase in the wall thickness of spruce tracheids during the growth period is shown in Figure 2.

The structure of the tissue elements influences the technological properties of the resulting paper in the following manner. In papermaking, the fibers suspended in water deposit on the wire of the paper machine to form a fiber web. Hydrogen bonds are responsible for bonding the fibers together. Apart from the presence of water, formation of hydrogen bonds requires hy-

drophilic groups for contact between the fiber surfaces, and small interfiber distances. The removal of the hydrophobic lignin from the surface of the fiber exposes the cellulose and hemicelluloses with their hydrophilic OH groups. The tensile strength and burst strength of a paper sheet depend primarily on the number of hydrogen bonds per unit volume between the fiber surfaces. Therefore, during paper sheet formation it must be ensured that the interfiber distance required for the formation of hydrogen bonds is attained. Springwood fibers with thin walls and large diameters (i.e., with large volumes) collapse during paper sheet formation because the lignin responsible for the stiffness of the cell wall was dissolved during digestion. Hence, the fiber becomes much more flexible, and its surface can touch neighboring fibers in large areas of the paper web, leading to increased hydrogen bond formation. This effect can be increased still further by mechanical treatment of the pulp in a beating step.

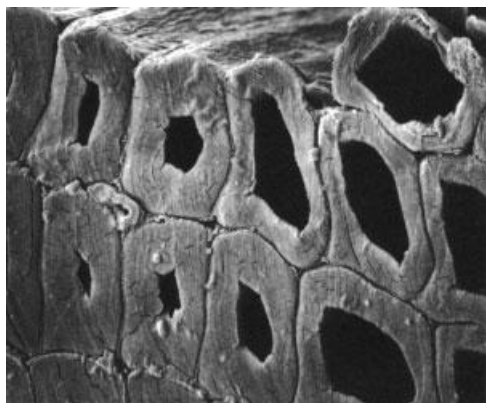


Figure 2. Increase of the cell wall thickness of spruce tracheids during the growth period

Summerwood fibers, having thick cell walls and being less flexible, hardly collapse and therefore form fewer hydrogen bonds per unit volume. However, they contribute greatly to the tear strength of the fiber web because of their inherent high fiber strength. In addition, they increase the volume of the paper and improve the optical properties by increasing the opacity of the paper. Thus, long, thick-walled fibers are required for high tear resistance of the pulp, while high fiber flexibility and a large surface-to-volume ratio are required for good interfiber

bonding and high tensile strength. Therefore, fibers with a good length-to-width ratio have optimal properties for papermaking. This ratio should be at least 100 : 1. Figures 3 and 4 show the embedding of unbeaten and slightly beaten fibers in a paper web.

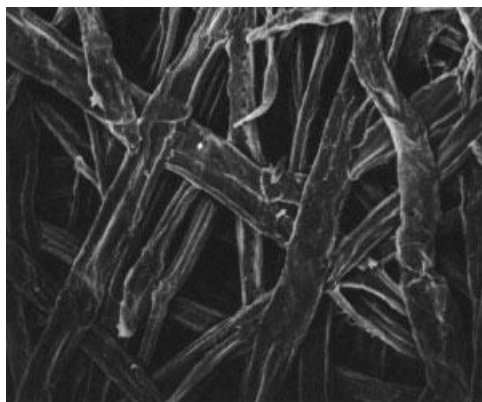


Figure 3. Electron micrograph of a test sheet made of unbeaten oak pulp

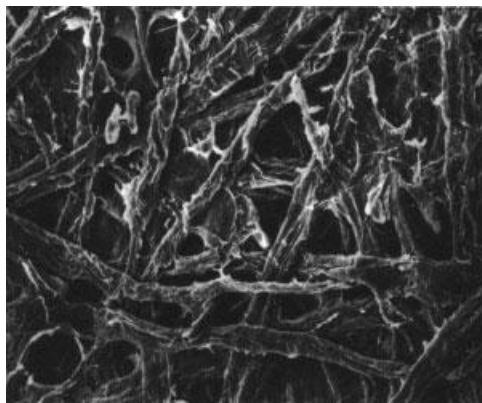


Figure 4. Electron micrograph of a test sheet made of oak pulp after 20 min beating

In Europe, sawmill residues and wood from thinning of forests are used in the production of wood pulp. In countries with good growth conditions, wood for pulp production is predominantly cultivated on plantations. Conifers, particularly spruce and pine, are preferentially used because of their favorable morphological structure. However, pulps of good quality can also be made from hardwoods, such as birch, beech, eucalyptus, and poplar (see Tables 1 and 2). In

particular, the importance of eucalyptus for the fiber industry should increase steadily because of its high growth rate and the excellent properties of pulps made from this wood [18–20]. Each type of wood is normally processed separately because, to achieve optimal pulp properties, the production process must be adjusted to the specific requirements of that particular type of wood. Mixtures of woods of greatly varying morphology and chemical composition, e.g., mixtures of hardwoods and softwoods or mixtures of hardwoods of widely varying wood density, lead to unsatisfactory digestion results and pulp properties.

1.2. Processing of Raw Materials

1.2.1. Processing of Wood

Wood is the most important raw material for the pulp industry and is obtained as logs, saw-mill residues, and chips. Logs normally enter the pulp mill with bark, but industrial residues should be bark-free.

Storage of Wood. Weeks and months often pass between wood harvesting and its processing in the pulp mill. In this time, biological respiration of living cells, chemical reactions, and attack by microorganisms can degrade the wood. The extent of wood degradation depends on many factors, the most important being the duration of storage, the storage conditions, the climate, and the type of wood.

In the storage of very fresh wood, especially from summer felling, the respiration of nutrients still present in the wood continues, generating heat, especially in the center of wood chip piles. Temperatures of 60 °C can be reached in only one to two weeks and in extreme cases temperatures as high as 90 °C have been observed. Spontaneous ignition can even occur under these conditions. After this increase in temperature, fungi and bacteria attack the wood, reducing the temperature again. Normally a temperature gradient arises, with the highest temperatures in the upper part of the pile.

Apart from microbial oxidation, chemical autooxidative and hydrolytic degradations also occur. In autooxidation, the wood components react with atmospheric oxygen; the final products are frequently organic acids. Substances

that primarily undergo autooxidation are wood extractives, especially unsaturated fatty acids, resin acids, and terpenes. Although hydrolysis, particularly of carbohydrates, contributes only to a small extent to the generation of heat, it releases acetic acid from the hemicelluloses, which causes further hydrolysis.

Fungi and bacteria have the greatest destructive effect on wood. Most of the microorganisms that destroy wood have an optimum temperature between 25 and 50 °C; the most damaging microorganisms have an optimum of 30 °C. The optimal moisture content for microbial attack is 24–32 %. Degradation is accompanied by a reduction of strength of the wood and of the individual tissue components. Frequently, discoloration of the wood also occurs.

No general statements can be made about the losses of wood incurred during storage because of a great variety of interconnected factors. However, it can be assumed that wood losses of at least 1 % occur for each month of storage. Considerably higher values are observed for hardwoods than for softwoods, and the degradation of sapwood is greater than that of heartwood. The loss in digestion yield resulting from the decay of wood during storage is substantially greater. Microbial attack results not only in the loss of wood substance, but also in the reduction of the degree of polymerization of cellulose. This results in decreased pulp strengths. In addition, condensation reactions occur in lignin which lead to darkening of the wood and reduction of lignin reactivity. Hence, stronger digestion and bleaching conditions are required, which result in an increased degradation of carbohydrates.

The duration of storage of wood should be limited to two to three months to prevent storage damage. Since fungi do not attack highly moist wood, it is of advantage to store wood in a water saturated state. This applies in particular to the storage of chips. In principle, chemical treatment with wood preservatives is possible, but is now hardly considered for economic and environmental reasons.

Wood Debarking. The bark of a tree accounts for 10–20 % of the trunk, depending on the type of tree, its age, and the growth conditions. The bark must be removed before the

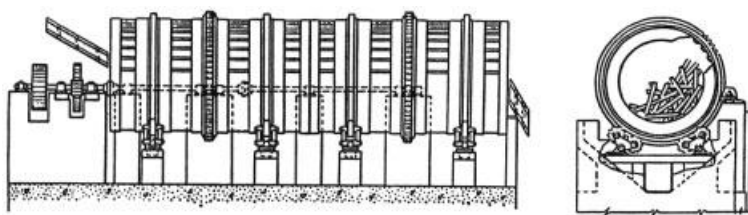


Figure 5. Drum barker

wood is cooked because it interferes with the digestion process and reduces the quality of the pulp. Bark has a higher content of lignin and extractives and a much lower content of cellulose than wood. Up to 25 % of the tissue components of hardwood barks is fiber. However, softwood barks have a fiber content of at most 5 %. The presence of bark leads to an increased consumption of digestion chemicals, and reduces not only pulp yield, but also the technological properties and the brightness of the pulp. In addition, acidic digestion processes can only degrade and dissolve bark to a limited extent. Hence, the resulting pulp contains more impurities and requires stronger bleaching conditions. Bark, especially outer bark, contains considerable amounts of colored substances which usually have a phenolic structure. Bark phenols can cause serious digestion problems in the sulfite process. They react with lignin, preventing its sulfonation and dissolution. The kraft process can cope with the largest proportions of bark because most of the bark components are quite readily soluble in alkali. The higher the quality of pulp required, the lower the content of bark that can be tolerated. The use of bark-containing wood also has the disadvantage that dirt such as sand and stones enters the pulping process, and must subsequently be removed.

The efficiency of debarking depends on the structure of the bark, the strength of bonding between the bark and the wood, and the shape of the trunk. The most important influencing factor is the bonding between the bark and the wood, which depends on the time of felling and storage influences. In most cases, wood felled during the vegetation period can be debarked in the fresh state rather easily. Wood which is felled in summer and allowed to dry in its bark can be debarked only with great difficulty. However, considerable differences are observed between dif-

ferent types of wood. After exceptionally long storage, the bark can be removed from the wood without additional mechanical effort because of microbial degradation. However, overstored wood should not be used for the production of pulp. The debarking of wood during periods of frost causes great problems as frozen bark can hardly be removed from the wood. Therefore, wood of this type must be subjected to steam treatment before debarking. Wood which is suitable for debarking should be as straight as possible and contain only a few depressions and knots. Before debarking, the wood is cut into segments.

In the pulp industry, drum barking is the most frequently used debarking process (Fig. 5). In this process, small short logs are continuously fed into a slightly-inclined, horizontally rotating drum. The bark is sheared off by friction between the logs and between the logs and the inner wall of the drum. The bark falls through slots in the drum wall onto a conveyor belt below the drum. Although the spraying of water improves debarking, this process is usually not employed today because the resulting wastewater is polluted and the heating value of the bark is reduced because of the increased moisture content. Drum barkers have diameters of 3–5 m, lengths of up to 30 m, and rotate at 5–10 rpm. Since the wood is subjected to intense mechanical stress in the drum, losses occur, but these do not normally exceed 3 % for normal wood. However, losses are much higher if the wood has been damaged by fungi or is very thin.

Ring barkers are normally used only for barking large-diameter logs (Fig. 6). In this process, logs are passed through a rotating ring and scrapers are hydraulically pressed against the surface of the trunk. Wood losses of 3–5 % can occur and, in addition, the barking efficiency for strongly adhering bark is frequently inadequate.

Knife barking machines and hydraulic barkers are no longer used in the debarking of wood. The output of knife barkers is too low and wood losses too high, while hydraulic barkers require too much energy and cause wastewater problems.

The debarking efficiency should be in the range of 85 to 95 %, depending on the digestion process used.

The bark obtained from the debarking process is usually utilized, either directly or after press dewatering, for the production of power in a bark combustion furnace.

The debarking of chips has been the subject of intensive studies, but the results were unsatisfactory. The debarking of chips is still an unsolved problem.

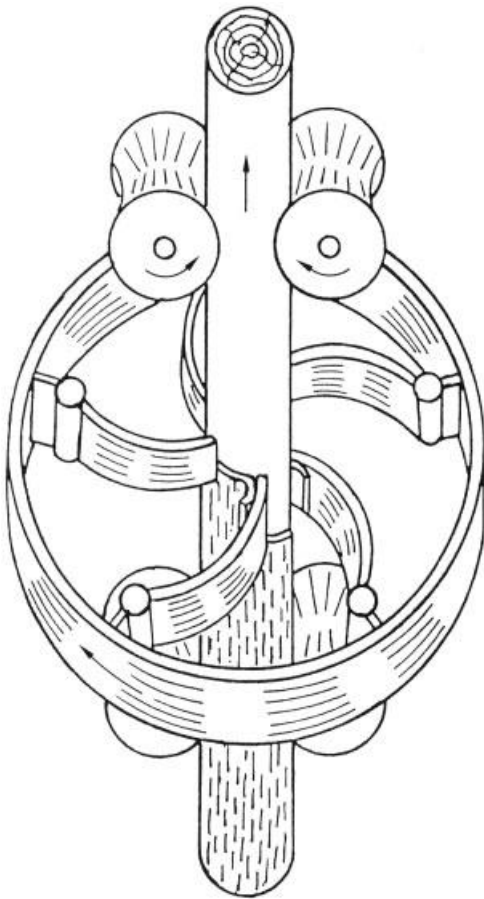


Figure 6. Ring barker

Production of Chips. In pulp production, the digestion of wood requires homogeneous impregnation with digestion chemicals. Therefore, chipping of wood is necessary. However, in the mechanical production of chips the wood can be damaged in various ways, and the resulting fiber damage influences the pulp quality. The smaller the chips, the more often the fibers are cut. The extent to which chipping reduces the average fiber length also depends on the average native length of the wood fiber. The smaller the average fiber length of the wood, the smaller the chips can be cut without reducing the average fiber length. Therefore, the chip size is always a compromise between the demand for chips that are mechanically as undamaged as possible and the necessity of achieving the quickest and most extensive impregnation with the digestion liquor. Moreover, the chips produced should have as homogeneous a size distribution as possible. Optimally dimensioned chips are 25 – 35 mm long and 3 – 7 mm thick.

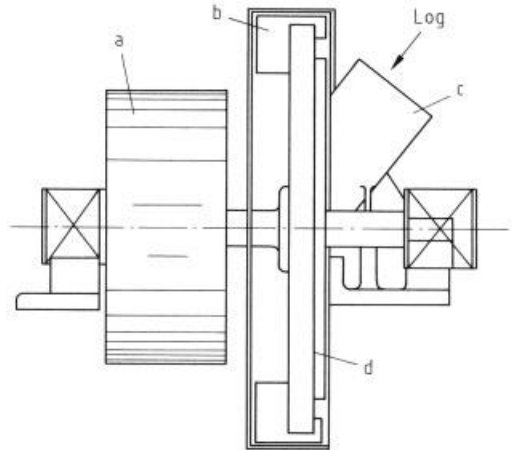


Figure 7. Schematic of a disk chipper
a) Flywheel; b) Crushers; c) Spout; d) Disk with knives

The machines used most frequently are disk chippers (Fig. 7). They have a disk diameter of 1.2 – 4.5 m, with chopping knives fastened in holes in the disk. The number of knives per disk varies between 4 and 14 and the speed between 300 and 900 rpm. The wood is transported towards the rotating disk at an angle of about 45° to the longitudinal direction of the wood, and chopped into slices. Due to the wedge-shaped form of the knife and the position of the knife

with respect to the cutting surface, the knife blade applies a shearing force in the longitudinal direction of the wood which results in a predetermined chip thickness. The length of the chips depends on how far the knife projects out of the chopping disk. The cut slices are flung outwards, and are then disintegrated into chips by a crusher fastened at the periphery of the chipping disk. Disk chippers have a capacity of more than 100 m^3 of wood per hour.

Drum chippers (Fig. 8) are used for chopping round wood and sawmill scraps in particular. The knives of a drum chipper are arranged on a rotating drum. They penetrate the wood from above at an angle of about 40° ; during chopping, the cutting angle changes constantly because of the rotary motion. The wood is transported into the chopper at right angles to the drum axis. Depending on the cutting angle, the chips have surfaces that are compressed to a greater or lesser extent. The proportion of fines is high.

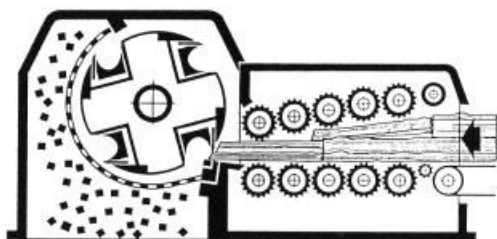


Figure 8. Schematic of a drum chipper (Courtesy of Pallmann Maschinenfabrik, Zweibrücken, Germany)

A development that has considerably influenced sawmill techniques in the last years is the headrig cutter (Fig. 9). By using two parallel cutter heads of greatly varying shape, chips can be cut directly out of the trunk surface, resulting in a beam with two smooth cut surfaces. The knives can be arranged on a conical cutter head in spirals or rings. The space between the cutter heads can be varied, depending on the dimensions of the log to be cut. The knives penetrate the wood at an angle of $35-40^\circ$. As in the drum chipper, the cutting angle changes constantly due to the rotation of the cutting heads. In the final phase of cutting, the chips are removed from the wood parallel to the fiber direction, resulting in little fiber damage. The design of the knives determines both the length of the chips and their thickness, so that the production

of chips with a homogeneous size distribution is possible.

The CCL chipper functions in a similar manner to the cutting heads of the headrig cutter. The two cutting heads are fitted together to form a V-shaped opening on the surface. The trunk is transported horizontally towards the rotating disk, and the knives cut in the same way as in the headrig cutter, except that the entire log is cut. With well-dimensioned wood and a constant cutting geometry, very homogeneously dimensioned chips having little fiber damage can be produced.

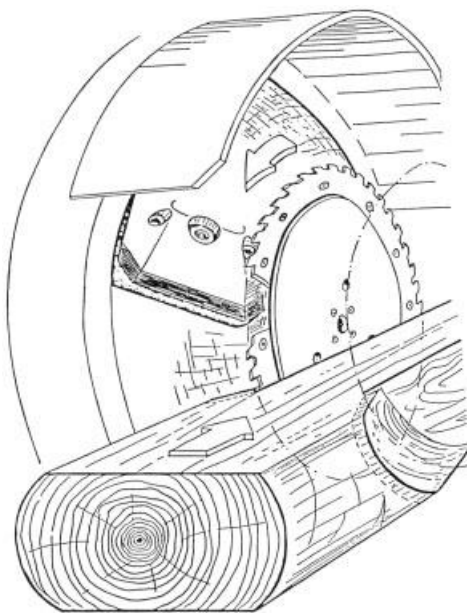


Figure 9. Schematic of a headrig cutter (Courtesy of Linck Holzbearbeitungstechnik, Oberkirch, Germany)

In chip production, not only are fibers shortened due to cutting, but damage also occurs within the chips. This damage includes primarily cracks in the middle lamella, and cracks and breaks in the inner, cellulose-rich cell wall layers due to the slipping of the parallel fibril layers. The latter, in particular, represents irreversible damage and allows the digestion chemicals to attack the carbohydrates directly. This results in poorer yields and strength losses. In thin-walled springwood fibers, damage is more pronounced than in the more stable summerwood fibers. This mechanical damage is particularly evident in

acid sulfite digestion. It can reduce the strength of sulfite pulps by 10–20 %. Fewer negative effects are observed in alkaline digestion.

Chips must be screened after production. Oversized and fine components are normally separated by rotating or vibrating screens (Figs. 10 and 11). Oversized chips are rechipped and the sawdust fraction is used for another purpose, e.g., production of chipboard and fiberboard. The entire course of wood processing is shown in Figure 12.

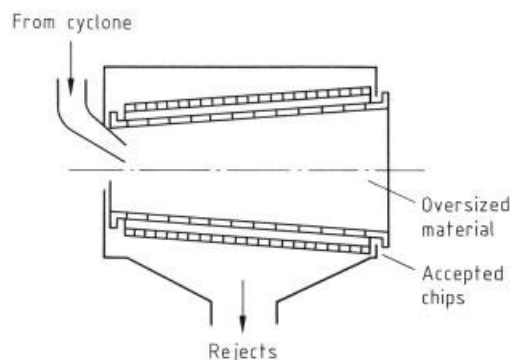


Figure 10. Rotary screen

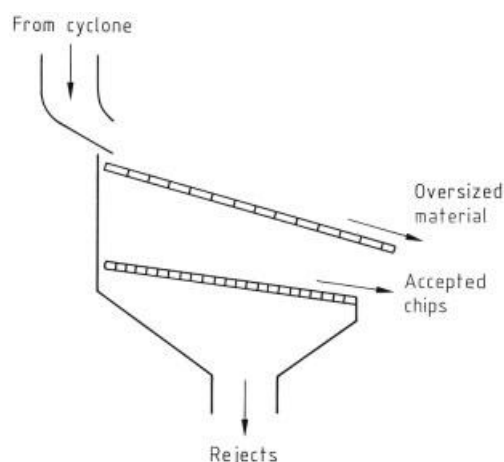


Figure 11. Vibratory screen

1.2.2. Processing of Annual Plants

The processing of annual plants for pulp production poses specific problems [21]. Harvesting is limited to a few weeks a year; hence, a

pulp mill requires an extensive store capacity to ensure an all-year supply. As a result of their morphological and chemical structure, most annual plants are attacked rapidly and intensively by microorganisms. To minimize degradation, these plants should be stored as dry as possible or in a water-saturated state. Straw and strawlike annual plants are usually stored as bales.

It is essential that the plants be thoroughly washed before processing to remove adhering soil and other impurities. Chopping to lengths of about 4 cm is usually carried out in a chipper.

Plant material of high pith content, especially sugarcane, must be subjected to pith removal because the parenchyma pith cells are unsuitable for papermaking. Pith removal can be achieved either in the moist or in the dry state. Wet pith removal in hammer mills and screens is more intensive, but pollutes the wastewater considerably. In the dry process, the starting material is crushed in disk mills and the pith is removed with screens or by air separation.

1.3. Pulping Processes

At elevated temperatures lignin, a large proportion of the hemicelluloses, and some of the cellulose are dissolved by the action of pulping chemicals on wood. The fiber yield is 45–90 %, depending on the intensity of the chemical action. The dissolution of lignin weakens the fiber matrix. The fibers can be separated easily after about 40–45 % of the wood substance has been dissolved. This stage is depicted in Figure 13 for the pulping of spruce chips.

The corresponding pulps are called chemical pulps. If the pulping process is continued and if in addition to lignin, the hemicelluloses are also dissolved extensively, pulp yields of less than 45 % are obtained, but the pure cellulose content is high. Pulps of this type are processed further into chemical products. Very mild pulping conditions result in high yield pulps or semichemical pulps. The yields are in the range of 60–90 %, and the defibration point is not reached during digestion, i.e., the bonding substances in the wood are not rendered sufficiently soluble to disrupt the fiber binding and separate the cells from one another. Therefore, mechanical defibration must follow digestion. A survey

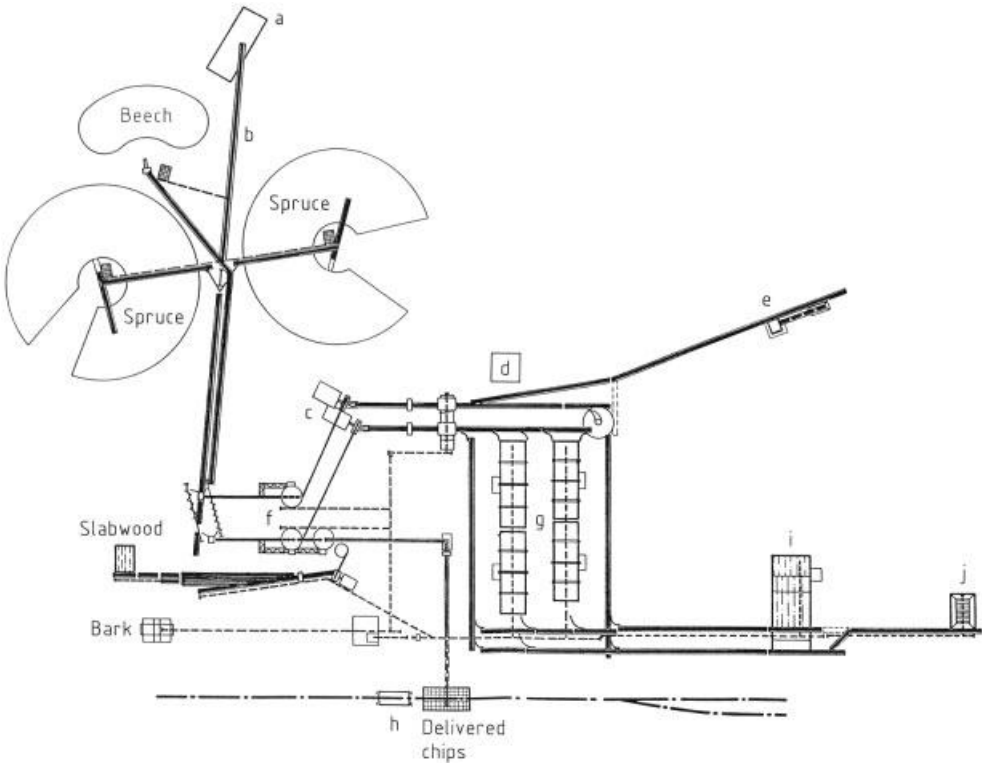


Figure 12. Schematic of wood processing (LEYKAM-Mürztaler)
a) Digester house; b) Chip storage; c) Chipper; d) Control room; e) Intermediate storage for debarked beech wood; f) Screening; g) Debarking; h) Tipping device; i) Saw; j) Log feeder

of the various processes involved in pulp production is given in Table 3.

The most important pulping processes are the sulfate or kraft process, the acid sulfite process, and the soda process. The advantages and disadvantages of the kraft and sulfite processes are listed in Tables 4 and 5, respectively.

The sulfate or kraft process has become increasingly important and is now the principal pulping process, accounting for ca. 80 % of world pulp production. In comparison, the importance of the sulfite process has decreased steadily. Today, only 10 % of the world pulp production is obtained by this method. The soda process is used primarily for the pulping of annual plants and is responsible for 5 % of the total pulp production. The remaining pulp production is based on other processes.

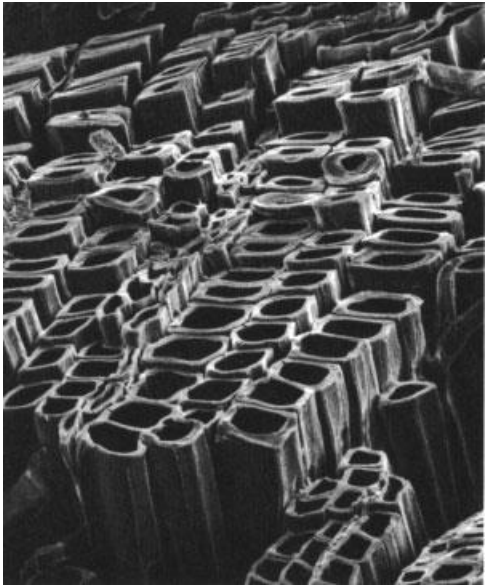


Figure 13. Electron micrograph of a spruce chip after the defibration point has been reached

Table 3. Pulp production processes

Process	Raw material	Yield, %	Brightness, % ISO	Breaking length ^a , m	Tear strength ^a , cN	Uses
High-yield neutral sulfite	softwood	85–93	60–80	6000–7000	80–100	wood-containing printing paper tissue, fluff
Neutral alkaline sulfite		85–90	60–80	4000	60	writing and printing paper tissue
Neutral sulfite, semi-chemical	hardwood	70–80	60–80	7000	80	fluting for corrugated board
Sulfate, semichemical	softwood	55–70	30	8000	150	liner for corrugated cardboard
Sulfite, chemical	softwood	48	90	7000	70	wood-containing papers and boards
	hardwood	43	90	5500	60	wood-free papers
Kraft	softwood	43	88	9000	130	wood-free and wood-containing papers and boards
	hardwood	50	90	8000	90	wood-containing and wood-free papers and boards
Soda	straw	43	90	6000	45	wood-free fine papers

^a Strength values based on a degree of beating of 30°SR.

Table 4. Advantages and disadvantages of kraft pulping

Advantages	Disadvantages
Universal raw material basis	Small process flexibility
High insensitivity to bark	Low yields for softwoods
Fast pulping process, short cover-to-cover times	High residual lignin content and poor bleachability of the pulps
High yields for hardwoods	High bleaching chemicals demand
Good pulp strength	Indispensable use of chlorine-containing bleaching agents; high water pollution
Low extract content of the pulps	Offensive smell due to volatile reduced sulfur compounds

Table 5. Advantages and disadvantages of sulfite pulping

Advantages	Disadvantages
High process flexibility	Limited raw material basis
High yields for softwoods	High requirements on raw material quality, especially high sensitivity to bark
Good bleachability	Poor pulp strength
Low water pollution	Low pulping yields for hardwoods
Possible utilization of dissolved carbohydrates	Air pollution by SO ₂ emission

1.3.1. Alkaline Pulping Processes

1.3.1.1. Kraft (Sulfate) Pulping

The sulfate or kraft process exhibits a higher selectivity of delignification and, for this reason, has almost completely replaced the older soda or sodium hydroxide pulping process. Only in the case of annual plants that are easily cooked has the soda process been able to assert itself because the sulfate process offers no distinct advantages [22].

The predominant position of the kraft process is, above all, due to its applicability to almost all lignocellulose-containing raw materials, its low sensitivity to variations in the quality of raw materials, and the excellent technological properties of the resulting pulps (see also Table 4). Furthermore, the original disadvantages of the kraft process, such as poor bleachability of the pulps and complicated recovery of chemicals, have now largely been eliminated.

The terms “sulfate” and “soda” process are derived from the make-up chemicals, sodium

sulfate and sodium carbonate, which are added in the recovery cycle to compensate for chemical losses.

Pulping Conditions. The digestion liquor (white liquor) used in the kraft process consists of sodium hydroxide and sodium sulfide as active pulping chemicals, as well as sodium carbonate as residue from the causticizing step. Furthermore, small amounts of Na_2SO_4 , Na_2SO_3 , and $\text{Na}_2\text{S}_2\text{O}_3$ from side reactions are present in the pulping liquor. The following definitions are used to characterize white liquor, sodium equivalents expressed as Na_2O or NaOH being used to calculate the chemicals employed.

Titrateable alkali = $\text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3$

Active alkali = $\text{NaOH} + \text{Na}_2\text{S}$

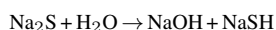
Effective alkali = $\text{NaOH} + 1/2 \text{Na}_2\text{S}$

Sulfidity, % = $100 \times \frac{\text{Na}_2\text{S}}{\text{NaOH} + \text{Na}_2\text{S}}$

Causticizing efficiency, %
= $100 \times \frac{\text{NaOH}}{\text{NaOH} + \text{Na}_2\text{CO}_3}$

Degree of reduction = $100 \times \frac{\text{Na}_2\text{S}}{\text{Na}_2\text{S} + \text{Na}_2\text{SO}_4}$

The sodium sulfide added is hydrolyzed almost completely to sodium hydroxide and sodium hydrogen sulfide



and, therefore, only half of the Na_2S is effective available alkali.

In comparison with the sulfite process (see Table 5), the kraft process is a very uniform method that exhibits little flexibility and is well suited to continuous production of a given quality of pulp. In particular, pH adjustments over a wide range are not possible. As a result of the large amounts of sodium hydroxide used, the pH value at the start of the digestion is between 13 and 14. It decreases continuously during the course of digestion because organic acids are liberated from lignin and carbohydrates during the pulping reaction.

The amount of chemicals required for pulping, their composition and the pulping parameters to be applied depend on the type of raw material used, the quality of pulp desired, and especially on the extent of delignification required. The production of semichemical or high-yield pulps requires between 10–15 % of active alkali, chemical pulp based on hardwoods requires

18–22 %, and the corresponding softwood pulp 20–25 %, calculated in each case as NaOH . The amount of sodium solution used should be calculated such that the pH does not fall below 10, because otherwise the dissolved lignin would reprecipitate on the pulp fibers. Nevertheless, a drop in pH towards the end of the digestion process is, as a rule, desired because then dissolved xylan fragments reprecipitate on the cellulose fibers [23–26].

A very important pulping parameter is the sulfidity of the white liquor. The optimal sulfidity depends on the raw material, the amount of chemicals used, and the pulping temperature. Since the Na_2S used in the kraft process improves the selectivity of pulping by accelerating the delignification reactions without simultaneously enhancing the dissolution of carbohydrates, pulping time can be shortened by maintaining a high sulfidity. This raises the pulp yield, and the higher hemicellulose content increases the tensile strength of the pulp. However, using more sodium sulfide leads to more odors due to the formation of reduced sulfur-containing gases, and increases the corrosiveness of the digestion liquor. A sulfidity of 25–40 % is normally applied in softwood pulping, while a lower sulfidity in the range 20–30 % is chosen for hardwoods.

Kraft pulping is usually carried out at 165–175 °C. The digestion time at the maximum temperature is in the range of 1–2 h, depending on the type of wood, the extent of delignification desired, and the digestion temperature. The heating of the digester can be carried out relatively quickly because, as a rule, the impregnation of the chips poses no problem due to the strong swelling of the fiber walls under the strongly alkaline conditions. The liquor to wood ratio influences the intensity of pulping through the chemical concentration. Depending on the chip size and the packing density of the chips in the digester, the pulping process (continuous or batch) etc., the liquor to wood ratio is adjusted to 2.5–4.5. A higher ratio favors uniform impregnation of the chips but reduces the delignification rate. As a result of the poor bleachability of kraft pulps and the pollution caused by pulp bleaching, efforts are being made to continue digestion to give the lowest possible kappa number so as to achieve an easier bleachability of the pulp. The kappa number is a measure of the residual

lignin content of the pulp. The amount of lignin that remains in the pulp can be determined approximately by multiplying this number by the factor 0.15 for sulfate pulp and 0.165 for sulfite pulp.

Chemical pulps made from conifers (spruce and pine) are cooked to kappa numbers of 25–30, giving yields between 45 and 47 %. In comparison, hardwoods give yields of >50 % when delignified to kappa numbers of 15–20.

Pulping Reactions. Lignin is a macromolecule based on phenylpropane units, three-dimensionally cross-linked through various ether and C–C bonds ($\rightarrow$ Lignin). The dominant bonds are α - and, above all, β -arylether bonds. A large proportion of these bonds must be cleaved in the pulping process to achieve the fragmentation and subsequent dissolution of lignin. Compared with the soda process, delignification is accelerated in the kraft process by the presence of strongly nucleophilic hydrogen sulfide ions, and the extent of lignin breakdown is increased, especially in the case of softwoods. Phenylpropane units with free phenolic OH groups are very quickly attacked. The initial step is the formation of a quinone methide structure, which already results in lignin degradation by cleavage of α -arylether bonds. The HS⁻ ion (OH⁻ ion) can subsequently add to the quinone methide intermediate and, as a strong nucleophile, can initiate the cleavage of an arylether bound to a neighboring β -C atom (Fig. 14). Phenolate anions formed by this cleavage reaction favor the continued breakdown of lignin.

Even β -arylether bonds in nonphenolic lignin units are cleaved, albeit more slowly, if an adjacent ionized hydroxyl group was originally present (OH groups in α - or γ -position) or were formed during the pulping reaction. During kraft pulping, some of the methoxyl groups of the phenolic ring are split off to give methyl mercaptan (CH₃SH), which can be converted subsequently to dimethyl sulfide (CH₃SCH₃) or dimethyl disulfide (CH₃SSCH₃). These compounds are responsible for the unpleasant odor surrounding kraft pulp mills. Apart from the cleavage of arylether bonds, carbon–carbon bonds are also cleaved to some extent. The degradation of lignin by the pulping chemicals competes with condensation reactions caused by internal nucle-

ophiles, especially in the final phase of digestion. These reactions counteract further delignification by forming C–C bonds and greatly reduce the bleachability of the pulp produced [27–36].

The polysaccharides in the raw material are also attacked and degraded under the conditions of alkaline pulping. The carbohydrate losses incurred and the reduction of the degree of polymerization are caused essentially by two reactions: the depolymerization reaction and alkaline hydrolysis. The former is primarily responsible for yield losses, while the latter mainly causes a reduction of the chain length. In particular, the hemicelluloses are subject to degradation reactions because of their amorphous structure and their lower degree of polymerization. Galactoglucomannans and glucomannans are dissolved much faster than the fairly alkali resistant xylans [37], [38]. For this reason, the xylan-rich hardwoods give higher yields in alkaline pulping than the low-xylan conifers.

The acetyl side groups of the xylans of hardwoods and the galactoglucomannans of softwoods are hydrolyzed at the very start of digestion. The primary depolymerization reaction begins above ca. 100 °C. In this process, sugar units are successively cleaved in a β -alkoxy elimination reaction, commencing at the reducing end of the carbohydrate chains [39–42]. An average of 50–60 units are cleaved from the cellulose chain molecules until depolymerization is stopped by competing stopping reactions and formation of an alkali-stable carboxyl group at the end of the chain [43–45]. Chain scission reactions occur at temperatures above ca. 150 °C due to alkaline hydrolysis, which lowers the degree of polymerization of cellulose [46–48]. The ends of the chains, exposed by the hydrolytic cleavage of glycosidic bonds, are the starting point for the secondary depolymerization reaction. With increasing digestion time and more extensive lignin dissolution, the carbohydrate degradation reactions dominate and, because of the reduced selectivity of the pulping reaction, digestion must be terminated to avoid excessive losses of yield and pulp strength.

The carbohydrate losses caused by the depolymerization reactions can be limited by reduction or oxidation of the aldehydic end groups of the cellulose to give alkali-stable alcohol or carboxyl groups [49–52]. Although reduction by the addition of 1–2 % sodium borohydride,

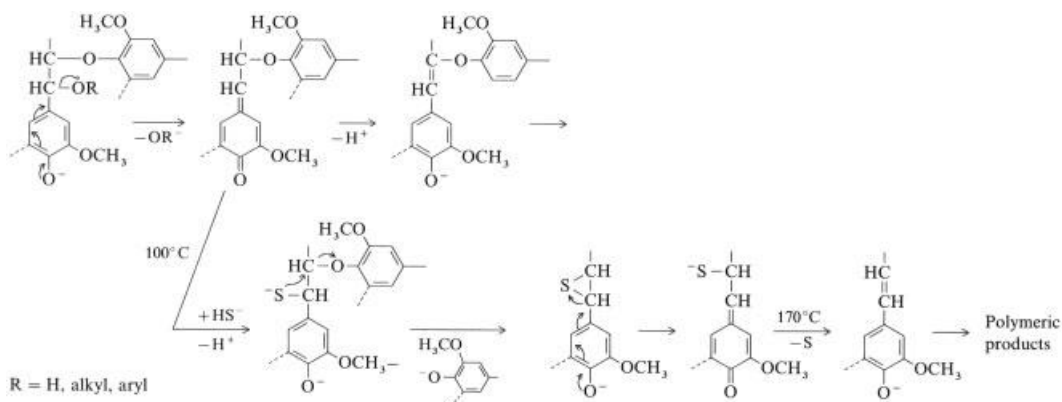


Figure 14. Main reactions of lignin during soda and kraft pulping

based on o.d. (oven dry) raw material, produces up to 6 % higher pulp yields [53], [54], the high cost make this process uneconomical. In comparison, oxidation by the addition of 3–4 % polysulfide is used on an industrial scale in some cases. A 6 % increase in yield can be obtained by polysulfide digestion, which, however, also leads to an increased emission of odorous sulfur compounds [55–59]. The use of anthraquinone (AQ-catalyzed pulping) stabilizes carbohydrates against degradation by oxidizing the end groups.

Anthraquinone-Catalyzed Pulping. Anthraquinone (AQ) which, when used in catalytic amounts of 0.05–0.2 % based on o.d. wood in alkaline pulping, causes efficient stabilization of carbohydrates and simultaneous acceleration of the delignification reaction [60], [61]. The addition of 0.05 % AQ to softwood pulping increases pulp yield at a given kappa number by 2–3 % [62], [63]. Although various AQ derivatives are also effective catalysts for alkaline pulping, they are less cost effective than anthraquinone [64].

The effect of anthraquinone is based on the AQ/AHQ (AHQ=anthrahydroquinone) redox system. Already in the initial phase of pulping, anthraquinone oxidizes the reducing end groups of the carbohydrates to give aldonic acid end groups and thus stabilizes them towards degradation by the depolymerization reaction. The monoanion of the anthrahydroquinone produced in this reaction can add to the α -C atom of the lignin quinone methide intermediate. AHQ monoanion can initiate the cleavage of β -arylether

bonds in the same way as HS^- ions. AHQ is oxidized in this redox reaction, regenerating AQ for further redox cycles [65–70].

Anthraquinone was first used on an industrial scale in 1977. In the meantime it has been employed in more than 70 pulp mills on a temporary or permanent basis [71], [72]. Since anthraquinone is relatively expensive and cannot be recovered because it is decomposed extensively in the pulping process, the decision to use AQ depends on the wood costs, the pulp prices attainable, and on the specific production conditions. In principle, many different objectives can be pursued with the use of AQ in the sulfate process:

- 1) Increase in pulp yield and therefore enhanced production in the case of limited capacity for evaporation or combustion of waste liquor
- 2) Reduced wood consumption per tonne of pulp
- 3) Energy savings by use of lower pulping temperatures or shorter digestion times
- 4) Reduced pulping chemicals demand per tonne of pulp
- 5) Reduction of sulfidity in order to reduce the formation of volatile, odorous sulfur compounds
- 6) Increase in the extent of delignification in order to improve the bleachability and reduce water pollution caused by bleaching effluents

In comparison to kraft pulping, a far greater effect can be achieved by the use of anthraquinone

in the soda process. During lignin degradation, AHQ acts in a similar way to hydrogen sulfide ions. Therefore, the rate and extent of delignification is increased to a much greater amount by the addition of AQ to the soda process. In fact, the application of the soda AQ process permits the production of bleachable chemical pulp from softwoods. The same applies to alkaline and semialkaline sulfite pulping (see Section 1.3.2.4) [73–78].

Prehydrolysis Kraft Process. The chemical industry requires dissolving pulps with a high α -cellulose content for processing into cellulose products. If the kraft process is used, the wood hemicelluloses must be degraded by acid hydrolysis prior to digestion because the alkaline pulping conditions stabilize the hemicelluloses remaining in the pulp towards further alkaline attack. In contrast, the hemicelluloses in sulfite dissolving pulps can be removed from the fiber matrix by an alkaline purification step. Prehydrolysis can be carried out by using mineral acids (e.g. 0.25–0.5 % H_2SO_4 based on o.d. wood) at 120–140 °C, or by steam or water treatment at 160–170 °C. In the latter case, acetyl groups are split off from the xylans of hardwoods or the galactoglucomannans of softwoods, resulting in a pH of 3–4. Whereas cellulose is very stable to such acid treatment, hemicelluloses are broken down into smaller, water-soluble chains. Bonds between hemicelluloses and cellulose and lignin are hydrolyzed as well. The average degree of polymerization of the hemicelluloses is decreased by about 30 % during prehydrolysis. If softwoods are used, ca. 10–15 % of the organic matter is dissolved in this step, and with deciduous woods the losses are 15–20 %. In particular when hemicellulose-rich hardwoods are used, the large-scale utilization of the hydrolysate obtained is of interest. Dissolved sugars and their degradation products, such as furfural, hydroxy-methylfurfural, levulinic acid, acetic acid, formic acid, and methanol, are present in the hydrolysate.

The subsequent kraft pulping is carried out analogously to the process used in the production of paper pulps. The digestion conditions depend primarily on the required α -cellulose content of the pulp. The hemicelluloses still present in the wood after prehydrolysis are subject to intensive degradation, especially through the de-

polymerization reaction that can commence at the numerous carbonyl groups formed during prehydrolysis.

Softwoods, and hardwoods, and low-ash annual plants are suitable raw materials for prehydrolysis kraft pulping. Hardwoods have a higher hemicellulose content than softwoods and usually give lower yields, but they can be much more easily and extensively delignified. Also, the risk of lignin condensations occurring during prehydrolysis is far lower. These condensations impede the subsequent pulping and bleaching steps. The conditions for the prehydrolysis of hardwoods and softwoods are summarized in Table 6 [79–85].

1.3.1.2. Soda Pulping of Annual Plants

The most important annual plants for the pulp industry are agricultural waste materials (bagasse and straw) and naturally occurring or cultivated bagasse and reeds. Cultivated fiber plants, such as kenaf, sisal, jute, hemp, and cotton, are valuable raw materials for the production of specialty pulps [16], [21], [86–88].

For the pulping of annual plants, the soda process is usually employed. The kraft and neutral sulfite processes are used less frequently. The acid sulfite process is not applied because it produces brittle pulps with a high ash content and inadequate strength properties.

Since annual plants are impregnated easily and have a low content of reactive lignin, the amount of chemicals required is lower than in wood pulping. In soda pulping, 10–15 % NaOH, based on the raw material, is normally employed at a pulping temperature of 160–170 °C. The yields attainable are in the range 40–55 % and are influenced greatly by the type and quality of the raw material, especially by the lignin content and the proportion of parenchyma cells. A high parenchyma content of the raw material not only reduces the yield, but also increases alkali consumption and diminishes the dewatering properties and strength of the pulp by increasing the formation of fines. For this reason, bagasse is subjected to a depithing process to eliminate parenchyma pith cells before pulping.

While various fiber plants such as hemp, kenaf, jute, and sisal give high strength pulps,

Table 6. Prehydrolysis conditions for hard- and softwood

	Charge, %/o.d. wood	Temperature, °C	Time, h
<i>Prehydrolysis with mineral acids</i>			
Hardwood, H ₂ SO ₄	10–30	70–80	0.5–3
Hardwood, H ₂ SO ₄	0.3–0.5	120–140	0.5–3
Hardwood, HCl	0.5–0.7	95	0.5–3
Softwood, H ₂ SO ₄	0.25–0.5	130–140	0.5–1
<i>Prehydrolysis with liberated organic acids</i>			
Hardwood		160–170	0.5–3
Softwood		170–175	0.5–1

sugar-cane bagasse and straw pulps have lower strengths than wood pulps because of their short, thin-walled fibers. However, these pulps are commonly added in the production of fine papers to give the paper certain characteristics, e.g., a smooth, closed surface [89].

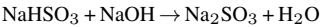
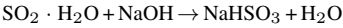
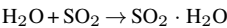
1.3.2. Sulfite Process

The sulfite process is characterized by its high flexibility. In principle, the entire pH range can be used for pulping by changing the dosage and composition of the chemicals. In comparison, kraft pulping can be carried out only with highly alkaline digestion liquor. Thus, the use of sulfite pulping permits the production of many different types and qualities of pulps for a broad range of applications (Table 7).

Today, the term sulfite process also refers to the many different variations of this process. Previously, this term was reserved for the acid (calcium) bisulfite process, which was used almost universally. The sulfite process can be subdivided into the following types of pulping:

- 1) acid bisulfite pulping,
- 2) bisulfite pulping,
- 3) neutral sulfite pulping,
- 4) alkaline sulfite pulping,
- 5) multistage sulfite pulping, and
- 6) anthraquinone-catalyzed sulfite pulping.

All these processes are based on the use of aqueous sulfur dioxide and a so-called base, i.e., calcium, magnesium, sodium, or ammonium. In the pulping system, pH-dependent equilibrium reactions occur that depend on the ratio of SO₂ to base. If sodium hydroxide is added to the aqueous sulfur dioxide, first bisulfite and then sulfite are formed:



A pure bisulfite solution is present at pH 4.5 and a pure unbuffered sulfite solution at approximately pH 9 (see Fig. 15). At these inflection points, a slight change in the chemical composition leads to a large pH shift [90]. As shown below, practically the entire pH range can be used for sulfite pulping with Na as “soluble” base (the same applies to NH₄).

Chemical composition	pH
SO ₂ · H ₂ O/NaHSO ₃	1.5–4.5
NaHSO ₃	4.5
NaHSO ₃ /Na ₂ SO ₃	4.5–9.0
Na ₂ SO ₃	9.0
Na ₂ SO ₃ /Na ₂ CO ₃	9–12.5
Na ₂ SO ₃ /Na ₂ CO ₃ /NaOH	10–13
Na ₂ SO ₃ /NaOH	13–14

Since calcium sulfite is only slightly soluble, this base can only be used in acid bisulfite pulping, i.e., in the presence of excess SO₂; Ca(HSO₃)₂ precipitates at pH values above 2.0–2.3. In comparison, magnesium bisulfite solutions are stable up to pH 5–6, so that acid bisulfite as well as the bisulfite (magnefite) and multistage pulpings can be carried out. Due to the rise in the pH value with increasing pulping temperatures [91], the pH of the cold pulping liquor must be in the range of 1.5 (acid bisulfite) and 4.0 (bisulfite) to avoid precipitation in the digestion phase.

Table 7. Sulfite pulping processes

Process	pH range	Base	Active agent	Digestion temperature, °C	Digestion time, min	Pulp yield, %	Special applications
Acid (bi)sulfite	1–2	Ca^{2+} , Mg^{2+} , Na^+ , NH_4^+	$\text{SO}_2 \cdot \text{H}_2\text{O}$, H^+ , HSO_3^-	125–143	180–420	40–50	dissolving pulp, tissue, printing paper
Bisulfite	3–5	Mg^{2+} , Na^+ , NH_4^+	HSO_3^- , H^+	150–170	60–180	50–65	printing paper
Neutral sulfite (NSSC)	5–7	Na^+ , NH_4^+	HSO_3^- , SO_3^{2-}	160–180	25–180	75–90	corrugated medium
Alkaline sulfite	9–13.5	Na^+	SO_3^{2-} , OH^-	160–180	180–300	45–60	kraft-type pulp
Two-stage sulfite							
Stora							
1st stage	6–8	Na^+	HSO_3^- , SO_3^{2-}	135–145	126–360		
2nd stage	1–2		$\text{SO}_2 \cdot \text{H}_2\text{O}$, H^+ , HSO_3^-	125–140	120–240	50–60	greaseproof paper
Sivola							
1st stage	3–4	Na^+	HSO_3^- , H^+	140–150			
2nd stage	7–10		SO_3^{2-}	160–180	60–180	35–45	dissolving pulp
AQ-sulfite (NS–AQ, AS–AQ)	9–13	Na^+	SO_3^{2-} , OH^- , AHQ^-	170–175	150–240	55–65	kraft-type pulp

In practice, apart from the chemical composition and the pH values, the terms free, combined, and total SO_2 are used to characterize sulfite solutions. The content of theoretically base bound bisulfite and sulfite ions is referred to as combined SO_2 . The difference between the total SO_2 and the combined SO_2 is then free SO_2 . According to this definition, half of a pure bisulfite solution is free and the other half is bound SO_2 .

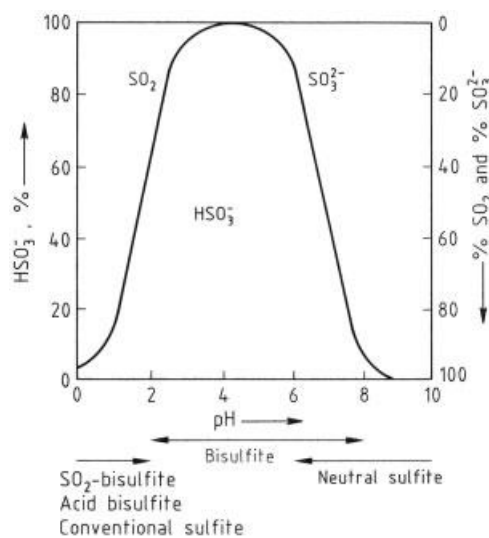


Figure 15. Composition of a dilute SO_2 – H_2O solution versus pH at 20 °C

1.3.2.1. Reactions in Sulfite Pulping

In sulfite pulping, the reactivity of lignin is essentially determined by the pH of the pulping liquor. Fundamental differences exist in the mechanism, rate, and extent of delignification under acidic, neutral, and alkaline conditions. Regardless of the pH, the α -position of the quinone methide intermediate formed from the lignin phenylpropane units is always the most reactive site for attack.

Under acidic pulping conditions, aqueous sulfur dioxide is the active pulping chemical that causes extensive sulfonation, especially by addition to the α -C of the propane side chain. Bisulfite ions can also take part in the sulfonation reactions. The initial step involves the protonation and subsequent cleavage of α -

hydroxy, α -alkoxy, and α -aroxy groups leading to the formation of resonance stabilized carbonium–oxonium ions. Since these ions are very reactive, the weakly nucleophilic pulping reagents can readily add to the α -C atom (Fig. 16).

Other sulfonation reactions can occur on the γ -C aldehyde groups or on the α -C carbonyl groups of the propane side chain. The solubility of the lignin molecule is increased by the hydrophilic sulfo groups. However, the fragmentation of lignin is restricted to the cleavage of non-cyclic α -arylether bonds between the lignin units. In acid sulfite pulping, the β -arylether bonds are essentially stable due to the absence of strong nucleophiles, and methoxy groups attached to the phenolic ring are also not subject to cleavage [36], [92–94].

Condensation reactions of nucleophilic lignin fragments compete with the sulfonation reaction. Both reactions are favored by low pH values. The danger of lignin fragments undergoing recondensation to give higher molecular, partially degradable units exists, especially if the amount of combined SO_2 available at the end of digestion is not sufficient. The resulting “black digest” can be avoided by raising the bisulfite ion concentration, i.e., by increased addition of base. Phenolic extractives from the bark or heartwood constituents such as pinosylvins (3,5-dihydroxystilbene) and its methyl ether from pine heartwood, or taxifolin from the heartwood of larch and Douglas fir, readily condense with lignin and can greatly impede acid bisulfite pulping or bring it to a complete standstill.

In bisulfite pulping (pH ca. 4), these condensation reactions can be largely suppressed, and a more selective, but slower sulfonation is achieved by the bisulfite ions. The main disadvantage of bisulfite pulping is the lower degree of delignification that can be attained.

In the neutral sulfite process, the reactions of lignin are restricted to the phenolic structural units, which are converted to quinone methide structures, as in alkaline pulping. After sulfonation at the α -C atom, the neighboring β -aroxy group can be slowly cleaved sulfolytically [95]. The nonphenolic β -arylether units, however, are resistant to neutral sulfite pulping [29]. Since practically only phenolic lignin structures react, only semichemical pulps with a high residual lignin content can be produced.

In the alkaline sulfite process, which is carried out in the presence of NaOH (NH_4OH), the cleavage of α -ether bonds is also restricted to the phenolic lignin structures. Apart from the sulfolytic β -arylether cleavage described above for the neutral sulfite process, β -aryl ether (β -O-4) bonds of nonphenolic units are also cleaved to a certain extent by the action of alkali, analogous to the reaction in the soda process. Consequently, chemical pulps similar to kraft pulps can be produced by alkaline sulfite pulping.

The reactions of carbohydrates in sulfite pulping are also determined by the pH value. At high pH values, rapid deacetylation of hemicelluloses takes place and alkali-induced degradation reactions (see Section 1.3.1) occur. In the neutral pH range, carbohydrates are attacked to the lowest extent, but their susceptibility increases considerably with increasing acidity. The glucosidic bonds are readily cleaved by acid, especially under the conditions of acid bisulfite pulping. Hemicelluloses in particular are subject to hydrolytic degradation because their glycosidic bonds are more easily accessible and less resistant than the bonds of cellulose. With increasing degradation, highly depolymerized hemicelluloses dissolve and are hydrolyzed step by step until monomeric sugar building blocks are obtained. The depolymerization of cellulose leads essentially to a reduction in the degree of polymerization (DP value); only under drastic conditions are soluble cellulose fragments formed. In general, acid pulping of softwoods gives higher yields because galactoglucomannans, the dominant hemicelluloses, are relatively acid resistant, whereas the xylans occurring predominantly in hardwoods are degraded much faster [96–98].

The monosaccharides formed in pulping are not completely stable and are partially dehydrated and oxidized. Aldonic acids in particular are produced by bisulfite oxidation. The thiosulfate formed by the reduction of bisulfite can, in turn, react with reactive lignin structures and contribute to lignin condensation [99–101].

1.3.2.2. The Various Sulfite Processes

Acid Bisulfite Process. In the acid bisulfite process, pulping is performed with a large excess of free SO_2 at pH 1.2–1.8. All of the above-

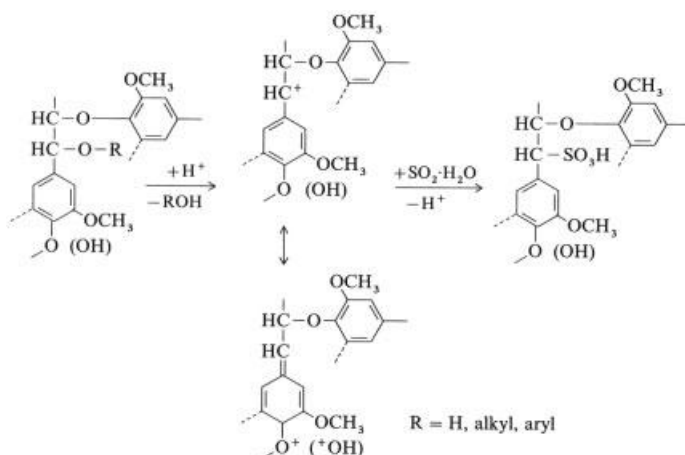


Figure 16. Reactions of lignin during acid sulfite pulping

mentioned bases can be employed. No basic differences in their mode of action exist, but the pulping conditions considered to be optimal vary slightly. The course and the result of pulping are influenced by the base selected [102], [103]. For instance, magnesium bisulfite pulping results in the best yields and the highest pulp brightness. Use of the monovalent bases Na^+ and NH_4^+ results in stronger pulps and a lower shive (fiber bundle; see section 2.4.1) content. If ammonium is used as base, the pulping process is very fast, but the pulps are dark in color and cannot be used in the unbleached state. Pulps of the lowest strength are obtained with calcium as base, and this pulping process must be controlled more carefully because calcium precipitates readily.

The total SO_2 used in acid bisulfite pulping is in the range 18–25 %, depending on the type of wood used, degree of digestion desired etc., and the SO_2 to base ratio is adjusted to 4.5–6.0. During the digestion phase, the liquor to wood ratio is usually 3–4 : 1. The chips are first impregnated with a higher liquor ratio to achieve a homogeneous distribution of the pulping liquor. A part of the pulping liquor (side relief) and the SO_2 gas (top relief) is then removed after impregnation and returned to the accumulator to prepare fresh digestion liquor. Pulping temperatures of 125–140 °C are used for the production of paper pulps. Unlike bisulfite pulping, the acid bisulfite process is also well suited to the production of dissolving pulps because the hemicelluloses can be dissolved to a

large extent in the highly acidic pulping process. However, higher maximum temperatures of 145–150 °C are employed for this process. The digestion time is usually 2–5 h at this pulping temperature, but can be extended to more than 7 h at lower pulping temperatures. A long heating time is also necessary because the SO_2 penetrates into the wood much faster than the base due to the high vapor pressure of the excess free SO_2 . Rapid heating can result in lignin condensations due to the high acidity within the chip centers. Since digester relief must also be effected slowly so that the excess SO_2 can be reused in the subsequent digestion, the result is a longer cover-to-cover cycle of 8–12 h.

From its first industrial application in 1874 until the end of World War II, the calcium bisulfite process was the principal process for wood pulping used worldwide because of the low costs and good availability of limestone and sulfur dioxide as basic materials for the production of the digestion acid. Since the pulping chemicals were inexpensive, it was not necessary to recover them before discharging the sulfite waste liquor into rivers or lakes. At the beginning of the 1950s, factories in North America started using ammonium as the base and it was possible to use the resultant waste liquor as fertilizer. Today, calcium bisulfite pulping, ammonium bisulfite pulping, and other sulfite pulping processes based on ammonium are of very little importance. If there is no possibility of utilizing the waste liquor, it is burnt for reasons of environ-

mental protection and process energy production. However, base recovery is pursued neither in the calcium bisulfite process nor in the ammonium sulfite process.

The recovery of calcium fails because of the high temperatures of more than 1150 °C required to completely decompose the gypsum, formed during waste liquor combustion, to calcium oxide and sulfur dioxide. For ammonium sulfite waste liquor, semitechnical recovery processes based on ion exchange have been developed. However, these processes have not gained acceptance in industry because of high costs. Thus, recovery in both processes is limited to the portion of SO₂ that is not bound to the base, i.e., a maximum of 80 % of the sulfur dioxide charge is recoverable.

Therefore, the use of ammonium as base was only a temporary alternative. With the development of recovery processes for magnesium and sodium sulfite liquors the corresponding pulping processes have increasingly gained acceptance for economic and environmental reasons. Moreover, compared with the calcium bisulfite process, the possibility exists that improved paper pulp qualities and higher yields can be achieved and the utilizable range of raw materials can be extended by increasing the pH value of the pulping liquor.

Bisulfite Pulping. The pulping liquor used in the bisulfite process consists of approximately equal parts of free and combined SO₂, i.e., it contains no excess free SO₂. The pH value is between 3.5 and 5.5, depending on the temperature and the chemical concentration. The use of calcium as base in this pH range is not possible. Magnesium is usually employed as base (magnefite process) [104] because the recovery of chemicals is easy and inexpensive. Ammonium bisulfite [105] and sodium bisulfite pulping [106] (Arbiso process) have also found industrial applications in individual cases.

Bisulfite pulping is normally carried out with 4–5 % total SO₂ in the digestion liquor and a liquor to wood ratio of 4 : 1, i.e., the total SO₂ used, based on wood, is 16–20 %. The pulping temperature is ca. 155 °C for hardwoods and 165 °C for softwoods. The higher temperatures required, compared with the acid bisulfite process, compensate for the lower rate of delignification caused by the lower acidity of the pulp-

ing liquor. However, carbohydrates are also dissolved to a smaller extent during bisulfite pulping. Hence, these pulps have a high hemicellulose content, and yields can reach 60 %. In comparison with acid bisulfite pulping, shorter digestion times of 1–3 h are required because of the higher digestion temperatures. The heating period is also considerably shorter since the risk of lignin condensation is lower and, therefore, the digestion liquor can be pumped at higher temperature into the digester and heated more quickly to the maximum temperature. On the whole, the cover-to-cover cycle is much shorter (approx. 6–8 h), which increases the production capacity.

Since phenolic components of bark and heartwood interfere with bisulfite pulping only to a small extent, the raw material base is considerably wider than for the acid bisulfite process. In addition to spruce and fir, pine, Douglas fir, and larch can be used in the production of long-fiber pulps. Bisulfite pulps are brighter, stronger, and better suited to papermaking than the corresponding acid bisulfite pulps. However, these pulps are not suitable for further processing in the chemical industry because of their high hemicellulose contents. A serious disadvantage of the bisulfite process is that the extent of delignification attainable is lower than that obtained under highly acidic pulping conditions, since otherwise the losses of yield and strength that occur are excessively high. The higher residual lignin content of the pulp requires the use of more bleaching chemicals and hence produces a greater effluent charge. As a result of stricter environmental controls, many mills that had already switched from the acid bisulfite to the bisulfite process reversed their decision.

Neutral Sulfite Process. The NSSC (neutral sulfite semichemical) process is not suited for making chemical pulp because the degree of delignification attainable is too low. This process uses sodium as base and is widely applied in the production of semichemical pulps, especially in North America. These pulps are employed mainly for the middle layers of corrugated cardboard and in newsprint [107], [108]. Neutral sulfite pulp mills are sometimes used in combination with kraft mills, which allows the combined recovery of chemicals (cross recovery). The NSSC waste liquor can be used as

make-up chemical to compensate for losses of chemicals in the kraft process.

The neutral sulfite process is a two-stage process with a chemical delignification step followed by mechanical defibration. In the chemical treatment, neutral to slightly alkaline sulfite solutions are used to dissolve hemicelluloses and lignins and, thus, weaken the bonds between the fibers. In this way, the mechanical effort required to expose fiber bundles and individual fibers is reduced considerably.

Hardwood is the raw material of choice; it can be digested easily and gives bright pulps with high stiffness and crush strength. Annual plants, such as straw and bagasse, and softwoods can also be used. Conifers produce pulps of good quality, but the chemicals requirement is higher and more energy is needed for defibration and subsequent beating.

In the neutral sulfite pulping of hardwood, between 8 and 18 % of sodium sulfite or ammonium sulfite is used, based on o.d. wood. To maintain the pH in the range 7–9, the digestion liquor must be buffered by the addition of 2.5–5 % of alkali (NaHCO_3 , Na_2CO_3 , or NaOH) because acids are released during digestion, particularly acetic acid by the cleavage of acetyl groups from hemicelluloses. The digestion time is 30–180 min at the maximum temperature (ca. 170 °C). The reaction proceeds very slowly and only 25–50 % of the lignin and about 30–45 % of the hemicelluloses are dissolved. Accordingly, high yields of about 65–75 % are obtained for deciduous woods and up to 85 % for conifers.

Alkaline Sulfite Pulping. Alkaline sulfite pulping is carried out with liquors containing sodium sulfite and sodium hydroxide (sodium carbonate) at initial pH values of 9–13. When, as in NSSC pulping, a low chemical charge, low alkalinity, and low temperature are applied, semichemical pulps can be prepared, especially from annual plants. The boundaries between the two processes are fluid. If the pulping liquor consists of approximately equal amounts of sodium sulfite and NaOH , and if strongly alkaline conditions ($\text{pH} > 13$) are chosen, chemical pulps can be produced as well. This pulping exhibits characteristics typical of both the sulfite process (no odors due to formation of reduced sulfur compounds; good bleachability of pulps) and the kraft process (no raw material restric-

tions, high pulp strengths, low yields, and low brightness) [109]. However, the higher chemicals requirement, longer pulping times, higher residual lignin content, and the more complicated chemicals recovery, compared to the kraft process, prevented establishment of this process in industrial practice. However, the especially pronounced effect of anthraquinone in alkaline sulfate pulping may lead to renewed interest in this process.

1.3.2.3. Multistage Sulfite Processes

The various modifications that can be achieved in the sulfite pulping system by adjustment of the pH can be advantageously combined by changing the pH during pulping. In this way, it is possible to produce special pulps that are ideally suited to certain fields of application. Sodium, as a soluble base, is particularly suitable for multistage digestions of this type. Magnesium can be used as base within limits. In the two-stage systems, pulping is either carried out first at a higher pH and the pH is subsequently decreased or vice versa. The Stora process, applied for the first time in the Skutskär factory of Stora-Kopparsberg, has achieved commercial importance [110], [111]. In this process, a sodium bisulfite–sulfite solution at pH 6–8 is used in the impregnation and first digestion stages. Subsequently, excess pulping liquor is removed and the pH is adjusted to ca. 1.5 by introducing SO_2 . This is followed by normal acid bisulfite pulping as the main delignification step. The reactive centers of lignin are sulfonated practically completely in the first stage, and thus condensation reactions with phenolic extractives under strongly acidic conditions are blocked, so that even pine heartwood, for instance, can be digested satisfactorily by this method. Furthermore, glucomannan stabilization takes place in the bisulfite–sulfite step such that the acetyl groups are cleaved first, allowing the glucomannans to attach themselves firmly to the cellulose fibrils by increased formation of hydrogen bonds [112–114]. The resistance to acid hydrolysis is thereby increased. However, this stabilization effect is restricted essentially to softwoods, with their high galactoglucomannan content. An increase in yield of over 5 % can be achieved in this manner. The very bright, easily bleachable pulps

are specially suited to the production of grease-proof paper because of their high hemicellulose contents and their resultant fast beatability.

A corresponding process can be carried out with magnesium as base [115]. The term FB process results from the very fast beatability, a characteristic property of these pulps. Analogous to the process based on sodium, pretreatment in a slightly acidic to neutral medium is followed by pulping at a highly acidic pH. As a result of the limited solubility of magnesium sulfite, the pulping liquor is pumped into the digester at pH 5 for the first step. The required pH value of 5.5–6 is then adjusted in the digester by the direct addition of magnesium hydroxide. In the second pulping stage, the pH is lowered by addition of SO_2 .

The second type of process involving an increase in the pH in the second pulping stage is the Sivola (Rauma) process [116–118]. In a two-stage procedure, a pH 3–4 sodium bisulfite solution is applied in the first stage, and the pH value is subsequently adjusted to 7–10 with sodium hydroxide. A three-stage variant of the Sivola process, with a somewhat higher pH in the first stage, an intermediate acid bisulfite stage, and a final neutral or slightly alkaline stage is especially suited to extractive-rich wood species, such as pine. This method can be used to produce dissolving pulps with a particularly high α -cellulose content [119], [120]. Dissolving pulps can also be produced by the two-step process, and it is also possible to make many different paper pulps by altering the pulping conditions. Hemicelluloses can be dissolved to a great extent by using a high pH in the second stage. The tear strength of the pulps thus obtained rivals that of kraft pulps. On the other hand, the hemicelluloses are largely retained in the pulp by second-stage digestion under neutral conditions, so that higher yields are achieved.

A corresponding two-stage process based on magnesium is called the HO process (high opacity). Impregnation with a bisulfite solution (pH 3.8–4) is carried out in the first stage. The pH is then adjusted to 6.5–7 by the injection of magnesium oxide milk and digestion is completed at a high pulping temperature (170 °C) [121]. Since dissolved organic acids apparently stabilize the pulping liquor, no precipitation occurs in spite of the high pH.

1.3.2.4. Anthraquinone-Catalyzed Sulfite Pulping

An exceptional feature of the sulfite pulping system is that the catalytic activity of anthraquinone is also exerted at slightly alkaline to neutral pH values, whereas effective acceleration of delignification in soda pulping requires a pH above 13 [122], [123]. This explains how sulfite pulping in a moderately alkaline pH range, which would otherwise permit only inadequate delignification, can be used for the production of chemical pulps if small amounts of AQ (0.1–0.2 %) are added [124–127], [73–78]. The pulping liquor used in this process consists predominantly of sodium sulfite. Sodium hydroxide solution and/or sodium carbonate is added as additional alkali. The alkali ratio (sodium sulfite/total alkali) is preferably 0.8–0.9. In comparison with the AS–AQ process with NaOH (pH 10–13.5), the term NS–(neutral sulfite) AQ process is frequently used when sodium carbonate is employed as the buffer below pH 10. The transition is, however, fluid and both process variants require alkaline conditions (final pH 7–10.5).

This pulping procedure is faster and more selective than alkaline sulfite pulping with approximately equal sodium sulfite and sodium hydroxide charges and without AQ. Better delignification is achieved in spite of the lower chemicals demand (20–25 % calculated as NaOH/o.d. wood) and shortened digestion times (150–240 minutes).

AQ-catalyzed sulfite pulping combines the advantages of the sulfite and kraft processes. First, there is no raw material restriction and high pulp strengths are achieved. Second, high yields are obtained, the pulps are easily bleachable and the emission of malodorous sulfur compounds is avoided. The main disadvantage of this process is the relatively high residual lignin content in the pulps, which have a high chemicals demand for bleaching and require the use of chlorine-containing bleaching agents.

1.3.3. Other Pulping Processes

Environmental problems and the high investment costs for pulp mills (€1500–2000 t⁻¹ a⁻¹)

have led to the development of new pulping processes. The aim is to develop a process that can produce high strength pulps with good yields from all lignocellulose-containing raw materials that are suited to fiber production. The lignin content of these pulps must be low and the residual lignin must be highly reactive to permit easy, high-brightness bleaching. An important criterion is also the bleachability with chlorine-free chemicals. This makes possible the treatment of the bleach effluent together with the waste digest liquor in the recovery stage and reduces the fresh water demand of a pulp mill to a minimum. Other aims are to reduce the cost of pulp production by reducing investment costs, e.g., in the fields of chemical recovery and utilization of useful byproducts from the dissolved wood components present in the black liquor.

1.3.3.1. Nitric Acid Pulping

The first investigations made by PAYEN (1838) showed that wood can be delignified with nitric acid. The breakdown of lignin proceeds via electrophilic substitution on the aromatic rings and subsequent oxidation reactions. Apart from the partial cleavage of methoxy groups and propane side chains, the ether bonds between the lignin units are also partially cleaved. As a result of the oxidation reaction, the nitrated lignin fragments possess mainly a quinoid structure and are highly colored. Alkali treatment is required to dissolve the partially water soluble nitrolignin.

Nitric acid pulping has achieved importance only to a modest extent in small pulp mills for the pulping of hardwoods and annual plants. The process was used for the first time on an industrial scale in the 1930s in Wolfen, Germany. Dissolving pulps with a high cellulose content (98–99 %) were produced from beech wood with a yield of ca. 40 %. The chips were first impregnated for 3 h under pressure at 40–45 °C with 15 % nitric acid. After the removal of excess acid and reduction of the acid concentration to 4 %, the chips were digested for 7 h at 70–95 °C. To dissolve the nitrated lignin, a two-step alkali extraction was then performed with 1 % NaOH for 60 min at 70 °C, followed by 3 % NaOH for 180 min at 80 °C.

Apart from this process, numerous other nitric acid pulping processes and modifications

have been developed which differ primarily in the acid concentration, pulping temperature and time, and the extraction conditions [128–132].

Nitric acid pulping can be accelerated greatly by the addition of sulfuric acid or aluminum sulfate so that the digestion time for pressured digestion at 110 °C can be reduced to a few minutes. The alkali extraction step can be enhanced by the addition of oxygen, and ammonium hydroxide can be used instead of sodium hydroxide. The black liquor obtained in this way has a high nitrogen content and can be utilized as long-term fertilizer. Although the amount of nitric acid required has been reduced drastically from 550 kg/t, e.g., to 130 kg/t of pulp, by changing the original pulping procedure, this method may be considered economical only if cheap nitric acid is available and special pulps with a high market value can be made.

1.3.3.2. Pulping with Organic Solvents

Alcell Process. The use of low-boiling alcohols in wood pulping was proposed in the 1930s by KLEINERT, who applied mixtures of ethanol and water to dissolve lignin [133]. In the 1970s, this method [134–136], in a modified form, was adopted in many new pulping processes [137–159]. The Alcell process [137–141] comes closest to Kleinert's original idea: hardwoods are cooked with a 50:50 ethanol–water mixture. Three extractors in series are used in which the chips are delignified by successive exposure to different pulping liquors. Since the solution applied first has already been used previously in two extraction stages, it has the highest content of dissolved wood components. Fresh solution is employed in the third delignification stage. The exchange of pulping liquor is effected by displacement. The alcohol is recovered by condensation of the gases during relief of the digester after the third extraction stage. The alcohol remaining in the pulped material is recovered by introducing steam into the extractor.

The waste liquor from the first extraction step is processed, the alcohol is distilled off, and the lignin that then precipitates is separated from the carbohydrates remaining in the aqueous solution by centrifugation. In this process, lignin and low-molecular carbohydrates and their reaction products can be recovered in addition to

pulp. Depending on the type of wood, 15–20 % lignin, 7–10 % xylose, and 1–3 % of other sugars based on o.d. wood are recovered from the black liquor.

At still acceptable pulp strength, the kappa number of the pulps is in the range 25–30. The yield for beechwood pulping is 50 % (based on o.d. wood) and thus, less than that given by kraft pulping. The relatively high lignin contents make it difficult to bleach the pulp to high brightness when exclusively chlorine-free bleaching agents are used. Alcell pulps subjected to conventional bleaching with chlorine-containing chemicals have a 10 % lower breaking length and at least 20 % lower tear strength than comparable kraft pulps. Until now, use of the Alcell process has been restricted to the pulping of hardwoods, which are easy to delignify. Due to lower costs for recovery of chemicals, it can be assumed that plant costs are 10–15 % lower than those of kraft pulp mills. The economy of this process can be further improved by alternative use of lignin and carbohydrates. However, this process cannot be regarded as a generally applicable alternative to the kraft process because the strength properties of the pulps are markedly lower than those of kraft pulps. Also, the restriction to hardwoods limits the applicability of the process.

Organocell Process. The limited capacity of aqueous alcohol solutions to dissolve lignin led to the development of organosolv processes, which involve the addition of conventional pulping chemicals. The Organocell process is a two-stage process [143–145]. In the first pulping stage, the chips are treated with a mixture of methanol and water (50:50) at 190 °C for 20–40 min. In this stage, equal amounts of lignin and carbohydrates, accounting for 10–20 % of the wood substance, are dissolved.

In the main pulping stage, the methanol content of the liquor is lowered to 35 vol % and ca. 20 % sodium hydroxide and 0.1–0.2 % anthraquinone based on o.d. wood are added. In this stage, the pulping time for softwoods is 40–60 min at ca. 170 °C. The yield and the residual lignin content of the pulp are comparable to the kraft process. Apart from pulp production, the utilization of substances in the black liquor is an objective of this process. Distillation is used to separate the alcohol from the pulping

liquor from the first stage. Lignin precipitates in this process and can be removed by centrifugation. The carbohydrates remain in the aqueous solution. In this manner, about 6 % lignin and 5 % carbohydrates based on o.d. wood can be recovered in softwood pulping. Since the second stage requires sodium hydroxide, the carbohydrates dissolved in this stage are degraded extensively, and only lignin can be recovered from the black liquor. After methanol distillation, lignin precipitates after acid treatment or in the electrolytic recovery of sodium hydroxide. Since the recovery of sodium hydroxide by electrolysis consumes a lot of energy and the lignin recovered cannot be sold at a cost-covering price, the simplest solution is conventional black liquor treatment with evaporation, combustion, and recovery of chemicals. The recovery process, being free of sulfur, is unproblematic.

Organocell pulping can be used to process the same range of raw materials as the kraft process. However, it has disadvantages with regard to the pulp yields and the extent of delignification. The tear strengths of organocell pulps are comparable to those of kraft pulps, but the tensile strengths are much lower.

ASAM Process. Like the AS–AQ (NS–AQ) process, sodium sulfite is used as the main delignification agent in the alkaline sulfite process with the addition of anthraquinone and methanol (ASAM). Sodium hydroxide, sodium carbonate, or a mixture of the two can be added to increase the alkalinity of the pulping liquor. The optimal ratio of sodium sulfite to added alkali varies between 70:30 and 80:20, depending on the type of wood to be pulped and the desired pulping result. In addition to anthraquinone, used in amounts of 0.1 % based on o.d. wood, 10–25 vol % of methanol is added to the pulping liquor to intensify the delignification process.

The same range of raw materials as in the kraft process can be digested at 175–180 °C in 2–3 h. Both the yield and the pulp strength, especially the breaking length, are superior to those obtained from the kraft process. However, the essential advantages of the ASAM pulps are the lower residual lignin content (kappa numbers between 10 and 20), the relatively high brightness and the easy bleachability. Even completely

chlorine-free bleaching sequences can produce high brightness levels [152–155].

1.3.3.3. Pulping with Organic Acids

Both formic acid and acetic acid, with or without the addition of peroxides, can extensively remove lignin from wood. In all cases, concentrated acids are required, and temperatures range from 100 to 190 °C. The use of lower temperatures has the advantage that pressureless systems can be employed. In this case, however, an acid catalyst (e.g., HCl, aluminum chloride) or the addition of peroxide is required. Very low kappa numbers can be achieved in acetic acid pulping. The pulps as well as the dissolved lignin and the hemicelluloses are acetylated. Dissolved carbohydrates and lignin components can be separated and processed into byproducts. Chlorine-free bleaching in the acetic acid system can follow directly if peroxides are used. Another bleaching chemical that has proved effective under these conditions is ozone. The pulps have fairly good tensile strengths; the tear strengths are similar to those of sulfite pulps [160–167].

1.4. Technology of Pulp Production

1.4.1. Pulping

Wood pulping can be carried out in a continuous or batch process. The steel digesters are protected internally against the corrosive digestion liquor. In older batch digesters, acid resistant tiles or carbon bricks were used for the digester lining. A lining of this type reduces the digester volume by 7–15 %. In addition, the bricks and tiles must be inspected regularly because they can crack easily, especially at the joints, due to the high temperature differences during heating up and cooling down. Today, digesters are usually plated on the inside with stainless steel. Batch digesters (Fig. 17) have a volume in the range of 100–400 m³. Rotary digesters are older types with smaller volumes. They are rotated head over in order to thoroughly mix the chips with the digestion liquor, and are heated directly by the introduction of steam into the digester. In this way, the liquid volume increases and the concentration of chemicals is reduced.

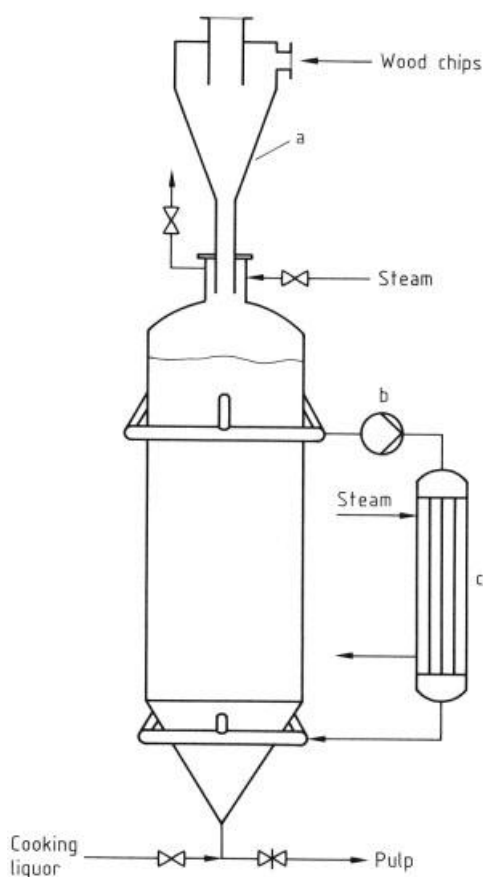


Figure 17. Batch digester
a) Wood chip collector; b) Circulation pump for digestion liquor; c) Heat exchanger

In more modern pulp mills that use batch pulping systems, the digesters are arranged upright in batteries and each is equipped with a liquor circulation system. The liquor is removed at the bottom of the digester and pumped into the top of the digester. A heat exchanger in the circulation cycle is used for indirect heating. Digesters with liquor circulation systems and direct heating are very rare.

The investment costs for conventional batch pulping systems are lower than for continuous systems. However, it is more difficult to maintain the constant process conditions that are required for uniform pulping results. Moreover, the heat economy of batch pulping systems is unfavorable. To reduce or completely eliminate these disadvantages, energy saving systems have been developed for batch digestion systems, which

use the heat content of the waste liquor to heat up the next digester. This can be achieved either by heat exchangers or by collecting the black liquor in thermally insulated collecting tanks and using it for heating chips. In this way, the residual pulping chemicals in the black liquor are also made available for pulping. Apart from improved heat economy, impregnation of the pulping material is also increased. The chemical dosing during the entire cook can be better adjusted to the pulping requirements, reducing side reactions, especially with the carbohydrates. Pulps made by such liquor displacement can be delignified to a greater extent. They have better yields and very good strengths.

Modern pulp technology is dominated by continuous digesters. The leading system worldwide was developed by Kamyr (Fig. 18). In this process, chips are continuously fed into upright digestion tubes from the top while the pulp is removed at the bottom of the digester. Digestion systems of this type have a very wide capacity range of 200–2000 t/d. All conventional pulping processes can be conducted in this system, and many different types of pulp, ranging from semichemical pulp to dissolving pulp, can be produced. Accordingly, both the design and the process mode of this system can be modified.

The standard design functions as follows. Chips are introduced continuously via a low-pressure valve into a presteaming vessel, in which they are heated with low-pressure steam (150 kPa) to prepare them for subsequent impregnation. The chips are transferred to an impregnation tower through the chip chute together with the pulping liquor via a high-pressure valve. Complete impregnation of the chips takes place here. The chips are discharged from the bottom of the system and are conveyed to the digester together with the liquor. They are then heated to the maximum digestion temperature. The chips are transported from the top of the digester downwards and pulped in the process. The pulping occurs in the interchanging action of liquid and vapor phase digestion. Recirculation of the pulping liquor is achieved by means of a system of concentric tubes in the center of the digester and outlet screens set in the wall. Varying numbers of these screens are arranged at different levels in the digester. In each case, the inlet tubes end slightly above the outlet screens, and the pulping liquor is fed centrally into the

digester. As a result of pressure differences, it flows from the center to the outlet screens in the wall. This liquid cycle causes the reaction products to be washed out of the chips and replaced by new pulping chemicals, which react in the vapor phase between the screens.

Wash liquor is added in the lower part of the digester and moves upwards countercurrently to the stream of chips. Thus the spent liquor present in this region is displaced, and the pulp is subjected to preliminary washing. In addition, this technique serves to reduce the fiber temperature, and only little fiber damage occurs during pulp discharge through a valve by rapid pressure relief. The wash liquor used comes from washers located behind the digester. The black liquor is withdrawn through the last screen ring and fed into the liquor evaporation system via a heat exchanger.

Apart from the Kamyr system, various companies have developed continuous pulping systems for the production of semichemical and chemical pulps based on both wood and annual plants. In addition to upright digesters, inclined and horizontal digesters are also employed, in which a conveyor system such as a screw, is used to transport chips and chemicals. All these systems are only partially suited to the production of chemical pulps from wood because liquid-phase pulping cannot be carried out due to the lack of liquor recycling systems. All the pulping chemicals must be homogeneously distributed throughout the raw material before pulping starts. Subsequently, pulping occurs in the vapor phase without exchange of chemicals.

1.4.2. Washing and Screening of Pulp

Brown-Stock Washing. In the production of chemical pulps, 45–55 % of the wood substance fed into the digester is dissolved. The remainder is present as fibers, largely still in the form of the original chips. In addition, ca. 200–500 kg of pulping chemicals per tonne of pulp are present, depending on the process and the extent of delignification. It is essential for economic and environmental reasons that the dissolved wood substances and the pulping chemicals are separated from the pulp as completely as possible with a minimum amount of wash water. The black liquor contains organic components

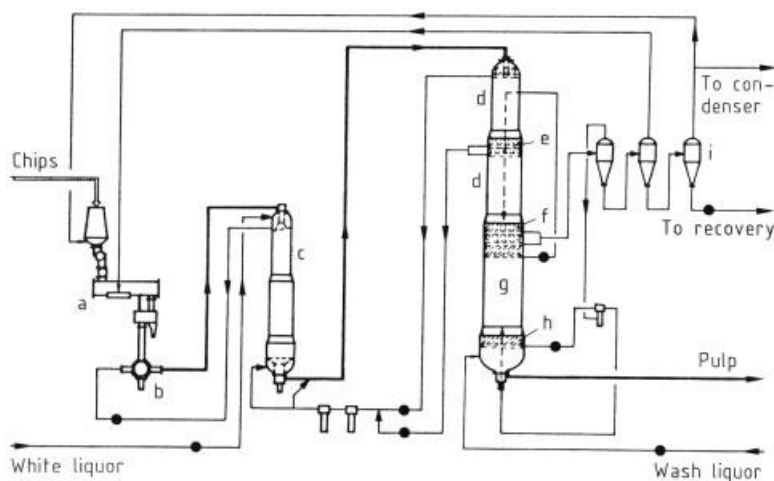


Figure 18. Continuous digester (Kamyr system)

a) Presteaming vessel; b) High pressure valve; c) Impregnation tower; d) Digester; e) Strainers for recirculation of digestion liquor; f) Strainers for waste black liquor; g) Washing zone; h) digestion liquor outlet; i) Heat exchangers

of high heating value, whose combustion can cover all or most of the energy requirements of a pulp mill. For economic operation of the mill, the digestion chemical make-up demand should be as low as possible. The washing efficiency must be as high as possible to minimize the pollution load of the mill effluent stream. However, this objective must be achieved with a minimum of wash water because its evaporation before the subsequent black liquor combustion is an energy consuming process.

The washing process is influenced by many factors, e.g., the type of wood, the chip size, the packing density of the chips in the digester, the extent of delignification, the concentration of the black liquor, amount of wash water, flow rate, temperature, washing time, diffusion gradient, and the pH.

Pulp washing can be divided into two steps. The first stage involves the displacement of the free spent digest liquor. This occurs either with the wash water or by pressing the pulped material. The second step involves the removal of the black liquor from the chips or fibers. The washing process occurs largely by diffusion since the free flow of the wash water is impeded by the tissue structure of the wood. The washing process must be controlled such that both steps are carried out under optimal conditions. In other words, the free black liquor must first be displaced from the brown stock to establish a con-

centration gradient between the liquor inside the chips and the liquor surrounding the chips. Then optimal diffusion conditions must exist to ensure the fastest possible removal of the dissolved wood substances and the pulping chemicals from inside the chips and fibers. In practice, these two washing steps, displacement of free waste liquor and subsequent diffusion, cannot be clearly separated from the viewpoint of time and space. In the displacement of free black liquor, it is unavoidable that the black liquor mixes with the wash liquor. A region of low black liquor concentration is established where diffusion occurs again on account of the concentration gradient. The washing is influenced considerably by the accessibility of the chips and the individual fibers after pulping. The higher the delignification, the easier it is to wash the black liquor solids and the chemicals out of the chips. A very important factor for the washing efficiency is whether the process is dominated more by displacement washing or by diffusion. If the wood substance is still present as chips, the dissolved substances require a correspondingly longer time to find their way out of the chips and into the wash water. Diffusion is of importance primarily in the removal of dissolved substances from the cells. The rate of diffusion depends on the concentration gradient between the black liquor in the cell wall and in the wash water. Moreover, the washing temperature is of significance. At elevated

temperatures, the solubility of the substances to be washed out increases and the viscosity of the wash water decreases. The diffusion rate can be doubled by increasing the temperature by 30 %, which favors high-temperature washing. However, this can be carried out only in closed systems. If the pulped material is still present as chips during washing, diffusion plays the dominant role and the time required to achieve the effective removal of black liquor is relatively high. In the case of defibrated material, displacement of black liquor by the wash water dominates.

Washing Systems. In the early days of pulping, washing was carried out in the digester or in the blow pit into which the digesters were emptied. The amount of wash water used did not have to be restricted because the waste liquor was not monitored; the dissolved wood substance and the pulping chemicals were simply discharged into the receiving stream. Today, a washing efficiency of 99 % must be attained with dilution factors of 2 (wash water/pulp) or less. This is possible only in closed systems in which the repeated use of the wash water takes place in a countercurrent washing process.

In the continuous pulping system described above, pulp is prewashed in the lower part of the digester with wash filtrate from a subsequent washing stage. The washing efficiency attainable at this stage is already above 80 %. The pulp is then fed into a single- or multistage diffusion washer (Fig. 19). Since this is a closed system, effective, high-temperature washing can be performed above 100 °C. The pulp enters the diffuser at the bottom with a consistency of 5–10 %. In the interior, concentric perforated outlet screens are to be found over the entire area. The wash water is injected into the system by rotating jets between the outlet screens and diffuses through the pulp to the outlet screens, where the waste liquor is withdrawn. Several of these washing units can be placed at different levels in one diffuser and operated in series, with fresh water being used only in the last step. The system is operated countercurrently and the pulp leaves the diffuser from the top. The digester washing and a subsequent two-step diffuser give a washing efficiency of more than 99 %.

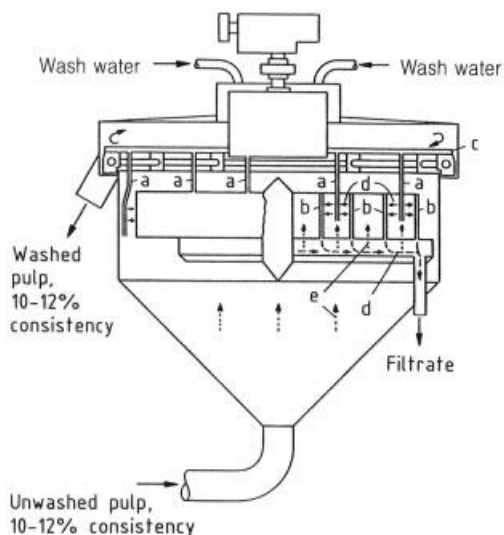


Figure 19. Diffusion washer

a) Rotating nozzle for wash water addition (attached to (c)); b) Concentric screen rings for removal of wash water; c) Rotating pulp scraper; d) Wash water outlet; e) Upflowing pulp

The standard washing in a pulp mill is carried out in a washing line which operates with rotary filters (Fig. 20). In this process, drums are used that are closed at the sides and have a screen spanned over their shell surfaces. The drum dips into a chest containing the pulp suspension at a consistency of ca. 4 %. During rotation through the suspension, the fibers become attached to the filter surface, while the waste liquor enters the filter and is pumped off. The fiber mat on the filter surface is removed by a scraper. Modern filters are closed and can be operated above 100 °C at an overpressure. The washing effect is increased by spraying wash water onto the pulp web on the filter surface. In modern filter designs, several washing steps are installed in a single unit. A washing line consists of several filters operating in series. Fresh water is used only in the last filter, the preceding filters each operate with the filtrate from the following washing step. This countercurrent operation minimizes water consumption. The filtrate from the first washing stage, which is polluted to the greatest extent, is used to dilute the pulp in the digester.

Double-sieve presses and double-roll presses have also proved effective in pulp washing. In the former, the pulp is dewatered between two flat sieves which run on pressure rollers. The second system involves double presses with perfo-

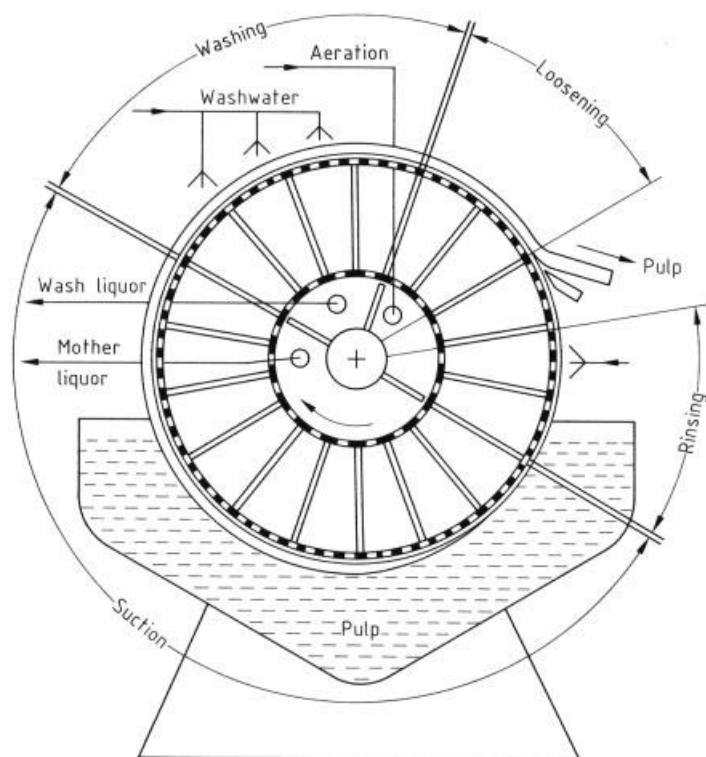


Figure 20. Rotary filter for washing pulp and recovering waste liquor

rated surfaces. They dip into a pulp suspension and their surfaces are pressed together. While ca. 15 % solids content can be achieved in a pulp suspension by dewatering filters, the pulp consistency attainable with double sieves reaches 40 % and with double-roll presses >40 %.

Fiber Screening. After the removal of dissolved substances from the pulp, all solid impurities that are not part of the fibrous material must be removed. These include bark residues and undercooked wood particles such as knots and shives, as well as external impurities such as sand, stones, and even metal objects.

As a result of the varying size ranges and other sorting criteria, e.g., specific weight, screening and cleaning must be carried out with different separating aggregates in a multistage process.

Coarse screens or knotters, commonly of vibratory design, are used to separate large rejects (Fig. 21). The flat screens have perforations in the form of slots or round holes. The screen vi-

brates elliptically, and the pulp flows onto the screen with a consistency of 1–2 %. The accepts pass through the screen, while the rejects, owing to the vibration direction of the screen, are transported over its surface to the outlet. The spraying of water on the surface of the screen intensifies the screening process.

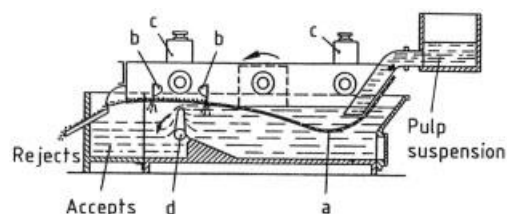


Figure 21. Jönsson shaker

a) Vibrating screen; b) Canned sprayer; c) Casing for spring; d) Overflow control

Vibrating screens can also be designed in cylindrical form. They consist of perforated, vibrating cylinders that have a longitudinal axis of rotation. Depending on the design of the screen

surface, they can be used in both coarse and fine screening.

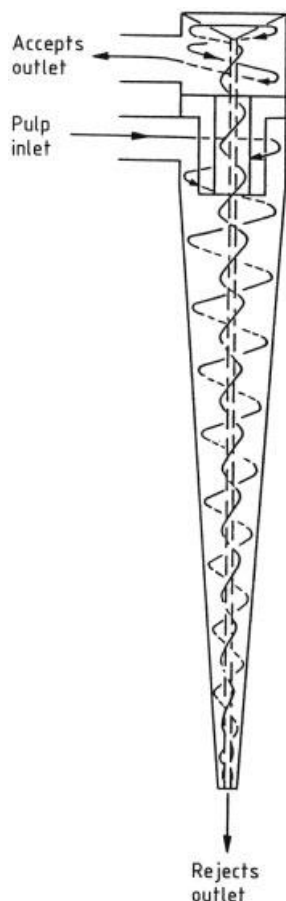


Figure 22. Schematic of a centrifugal cleaner (hydrocyclone)

Centrifugal strainers have a stationary horizontal cylindrical screen. The pulp suspension enters this body with a stock consistency of less than 1 %. The rotating suspension is flung against the screen, causing the fibers to pass through it. To improve the screening process, water can be injected into the drum. Multistage screening in one aggregate is possible by using screen perforations of different sizes at different levels in the cylinder.

Today, pressure screens are most often used for pulp screening. They have a high output and produce excellent separation. These are vertical centrifugal screens with a vertical shaft and a fixed screen basket. The stock is introduced tan-

gentially from the top. The centrifugal motion of the stock is intensified by the propeller blades rotating at the bottom of the screen. Very effective screening is possible because of the pressure pulsation that occurs due to the scraper closely passing the screen. Moreover, the blades keep the screen surface free. Since screening is accelerated by applying overpressure, the rejects must be removed batchwise. On the other hand, the accepts go into a chest or directly to the paper machine, thus maintaining the pressure in the system. Pressure screens are used almost entirely for fine screening.

The screens described above remove impurities primarily on the basis of particle size. Unwanted accompanying substances with the same dimensions as fibers, e.g., sand or bark residues, cannot be separated in this way. Centrifugal cleaners (hydrocyclones) are suitable for the separation of these contaminants. A cleaner of this type is shown in Figure 22. The stock enters tangentially so that a vortex flow is produced in the tube. The tangential, axial, and radial velocity components of the swirling motion of the suspension are dependent on the location. The suspension near the cyclone wall moves predominantly towards the rejects outlet, while that in the interior moves towards the accepts outlet.

It can be assumed that in the cyclone, fibers and impurities move approximately with the tangential and axial velocity of the carrier liquid. In the radial direction, however, considerable differences in velocity occur which are responsible for the separation process. If a particle moves towards the cyclone wall as a result of the centrifugal force and the radial pressure gradient, this motion counteracts the resistance to fluid flow because the particle must move through the carrier liquid. The larger the projection area of a particle, the higher the resistance. In addition, the migration velocity of the particle depends on its specific weight. The higher the mass per unit projection area, the quicker it migrates to and along the wall to the rejects outlet. Hence, specifically heavy particles such as sand are removed from the stock flow relatively early. In the case of particles of the same specific gravity, e.g., fibers and some bark components, separation is based on the different ratio of projection area to volume. The larger the projection area of a particle, the higher the power of resistance of the liquid. As a result, even in an early

phase of the separation process, large fibers with correspondingly large projection surfaces reach the fiber outflow in the center of the cleaner. In comparison, smaller particles are carried further down and then pass into the rising accepted stock flow. By using a particular entry velocity and dimensions of the centricleaner, particles with defined length to thickness ratios can be eliminated. Since fibers or fiber fragments and bark components can have the same dimensions, separation can be achieved only incompletely in a single step. For this reason, cleaners are arranged in several stages and the rejects are after-screened in each case. Cleaners normally operate with dilute suspensions with pulp consistencies of less than 1 %.

The arrangement and operation of the different screening systems in a pulp mill can vary considerably, and are determined largely by the type of pulp being made. Thus, in the prescreening of unbleached pulp, swinging perforated sieves and centrifugal sorting machines are used to remove knots and other coarse impurities. In final screening, however, swinging cylindrical sieves and centrifugal cleaners are used.

1.4.3. Pulp Drying

After being cleaned in the screening process, pulp is usually dried either in the bleached or unbleached state. This drying to a solids content of ca. 90 % is required in all cases for pulp that is to be marketed. Also, in the case of integrated pulp and paper mills, the pulp is sometimes dried because the fiber properties of interest for papermaking are changed by drying. Pulp that has been subjected to intermediate drying swells to a lower extent and can be drained more easily on the paper machine. The opacity of paper made from this pulp is higher. Intermediate storage in the dried state poses no problems.

Conventional dewatering and pulp drying is carried out on a Fourdrinier. As in the production of paper and board, the fiber suspension flows through a stock inlet onto the wire and is then drained. The single-layer mat of pulp thus formed is removed at the end of the wire, passed through presses onto conventional steam-heated drying cylinders where the final drying to a predetermined moisture content takes place. To increase drying efficiency, the final drying of the

pulp, after web formation and pressing, is often completed in flakt or jet dryers. These are usually arranged in several levels one above the other. The pulp passes through them and is dried in a stream of hot air. After drying, the mat of pulp is cut into sheets, stacked, pressed, and packed in bales.

Fiber Flash Drying. In fiber flash drying, the moisture content of the pulp is first reduced to about 50 % in double-screen, disc, or double-roll presses. The predrained pulp is then flaked in a shredder. The pulp flakes are subsequently blown into a hot-gas channel and dried in two steps. The drying stages involve ventilators, high-performance suspension towers, and cyclone separators. The dried flakes are fed continuously into a bale press, which produces bales with a specific weight of about 0.5 g/cm^3 . The bulk density is increased to at least 0.8 g/cm^3 by repressing the bales in a hydraulic bale press. As a result of the relatively severe drying conditions, the fibers can become horny, especially if the hemicellulose content of the pulps is high.

1.5. Waste Liquor Treatment

The waste liquor obtained from the production of chemical pulps contains at least 50 % of the wood substance and pulping chemicals. For environmental and economic reasons, this waste liquor must be utilized as far as possible. Indeed, its utilization to cover the energy requirement of pulp production is of primary importance, and in most processes, this is combined with the recovery of the pulping chemicals. In addition, part or all of the waste liquor can be utilized directly or after chemical or biological treatment.

1.5.1. Recovery of Useful Products from Waste Liquor

The composition of waste liquor depends on the raw material and pulping process used. For instance, utilizable carbohydrates are found only in waste liquor from acid pulping processes, while resin acids and fatty acids occur only in black liquor from alkaline pulping processes that use resin-containing softwoods. The lignin structure is also influenced by the

pulping process. Thus, water soluble lignosulfonates are found in the sulfite process, whereas alkali lignins are formed in the kraft or soda process. The composition of typical sulfite and kraft waste liquors from softwoods is shown in Tables 8 and 9.

Table 8. Composition of softwood sulfite spent liquor

Product	Quantity, kg/t pulp
Methanol	7–10
Acetic acid	30–90
Formic acid	0.5–1
Formaldehyde	2–6
Furfural	5–6
Sugar sulfonic acids and aldonic acids	150–250
Sugars	200–400
Cyrenes	0.3–1
Lignosulfonates	600–800

Table 9. Composition of softwood kraft black liquor

Product	Quantity, kg/t pulp
Methanol	5
Acetates	100–200
Carbohydrate degradation products (lactones, sugar acids, etc.)	350–400
Aliphatic sulfur compounds (methyl mercaptan, dimethyl sulfide, dimethyl disulfide)	1
Terpentine	8–10
Tall oil	20–100
Alkali lignin	400–600

Waste liquor from the sulfite process is better suited to the nonenergetical waste liquor utilization than kraft black liquor. Concentrated sulfite waste liquor is used both as a pelletizing agent in the feed industry as well as in the pelletizing of coal and ore. The carbohydrates obtained in the sulfite process can be utilized as shown in Figure 23. Hexoses are fermented to ethanol, while the pentoses are converted to yeast, or reduced to xylitol, or converted to furfural [168], [169].

The lignosulfonates in sulfite waste liquor can be used in many ways, e.g., they are employed as concrete additives to improve the viscosity. The dispersing properties of lignosulfonates are exploited in the dispersion of pigments in dyes, as dispersing agents for water insoluble compounds in pesticides, as drilling

agents, and as additives in the production of adhesives for the wood industry. The residual waste liquor components are present in amounts that are usually too small for cost-effective utilization. However, the elimination of these substances from waste liquor may be necessary for pollution control.

In the recovery of byproducts from kraft black liquor, only two groups of substances are of economic interest: alkali lignins and the resins and terpenes. The terpene fraction is steam volatile, so when the digester is relieved, this fraction is found in the gas phase and can be recovered by condensing the digester gases. The wood resins are dissolved in the black liquor. During concentration in black liquor evaporation plants, the resins can be skimmed off the waste liquor as sodium soaps with a solids content of ca. 28 %. They are salted out and separated by distillation.

Alkali lignins as such are of little interest economically. They are, however, subjected to fractional precipitation and sulfonation to give high-quality lignosulfonates. They can also be converted to polymers. The following reactions are of potential interest: lignin and formaldehyde to give phenolic plastics; lignin and epichlorohydrin to give epoxide resins; and lignin and epoxides to give polyalcohols, followed by reaction with diisocyanates to polyurethanes [170], [171]. However, these have not been used until now because products recovered from fossil raw materials can be produced in higher quality and often more cheaply. Lignin can be converted to a nitrogen-yielding fertilizer by reaction with ammonia and oxygen under pressure. A series of low molecular mass products based on lignin can also be produced. Vanillin and dimethyl sulfoxide are recovered on an industrial scale. Due to low demand, however, only a very small part of the waste liquor lignin obtained can be used for this purpose. Potential alternative uses include hydrogenolysis of lignin to give phenols, and high-temperature pyrolysis for the recovery of gaseous or liquid products such as carbon monoxide or ethane and methane. However, these processes are not used industrially because they are not cost effective.

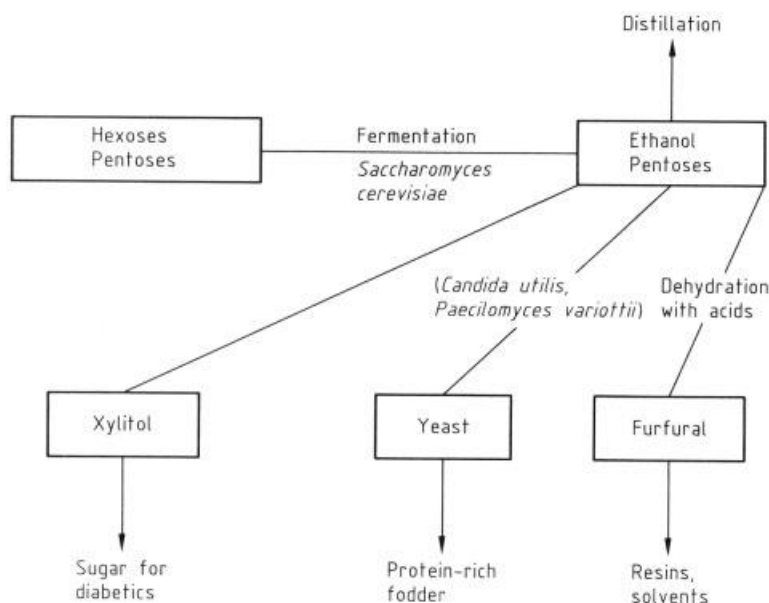


Figure 23. Processing of pentoses and hexoses

1.5.2. Energy Generation from Waste Liquor

After pulp washing the black liquor has a solids concentration of 10–18 %. The solids content must be increased to 55–70 % before utilization for energy. Counterflow multistage vacuum systems are the most frequently used liquor evaporating systems. They consist of 4 to 7 evaporators arranged in series. The individual evaporators usually comprise a lower evaporating part and an upper vapor space. The dilute black liquor flows between the vapor space and the evaporating part into the evaporating body. The evaporating part consists of either a steam-heated tube bundle or falling-film evaporators. The waste liquor is heated in these systems, which operate as heat exchangers, and the steam produced is withdrawn through the vapor space and later removed from the system as vapor condensate. The waste liquor concentrated in this manner passes into the next evaporating body and is concentrated further with steam. It flows through the entire evaporating system in this way and leaves with the required final concentration. Because the steam is reused repeatedly, its temperature decreases. To maintain the evaporation capacity, this loss of temperature is compensated for by operating the evaporators under vacuum; the

lower the steam temperature, the higher the vacuum employed. The higher the rise in concentration of waste liquor in the individual evaporating steps, the higher the evaporation temperature used. In this way a sufficiently high evaporating efficiency is ensured and, at high solids concentrations, the viscosity of the waste liquor is maintained at such a level that precipitation and deposition on the heat exchangers is avoided. A flow sheet of an evaporation plant is shown in Figure 24.

The risk of precipitation in the liquor evaporating system is especially high for more concentrated liquor. This problem can be combated by rinsing the evaporating system from time to time with vapor condensate. During this time, the evaporating body being rinsed cannot be used for evaporation. The evaporating system can be designed so that half of it is used for evaporation while vapor condensate flows through the other half. The two systems can be used alternately by changing from one to the other. Moreover, systems exist that operate without vacuum. In these systems, evaporation is also carried out in counterflow but at correspondingly higher temperatures. The lowest steam temperature of a system of this type used to concentrate the dilute black liquor flowing into the first stage must

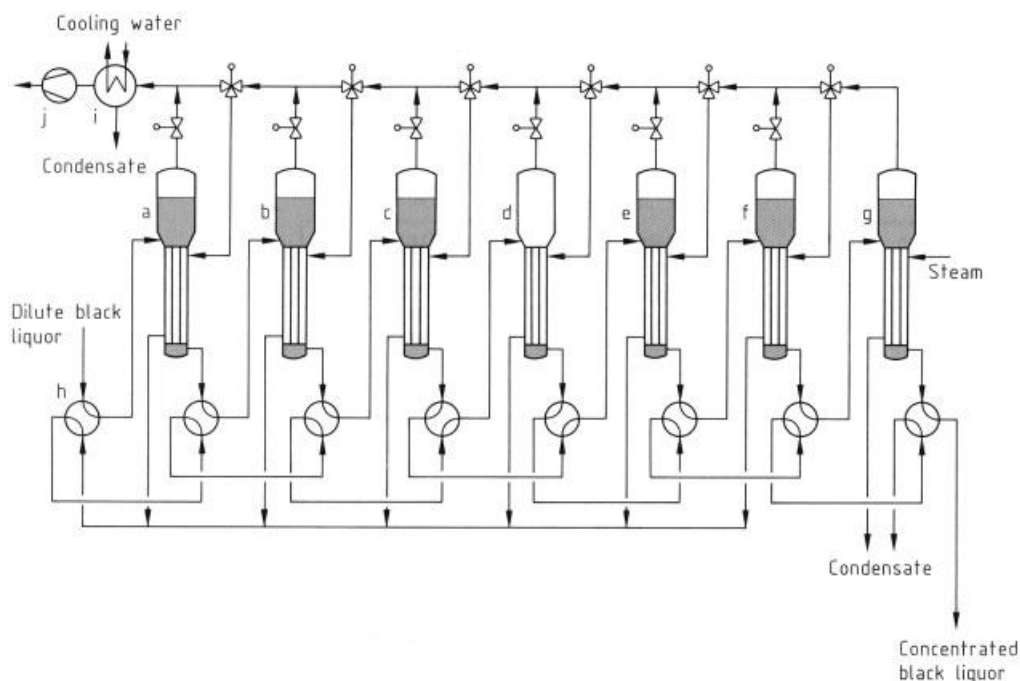


Figure 24. Schematic of a multistage vacuum evaporating plant

a) – g) Evaporators (Evaporator d is switched to washing); h) Reversing valve; i) Condenser; j) Compressor

be well above 100°C . Although the energy requirement in the individual evaporating stages is quite favorable in a system of this type, utilization of the waste steam is necessary if the total energy requirement is to be minimized. This often causes problems in a pulp mill, because most mill operations require higher steam temperatures.

In modern evaporating plants, liquor concentrations of up to ca. 80 % are attainable. However, the composition of the liquor plays a considerable part in concentration. The viscosity is very important as is the concentration-dependent solubility. Here, the molecular structure of lignin and its solubility in water and alkali are of significance. The concentration and composition of inorganic components in the waste liquor are also important. Silicates, which are present in large amounts particularly in annual plants, are extremely critical because they deposit as sodium silicates on heat exchanger surfaces during alkaline pulping. The concentration of problematic waste liquor of this type to a high solids content is possible only by direct evaporation. In this process, the liquor is dried directly in a hot-

air drier, which is fed with waste gas from the black liquor combustion stage. This can lead to air pollution problems because reduced or oxidized gaseous sulfur compounds are liberated from the waste liquor. These must then be introduced into the liquor combustion system or the off-gas purification system.

Combustion of Concentrated Liquor.

Liquor combustion combines several objectives. It is a means of disposal; serves the recovery of energy, making pulp production self-sufficient; and allows the recovery of the majority of the pulping chemicals charged. Combustion is carried out in a special combustion furnace which functions as a thermal power station and is equipped with a chemical recovery system. Both the combustion furnace and the following chemical regenerating system are adapted to a particular type of waste liquor. A furnace suited to the combustion of waste liquor based on sodium is shown in Figure 25.

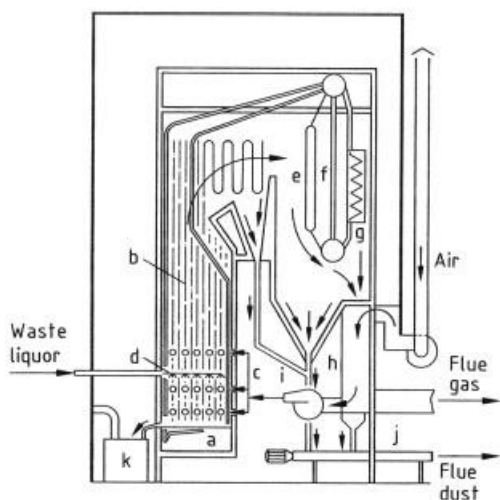


Figure 25. Black liquor combustion furnace

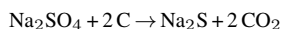
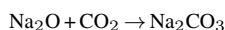
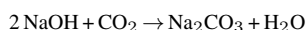
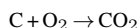
a) Melting zone; b) Boiling tubes; c) Nozzle for combustion air; d) Nozzle for black liquor; e) Superheater; f) Preevaporator; g) Fresh water preheater; h) Air preheater; i) Pipes for flue gas transport; j) Transport system; k) Smelt dissolver

The concentrated waste liquor is injected into the lower part of the furnace. In the combustion of waste liquor with a low content of organic components (e.g., waste liquor from the production of semichemical pulp), the simultaneous combustion of heavy fuel oil or coal dust is required. Injection occurs through oscillating nozzles to achieve uniform distribution on the furnace walls where the remaining water evaporates. The organic components of the liquor burn at ca. 1000 °C. The dosing of oxygen during the combustion process is of considerable importance. Sodium-containing waste liquor is normally burnt under reducing conditions in the furnace bed. This means that enough oxygen must be present in the combustion air, so that a complete conversion of organic substance to CO₂ and water occurs. However, the sulfur compounds in the waste liquor should be present in the reduced form, i.e., bound to sodium as sodium sulfide in the smelt. In contrast, in sulfite waste liquor based on magnesium, combustion conditions must be regulated so that magnesium oxide is present as ash, and SO₂ in the gas phase. Both compounds must be separated from the combustion gas. In the combustion of kraft black liquor, most of the pulping chemicals are present in the form of sodium sulfide and sodium carbonate in the smelt at

the bottom of the furnace and are then transferred to a dissolving tank. The flue gases pass through heat exchangers in which high-pressure steam is produced. The gases contain a considerable amount of entrained dust and must therefore be purified in mechanical dust collectors and electrostatic filters. An additional gas purification step is required to meet environmental regulations. Sulfur-containing gaseous compounds, in particular, must be eliminated. This is achieved by wet cleaning in scrubbers. The solid and gaseous combustion products which contain pulping chemicals can either be reused directly in the production of pulping liquor or they must be first subjected to chemical conversion.

1.5.3. Chemicals Recovery

Kraft Process. A series of reactions take place in the combustion furnace during the combustion of kraft black liquor. The carbon in the organic material combines with oxygen to form carbon dioxide, which can react with free NaOH to give sodium carbonate. Since combustion partly takes place under reducing conditions, sodium compounds react with the sulfur to form sodium sulfide. The chemical losses that have occurred in the entire pulping process are compensated by addition of sodium sulfate as make-up before combustion. This sodium sulfate is reduced to sodium sulfide in the combustion furnace. For economic reasons, other sodium and sulfur-containing materials are often used to compensate for losses. In modern mills, the chemical losses, calculated as sodium sulfate, are 10–20 kg per tonne of pulp. This corresponds to >90 % recovery of the pulping chemicals used. The reactions occurring in the combustion furnace can be simplified as follows:



Therefore, the smelt present at the bottom of the combustion furnace consists primarily of sodium carbonate and sodium sulfide. A solution of this smelt in water is referred to as green

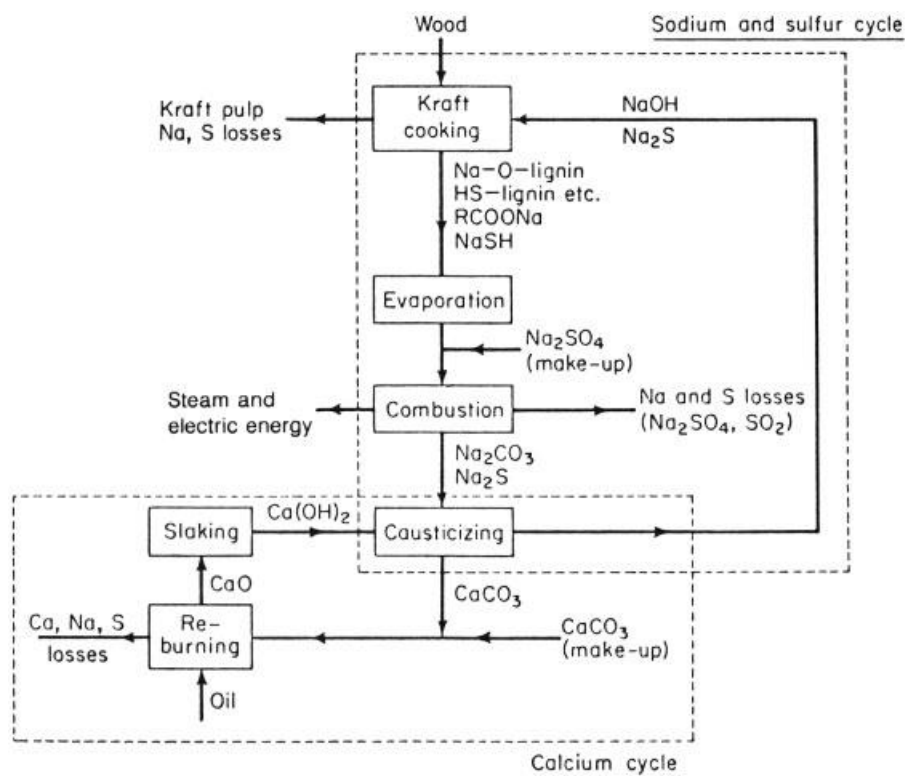
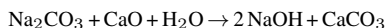


Figure 26. Recovery cycles for a kraft mill

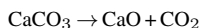
liquor. The greenish color is due to iron sulfides contained in the solution.

To recover the pulping chemicals used, sodium carbonate must be converted to sodium hydroxide. This takes place in the causticization step, in which sodium carbonate reacts with slaked lime to give sodium hydroxide and calcium carbonate:



This is an equilibrium reaction which, under normal conditions, produces degrees of causticization of 85 to 90 %. The solubility of calcium carbonate increases with increasing OH^- content, and the reaction equilibrium is shifted to the right. Normally 2–3 % of calcium oxide remains in the sludge produced by causticization. Although the addition of more quicklime improves the degree of causticization slightly, a multistage causticization process is more effective. The calcium carbonate formed is separated from the white liquor and rewashed to reduce chemical losses. About 250 kg quicklime

per tonne of pulp are required for causticization. Amounts of this magnitude are very expensive and the large capacity of kraft pulp mills makes this not only a procurement problem, but also a waste problem. Therefore, the lime sludge is re-burnt in a rotary kiln in the plant, converting the calcium carbonate in an endothermic reaction to calcium oxide:



The lime kilns are a major source of air pollution because mercaptans are released from liquor residues in the sludge. The outlet air from the kilns can be returned to the liquor combustion furnace to reduce odors. A chemical recovery system for the kraft process is shown in Figure 26.

Calcium Bisulfite Process. Apart from calcium oxide and sulfur dioxide, calcium sulfate is formed predominantly in the combustion of calcium bisulfite liquors. The complete

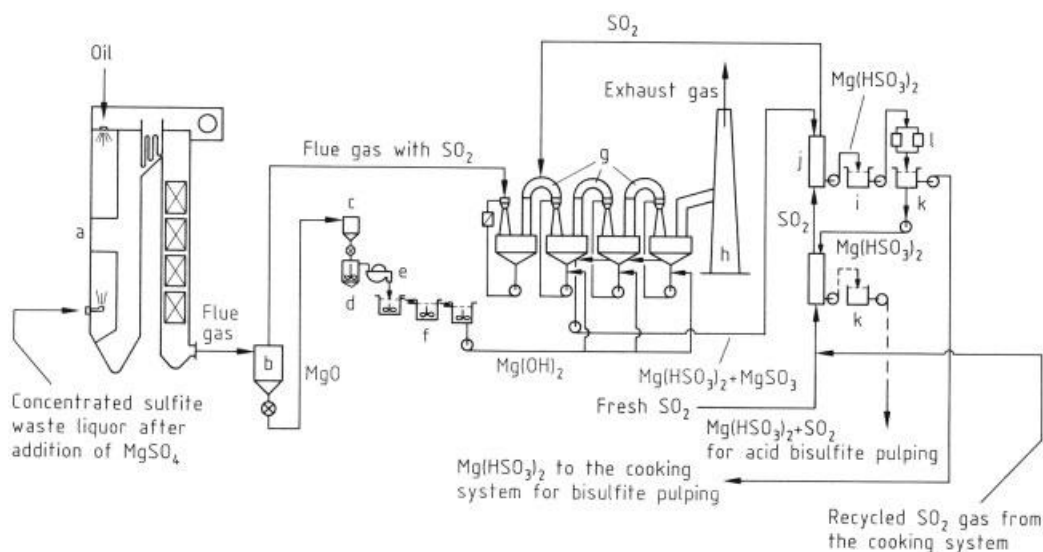


Figure 27. Recovery of the chemicals from the spent liquor from the magnesium bisulfite process

a) Waste liquor combustion furnace; b) Dust collector; c) MgO silo; d) Slurry tank; e) Wash filter; f) Hydration vessels; g) Flue gas scrubber; h) Stack; i) Sedimentation tank; j) Fortification tower; k) Storage tank; l) Filter

thermal decomposition of calcium sulfate occurs only above 1150 °C; temperatures above 1200 °C must be used to achieve an essentially quantitative decomposition. This causes problems because dead burning of lime occurs at these high temperatures, changing its crystal structure and reducing its reactivity.

Magnesium Bisulfite Process. In comparison with calcium sulfate, the magnesium sulfate obtained from the combustion of magnesium sulfite waste liquor can be decomposed thermally at normal combustion temperatures to give gaseous SO₂ and magnesium oxide. The latter can be separated from the combustion gases in powder form. In slaking tanks, the magnesium oxide is converted to magnesium hydroxide, which reacts with SO₂ to form a mixture of magnesium sulfite and magnesium bisulfite. In the fortification tower, this solution is treated with SO₂ so that either a pure magnesium bisulfite solution is formed which can then be used in the magnesite process, or a magnesium bisulfite solution with excess SO₂ for acid magnesium bisulfite pulping. A schematic of the process is shown in Figure 27.

Flue gas purification using electrostatic filters is not widely employed because chlorides, for example, are not removed in this process.

Instead, the pulp particles are discharged from the gas flow in mechanical purification units or multiple cyclones. In the subsequent wet cleaning, water-soluble solid components of the flue gases are removed. The flue gases then again pass through wet dust separators, which precipitate further chlorides. Chloride discharging occurs in a retention tank for magnesium oxide. The chloride level of the chemical cycle can be controlled by regulating the overflow.

In sulfite mills, the spent liquor contains considerable amounts of acetic acid, furfural, and methanol, especially when hardwoods are used for pulping. For this reason, the vapor condensate obtained on evaporation is highly polluted. Therefore, the digestion spent liquor is usually neutralized before evaporation to convert the low-boiling, acidic components to salts and thus prevent their transfer to the vapor condensate. For waste liquor neutralization in magnesium bisulfite mills, the amounts of MgO required are of the same order of magnitude as the amounts of magnesium oxide used in digestion liquor preparation. The volatile compounds can also be separated by stripping the vapor condensates. Acetic acid can also be recovered by liquid–liquid extraction.

The degree of chemicals recovery in the magnesium bisulfite process is 80–90 % for both

magnesium and sulfur. Therefore, the make-up requirement is 10–15 kg magnesium oxide and SO_2 per tonne of pulp.

Sodium-Based Sulfite Process. The recovery of chemicals in sodium-based sulfite processes is relatively complicated. For this reason, many different methods have been developed. Until now, only a few processes have proved useful in industrial practice. These are based on the principle of carbonation or pyrolysis. Direct sulfitation is a very interesting process, but it has never been used in a large-scale operation.

Carbonation. The concentrated liquor is burnt in a kraft-type furnace under reducing conditions. Sodium sulfide and sodium carbonate are present in the smelt. The sodium sulfide reacts with CO_2 from the flue gases or pure CO_2 or bicarbonate to yield sodium carbonate and hydrogen sulfide. The gaseous hydrogen sulfide is withdrawn and burnt to give SO_2 . In an absorption tower, SO_2 reacts with sodium carbonate to give sodium sulfite or sodium bisulfite, depending on the stoichiometry. Carbonation processes in various modifications are still the only large-scale recovery processes for sodium sulfite liquor [172], [174].

Pyrolysis. Sodium and sulfur can be separated in a single step by pyrolysis of sodium sulfite waste liquor to produce sodium carbonate and solid carbon, while sulfur is obtained as gaseous hydrogen sulfide, which gives SO_2 on combustion. In comparison with other combustion processes, the pyrolysis temperatures are relatively low because no smelt should be formed in this process. Sodium carbonate is then dissolved in water and the carbon is filtered off and burnt in a separate step. Sodium carbonate and SO_2 are recombined to give the pulping liquor. In the industrial application of this process, however, substantial oxidation of sodium sulfur compounds occurs during pyrolysis, forming sodium sulfate. This must be carried through the process cycle as a chemical inert for pulping. Temperature control is also a problem in this process. If the temperature is too low, incomplete chemical conversion occurs. On the other hand, if the temperature is too high, a smelt is formed which contains sodium sulfides [175].

Direct Sulfitation. In the direct sulfitation, the smelt containing sodium sulfide and sodium carbonate, formed after spent liquor combustion

under reducing conditions, is reacted directly with SO_2 to yield sodium sulfite. Sodium sulfide reacts to give sodium sulfite and H_2S , which is in turn converted to SO_2 by combustion. The industrial application of this process failed because thiosulfate is formed in considerable amounts from sodium sulfide, SO_2 , and sodium sulfite in side reactions. Thiosulfate catalytically decomposes bisulfite during the digestion process.

Ammonium Sulfite Process. Today, ammonium sulfite solutions are seldom used for pulp production. The main reasons for this are the relatively high price of ammonia and the fact that base recovery is not cost effective. However, after combustion of the waste liquor the SO_2 can be recovered from the gas flow.

1.6. Pulp Bleaching

Lignin cannot be completely dissolved out of the wood in a pulping process because the rate of carbohydrate degradation in the final phase of delignification exceeds the rate of lignin dissolution. This leads to high yield losses and reduced pulp strengths due to the depolymerizing attack on the carbohydrates. For this reason, pulping must be stopped and the lignin that remains in the pulp must be removed by selective lignin dissolving chemicals. The residual lignin content of pulps depends on the type of raw material, the pulping process, and the required pulp properties. The residual lignin content of softwood pulps is normally higher than that of hardwood pulps, and sulfite processes can delignify more extensively than the kraft process. The normal residual lignin content of unbleached pulps is in the range 2–5 %. The elimination of this residual lignin is required primarily to brighten the pulps. However, mainly the structure and not the content of residual lignin is responsible for the color of unbleached pulp. Depending on the pulping reactions, more or less chromophoric groups are formed. Sulfite pulps always have a higher brightness than kraft pulps. Table 10 lists residual lignin contents and pulp brightnesses for various pulps.

Pulp bleaching is carried out in several stages, with the elimination of residual lignin as far as possible being the primary objective of the first

stages. The subsequent bleaching stages are responsible for brightening the pulp. Accordingly, bleaching is divided into prebleaching and final bleaching. The following abbreviations have been introduced for the bleaching stages:

- C—chlorination
- E—alkaline extraction
- H—sodium or calcium hypochlorite bleaching
- D—chlorine dioxide bleaching
- O—oxygen bleaching in alkaline medium
- P—peroxide bleaching
- Z—ozone bleaching
- Y—dithionite (hydrosulfite) bleaching

Table 10. Residual lignin content and brightness of various pulps

Type of pulp	Residual lignin content (kappa number)	Brightness, % ISO
Softwood kraft	27–33	25–30
Hardwood kraft	17–20	25–35
Softwood sulfite	15–25	55–60
Hardwood sulfite	12–22	55–65
Semichemical pulp/neutral sulfite	> 80	50–60
Semibleached pulps	1–5	70–85
Fully bleached pulps	< 1	85–92

1.6.1. Conventional Bleaching

In conventional pulp bleaching, chlorine, hypochlorite, and chlorine dioxide are used with or without intermediate alkaline extraction steps. For purposes of comparison, the amounts of chlorine chemicals employed are expressed as active chlorine, the varying molecular weight and oxidation potential of the chlorine-containing bleaching agents being taken into account. Thus, the oxidation potential of chlorine in hypochlorite is twice that of chlorine and the oxidation potential of chlorine in chlorine dioxide is five times that of chlorine. Taking into consideration the different molecular masses of the various chlorine compounds, the chemical equivalence compared to molecular chlorine is 1.05 for sodium hypochlorite and 2.63 for chlorine dioxide.

The use of chlorine and chlorine-containing compounds in pulp bleaching is ecologically the

most problematic step in the entire process of pulp production. The chlorine compounds react in various ways with the lignin of pulp. Substitution reactions on the phenol rings of lignin, which occur to a large extent especially in chlorination, are particularly critical with regard to environmental pollution. The effluents from the bleaching process contain chlorinated organic compounds and cannot be disposed of by combustion with the spent digestion liquor. It must be released into the receiving stream, possibly after being subjected to biological treatment. It pollutes this stream considerably with its oxygen demand and its toxic and genotoxic effects [176–179]. Among others, various dibenzofurans and dioxins and even the extremely toxic 3,4,7,8-tetrachlorodibenzo-*p*-dioxin have been detected in small concentrations [179–183]. The combustion of bleaching waste liquor of this type would cause corrosion problems because of the formation of hydrochloric acid and would lead to the production of other highly toxic chlorinated products.

Chlorination. The first step in conventional lignin-dissolving bleaching is usually chlorination [184]. Chlorine is an effective, selective, and inexpensive bleaching agent that reacts exceptionally quickly with lignin. However, instead of brightening the pulp it usually causes a decrease in the brightness. Chlorination is normally carried out at a low temperature (ca. 30 °C). A short reaction time is sufficient, usually 30 min for sulfite pulp and up to 60 min for kraft pulp. The stock density for chlorination is usually ca. 3 %. Due to the fast reaction of chlorine with pulp, this low stock consistency is required to guarantee quick chlorine mixing and, hence, a uniform reaction. In particular, overchlorination of parts of the pulp and the resultant fiber damage should be avoided. However, the development of high performance mixers has made chlorine bleaching possible even at higher pulp consistencies of up to 10 % [185].

Chlorine water is normally used for chlorination. As a result of the more favorable reaction conditions and the possibilities now available for the optimal mixing of chlorine and pulp, chlorine gas has also been used recently on an industrial scale.

The most important function of chlorination is the conversion of the residual lignin in the pulp

to products that are soluble in water and alkali. Chlorine reacts primarily with the benzene rings of lignin in a nonradical reaction, in which both substitution and oxidation reactions take place. At the same time, addition reactions occur on the propane side chains of the lignin monomers if double bonds are present. However, since this is very seldom the case, addition reactions play only a minor role.

Electrophilic substitution with the chloronium ions formed by heterolytic cleavage of the Cl–Cl bond results in the replacement of the hydrogen atoms of the benzene ring by chlorine atoms [36], [186–189]. The number of chlorine atoms and their position on the ring depend on the structure of the lignin molecule. The use of excess chlorine can result in the maximum replacement of the three ring hydrogens at positions 5, 6, and 2 of the aromatic nucleus by chlorine atoms; 50–70 % of the total chlorine requirement of a bleaching sequence is consumed in chlorination.

The amount of chlorine used for different pulps is normally in the range of 1.0–1.7 g active chlorine per gram residual lignin. Lower amounts are required for sulfite pulps, which contain more reactive residual lignin, than for kraft pulps. Independent of the pulping process, softwood pulps require more chlorine than hardwood pulps. Under industrial chlorination conditions, ca. 1–2 chlorine atoms per lignin unit are attached to the phenol ring in substitution reactions. If the phenolic OH group in *para*-position to the side chain is not etherified, the substitution reaction occurs preferentially at the 5-position of the aromatic ring. If there is an alkyl, aryl, or methoxy group at position 5 of the ring, substitution occurs only at positions 6 or 2. The substitution of chlorine on the guaiacyl ring has the following priority: 6 > 5 > 2.

Electrophilic substitution can also occur at position 1 of the phenol ring if the α -C atom of the side chain bears an OH or OR group. In this reaction, the aliphatic moiety is cleaved from the aromatic ring of the lignin phenylpropane unit (side-chain elimination). In contrast to the substitution of hydrogen atoms on the aromatic ring, the lignin molecule is fragmented in this reaction. Apart from the substitution reaction, oxidation also occurs during chlorination [190]. The initial step in the oxidation reaction is again the electrophilic addition of chlorine.

Subsequent demethylation gives rise to quinoid intermediates, which can be oxidized further to dicarboxylic acids upon ring opening. The reactions occurring on the aromatic rings during chlorination of lignin are shown in Figure 28 [36].

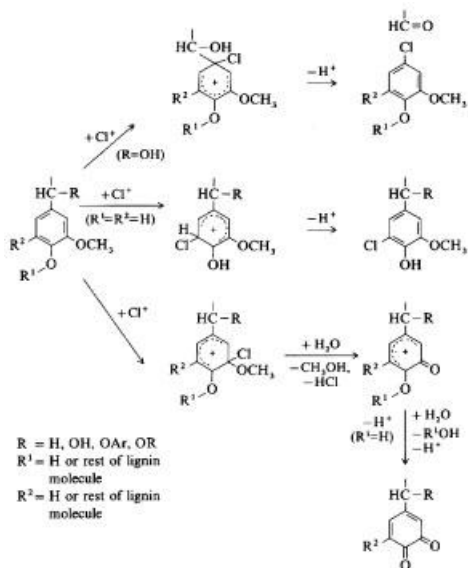


Figure 28. Substitution and dealkylation of phenolic and nonphenolic units by chloronium ions

Apart from the reactions described above, a large number of side reactions occur which give rise to many different chlorinated compounds, some of which are toxic, resistant to biological degradation, or potentially mutagenic or carcinogenic.

In industrial chlorination processes, the ratio of substitution to oxidation reactions is about 50 : 50. The chlorination conditions chosen previously favored the substitution reaction because carbohydrates are attacked thereby only to a minor extent. However, the chlorination process is now operated increasingly such that the oxidation reactions dominate, thus avoiding the aromatic chlorine compounds produced in the substitution reactions. This can be achieved by increasing the reaction temperature and pH.

Chlorine is a selective bleaching agent that reacts faster with lignin than with cellulose. Nevertheless, carbohydrates are also subject to attack by the chlorine radicals formed [184]. Carbohydrate degradation occurs via oxidation as well

as hydrolysis. The positions 1, 2, 3 and 6 of anhydroglucose units are very sensitive. If oxidation occurs at position 1, depolymerization takes place by cleavage of the β -1,4-glycosidic bond.

In other oxidation reactions, primary and secondary alcohol groups can be converted to aldehyde and keto groups, which facilitates depolymerization of the cellulose chains in subsequent bleaching steps.

Alkaline Extraction. Chlorination makes lignin partially soluble in water and alkali. After chlorination, in fact, sulfite lignin is for the most part already soluble in water, whereas the majority of kraft lignin can be dissolved only in alkali [191]. Due to the action of alkali, chlorine atoms bound to the aromatic nuclei are partially replaced by hydroxyl groups, increasing lignin solubility. Apart from the dissolving of chlorolignin, the function of alkali extraction in the production of dissolving pulps is to remove the hemicelluloses from the pulp as extensively as possible. For this purpose, higher amounts of alkali and severer conditions are required. In the production of paper pulps, however, hemicelluloses should remain in the pulp as far as possible and the DP value of the cellulose should be maintained at the highest possible level. Therefore, alkali extraction should be carried out gently.

In the extraction step, 1–1.5 % NaOH based on o.d. pulp is used for sulfite pulps, and up to 3 % for kraft pulps. The extraction time is 60–90 min at 40–60 °C. For dissolving pulps, temperatures up to 90 °C and up to 15 % sodium hydroxide based on o.d. pulp are used if pulps with extremely high α -cellulose contents are to be made. The consistency in the extraction stage is generally ca. 10 %.

As a result of the intensive dissolution of lignins and carbohydrates in the chlorination and extraction stages of pulp bleaching, highly polluted wastewater is produced which accounts for up to 90 % of the COD of the total bleach and ca. 100 % of the color load. The chlorinated lignin degradation products have, in part, a potential toxic effect on living organisms as well as a mutagenic effect. In particular, chlorine compounds with molecular masses of less than 1000 are problematic because they are small enough to diffuse through the membranes of living cells and can accumulate in fat tissues. The effluents from the chlorination and extraction steps can be

degraded only to a limited extent by biological treatment. In single-stage plants, rates of degradation of approximately 50 % can be achieved, carbohydrates being broken down preferentially.

Hypochlorite Bleaching. After chlorination and alkaline extraction, the delignification of pulp is almost complete. The residual lignin content of the pulp is ca. 0.5–0.8 %. In conventional bleaching, this lignin is dissolved with oxidizing bleaching agents. In the past, hypochlorite was the agent of choice, but today chlorine dioxide is used almost exclusively, especially for kraft pulps. If both bleaching agents are used, hypochlorite is usually used first, followed by chlorine dioxide. Whereas calcium hypochlorite was used predominantly in the past, especially in calcium bisulfite pulp mills, sodium hypochlorite is used almost exclusively today in pulp bleaching [192].

In the hypochlorite bleaching step, the pH is the most important influencing factor. It can be varied within a wide range by varying the ratio of alkali to chlorine. At pH values less than 2, only elemental chlorine is present in the bleaching liquor. However, HOCl is formed at higher pH values, and the dissociation of this acid produces OCl^- ions at still higher pH values. Above pH 9.5, only OCl^- ions are present. Chlorination reactions take place predominantly at acidic pH values, whereas oxidation reactions occur preferentially at higher pH values. Since the latter are preferred, the initial pH of the hypochlorite solution should be adjusted to 11–12. The pH drops during bleaching owing to the formation of acidic products such as carbonic acid and oxalic acid. The pH should not fall below 8 at the end of the reaction because cellulose is also attacked extensively at lower pH values.

Normally, 1–2 % hypochlorite based on o.d. pulp is used at 30–50 °C. Temperatures up to 70 °C are also acceptable if the pH does not fall below 11 during bleaching. The consistency in the hypochlorite stage is 10 %, and the bleaching time is 2–4 h, depending on the raw material used, the pulping process, and the pulp properties required.

The oxidation reactions occurring at high pH in hypochlorite bleaching attack the free phenolic hydroxyl groups or the phenolic ethers at positions α and β of the phenylpropane side chain. The products of lignin degradation from

hypochlorite bleaching are methanol, organic acids, and carbon dioxide.

Hypochlorite is, however, not a selective oxidizing agent; it also reacts with carbohydrates. The following reactions can occur [192], [193]:

- 1) Oxidation of primary hydroxyl groups at C₆ to carbonyl and further oxidation to carboxyl groups
- 2) Formation of keto groups at atoms C₂ and C₃; ring cleavage to give dicarboxylic acids
- 3) Cleavage of the β -1,4-glycosidic bond and oxidation of the reducing end groups to carboxyl groups
- 4) Ring fission between C₁ and C₂ with formation of an aldehyde group at position 2 and a carboxylic ester at position 1; further oxidation to a carboxyl group at position 2 is possible

Depolymerization, which leads to poorer technological pulp properties, can be limited by using high pH values and lower reaction temperatures.

Chlorine Dioxide. Chlorine dioxide is an extremely effective and selective, but also expensive bleaching chemical. In the gas phase, chlorine dioxide is explosive at concentrations above ca. 12 %. It is, however, uncritical in dilute aqueous solution. The production of chlorine dioxide is carried out at the pulp mill by reduction of sodium chlorate. For a long time, it was not possible to use chlorine dioxide in pulp bleaching because of its toxicity, corrosivity, and the risk of explosion. It was the industrial application of chlorine dioxide shortly after World War II that made it possible to bleach even kraft pulps to high brightness, and led to the dominance of kraft pulping.

Chlorine dioxide has five oxidation equivalents. It can develop its full oxidation potential at a pH of 4 because all five oxidation equivalents can be used. In practice, the highest brightness is obtained when the pH at the beginning of bleaching is adjusted to approximately 6 and is around 4 at the end of the process [194].

The bleaching effect of chlorine dioxide is based on the oxidation of lignin. The initial step in lignin breakdown involves radical attack on structures with phenolic OH groups, forming phenoxy radicals, which undergo further reactions to give quinoid structures or, after ring

cleavage, to form muconic acid derivatives [36], [195]. Ring chlorination reactions are caused by elemental chlorine, which is either contained in technical chlorine dioxide or formed by its decomposition.

Under normal bleaching conditions, chlorine dioxide hardly degrades carbohydrates. However, carbohydrate degradation can occur at temperatures above 80 °C, pH values above 7, and in the presence of excess chlorine dioxide, especially if the carbohydrates have already been attacked in the preceding bleaching stages.

The application of chlorine dioxide is a first response to the necessity of using environmentally harmless bleaching agents. The amount of bleaching agent used is small. Extensive degradation of lignin to aliphatic compounds occurs and chlorinated compounds are formed only to a very small extent.

Chlorine dioxide has an exceptionally positive effect on pulp brightness. It can degrade even largely unreactive lignin structures and is indispensable for the elimination of dirt specks in pulp.

The temperature during chlorine dioxide bleaching is between 70 and 80 °C and the bleaching time is 3–4 h. The pulp consistency is ca. 10–12 %. The amount of chemicals used can vary considerably depending on the position of the chlorine dioxide stage in the bleaching sequence and the type of pulp to be bleached. Normally, the amounts used are between 0.5 and 1.5 % active chlorine based on o.d. pulp.

Conventional Bleaching Sequences for Various Pulps. Depending on the type of wood, the pulping process used, the residual lignin content of the pulp, and the target brightness, different bleaching sequences must be used in the production of the various pulps. In pulps of all types, conventional bleaching starts with chlorination and extraction stages. In the case of readily bleachable sulfite pulps having low residual lignin contents, a hypochlorite stage follows CE prebleaching, and chlorine dioxide is used in the final bleaching. The bleaching of sulfite pulps to brightnesses of 90 % ISO and higher is possible with this CEHD standard sequence. Semi-bleached pulps having brightnesses of 80 % can be produced by using the sequence CEH.

In the conventional bleaching of kraft pulps, the sequence CEDED has become established.

Brightnesses of 90 % can be achieved while maintaining good pulp quality. Bleaching yields of ca. 93 % are obtained for softwood kraft pulps with an initial kappa number of about 30 (residual lignin content ca. 4.5 %). Bleaching yields of 96–97 % are achieved for sulfite pulps with low unbleached kappa numbers in the range 12–15.

The properties of pulp change during bleaching in a characteristic manner. As a result of the removal of hemicelluloses, the bonding potential of the fibers is reduced, which, in turn, reduces the breaking length in particular. On the other hand, the tear strength can increase.

1.6.2. Chlorine-Reduced and Chlorine-Free Pulp Bleaching

In response to pollution linked to the use of chlorine in pulp bleaching, considerable efforts have been made to replace chlorine by an environmentally less harmful chemical. Moreover, efforts are also being made to replace as far as possible the other chlorine containing bleaching agents and to develop bleaching sequences that require no chlorine-containing compounds. Then, the requirements would be met not only for the combined evaporation and combustion of waste liquor from bleaching and digestion, but also for the recovery of the alkali used in the various bleaching stages and for carrying out pulp production with a greatly reduced water consumption.

At the beginning of this development, attempts were made to replace the highly polluting CE prebleaching by chlorine-reduced or even chlorine-free alternatives. The first steps in this direction were the partial or complete replacement of chlorine by chlorine dioxide and the introduction of oxygen delignification. Ozone has also been employed on a laboratory and pilot scale. Peroxide has proved useful in enhancing oxygen delignification and is also being used increasingly in final bleaching.

Substitution of Chlorine Dioxide for Chlorine in Prebleaching. Owing to the different modes of reaction of chlorine and chlorine dioxide, the formation of chloroorganic compounds decreases with increasing use of chlorine dioxide [196–201]. At the same time, the selectivity of the bleaching reaction is improved [202–

208]. Even small amounts of chlorine dioxide added in a chlorination stage reduce carbohydrate degradation considerably because chlorine dioxide functions as a radical scavenger and suppresses the oxidation of alcoholic OH groups to carbonyl groups by chlorine radicals [209], [210].

In industrial prebleaching, up to 70 % of the chlorine is replaced by chlorine dioxide. Especially in the case of kraft pulps, the complete replacement of chlorine is impracticable because the delignifying effect of chlorine dioxide is much lower than that of chlorine. The use of mixtures of chlorine dioxide with chlorine has the following advantages:

- 1) The process can be carried out at higher temperatures (60–70 °C) and higher consistencies (10–15 %). This corresponds to the conditions used in the following bleaching stages. Thus, a reduction of the energy and water requirements is possible.
- 2) Since chlorine dioxide has five oxidation equivalents, the use of this agent, compared to chlorine, corresponds to a reduction of the chloride ion content to 20 %.
- 3) The oxidative attack of chlorine dioxide on lignin leads to water-soluble degradation products, so that the amount of alkali used in the subsequent extraction stage can be reduced.
- 4) The use of chlorine dioxide produces effluents that are less chlorinated, less colored, and contain smaller amounts of toxic and genotoxic substances.
- 5) Pulps bleached with chlorine dioxide are of a better quality. Their extractives content is lower, and the brightness, viscosity, brightness stability, and technological properties are improved. Yields increase since chlorine dioxide attacks the carbohydrates in pulp to a lesser extent.

Alkali/Oxygen Bleaching. The increased use of chlorine dioxide also has disadvantages in that the investment and chemical costs are higher. Because of the high oxidizing power of chlorine dioxide, bleaching equipment must be made of corrosion-resistant material.

The treatment of pulp with oxygen under alkaline conditions is a chlorine-free alternative to prebleaching [211–219]. Sodium hydroxide is

usually used as alkali; magnesium hydroxide can be used in magnesium-based sulfite mills. The bleaching agent employed is gaseous oxygen, which is a very inexpensive chemical. However, oxygen is only very slightly soluble in water, especially at the high bleaching temperatures that must be used in the oxygen stage to achieve an adequate reaction rate. Therefore, the process must be carried out under pressure for a sufficient amount of oxygen to be available in the bleaching liquor. Oxygen in alkaline medium is, under these conditions, a relatively strong oxidizing agent. As a biradical, it can remove an electron from the phenolate ions present in the alkaline medium. The phenoxy radical thus formed is subject to further reactions. Hydroperoxides are produced which are further degraded by intramolecular nucleophilic attack of the peroxide anions [36], [218–221].

Oxygen does not, however, react selectively with lignin, but also attacks carbohydrates to a considerable extent [122], [123]. Above all, oxidations at atoms C 2 and C 3 of the anhydroglucose units occur. The unstable carbonyl compounds facilitate further degradation, which can result in the cleavage of the glycosidic bonds. To reduce carbohydrate degradation, the extent of delignification occurring in this stage must be limited. Inhibitors such as magnesium sulfate can be added to protect the carbohydrates. In industrial operation, delignification in the oxygen stage is restricted to about 50 % in spite of these additives. Consequently, oxygen bleaching is less effective than conventional prebleaching with chlorine.

Oxygen bleaching was originally developed as a high consistency bleaching process for pulp consistencies of 30–35 %. However, newly installed large-scale plants operate almost exclusively in the MC range (medium consistency), i.e., at consistencies of 10–15 % [224–227]. While high consistency bleaching requires temperatures above 100 °C and pressures up to 0.8 MPa, MC oxygen bleaching is carried out at temperatures below 100 °C and pressures of 0.2–0.4 MPa. The temperature can be reduced further to 70 °C in the bleaching of sulfite pulps. Modern MC oxygen stages usually operate under hydrostatic pressure. The oxygen is mixed in at the bottom of the bleaching tower under the hydrostatic pressure of the reactor. Thus, a

reactor height of 20 m, for instance, results in a pressure of 0.2 MPa.

The reaction time in the oxygen stage is 30–90 min, and 20–40 kg alkali per tonne o.d. pulp and about 0.5–2.5 kg magnesium sulfate are charged. Depending on the delignification efficiency, 10–25 kg oxygen per tonne of pulp are consumed.

In order to improve delignification and to apply milder conditions, especially lower temperatures, hydrogen peroxide is added to the oxygen stage, particularly in sulfite pulp bleaching [228–231]. Sulfite pulps can be delignified by 50–60 % at 70–80 °C in the oxygen stage by adding 1 % peroxide. Moreover, the pulp properties profit from the milder reaction conditions.

Pulp Bleaching with Ozone. Since oxygen delignification is limited, other delignifying agents must additionally be used before final bleaching is performed. In practice, especially in kraft pulp bleaching, chlorine and chlorine dioxide are used today in varying proportions. Ozone has been tested for this purpose both on a laboratory and pilot-plant scale [232–240]. However, the use of ozone in pulp bleaching requires new technology. Like oxygen, ozone is only slightly soluble in water. Ozone is also very unstable and must be prepared at the mill by electrical discharge in air or oxygen. The ozone concentration in the air flow reaches 3–5 %, while concentrations of 6–10 % can be achieved with oxygen. In order that sufficient amounts of ozone reach the fibers, extremely low pulp consistencies of less than 2 % must be used; otherwise this process must be carried out in the gas phase at consistencies above 35 %. Pressurized medium consistency ozone bleaching is also possible. The water should be as free as possible of heavy metals to minimize catalytic decomposition of ozone.

The most important reaction of ozone with lignin is the cleavage of the β -O-4 bonds between the lignin units. Ozone can attack both the aryl and the alkyl moieties of the molecule. The attack on the aromatic rings can lead to ring cleavage between the C 3 and C 4 atoms. Double bonds in the aliphatic side chain are also attacked, forming carbonyl and peroxide structures [36], [241–244].

The intense attack on the carbohydrates is a disadvantage. The dominant reactions are cleavage of the glycosidic bonds and oxidations at

the C 2 and C 3 atoms, which facilitate further chain breakdown in subsequent alkaline treatment [222], [245], [246].

The formation of hydroxyl and perhydroxyl radicals is of considerable importance in these reactions. The hydroxy radicals in particular react very unspecifically and lead to severe carbohydrate degradation. Since the formation of these radicals is favored by hydroxyl ions, the ozone treatment should be carried out under acidic conditions. For this reason, the pulp must be acidified, and SO_2 and sulfuric acid have proved effective for this purpose. Since ozone is extremely reactive, a very short reaction time can be used, provided that thorough mixing of ozone and pulp takes place. If this is the case, the entire duration of treatment including an appropriate after-reaction time can be less than 10 min. The temperature in the ozone step should be as low as possible to avoid harmful side reactions. This applies in particular to low-consistency bleaching. In high-consistency ozone bleaching with very thorough mixing, temperatures up to 50°C can be used.

Low-consistency ozone bleaching is of advantage with regard to the selectivity of lignin degradation [247]. However, high-quality water and low temperatures are required. If the water cycle of the mill is largely closed, both requirements can be met only with difficulty. The stronger attack on carbohydrates in high consistency ozone bleaching must be restricted by limiting the amount of ozone charge. Amounts exceeding 1 % ozone based on o.d. pulp should not be applied. The pulp can be delignified by about 10 kappa numbers with this amount of ozone. Under these conditions, ozone can be used for pulps with a high lignin content as the second bleaching stage after oxygen prebleaching. Alternatively, it can be used as the sole delignifying agent for sulfite pulps with low initial kappa numbers. As a result of its higher delignifying capacity, ozone, unlike oxygen, is also well suited to the bleaching of low-residual-lignin pulps. The kappa number after the ozone stage should be in the range of 1.5–3.

An emerging technology is ozone bleaching at medium consistency. The MC ozone bleaching must be carried out under pressure to reduce the gas volume and to have a good mixing effect. On the other hand, the disadvantages of ozone bleaching at low or high consistency are greatly

eliminated. First pilot plant results have been satisfactory; in particular, carbohydrate degradation was substantially reduced.

Until now, ozone has not been used for large-scale bleaching of pulp. However, the existing laboratory and pilot plant results and the necessity for chlorine-free bleaching suggest that the industrial application of this bleaching agent is in the offing.

Peroxide Bleaching. Hydrogen peroxide in alkaline medium is well suited to the final bleaching of chemical pulps [248]. The bleaching of mechanical pulp has shown that it destroys the chromophoric groups present in lignin by cleaving conjugated double bonds. At $70\text{--}80^\circ\text{C}$, the highly nucleophilic perhydroxyl ion formed is capable of further degrading quinoid lignin structures, produced by the attack of electrophilic bleaching chemicals. This is generally accompanied by ring fission [36], [221], [249]. As mentioned above, peroxide is used in prebleaching as an intensifying agent in the oxygen stage. In final bleaching, it is often used as the concluding treatment. The amounts used are 1–2 % at consistencies of 10 % and temperatures of $70\text{--}80^\circ\text{C}$. An advantage of the use of peroxide in final bleaching is the high brightness stability of peroxide-bleached pulps.

Chlorine-Free Bleaching Sequences. The choice of the bleaching sequence to be used, if chlorine-free bleaching agents are applied exclusively, depends on the raw materials used in pulping, the pulping process, the residual lignin content of the pulp, and the demands made on the quality of the bleached pulp. The sequence OZEP is suitable for sulfite pulps with high residual lignin contents. After the oxygen stage, the kappa number of the pulp should be 10. The kappa number can then be reduced to ca. 3 by the use of 0.8 % ozone based on o.d. stock. These pulps can be brightened to 90 % ISO by subsequent alkaline extraction and the addition of 1 % hydrogen peroxide in the final bleaching step.

At present, kraft pulps still cannot be bleached economically to high brightness levels in a chlorine-free sequence. In the case of softwood kraft pulps, strength losses of 20–25 % must be accepted in chlorine-free bleaching on reaching brightness levels of 85 % ISO.

On the other hand, several sulfite mills have switched to completely chlorine-free bleaching sequences; oxygen and hydrogen peroxide are employed. Prebleaching is achieved with alkali/oxygen, partially intensified by hydrogen peroxide. Peroxide is used in final bleaching, usually in a two-step process. Bleaching sequences of this type give brightnesses up to 85 % ISO. Compared with conventional bleaching and ozone bleaching, however, strength losses must be accepted.

1.6.3. Technology of Bleaching

Today, bleaching is always carried out in a closed system. The individual bleaching stages take place in bleach towers in which the material flows either from top to bottom or vice versa (Fig. 29). Washing units (filters or sieve presses) located between the bleach towers remove the used chemicals and the reaction products from the pulp. The washing efficiency is about 80 %. Countercurrent operation is employed as far as possible to minimize water consumption. In modern plants, the tendency is to use similar reaction conditions in all bleaching stages. The bleaching stages are preferentially performed at a medium consistency of 10–15 %. Bleaching towers with an upward flow can be used for this purpose without problems. The addition of the chemicals occurs before the pulp enters the tower. An exception is the chlorination step, which is performed at consistencies of 3–5 % and at the lowest possible temperatures. However, the temperature and the consistency can be adapted to those of the other bleaching stages by partially replacing chlorine by chlorine dioxide. Chlorination towers are usually rubber lined, while chlorine dioxide towers are made of high-alloy stainless steel.

High-consistency oxygen bleaching requires a technology which differs from conventional bleaching stages. Alkali and the degradation inhibitor (magnesium sulfate) are charged before the pulp enters the reactor. After mixing, the stock is adjusted to a consistency of at least 30 % and then fluffed at the top of the reactor. The tower is operated from the top downwards at a high oxygen pressure. The tower can be equipped with movable trays over which the pulp moves and is gassed with oxygen. Before

being discharged, the pulp on the reactor floor is diluted to give a pumpable suspension and it then enters a washing stage.

On the other hand, the medium consistency oxygen stage used more frequently today uses an up-flow. Alkali and magnesium sulfate are added before the pulp enters the tower. Oxygen is added in an additional mixer. Bleaching occurs either at hydrostatic pressure or with oxygen overpressure. The stock is discharged continuously from the top of the tower and is transported to a washer. The MC oxygen bleaching technology is not problematic because no explosive mixtures of carbon monoxide/oxygen can form. Increasing the consistency in the bleaching stages saves energy and reduces water consumption, but problems with the mixing of bleaching chemicals and the stock can occur at higher consistencies. The water and energy requirements in the medium-consistency range can be reduced by adapting the reaction conditions in the different bleaching steps and by using countercurrent washing. A system of this type is shown in Figure 30.

A high-consistency ozone stage can be operated with the technology of the high-consistency oxygen stage. However, a pressure reactor is not required. Ozone can be added in the fluffer. On the other hand, up-flow towers can be used for low and medium consistency ozone bleaching.

1.7. Environmental Aspects of Pulp Production

The production of pulp is associated with considerable pollution. The type and extent of pollution depend on the pulping and bleaching processes used and on the internal and external measures taken to reduce pollutants. If all the possible and economically justifiable measures are taken to reduce the environmental burden in the production of kraft pulp, pulpmaking with a wastewater COD below 50 kg/t of pulp appears to be possible. The specific water requirements of a mill of this type is ca. 50 m³ per tonne of pulp. In the production of sulfite pulp, the COD burden is even lower. Values of 30 kg COD per tonne of pulp and water consumption corresponding to that of kraft pulp production are possible. Base losses of 1–1.5 % based on o.d. pulp and sulfur losses, measured as SO₂, that are

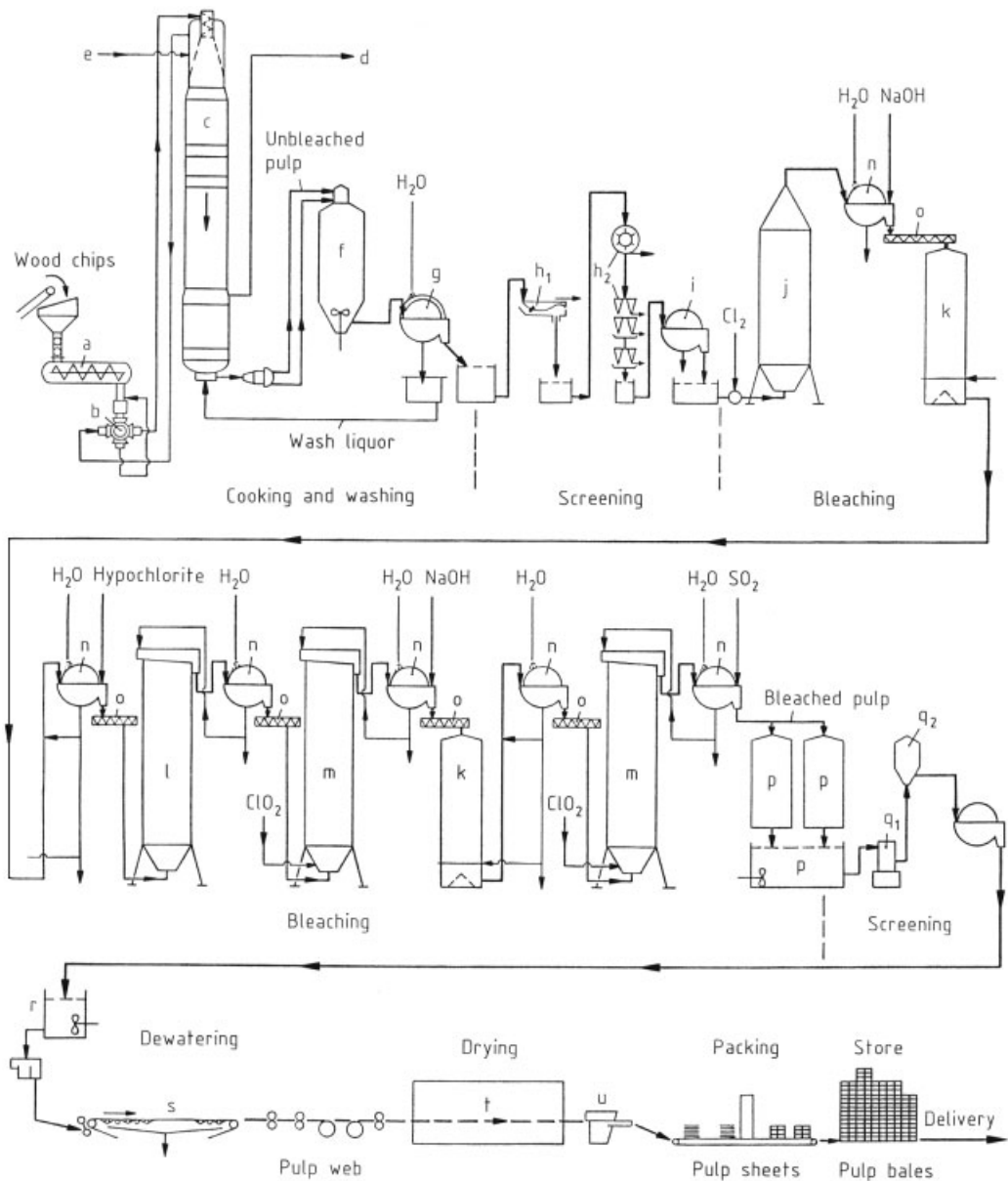


Figure 29. Schematic of a pulp mill

a) Steaming drum; b) High-pressure valve to the continuous digester; c) Continuous digester for kraft and bisulfite pulping; d) Waste liquor outlet; e) digestion liquor inlet; f) Blow tank; g) Filter for pulp washing; h₁) Coarse screening; h₂) Fine screening; i) Filter thickener; j) Chlorine bleaching tower; k) Bleaching tower for alkali treatment; l) Bleaching tower for hypochlorite treatment; m) Bleaching tower for chlorine dioxide treatment; n) Wash filters; o) Mixers; p) Storage tanks; q₁) Coarse postscreening; q₂) Fine postscreening; r) Machine chest; s) Dewatering machine; t) Tunnel dryer; u) Sheet cutter

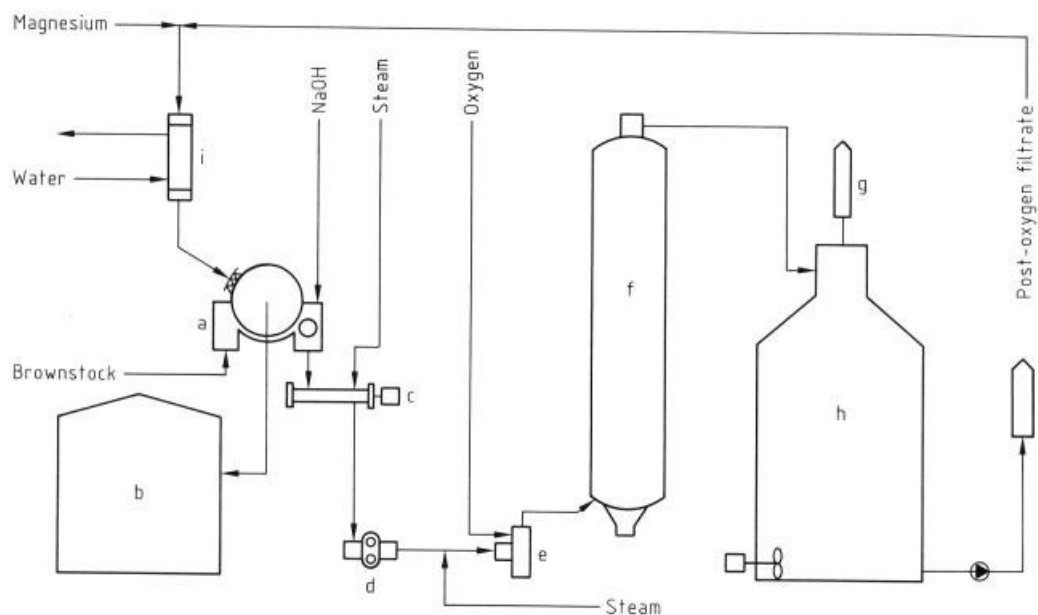


Figure 30. A medium consistency oxygen bleaching system
a) Brownstock washer; b) Seal tank; c) Steam mixer; d) Medium consistency pump; e) Oxygen mixer; f) Oxygen reactor; g) Vent; h) Oxygen blow tank; i) Post-oxygen washer

only insignificantly higher are incurred by modern kraft and sulfite pulp mills. Today, combustion furnaces operate with dust emissions below 50 mg/m^3 , NO_x emissions below 300 mg/m^3 , and SO_2 emissions below 1.5 g/m^3 .

Sources of Emission. In the pulping process, not only gaseous emissions, but also wastewater is produced. Today, the washing efficiency after the digestion process exceeds 99 %. The original load of the entire wood substance dissolved by pulping amounts to ca. 1500 kg COD per tonne of pulp and a final charge of ca. 15 kg COD is produced. Screening and liquor evaporation cause further pollution. In addition, pulp bleaching is a significant source of pollution. A rough assessment shows that about half of the COD of a pulp mill is caused by pulp production and the other half by pulp bleaching. In modern sulfite and kraft pulp mills, the gaseous sulfur compounds formed are withdrawn at the point of emission and charged into the chemical recovery system. The separation of gaseous sulfur compounds from the flue gases takes place in wet cleaners. The major sources of SO_2 in the sulfite process are the digester, the blow tank, the pulp wash, and the chemical recovery sys-

tem. In the kraft process, lime kilns are a further substantial source of emissions. Considerable amounts of chlorinated organic compounds are formed particularly in the chlorination and extraction stages of conventional bleaching. These compounds can be determined as organic halogens (AOX values) adsorbable on active charcoal. Ranges of AOX values for various hard- and softwood kraft pulps are listed in Table 11.

Table 11. AOX values from the bleaching of various pulp

Bleaching sequence	AOX, kg/t	
	Hardwood pulp	Softwood pulp
CEHDED	4–5	8–10
$\text{O}(\text{C}_{85}\text{D}_{15})$ EDED	2.5–5	4–5
$\text{O}(\text{D}_{70}/\text{C}_{30})$ (EO) DED	1–2	1.5–2.5

See Section 1.6 for abbreviations.

The chlorinated organic material can be divided into high and low molecular compounds, the dividing line being at a molecular mass of 1000. The high molecular mass fraction is not directly toxic. However, biological degradation

of these compounds can give rise to low molecular toxic products. The low molecular portion of the chlorinated organic compounds can, in turn, be divided into a water soluble, an ether soluble, and a highly volatile fraction. The ether soluble substances, particularly the chlorinated phenolic compounds, are especially hazardous, some of them being highly toxic, chemically very stable, and able to accumulate in the fatty tissue of water organisms via the food cycle. This fraction can also contain polychlorinated dibenzofurans and dibenzodioxins.

Prevention Measures. Pollution caused by pulping can be reduced by both internal and external measures. Internal measures refer to changes in the production process that lead to a reduction of pollution. These include extended digestion to reduce the residual lignin content of unbleached pulp, increasing the black liquor recovery rate by recycling the wastewater into the process, and switching to chlorine-free bleaching.

External basic prevention measures include the elimination of pollutants formed. Wastewater treatment for the reduction of pollutants can be carried out by filtration, sedimentation, flotation, and removal of solids. These processes can be supplemented by physicochemical procedures such as precipitation of dissolved compounds or flocculation.

Dissolved organic compounds can be degraded biologically in subsequent process steps. Both aerobic as well as anaerobic wastewater treatment are used for this purpose. Biological treatment is indispensable in modern pulp mills. To achieve the highest possible rate of degradation, multistage processes are frequently used; the sequence anaerobic/aerobic has proved to be especially effective. Depending on the wastewater composition, the COD of pulp mill effluents can be reduced by 50 % in single-stage plants. In two- or three-stage treatment plants, a decrease in the COD of up to 80 % and a AOX reduction of 50 % can be achieved.

In pulp production, the atmospheric emissions can be greatly reduced by rigorous detection of all flows of exhaust air and their return to the chemical recovery system, and by the purification of the flue gases.

1.8. Pulp Properties and Applications

Pulps have a wide range of properties and uses. The technological properties of pulps depend largely on the raw material, the pulping process, the extent of delignification, and the bleaching sequences applied. Basic differences exist between paper and dissolving pulps. The latter must not only be absolutely free of lignin, but the content of extractives, inorganic impurities, and hemicelluloses must not exceed relatively narrow limits. In addition, the degree of polymerization of cellulose must fall within a definite range, depending on the intended use. Dissolving pulps are produced by using the prehydrolysis–kraft process or the acid sulfite process. In the prehydrolysis–kraft process, the hemicelluloses are prehydrolyzed to such an extent that pulp with a high α -cellulose content is formed in subsequent digestion. The bleaching conditions, especially in the extraction stage, are also characterized by relatively stringent conditions. This refers to both the alkali dosing as well as the bleaching temperatures. A survey of the requirements to be met by dissolving pulps for the production of various products is given in Table 12.

For pulps used in the production of paper and board, the strength properties are of special importance. Kraft pulps are clearly superior to sulfite pulps in this respect, especially with regard to the tear strength. The pulp fibers form the supporting structure of paper and board, while mechanical pulp fibers improve the opacity and the volume of paper. Mineral fillers also increase the opacity and the surface smoothness of writing and printing papers. On the other hand, recycled fibers from wastepaper contributes little to paper strength. They are, however, inexpensive and their reutilization reduces waste problems. Indeed, wastepaper is used as a substitute for mechanical pulp in many cases. Today, the sulfite processes are of secondary importance in the making of paper pulp because their strength properties are inadequate for many applications. For instance, the tear strength of acid bisulfite pulps is only about two thirds that of kraft pulps. However, they have the advantage of easy bleachability and beatability. Semi-chemical pulps made by the bisulfite, neutral sulfite, or alkaline sulfite processes have good strength properties and, compared to competing

Table 12. Specifications of dissolving pulps for various products

Specifications	Viscose					Cellulose derivatives				
	Cordrayon	Modal fibers	Cellulose guts	Cellulose film	Acetyl cellulose	Cellulose ^c ethers	Cellulose ^d ethers	Cellulose nitrates	Methyl-cellulose	Carboxy-cellulose
Brightness, % ISO			>90	>90		89	93	>90	>88	>88
R ₁₈ ^a	>99	>96	>95	>93	96	93–95	92	>92	>92	>90
R ₁₀ ^a	>98	>93	>93	>91	94	91–94	89	>90	>90	89
Extract in CH ₂ Cl ₂ , %	0.02 ^b	0.02 ^b	<0.2	<0.2	0.1	0.1	0.4	<0.2	0.2	0.2
Ash	0.15	0.18		<0.1	0.1	<0.2	0.1	0.1	<0.2	0.2
DP _W ^e	760–860	460–520	900–1700	900–1200				900–4500	500–4500	700–4500
Specific density, kg/m ³					600	650–800	800	500–700	ca. 700	ca. 700

^a Residues in 10 or 18 % sodium hydroxide at 20 °C.

^b In ethanol.

^c Softwoods.

^d Hardwoods.

^e Degree of polymerization.

pulps made by the kraft process, better brightness levels. A survey of pulps made by various processes, their properties, and possible uses is presented in Table 3.

2. Mechanical Pulp

2.1. Introduction

Mechanical pulp denotes the semifinished product, used for the production of paper and board, which is made solely by the use of mechanical energy to separate the wood into individual fibers and fiber fragments. According to present findings, the internal processes occurring in such nonchemical production processes are predominantly of a physical nature.

There are two main processes used for the production of mechanical pulp. In the stone groundwood (SGW) process, logs are pressed against a rotating grinder stone with simultaneous addition of water. Refiner mechanical pulps (RMP, TMP) are produced by defiberizing wood chips between refiner disks to give fibers and fiber fragments.

High yields are characteristic for these two processes, i.e., the losses occurring during the processes, mainly in the form of dissolved ligneous substances, are low.

The most serious disadvantages associated with all types of mechanical pulp are their low

resistance to ageing, which results in loss of strength and the tendency to discolor. For this reason, the large scale use of this pulp is limited to “short-lived” paper such as newsprint.

In the Federal Republic of Germany mechanical pulp accounted for about 15 % of the total production of paper and board from 1986 to 1988 [250]. This percentage is also more or less valid for world production.

2.1.1. The Raw Material, Wood

For the production of mechanical pulps, which to a large extent are responsible for the structural stability of the paper produced, softwood is used worldwide. The most common woods used in Europe are spruce and fir, while in climatically more favorable countries, woods such as the fast growing *Pinus insignis*, *Pinus maritima*, hemlock, etc. are used. Softwoods have two predominant advantages over hardwoods. The fiber content of softwoods is ca. 90 % as compared to 50 % for hardwoods and, in addition, the fiber length of softwoods of 3–4 mm is considerably larger than the 1–2 mm of hardwoods. Under the same manufacturing conditions these two characteristics are always responsible for the higher strength of softwood mechanical pulps.

The logs required for the groundwood process are obtained by thinning out forests and are usually 10–20 cm in diameter. The bark has to be removed before the logs are processed. The

wood chips used for the production of refiner mechanical pulps are predominantly obtained from sawmill residues. It is of great importance for the quality of mechanical pulp that the moisture content of the wood is as high as possible. This results in a higher flexibility of the fibers, which improves their fibrillation.

2.1.2. Characteristics Required of Mechanical Pulps

About 90 % of the mechanical pulp produced is used to make graphic papers, such as newsprint; uncoated and coated magazine papers, e.g., SC (super calendered), and LWC (light weight coated) papers [251]. The desired properties of mechanical pulps, used for graphic papers, are as follows:

- 1) The mechanical pulp should contribute substantially to the structural strength of the paper. Newsprint, for example, may contain more than 80 % mechanical pulp.
- 2) The printability of the paper is mainly determined by the quality of the mechanical pulp.
- 3) Since graphic paper is usually printed on both sides, a very low show-through and strike-through of the printing ink is very important. In offset printing, the surface of the paper should have a high picking resistance and be free of dust.
- 4) The drainage ability (freeness) of mechanical pulp has to be high to allow the paper machines to be operated at high speeds (ca. 1400 m/min). Furthermore, the paper has to be able to cope with the stresses within the printing machines.

The technological data of mechanical pulp is determined by means of standardized test methods. The United States and its neighbors follow the TAPPI regulations [252], the Scandinavian countries use the Scan methods [253], and Germany and its neighbors, the Zellcheming regulations [254].

Although the methods used vary and the results are thus not directly comparable, all standards require determination of the following mechanical pulp properties:

- 1) Drainage characteristics
- 2) Stability properties such as tensile strength tearing strength, and picking resistance

- 3) Optical properties such as brightness and opacity
- 4) The quantitative composition with respect to the portions of long fibers, fiber fragments, and fines as well as the size of the shives

Furthermore, proof printing and other tests provide information about the suitability of a mechanical pulp.

All in all, the test methods in question permit adequate assessment of the mechanical pulp and are essential for mechanical pulp production.

2.2. Groundwood

Until the 19th century, used textiles were virtually the only raw material used for paper-making. With the constantly increasing demand for paper, the supply of new raw materials was an urgent and widely known problem. In 1843 a weaver from Saxony, F. G. KELLER, shredded wood by pressing it against a hand-driven grinder stone adding water to the grinding process. From the resulting pulp, he then made a sheet of paper. By using wood, KELLER found a raw material which is still the most important in the paper industry. After this discovery was adopted, the first mechanical grinder was put into operation in 1852.

It was not until 1930 that the internal processes involved in grinding were systematically studied with the aim of obtaining a higher quality groundwood [255]. The investigations carried out in Canada in the early 1960s on an experimental grinder operating under pressure led to the pressure grinding process for the production of pressure groundwood (PGW) [256]. The Tampella company of Finland then developed this process and introduced it in 1978 [257]. The thermogrinding process for the production of thermogroundwood (TGW) was introduced by the Voith company in 1984 [258]. This grinding process is carried out at a normal pressure and with process temperatures that reach the feasible upper limit.

Theory of the Grinding Process. The purpose of the grinding process is to disintegrate the wood fiber bond system. The logs are pressed against the rotating grinder stone with the wood

fibers parallel to the axis of the stone (Fig. 31) [259]. Based on the usual operating parameters, a stone particle requires about 0.02 s to pass the grinding zone, removing 0.03 mm of the wood substance. The total or partial separation of the fibers from the wood and the properties of the groundwood achieved with this process depend on a series of factors. These are, above all, the surface structure of the grinder stone, the nature of the abrasive particles (round or sharp-edged) and their depth of penetration into the wood. Fiber removal occurs as soon as the stone particles are in contact with the wood, and the availability of sufficient water is of basic importance for heat dissipation and friction reduction. When sliding along the wood surface, a stone particle not only causes deformation of the fibers, but simultaneously changes the direction of already separated fiber parts (Fig. 32). These deformations lead to the fracture of the fiber-to-fiber bonds and of the bonds within the fiber walls. The results of this effect, comparable to “brushing” of the deflected fiber parts, are the fibrillation of the fiber walls and the creation of fines [260].

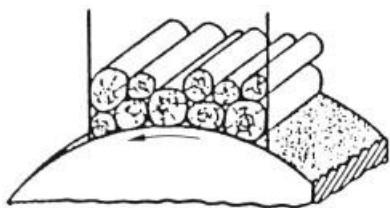


Figure 31. Arrangement of the wood on the grinding stone

It can be assumed that most of the energy put into the grinding process is transformed into heat; values of 90 to 99 % have been reported. The resulting increase in temperature is effective in the wood and in the grinding zone [261]. Due to the poor thermal conductivity of wood, temperatures of 180 °C or higher may develop within the wood directly above the grinding zone [262]. In the conventional grinding process at normal pressure, the average temperature in the grinding zone is below 100 °C. Evaporation may occur only in those areas where the amount of water present is insufficient to dissipate the heat [261].

During the development of grinding processes it was confirmed that the temperature is a

decisive factor in the production of groundwood. The explanation for this was given by GORING, who found that lignin with a water content of more than 30 % softens at temperatures as low as 90 °C (Fig. 33) [263]. Since the lignin-rich middle lamellae of the wood fibers contribute substantially to the mutual bonding of the fibers and to the structural stability of the wood, the softening of lignin must inevitably facilitate the exposure of the fibers.

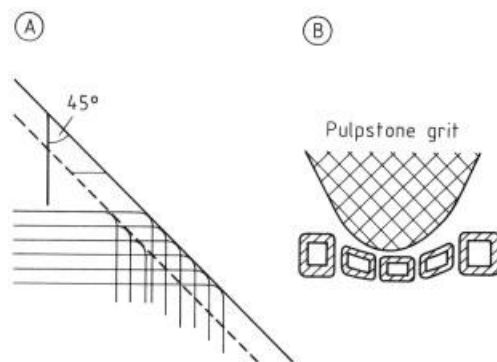


Figure 32. Processes occurring in the grinding zone
A) Angle of removal; B) Deformation of fibers by pulpstone grit

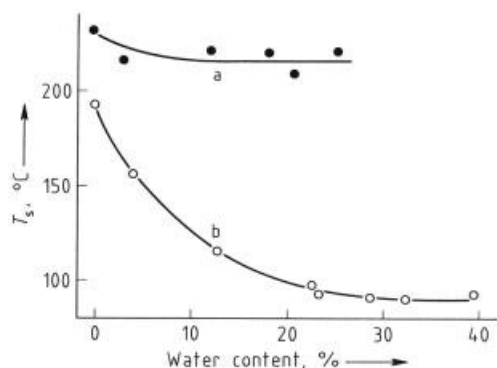


Figure 33. Variation of softening temperature T_s with water content
a) Sulfite pulp; b) Periodate lignin

A sharp-edged abrasive particle has an energy-saving cutting action on the wood structure, whereas round particles exert a predominantly fibrillating effect. The result is a groundwood with superior strength properties, but with the disadvantage of a lower production rate. The ratio of the motor energy to the amount

of groundwood produced is called the specific energy requirement (kWh/t), and is an important process parameter. An increase in the specific energy requirement is always linked with better strength properties, but also with a lower drainage capacity. The magnitude of the specific energy requirement depends on the interaction of all grinding conditions and the surface characteristics of the grinder stone. The effect of the grinding conditions – such as the grinding surface area, the peripheral speed, the specific grinding pressure, etc. – on the grinding process and on the groundwood quality has been the subject of detailed studies, which have in turn contributed to the optimization of the process [255], [264–266].

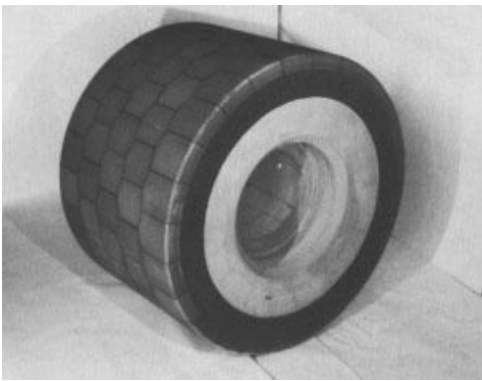


Figure 34. Ceramic-bound grinder stone

2.2.1. The Grinder Stone

Apart from the cement stones, now of declining importance, the grinder stones used are exclusively of the ceramic-bound type (Fig. 34) with a diameter 1.5–1.9 m. The stone surface consists of segments fastened to the concrete core of the stone [267]. The abrasive particles used consist either of sharp-edged carborundum (SiC) or, increasingly, of the softer and less sharp-edged corundum (Al_2O_3). A pattern is impressed on the grinder stone surface (Fig. 35) by traversing sharpening rollers, a procedure which has to be repeated periodically depending on the wear of the pattern. The intervals at which the stone is resharpened vary greatly between 1 and 100 d. This sharpening process must be carried out with extreme care because at present there is no prac-

tically useful technique available for measuring the pattern [268], [269]. This sharpening pattern has two functions. It meets the requirements for the separations of the fibers from the wood substances, and it transports the water needed in the grinding zone within the grooves of the sharpening pattern.

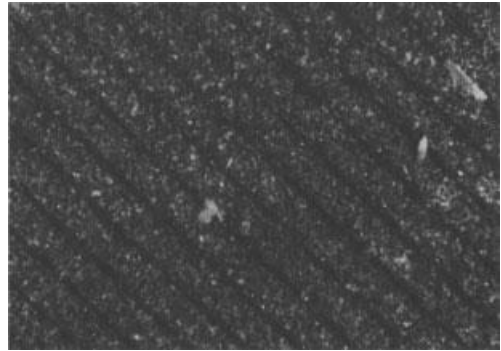


Figure 35. Pattern on a grinder stone surface

2.2.2. Groundwood Production

For the production of groundwood two grinder systems are predominantly used. In press grinders the logs are transported automatically into chambers, where they are pressed against a grinder stone by means of hydraulic presses (Fig. 36 A). In continuous grinders, logs are pressed against the stone by means of specifically shaped chains (Fig. 36 B) [270]. The advantage of the latter system is that the continuous grinding process better utilizes the motor load. The two-press grinder, on the other hand, has a higher specific production due to its larger grinding surface area. A comparison of the two grinding systems is given in Table 13.

Table 13. Comparison of the two types of grinder for wood of 1 m diameter

	Two-press	Continuous
Grinding surface, m ²	2.0	1.2
Motor output, kW	5000	3000
Motor output utilized, kW	4500	2700
Production (1250 kWh/t), t/d	78	50
Area required/unit, m ²	26	13
Space required/unit, m ³	100	80

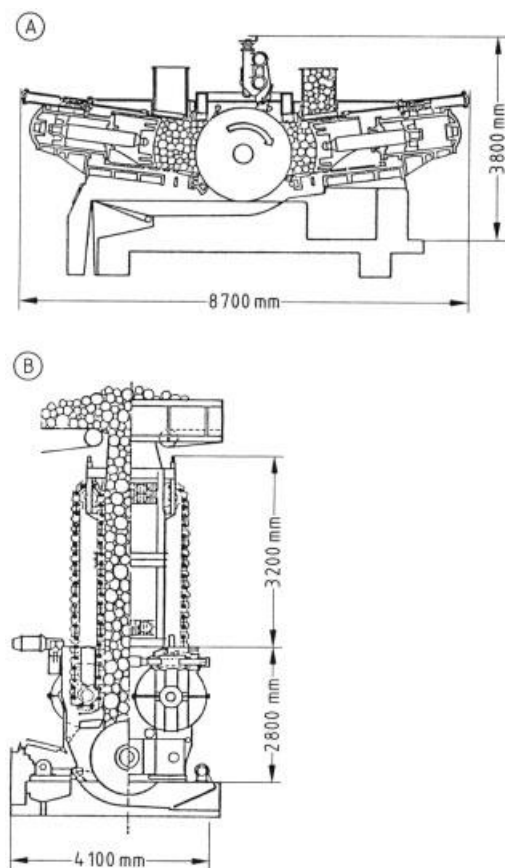


Figure 36. A) Tampella press grinder; B) Voith chain grinder

The grinders are equipped with control systems that keep the power input, the production rate, or the specific energy consumption constant. Each of these control systems has its advantages and disadvantages. In fact, combinations of two of the above control systems are usually applied.

2.2.3. Newer Methods of Groundwood Production

The superior strength properties of refiner mechanical pulps, especially of TMP, forced further development of the conventional grinding process if it was to remain competitive. The findings on the influence of process temperature [256] led to the development of the pressure grinding process (PGW process). In this process, the Tampella pocket grinder is

sealed so that the grinding process takes place at overpressure. Overpressures of up to 0.3 MPa, produced with compressed air, allow the process to be operated with white water temperatures of 95 °C and grinder pit temperatures of 125 °C. The more intensive softening of lignin associated with these temperatures results in improved groundwood qualities [271–275]. The strength of pressure groundwood is 30–35 % higher than that of conventional groundwoods produced with the same specific energy consumption. Although this process represents a tremendous improvement, the technical and financial requirements are considerably higher.

The manufacturers of continuous grinders were also compelled into improving the quality of their groundwood. This was achieved by reducing the heat losses [276] which result from evaporation in the grinding zone and by maximizing the process temperature, without using overpressure, by means of stability controllers [258]. The qualities of groundwood obtainable from the thermogrinding process (TGW process) are about 15–20 % higher than that of conventional groundwood and are comparable to lower-grade pressure groundwoods. A certain advantage is the fact that the conversion of existing grinders to the TGW process is relatively inexpensive.

2.3. Refiner Mechanical Pulps

2.3.1. Historical Survey

Refiners have been available since the thirties and were used particularly in the fiberboard industry. After 1955 they also found application in the paper industry for the production of mechanical pulps [277]. Sawmill residues are used as a cheap raw material by being transformed into wood chips. The refiner mechanical pulp (RMP) process, which is hardly used today, was the first stage within this development. After 1960, the advantages of higher process temperatures were exploited in the thermomechanical pulp (TMP) process. This process is still being improved and is used for the production of the majority of refiner mechanical pulps.

Since 1980, the chemothermomechanical pulp (CTMP) process is becoming increasingly

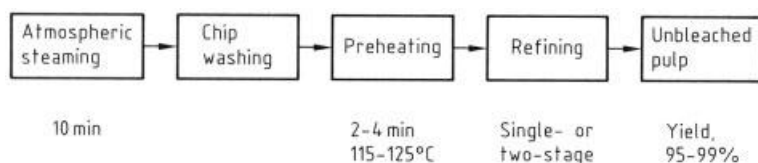


Figure 37. Schematic of the TMP process

important. Because wood chips are readily impregnated, small additions of chemicals give further improvements in the pulp properties. A further increase in the amount of chemicals used, as in the more recently developed CMP process, results in mechanical pulps comparable to semi-chemical pulps.

2.3.2. Theory of the Refiner Process

The objective of the refiner process is the same as that of groundwood production, i.e., the breaking loose and fibrillation of the wood fibers [278]. As a result of the large surface area of wood chips, the advantages of higher temperatures can be exploited to a much greater extent than in the grinding process. In the TMP process, the chips are subjected to thermal pretreatment, and the disintegration and defibration process is carried out in the refiner at overpressure. To obtain a large proportion of intact fibers, fiber separation should preferentially be a fiber-to-fiber action rather than an action between the refiner plates and the wood [279], [280]. Pulp consistencies in the refining zone of at least 40 % are suitable for this purpose. Nevertheless, the design of the refiner plate pattern exerts a marked influence on the quality of the wood pulp.

TMP with good strength properties is obtained as a result of the relatively small number of cutting actions. However, the specific energy consumption is 40–50 % higher than that of the grinding process. The temperatures resulting from the excess pressures of up to 5 bar in the refiners permit the recovery of the extra energy demand by means of heat exchangers [281], [282].

2.3.3. TMP Production

A schematic of the TMP process is shown in Figure 37 [283]. Since the pulping of wood chips to

the desired pulp quality is usually not possible in a single refiner stage, two stages are used. The pulping of screen rejects is often carried out in the second refiner stage.

The capacity of a two-stage refiner system is much higher than that of a grinder; 300 o.d. t/d of TMP can be produced at an installed motor power of 15 000 kW per refiner. The specific energy consumption, including that of the auxiliary machines is ca. 2100 kWh/o.d. t. The arrangement of the refiner disks can be quite different (Fig. 38) and each of these models has its advantages [284].

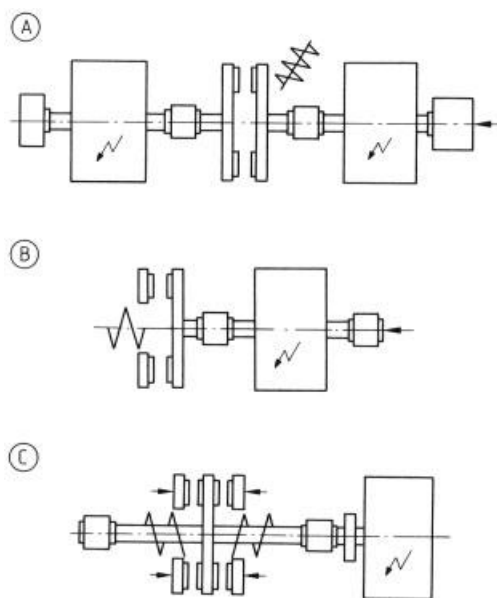


Figure 38. Refiner configurations

A) Double-disk refiner; B) Single-disk refiner; C) Twin refiner

The refiner disks consist of 6–12 segments and have a diameter of more than 1.5 m. The profile of the plates is designed such that the direction of disk rotation can be reversed, extending the plate life-time, which ranges between 1000 and 2000 h.

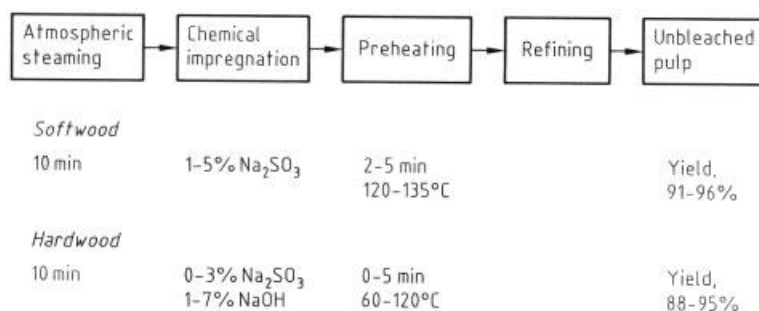


Figure 39. Schematic of the CTMP process

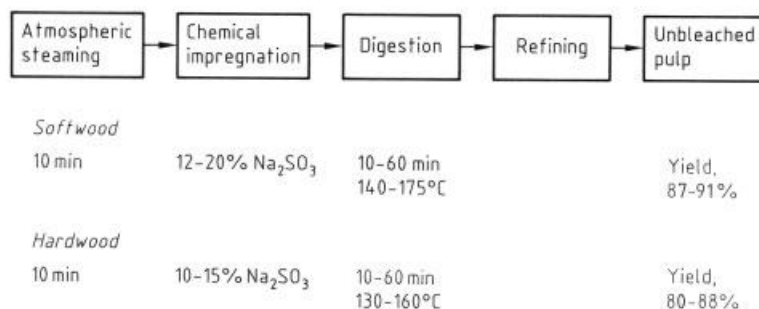


Figure 40. Schematic of the CMP process

The design of the refiner plates is also of great importance. This applies both to the optimum profile and to the alloy composition of the plate material [285]. The possibility of using elsewhere the heat generated in the process by means of heat exchangers has already been mentioned. In this way, 50–70 % of the motor energy can be saved [281], [282].

2.3.4. New Methods of Refiner Pulp Production

Although the addition of chemicals in the groundwood process did not prove worthwhile, their use in the refiner process has become increasingly important because wood chips can be impregnated very easily.

Sulfonation of the wood chips in combination with the TMP process has proved most effective. The properties of the CTMP can be varied to a great extent by changing the amount and the nature of the chemicals. CTMP has a wide field of application, ranging from tissue to LWC. A schematic of the process is given in Fig. 39 [286], [287].

Sulfonation results in permanent lignin softening which permits easy separation of the fibers. CTM pulps have a favorable dewaterability and are characterized by high strength, a large long fiber fraction, and a very low shive content [288].

A further development of the CTMP process is the CMP process. In this method, the process conditions are intensified, giving products comparable to semichemical pulps (Fig. 40) [286].

CTMP and CMP have the advantages of good strength properties and low shive content, but they also have the disadvantages of higher solvent losses and, therefore, environmental problems. Their tendency to yellowing is typical of all lignin-containing pulps [289]. For this reason, use of CTMP and CMP is limited to paper that is used for only a relatively short period of time.

2.4. Screening of Mechanical Pulps

2.4.1. Purpose of Screening

All mechanical pulps contain undesired components such as large, insufficiently pulped frag-

ments (i.e., coarse rejects) and the shives, which consist of many fiber bundles (Fig. 41).

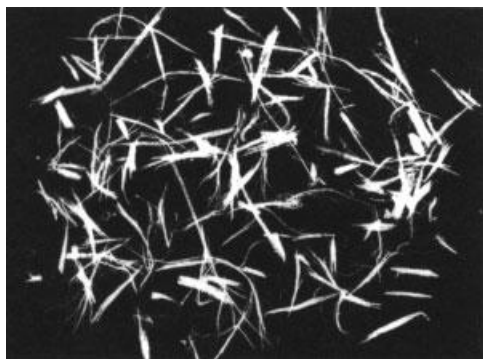


Figure 41. Fiber bundle or shives

The shives have to be removed because they reduce the strength and the printing quality of paper [251]. The screening out of the coarse rejects is easy to perform, but the removal of the shives requires a more elaborate technique. The shive content of unscreened mechanical pulp may be as high as 5 %, depending on the process used. The purpose of screening is to remove the shives to a large extent and, at the same time, to keep the simultaneous screening out of valuable long fibers as low as possible. The extent of the required shive removal depends on the type of paper to be produced. With increasing printing quality, priority is given to shive removal over the prevention of fiber losses [290].

For the evaluation of the action of a screen or a screening system, it is not sufficient to evaluate the accepts alone; the quality of the inflow and of the rejects also has to be taken into consideration. The higher the efficiency of a screen, the higher the relative shive retention at the lowest possible overflow [291], [292].

2.4.2. Mechanical Pulp Screening

Coarse rejects are removed by vibrating flat screens (bull screens) equipped with perforated plates (3 – 10 mm). Hammer mills or pulpers are used for the reduction of the coarse rejects, also called “sauerkraut”. The bull screen accepts mainly contain coarse shives and are usually added to the rejects of the fine screening system for further processing.

The screens used for the separation of shives usually have vertically arranged screen cylinders. The screening process is carried out at overpressure (Fig. 42). The size of the holes in the screen plates is chosen in such a manner that fibers and accepted stock pass through the screen, whereas shives above a certain size are retained. Depending on the type of paper required, screens with holes of 1.0 to 1.8 mm in diameter are employed, and the screening process is carried out at high dilutions (pulp consistencies below 1 %) to promote the screening action.

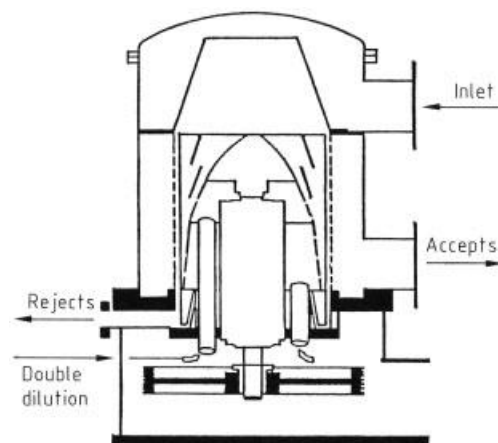


Figure 42. Hooper screen

Although older models are occasionally used, the new perforated plates equipped with slots (0.2 – 0.3 mm) instead of holes give an excellent screening effect [293], [294]. They relieve the cleaners, which are mainly used for the separation of cubelike particles, and are still an essential component of any multistage screening installation. The screening reject rate may be as high as 30 % of the inflow. A screening installation consists of various stages in order to reduce the strain on subsequent installations and to save most of the acceptable components contained in the rejects.

The rejects of the last stage, after thickening to ca. 20 % consistency, are processed in refiners and recycled to the screening process.

In the case of groundwood, the energy requirement for screening, for refining the screen rejects, and for subsequent thickening accounts

for ca. 25 % of the total energy. The value for refiner mechanical pulp is ca. 29 % [295].

2.5. Bleaching of Mechanical Pulps

Mechanical pulps need to be brightened to suit their intended use. Since higher process temperatures are always accompanied by a loss of brightness, the amount of wood pulp that requires bleaching is constantly increasing. Two bleaching processes or a combination of the two are used to achieve the desired final brightness [296–298].

Reductive bleaching uses sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) and can lead to an increase in brightness of up to 12 % ISO. Depending on the required final brightness, the amount of $\text{Na}_2\text{S}_2\text{O}_4$ used is 0.1 to 1.2 %, based on o.d. pulp. A suitable pH value is 5.6 to 6.5, and a temperature up to 70 °C accelerates the bleaching process. However, a further increase in temperature is detrimental. The optimum pulp consistency is 3–5 % and the bleaching time is ca. 1 h. The bleaching tower operates with an overflow and is charged from the bottom upstream, due to the detrimental effect of the presence of free oxygen on the process [296], [297].

Oxidative bleaching is carried out in the pH range 10–10.5. Sodium peroxide (Na_2O_2) or hydrogen peroxide (H_2O_2) is used in amounts of 0.4–4 % H_2O_2 (50 %), based on o.d. pulp. The bleaching time is 1–2 h at 50–60 °C. High pulp consistencies of 15–20 % are favorable and the maximum increase in brightness is 14 % ISO. However, an increase in brightness of 16–20 points can be achieved by combining the two bleaching processes in the order peroxide–dithionite (Fig. 43) [297], [299]. Both bleaching processes result in lower brightness in the presence of heavy metal ions. For this reason chelating agents (0.3–0.5 %) are added before bleaching [296], [297], [300], [301].

The technological properties of mechanical pulps are not changed appreciably by bleaching. However, solvent losses vary substantially, being distinctly lower with reductive bleaching. Finally, it should be mentioned that the tendency of mechanical pulps to yellowing is not changed by bleaching.

2.6. Comparison of Mechanical Pulps

Each mechanical pulping method results in very specific properties of the pulps produced. Furthermore, the pulp properties can be influenced to a certain extent by varying the pulping conditions or by additional treatments. A decision in favor of one or the other process is always a compromise because of the great variety of often contrasting properties.

It is generally valid that increasing process temperatures result in increased solvent losses and reduced brightnesses. Although the use of chemicals (CTMP, CMP) is of a certain advantage (for example, allowing the pulping of hardwoods) it causes a further increase in solvent losses.

Table 14 lists some technological characteristics of the various processes after thickening and before bleaching. These values are intended only to indicate the trends at about the same freeness level (excluding CMP and halfbleached sulfate pulp), and it should be mentioned that the values for the specific energy requirement, the strength, and fiber classification have a margin of error of ca. ± 10 %.

3. Wastepaper

Paper and board are indispensable resources for an information and distribution society. However, their production consumes large amounts of forest resources and energy. Furthermore, uncollected wastepaper which has been rapidly increasing is causing a large problem in the processing of urban waste materials. Although various proposals (e.g., specially designed incineration, biodegradation, and efficient landfill) will be performed for solving these problems in the future, a possible method may be to promote the utilization of all kinds of wastepaper immediately.

In 1987, worldwide production of paper and board was 25.6×10^6 t, of which 6.73×10^6 t was collected as wastepaper (collection rate = 30.9 %). 6.69×10^6 t of wastepaper was utilized (utilization rates = 30.7 %) as raw material for paper and board production, accounting for about one-third of the total raw materials. Wastepaper has thus become an indispensable raw material for the paper manufactur-

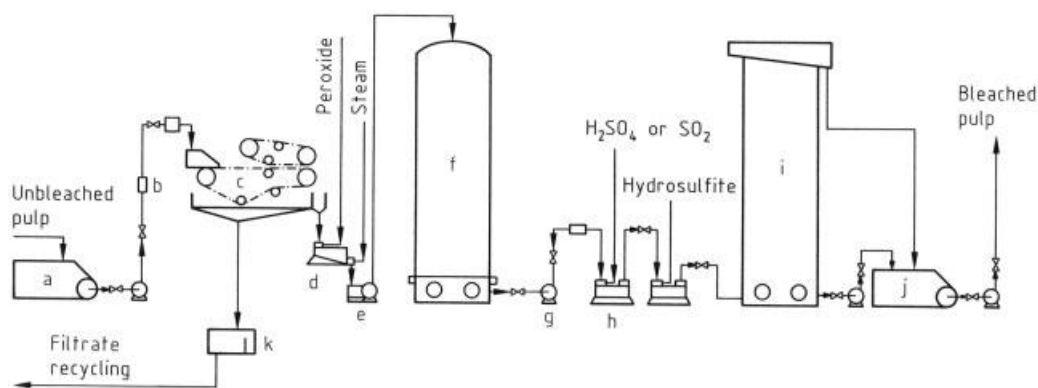


Figure 43. Schematic of a two-stage, continuous mechanical pulp bleaching process

a) Unbleached pulp chest; b) Pulp density regulator; c) Double wire press; d) High consistency mixer; e) High consistency pump; f) High consistency peroxide tower; g) Pump; h) Low consistency mixer; i) Low consistency hydrosulfite tower; j) Bleached pulp chest; k) Filtrate vessel

Table 14. Comparison of unbleached mechanical pulps (TAPPI standard)

	SGW	TGW	PGW	RMP	TMP	CTMP	CMP	Semibleached kraft pulp
Specific energy, kWh/t	1500	1530	1550	2100	2200	2100	1550	100
Process temperature, °C	75–80	93	115	90	120–140	120–140	150–160	
Yield, %	97–98	97–98	96–97	97–98	94–96	91–94	82–90	45
BOD, kg/t	7–15	9–16	10–17	ca. 15	18–25	30–40	50–85	200
Freeness (CSF), mL	100	100	100	100	110	110	300–400	350
Tensile index, Nm/g	30	34	37	36	42	47	54	65
Tear index, mN·m ² /g	3.4	3.9	4.7	3.9	7.3	7.3	9.0	14.0
Quality value (QV)*	98	112	131	114	188	193	234	345
Long fiber content (R 30), %	21	24	30	29	40	40		
Fines content (D 100), %	45	41	37	40	33	32		
Brightness, % ISO	63	62	60	58	56	60	52	

* QV = tensile index + 20 x tear index.

ing industry. The collection rates and utilization rates of wastepaper in some countries [302] are listed in Table 15. Both the collection and utilization rate are very high in EC countries. Although the collection rate is high in Scandinavian countries, the utilization rate is extremely low, because most of the paper and board produced is exported. In Asian countries wastepaper recovery and utilization are very high.

3.1. Types of Wastepaper

Wastepaper is generally classified according to origin, quality, and usage. The classifications vary according to country. For example, they are classified according to the 1983 NARI standards [303] in North America, the European wastepaper standards (CEPAC) [304] in Europe, and classification guides for wastepaper [305]

in Japan. In CEPAC the wastepaper is roughly classified into four groups, corresponding to ordinary, medium, high, and kraft qualities; these are further subclassified. However, these official classifications are rarely utilized as market nomenclature.

3.2. Origin, Collection, Handling, and Economic Aspects

Wastepaper contains contaminants such as inks, resins, and other substances. Since uniformity is important for pulp furnishes, the quantitative and qualitative variations of impurities should be as small as possible. Thus, the collecting methods and the segregation of the wastepaper at an early stage may be more important than the technical efforts to develop new processes for secondary fiber production.

Table 15. Wastepaper recovery and utilization in some countries in 1987

Country or region	Recovery rate, %	Utilization rate, %
EC	35	47
United Kingdom	30	55
Germany	41	44
Italy	23	41
Spain	41	58
Asia	37	47
Japan	50	51
Taiwan	40	87
China	21	25
Latin America	32	42
Mexico	40	67
North America	28	23
USA	29	26
Canada	20	11
Scandinavia	36	7
Sweden	40	10
Oceania	26	29
East Europe	26	25
Africa	17	27

The wastepaper collected from houses and markets etc., such as corrugated containers, newspapers, and magazines is usually called “collected wastepaper”, while the shavings (cuttings), brokes (waste materials), and overissued papers generated in printing, paper-container manufacture, and book binding mills are termed “industrial wastepaper”. Wastepaper occurring in supermarkets, department stores, and large office buildings are called “semi-industrial wastepaper” and are classified as industrial wastepaper.

Every country uses various collecting methods because the different climates influence wastepaper recycling. Most wastepapers are collected by dealers. However, in some countries collection boxes are provided without charge, and collection is carried out voluntarily by groups such as schools.

The collected wastepaper is brought to the collection yards, then weighed and sorted. They are compacted by baling machines (balers) which are installed in most collection yards. Small amounts of wastepaper are sometimes shipped in unbaled form. Industrial wastepapers from large generators are usually delivered to and processed in wastepaper yards integrated in the pulp mill. Detrimental substances (e.g., plastics; pressure sensitive and hotmelt adhesives; and carbonless copy, laminated, and thermosen-

sitive papers) are removed before baling. The baled wastepaper is stored in the yards until shipment.

Fluctuating moisture content may cause economic problems when the wastepapers are accepted by the mills, because wastepaper is bought and sold on the basis of weight. The property of secondary fiber furnishes also varies because chemicals are added on the basis of dry weight. Various measuring tools are being experimented with in all countries, for example, core-drillers and “aquaboy” which work by measuring electric resistance.

There are seasonal deviations in the occurrence of wastepapers; therefore storage sometimes causes problems. Unsuitable storage conditions result in an increased short fiber content. The processing of deteriorated wastepaper requires large amounts of drainage aids, the reduction of paper machine speed, and leads to decreased sheet strength. In this case the mill operators should optimize the turnover of wastepapers, and establish a maximum storage period.

Because the secondary fibers have already passed through stock-preparation equipment when the original paper was made, they require comparatively little energy for processing. Therefore, the capital investment for the mills and the running costs are lower than those of kraft or sulfite pulping mills. This means that secondary fibers are usually cheaper than other pulps.

Recent incentives for increased wastepaper utilization are a result of the favorable price of wastepaper in comparison with the corresponding grades of market pulp. However, in some countries wastepaper recycling is promoted by government assistance programs and policies for forest preservation and environmental protection. This trend will be accelerated more and more in the future.

4. Nonwood Plant Fibers

4.1. Rags

The textile fibers of cotton linters, flax, hemp, Manila hemp (abaca), sisal, and jute are used in papermaking. The fibers of cotton linters are the original fibers on cotton seeds. These fibers are

processed as original fibers or as cotton waste from the spinning factory.

The term rags refers to old or new fabrics produced from textile fibers, e.g., waste cloth, mailbags, foot cloth, ropes, binding twine, etc. Blended fabrics that contain plastic fibers or plastic coatings cannot be used. The amount of rags and cotton linters used by the pulp and paper industry in the Federal Republic of Germany was 92 000 t/a in 1962 and 38 000 t/a in 1988 (data from the Verband deutscher Papierfabriken).

The reasons for the replacement of rag and nonwood plant fibers are:

- 1) Wood fibers are substantially cheaper
- 2) Long-fiber softwood pulps are now of sufficiently high quality to compete with rag fibers in many applications
- 3) The very low availability of rag and nonwood plant fibers compared with wood fibers

Range of Use of Nonwood Plant Fibers in the Paper Industry. Rag fibers are used for thin and lightweight paper which must meet exacting demands with respect to strength, toughness, opacity, aging resistance (printing paper), absorbing capacity, chemical purity (linters), and runability. The following papers contain nonwood plant fibers:

cigarette paper (flax, hemp, and sisal)
 tea-bag paper (sisal, Manila hemp)
 casing paper (Manila hemp)
 thin carbon raw silk paper (flax, hemp)
 brush matrix (abaca, sisal)
 special filter papers (cotton linters)
 banknotes and security papers (hemp, cotton linters)
 paper for dust bags in vacuum cleaners (various rag fibers)
 special drawing, watercolor, and handmade paper (cotton linters)
 voluminous electrolyte paper (Manila, sisal)
 special thin Bible paper (flax, hemp)

Depending on the rag-fiber content these papers are designated as:

- 1) All-rag paper (100 % rags)
- 2) Rag paper (at least 50 % rags)
- 3) Rag-containing paper (at least 10 % rags)

The fiber additives are wood pulps and, in some cases, synthetic fibers.

The individual fibers are broken free from the fibrous material mainly by alkaline or neutral sulfite digestion. Stronger alkaline pulping is necessary to eliminate the lignified parts of fibers. In the case of rags, however, mild digestion is sufficient. The half-stock is subsequently bleached. The fiber yield is 40–50 %. Fiber yields exceeding 70 % can be achieved, depending on the quality of the rags.

Prospects. Efforts are being made to develop kenaf-hemp (*Hibiscus cannabinus*) and *Hibiscus sabdariffa* (Malvaceae family), also known as Mesta, Bimli, or Deccan hemp, Siam jute or Thai kenaf, into an industrially usable fiber plant for the paper and pulp industry. These plants occur in tropical and subtropical regions. *Kenaf rosella* is more robust, grows on poor soil more slowly, and gives lower fiber yields than kenaf (*Hibiscus cannabinus*).

4.2. Other Nonwood Plant Fibers

Other nonwood plant fibers used in the paper and pulp industry are:

bagasse
 bamboo
 esparto
 reeds
 rice straw
 wheat straw
 ramie
 papyrus (upper Sudan)

In 1987 the estimated worldwide production of pulp from the following nonwood plant fibers was:

straw	5.4×10^6 t
bagasse	2.1×10^6 t
bamboo	1.4×10^6 t
reeds	1.6×10^6 t

It is estimated that nonwood pulp products accounted for 8.1 % of total world pulp production in 1985 and showed a tendency to rise. The reasons for this are:

- 1) Saving of foreign exchange by the replacement of imported pulp by native fibrous raw materials

- 2) Creation of jobs in one's own country, both in agriculture as well as in the following industry
- 3) The consumption of wood-free fibers will increase on account of the progressive death of forests throughout the world and the growing demand for fiber raw materials
- 4) Efforts are being made to promote the cultivation of industrial plants to reduce agricultural surpluses
- 5) Recently developed, sulfur-free pulping methods could have a positive effect on the increased use of wood-free fibers in the pulp and paper industry

4.3. Synthetic Fibers

4.3.1. Survey

According to DIN 60 000 T 1, synthetic fibers belong to the group of man-made fibers that also includes fibers from natural polymers, e.g., viscose fibers. The term synthetic fibers covers a very wide spectrum of polymers, comparable to the range of plastics. The most important representatives are: PA 6 and 6.6, PETP, PAC, PP, PE, PVA, PTFE, PUE (elasthane), PVC, aramides, and PPS.

A comprehensive survey of the many different synthetic fibers available, their production, and properties is given in [306–309] (see also → Fibers, 4. Synthetic Organic).

The main application of synthetic fibers is textile production. Up to now, only a small quantity of synthetic fibers have been used in paper-making. The reasons for their use are as follows:

PA (6 & 6.6)	very high resistance against alternating bending, high strength, favorable dyeability
PETP	high strength (at a lower price compared to PA), favorable chemical stability, excellent electrical insulating capacity, very large selection of suppliers and types
PP, PE	very favorable chemical stability, low specific weight, relatively low melting point (ca. 160 °C or ca. 130 °C) which permits heat-sealing
PVA	used in the "unhardened" form due to the hot-water solubility, which can be used for pre-bonding of a web [310]

There are, in addition, some copolymer and mixed polymer fibers with low melting points

that can be used as binding fibers [309], [311], [312].

Papers containing synthetic fibers are:

- 1) Document papers with especially high resistance to alternating bending stresses. These papers are used for identity cards and maps. Types of fibers preferred: PA and PETP.
- 2) Papers that are subjected to high mechanical stress, e.g., for envelopes. Type of fiber preferred: PETP.
- 3) Filter papers (dry and wet filtration) with high chemical stability. Type of fiber preferred: PETP, PP.
- 4) Papers with an especially high dimensional stability under varying environmental conditions, used for stencils and cartridges. Type of fiber preferred: PETP.
- 5) Papers that are suitable for clean rooms because of low particle emission. Type of fiber preferred: PETP and PE.
- 6) Wrapping paper in food technology: for tea bags and sausage skins. Type of fiber preferred: PETP, PP, PE [313], [314].
- 7) Electrical insulating papers. Type of fiber preferred: PETP and PE.
- 8) Overlay papers for composites in plastic technology. Type of fiber preferred: PETP.
- 9) Decorative papers with colored fibers as part of the pattern. Type of fiber preferred: PA and PETP.
- 10) Roller coating papers with PA as additive.

This list is incomplete and the designation of these products as paper is also disputed.

According to DIN 60 000 T 1, glass fibers do not belong to the group of synthetic fibers. However, these fibers are of great importance for wet-laid nonwovens (cf. DIN 61 210).

A close relationship exists in part between paper and wet-laid nonwovens (→ Nonwoven Fabrics). According to DIN 61 210, two criteria serve to distinguish them: the pulp content and the bulk density. Thus, products that contain pulp and textile fibers are regarded as paper if:

- 1) the pulp content is at least 50 % and
- 2) the bulk density is at least 0.4 g/cm³.

If the pulp content is higher than 70 %, the product is generally considered to be paper and if it is lower than 50 %, the product is generally a non-

woven fabric. This definition has not yet been accepted internationally.

4.3.2. Marketing and Packages of Synthetic Fibers

In the case of several synthetic fibers, especially PETP and PA, many different types of each fiber are available. The properties of these various types can vary considerably even though they are made of the same polymer.

The main application of synthetic fibers is textile production. Accordingly, the package forms are adapted to textile process technology. They are characterized by:

- 1) crimped cut fibers, with fiber lengths $\geq$ ca. 30 mm; or flat or textured multifilament yarns with unlimited length; and
- 2) spin finishes, which determine the properties of the fiber surface.

As a rule, special package forms are required for paper production: lengths of 2–30 mm, uncrimped fibers, and a hydrophilic spin finish for quick wetting of the fibers. If necessary, further shortening is carried out by beating (Hollander).

The low demand for fibers of this type (less than one-thousandth of the total amount produced) by manufacturers of paper and wet-laid nonwovens limits the choice of fiber types drastically because efficient production in the usual large-scale plants is possible only in amounts larger than ca. 10 t.

4.3.3. Processing Properties and Characteristics of Synthetic Fibers

The demands made on synthetic fibers by paper process technology do not play an important part in textile technology. They include:

Fiber Length [309], [313], [315]. Fibers that are too long result in “interspinning” (fibers form bundles and knots) during the suspending process. Therefore, the length is restricted and, at the same time, depends on the degree of fiber fineness. A favorable degree of fineness (calculated as fiber length (mm)/fiber fineness (dtex)) is 4–8, which corresponds to a length of 6–10 mm for thin fibers (ca. 1.5 dtex) and

a length of up to 30 mm for coarse fibers (ca. 11 dtex). In view of this variation range, the varying polymer-dependent flexural rigidity does not have to be considered separately. Coarser fibers extend the range of processable fiber lengths.

Overlengths and Deformation of Cut Ends [309], [313], [315] arise through production defects. Overlengths are caused, in particular, by irregular fiber positioning and deformation is due to incorrectly adjusted or blunt blades. In the most unfavorable case, crushing of the cut ends can result in the welding together of neighboring fibers or entire fiber bundles, which cannot be opened during the suspension process.

Spin Finishes. Fibers free of spin finish are not produced. Spin finish—a multicomponent system of anionic or nonionic surfactants—cannot be quantitatively analyzed. It can only be described through its effects. The spin finish determines the wettability and suspendibility of the fibers [315], [316]. In fact, even polyolefin fibers (density < 1.0) can be processed without problems if the formulation is optimal. If the spin finish is unsuitable, air bubbles become attached to the fiber surface in the vat and result in the flotation of the synthetic fibers in the vat or in the headbox. Spin finishes are partially water soluble and can therefore accumulate in closed process water cycles.

4.3.4. Influence of Synthetic-Fiber Properties on Product Properties

4.3.4.1. Polymer-Dependent (Uninfluenceable) Fiber Properties

Density. The density of common synthetic fibers extends over a wide range from 0.9 g/cm³ for polyolefin fibers to 2.1 g/cm³ for PTFE fibers. This has an effect on the number of fibers in the product. The lower the density, the more synthetic fibers are contained in the product, fiber size being the same. Thus, fiber distribution in the paper web becomes increasingly uniform.

Chemical and Physical Stability. In principle, fibers and the corresponding plastics behave in the same way. In borderline cases, however, the synthetic fiber is always less stable because

the lower cross-sectional area of the fiber and the larger surface give rise to a higher rate of damage.

Adhesiveness. In contrast to pulp, synthetic fibers are not capable, to any appreciable extent, of forming hydrogen bonds. Auxiliary agents, e.g., binders (latices), are required to bond synthetic fibers with each other or with other fibers [314]. Alternatively, thermal treatment can be carried out, i.e., sealing or pressing in the softened state (warm calendering). The adhesion of the synthetic fiber surface to a binder film depends on the polymer. Moderate adhesion is observed with PTFE, PP, and PE fibers and good adhesion with PA and PAC fibers. PETP fibers occupy the mid-position.

Fibrillation. Treatment of some types of PAC, especially wet-spun types, in a pulper or Hollander causes fibrillation. A similar effect also occurs in the case of highly oriented (highly stretched) PP fibers. Fibrillation increases the surface areas of the fibers and the fiber flexibility. These are two desirable effects which increase paper strength and reduce flexural rigidity.

If fibrillation is carried out during fiber production, “fibrils” are produced. These are very thin, short fibers which cohere in large numbers due to stemlike linkages and give rise to net-shaped formations. Polyolefin and aramide fibers are especially suitable for this purpose.

Biocompatibility. In particular, PETP fibers have been intensively studied because they are used as implants (substitute for blood vessels). This material can be employed without reservations. It is suitable for use in the hygiene and food sectors provided that the spin finish has been carefully removed. PTFE and PP fibers can also be used for this purpose if they are free of spin finish. A general statement of this type cannot be made for any of the other synthetic fibers.

4.3.4.2. Type-Dependent (Influenceable) Fiber Properties

Fiber Fineness. As a rule, the fineness of fibers is adjustable within wide limits: between ca. 1 and 20 dtex in standard types. Melt-blown fibers extend this range to about 0.05 dtex and

coarse fibers to about 200 dtex. The fineness used depends on the type of paper, the most common range being 1.5 dtex to about 7 dtex.

Fiber Cross Section. Melt-spun fibers, such as PETP, PA, PP, and PE always have circular cross sections. However, other shapes can be produced by changing the shape of the nozzle: ring-shaped (i.e., hollow fibers), triangular, square, and star-shaped. These forms influence flexural rigidity and fiber gloss in particular. The circular cross section gives rise to the relatively lowest flexural rigidity and the most pronounced, sometimes “greasy” gloss. Multi-cornered or star-shaped cross sections stiffen the fibers and lower the gloss. For some synthetic fibers, e.g., PAC or PVA, the cross section depends on the spinning conditions. Consequently, a wide assortment of various noncircular cross sections can be formed, depending on the type and on the producer.

Strength. Strength can be adjusted within wide limits during fiber production by changing the spinning and aftertreatment conditions. As a rule, finer fibers have a higher strength per unit fineness than coarser fibers. The extent to which fiber strength influences paper strength depends primarily on the size of the fiber. Long, thin synthetic fibers increase paper strength to the greatest extent. The degree of fiber strength in itself is of minor importance.

Thermoshrinkage. Synthetic fibers shrink upon application of heat. The degree of shrinkage extends from <2 % for thermofixed types to ca. 40 % for high-shrinking types. The degree of shrinkage in boiling water corresponds to the degree of hot-air shrinkage at about 160 °C. Creases are formed in the product web if uncontrolled high shrinkage takes place during the drying process.

Crimp. In textile applications, fiber crimp helps to increase the volume of yarns and webs and also functions as a processing aid. In the paper and wet-laid nonwoven sector, it is the volume increasing effect, produced by a sawtooth shaped fiber, which is of interest [317]. (Note: three-dimensional screw-shaped crimp usually leads to disturbing “interspinning”). Only the

careful adjustment of crimping geometry (number of crimp curves per unit length, curve height) and spin finish guarantees problem-free processing in paper technology.

Delustering. Melt spun fibers (PETP, PA, PE, and PP) are usually glossy. This interferes with many textile applications. Therefore, the fibers are delustered by the addition of titanium dioxide. The degree of dulling extends from “micromatt” ($<0.1\%$ TiO_2) to “deep matt” ($>2.5\%$ TiO_2). Glossy fibers are usually supplied if the papermaker does not have any special requests when purchasing fibers.

Optical Brightening. “Pure white” fiber types are produced by the use of optical brighteners during spinning (“raw white” is the trade name without brighteners). Fibers of this type fluoresce on exposure to UV light, an effect that can be exploited, e.g., in document papers or used for quality control.

Color. Apart from a few exceptions (aramides, polyimides, PTFE), synthetic fibers are white. However, they can be dyed almost any color during production by means of pigments (spin dyeing). The availability of dyed fibers is still very restricted. This limitation is due to the producer requirement that minimum amounts in the range of 10 t per color have to be purchased. Colored synthetic fibers produce patterns in decorative paper.

Flammability. If high demands are made on the nonflammability, it is necessary to use special types of fibers or flame retardants, which are also widely used in paper technology. The available selection of these fiber types, especially those based on PETP and aramide, is constantly increasing because of worldwide growing demands for industrial and garment textiles.

Electrostatic Properties. Synthetic fibers that are free of spin finish become highly charged by friction and discharge very slowly. In the case of textiles, this unfavorable electrostatic property is reduced to an uncritical level by using antistatic agents, which are an essential component of all spin finishes, or by adding conductive fibers. The same solutions would also be appropriate for papers and wet-laid nonwovens if, as

a result of a high proportion of synthetic fibers, static charges are generated during use or if these papers are used in areas protected against explosion.

4.3.5. Special Fibers: Bonding Fibers [309], [310], [312], [313]

The extensive assortment of synthetic fibers includes special “bonding fibers”. For instance: hot-water soluble PVA fibers and low melting copolymer or mixed polymer fibers.

PVA fibers dissolve at water temperatures of 60°C – 80°C . This effect is utilized in the drying of a wet paper or nonwoven web. The PVA “solution” is distributed in the web during the drying process and then solidifies as a result of further heating after the water has evaporated.

Low-melting copolymer and mixed polymer fibers include copolyamide and copolyester fibers and mixed polymer fibers containing 85 % poly(vinyl chloride) and 15 % poly(vinyl acetate). The melting or softening point can be adjusted in each case by altering the mixing ratio. The typical temperature lies in the range 120 – 200°C for copolyamide and copolyester fibers, and at ca. 160°C for the mixed copolymer fibers. Softening can already occur in water at 100°C .

At least in the case of copolyamide fibers, the melting temperature in aqueous media is considerably lower, so that bonding can occur already during the drying of the wet webs due to the melt–water system formed.

PP and PE fibers are preferentially used as bonding fibers for dry-laid nonwovens. They are softened/melted under the influence of pressure and heat and then bond to other fibers such as PETP. Hot water or saturated steam are inadequate for the softening process. This fact distinguishes the PP and PE fibers from the special “bonding fibers”.

5. Raw Materials for Stock Preparation

5.1. Fibrous Raw Materials

Mulberry fibers, bamboo bark, China grass, cotton, hemp, and old rags were the first plant fibers

that were used for papermaking by the Chinese before the birth of Christ. Later, rice straw was employed, and the Japanese also used mulberry bark, Mitsumata, and Gampi. The Arabs adopted the technology and used linen and hemp as raw materials. Rags also played an important role in the early days of papermaking in Europe. In fact, old rags remained the only raw material till well into the nineteenth century. However, it became increasingly scarce with the invention of printing by GUTENBERG (1440), the publications of the reformation, the introduction and development of the postal service (after 1500), and the invention of the paper machine (patented in 1799 by ROBERT). The search for other fibrous raw materials resulted in a breakthrough in 1844, when KELLER succeeded in producing groundwood mechanically. However, the disadvantages of groundwood soon became apparent, and in the late 1800s methods were developed for the chemical production of pulp suitable for papermaking from annual and perennial fibrous raw material. Today, fibrous wood-based materials (residues from forestry and wood processing) are used almost exclusively for the production of bulk papers (printing papers, packaging papers) in North and South America, Europe, and Japan. Other raw materials are annual plants, such as wheat or maize straw and bagasse.

Today, the composition of the raw material used for paper is influenced more than ever before by the cost of the individual components. Since the cost of the raw materials for papermaking frequently accounts for more than 50 % of the total costs, changes in composition can have a major effect on the total production costs. Quality permitting, it is necessary to economize on fibrous materials not only because they are much more expensive than, e.g., mineral fillers, but also for reasons of environmental protection and better utilization of existing plant raw materials. This is particularly important in view of the fact that in the future the demand for paper can be expected to increase due to rising living standards and the growing world population.

Specialty papers still require fibrous materials that are otherwise too expensive to be used. For instance, document paper, banknotes and identification papers contain not only synthetic fibers, but also cotton and jute pulp from rags.

5.1.1. Pulp

The term chemical pulp for paper refers to fibrous material, usually obtained from wood, that only has a low lignin content as a result of chemical digestion. Paper containing only chemical pulp as the fiber component is called wood-free paper. In other words, this paper is free or largely free of the woody substance lignin. Pulps represent the most valuable constituent of the fiber component and are responsible for the highest attainable strengths. Owing to the elimination of lignin and the partial removal of hemicelluloses, hydrogen bonds can form between the fibers in the papermaking process. These bonds are responsible for the strength of paper, which results predominantly from fiber-to-fiber bonds. Fiber matting is practically of no importance for the very short fibers found in modern pulps. Furthermore, the quality of paper depends on whether the pulp was produced from softwood or hardwood. Softwood pulps have longer fibers (4–6 mm) and therefore give higher strengths, whereas hardwood pulps (fiber length ca. 1 mm and less) produce a more uniform sheet. In addition, the fibers are shortened and fibrillated by the mechanical treatment during beating. The shortening increases the uniformity of the resulting paper but can also lead to a slight loss of strength. On the other hand, fibrillation roughens the surface of the fiber, and the projecting fibrils can form more bonding points. The tensile strength, in particular, can be increased by this process. The type of digestion also plays a very important role here. Sulfite pulps can be beaten more easily, i.e., the strength potential can be increased more quickly by beating. In the case of kraft pulps, the increase in strength is slower but higher strengths can be achieved than with sulfite pulps, although this requires a correspondingly higher energy expenditure. For unbeaten or slightly beaten pulps, there is an increased danger of flocculation occurring in the liquid stock prior to sheet formation. This results in poor formation and nonuniform paper. Since beating also increases the flexibility of the fibers, a higher packing density can be achieved during sheet formation. This increases the strength, but the paper becomes more transparent because of the presence of small amounts of enclosed air. Although this is required for some specialty papers, for the majority of writing and printing papers,

pers it is a disadvantage because writing or pictures on the one side of the paper would interfere with those on the other side.

5.1.2. Mechanical Pulp

Papers that contain pulp produced by mechanical or chemomechanical processes are referred to as wood-containing papers. In the production of mechanical pulp, fibers are separated from the wood as gently as possible by mechanical processing. To produce useable fibrous material, the lignin binding the wood fibers together must be softened. This process is promoted by heating (friction heat) and is achieved more efficiently the higher the moisture content of the wood. The finished stock contains fibers as well as fiber fragments. For this reason, papers produced from pulps of this type have lower strengths than wood-free papers. Another reason for the lower strength is the high lignin content, which blocks hydrogen bonding sites on the fibers and stiffens the fibers themselves. Consequently, in the course of papermaking, fewer bonds can form during dewatering. However, the resulting paper has a higher specific volume. As a result of the higher volume and the presence of amorphous lignin, paper made from groundwood has a good opacity, which in turn allows even papers of low basis weight to be printed on both sides.

The residual lignin in mechanical pulp results in a poorer and less stable brightness level. Mechanical pulps cannot be brightened by oxidative and reductive bleaching to the same extent as chemical pulps because, in contrast to the bleaching of chemical pulp, no delignification takes place. The aging, or yellowing, is accompanied by a decrease in strength by which the paper becomes highly brittle. Therefore, fibrous materials of this type are not suitable for the production of paper for archives.

5.1.3. Wastepaper

In the paper industry, it is a very old tradition to make new paper from wastepaper. Today, wastepaper is also regarded as fibrous raw material because many types of paper either contain a large proportion of wastepaper or are produced entirely from it. There are many different types

of wastepaper, and these require exact classification and separation. This secondary fibrous material has various uses, depending on its history and degree of soiling. After being subjected to a dissolving process, pure grade, unprinted wastepaper can be used for the production of paper either directly or after a purification step. Mixed, unsorted paper, e.g., from household paper collections, can be used only in the production of paper whose quality is not reduced by the presence of many different fibers or accompanying waste paper components. These include, for instance, the middle layer of board or the components of corrugated cardboards. White papers such as newsprint can be made from wastepaper by using the deinking process. In this process, most of the printing ink is removed from printed old white paper (newspapers, magazines). Consequently, deinked stock is considerably whiter than stocks that have only been dissolved. Today, hygienic paper and writing paper are also made from wastepaper. It must be taken into account in the recycling of wastepaper that fibers of organic origin cannot be reused indefinitely because their strength is reduced by the stresses in production processes, such as dissolving, beating, sheet formation, drying and further processing (e.g., printing), and in use. For this reason, the addition of primary fibers (chemical or mechanical pulp) is necessary to maintain the strength of the paper. The stability of wastepaper-containing papers can also be limited because they can contain an uncontrolled, large proportion of mechanical pulp.

5.2. Stock Additives

5.2.1. Additives with Qualitative Effects

The demands made on the quality of many types of paper are very high because of the increased efficiency of modern processing machines. These requirements can no longer be met by natural raw materials alone. A large number of additives are available for altering and improving the properties of paper.

5.2.1.1. Fillers

Mineral fillers have long been used in papermaking. Previously, they were used to obtain a

more closed surface for writing papers and to improve the writing properties. Today, the main reason for the use of fillers in printing papers is to increase printability. They produce not only a higher smoothness and a higher gloss after calendering but also a higher brightness and opacity. In addition to improving quality and printability, mineral fillers are considerably cheaper than fibrous materials and, therefore, efforts are made to include as much filler as possible in the paper in order to reduce material costs. The limits are set by the properties of the sheet because the filler cannot form hydrogen bonds and so reduces the strength by blocking fiber-to-fiber bonds. This applies to both the tensile strength (breaking length, breaking load) and the surface strength (picking resistance), which is especially important in offset printing. If excessive amounts of filler are used, they can no longer be adequately fixed in the paper, resulting in dusting.

The demands made on fillers include the highest possible brightness level for the production of high-quality writing and printing paper, high refractive index so that the opacity is high enough even in thin papers to allow printing on both sides, chemical inertness so that no reactions occur between the filler and other paper components or dyes, and a defined particle size distribution to give a good surface finish. The particle size is also of importance for the production technology because, together with hardness and particle shape, particle size determines the abrasive wear of the paper machine wires. A survey of the properties of fillers is given in Table 16.

Kaolin, an aluminum silicate, is still the most frequently used filler. It is supplied as a slurry or dried in powder form. The hexagonal crystalline platelets of kaolin produce a high gloss in the finished paper after calendering. This gloss depends on the degree of delamination, i.e., the extent to which the platelet agglomerates are broken into individual platelets. The brightness of simple filler kaolins is not especially high. As a result of its chemical composition, kaolin can also be used as filler for papermaking under acid conditions. The retention of kaolin is better than that of granular fillers because of its plate structure.

Calcium carbonate is obtained by grinding limestone and has a granular structure. The greatest advantages here are the high brightness and the somewhat lower price compared to kaolin. This filler must be used in papermaking in the absence of alum because of its solubility in acid media. This still causes problems in the production of wood-containing papers. Calcium carbonate is used predominantly to produce papers with a matt surface. Precipitated grades are only employed for specialty papers, primarily because of its high cost.

Talc is hydrophobic and is therefore used when dealing with resin problems. Resin, which is problematic in paper production, is carried into the process with fresh fibers or on the sticky components of wastepaper. Talc particles are adsorbed on the resin and render these interfering substances harmless by covering them. As a result of its pronounced platelet structure, the use of talc as filler gives good retention and paper surfaces that have a high smoothness and gloss.

Titanium dioxide has the highest brightness and, because of its high refractive index, gives paper of the highest opacity. It is because of its excellent opacity that titanium dioxide, despite high cost and poor retention, is still indispensable as a filler especially in the production of thin printing papers. However, due to its high cost and for reasons of environmental protection, titanium dioxide is used in combination with extenders. These extenders are other minerals which are capable of replacing titanium dioxide to a limited extent while producing similar results.

Gypsum is currently not used on a large scale because of its high solubility in water and the resulting side reactions that occur in the circulation system of the paper machine. The high availability of gypsum, especially from flue-gas desulfurization, has stimulated intensive research in ways of using gypsum without these side effects.

Various other mineral fillers are used only for specialty papers because they are expensive or have special properties. *Barite* (rhombic barium sulfate) has high whiteness and is of importance for high-quality writing and printing papers, and for photographic papers. *Magnesite* (magnesium carbonate) is of some importance in the production of cigarette papers. *Diatomaceous*

Table 16. Properties of fillers

Filler	Chemical composition	Crystal form	Brightness, % ISO	Refractive index	Density, g/cm ³	Specific surface, m ² /g	Mohs hardness	Surface energy, 10 ⁻⁷ J/cm ²
Kaolin	Al ₄ (OH) ₈ [Si ₄ O ₁₀]	hexagonal platelets	70–90	1.56	2.8	4–7	1–2.5	508–668
Calcium carbonate	CaCO ₃	orthorhombic	82–92	1.58	2.7	3–4	3	78
Ppted.* calcium carbonate	CaCO ₃		95–98	1.56	2.7	3–10	3	
Talc	Mg ₃ (OH) ₂ [Si ₄ O ₁₀]	monoclinic lamellas	70–88	1.57	2.7	5–20	1	68
Titanium dioxide	TiO ₂	tetragonal	97–99	2.60	4.2	8–11	6–6.5	640
Gypsum	CaSO ₄	orthorhombic	92–98	1.58	2.8	0.7–2	2	39
Barite	BaSO ₄	rhombic	93–95	1.64	4.5	0.7–2	3–3.5	
Magnesite	MgCO ₃				2.9–3.1		4–4.5	
Diatomaceous earth	SiO ₂		60–90	1.33	2.3			
Synthetic ppted.* silicates	mostly Al or Ca silicates	mostly amorphous	94–96	1.54	2.1	30–150		
Aluminum hydroxide	Al(OH) ₃	platelets pseudo-hexagonal	96–98	1.58	2.4	5–9	2.5	

* Ppted. = precipitated.

earth, an amorphous silicium dioxide with a very low specific weight, can be used for very highly voluminous papers. *Synthetic precipitated silicates* and *aluminum hydroxide* also give a high specific paper volume and especially good printing properties.

Synthetic organic fillers can give a printability comparable to that attained with mineral fillers. In particular, the opacity is increased in combination with high volume. However, these fillers are seldom used partly because of problems with the uniform distribution in the paper and, above all, because of the high cost.

5.2.1.2. Strength Additives

It is possible to distinguish between three basic types of paper strength. The initial wet strength is the strength of the paper in the wet state before drying. It greatly influences the operational characteristics of the paper machine. The dry strength which the paper possesses in the finished state is responsible for a trouble-free running in further processing steps, e.g., in a printing press or packaging machine. Finally, the wet strength describes the strength of the paper after it has been wet.

Substances that improve dry strength are of the greatest importance in papermaking because they allow the use of cheaper raw materials, such as fillers. Dry-strength additives form additional

hydrogen bonds, which lead to stronger fiberto-fiber bonding. In this way, it is possible to compensate for the absence of hydrogen bonds due to the presence of mechanical pulps or fillers. Starches and their derivatives, plant gums, cellulose derivatives, and synthetic polymers are used for this purpose. These substances are usually added to the pulp slurry and, therefore, their retention in the stock often poses a problem. In general, the use of these additives is determined by economic considerations, i.e., whether it is more economical to use expensive raw materials or even more expensive binders, which, however, need only be used in small amounts to produce the desired strengths.

The wet strength of paper is essential for some of its applications. For instance, some packaging papers must be resistant to rainwater, while it should be possible to remove labels from bottles without turning the wash solution into a fiber slurry. Wet-strength additives protect the natural hydrogen bonds from attack by moisture and form additional water-resistant bonds. Wet-strength additives include poly(ethylene imines), polyamides, and urea– or melamine– formaldehyde condensates.

5.2.1.3. Sizing Agents

Paper usually has a high absorbing capacity for liquids because of its hygroscopic fibers and the many fine pores of the web. However, this has

a negative effect on the writing properties and printability of the paper. The absorptivity can be reduced by the addition of sizing agents to the pulp or by their application to the surface of the paper. Sizing makes the paper partially hydrophobic and prevents the spreading of ink or color, but not the receptivity for these fluids. In the production of hand-made paper, individual sheets were coated with starch or animal glue which covered the fine pores in the paper, resulting in a certain degree of sizing. This process corresponds to modern surface sizing, which is used either independently or to supplement pulp sizing, and is usually carried out with a size press in the paper machine. The most widely used sizing agent in pulp sizing is still rosin size, which is a partially saponified colloid or dispersion of colophonium. Sizing is achieved by distributing the size as finely as possible in the pulp slurry and subsequently precipitating it on the fibers as an aluminum resinate by adding aluminum sulfate. However, this process served as the basis for the paper disintegration (see Chap. 12) feared by libraries and archives because the acid residues remaining in the paper reduce the elasticity of the fibers and make the paper brittle and unusable. Today, printing paper is usually produced in neutral to slightly alkaline systems without the use of aluminum sulfate. This requires either synthetic sizing agents, primarily dimeric alkylketenes, or new precipitants for rosin size, which are in part still being developed.

Furthermore, aluminum sulfate is also an excellent precipitant for interfering substances and is therefore still very difficult to dispense with when producing wood-containing printing paper. The new precipitants such as polyDM-DAAC [poly(dimethyl diallyl ammonium chloride)] must also take over this role.

5.2.1.4. Dyes

The coloring of paper can be achieved by pulp dyeing, dip dyeing, or surface dyeing (see Chap. 10). A large number of physical and chemical forces are involved in each of these dyeing processes. The most important processes are:

- 1) Penetration of the dye molecules into the capillaries and cavities of the pulp fibers
- 2) Adsorption of the dye molecules onto the inner and outer fiber surface

- 3) Formation of a sparingly soluble complex in the presence of salts or fixing agents

The natural inorganic pigments possess a low dyeing power, but are very lightfast. The synthetic inorganic dyes have improved dyeing power. Natural organic dyes are no longer of importance. The synthetic organic dyes make up the most important group; they include basic, acid, and direct dyes, as well as pigments.

Basic dyes are salts of organic bases which cannot bond with pure cellulose. For this reason, they are usually used only for wood-containing papers because they form sparingly soluble colored lakes with the acidic groups of lignin.

Acid dyes are usually the alkali-metal salts of dye sulfonic acids. They have no affinity for plant fibers and must be precipitated as colored lakes in the paper stock. This is achieved with aluminum sulfate, a substance used frequently in the paper industry; however, the use of rosin size gives better binding.

Direct dyes are usually the sodium salts of azo dyes containing sulfo groups. They are absorbed by bleached pulp fibers without the addition of a fixing agent. However, they are not very suitable for the dyeing of wood-containing stocks because the incrusting components (binding substances) of wood prevent uniform dyeing. The lightfastness is usually good, but the colors attainable are generally not as brilliant as those produced by acid and basic dyes.

In pigments the colorant is present in a water insoluble, finely dispersed form. The binding of the pigment to the fibers is improved by rosin sizing and the use of aluminum sulfate. Fixing agents must be employed during paper-making in neutral or slightly alkaline systems. The lightfastness of pigments is excellent and mottling usually does not occur. Since these pigments are expensive, they are used only for specialty light-fast papers. The naturally occurring coloring pigments such as ochre, terra sienna, or umber are of little significance at present. However, the synthetic inorganic (iron oxide, cadmium, chromium oxide), the organic (azo and polycyclic), and the metal complex pigments are very important.

In combination dyeing, it should be taken into account that various dyes, e.g., acid and basic or direct and basic, must be dissolved separately

because they would otherwise precipitate each other during the dissolving process.

Dyeing is also of some importance for white papers, which are treated with small amounts of a blue dye to achieve a color shift and remove the yellowish tinge. This process is called shading.

5.2.1.5. Optical Brighteners

Optical brighteners are substances which transform ultraviolet light into visible blue light. Paper is treated with optical brighteners to achieve a whiter visual appearance. Although this effect can also be obtained with shading dyes, optical brighteners increase the luminosity as well. These substances are mainly derivatives of diaminostilbenedisulfonic acid and can form hydrogen bonds, allowing them to absorb onto cellulose fibers in the same way as direct dyes.

Optical brighteners act only when the light incident on the paper has an UV component, i.e., they do not act in artificial light. They lose their effect with increasing application of printing colors. Furthermore, they are not suitable for long-life papers because they are not resistant to sunlight. For this reason and because of pollution problems, the use of optical brighteners in paper is still controversial.

5.2.1.6. Chemicals for Specialty Papers

A large number of specialty papers exist for various applications. However, only a few specialty papers and the additives required in their production will be mentioned here.

Fire-resistant papers are used for wallpaper base materials, Chinese lanterns, and paper streamers. These papers are produced by the addition of flame retardants to the pulp or to the coating. The flame retardants either release incombustible gases on heating which prevent the entry of atmospheric oxygen, or produce a nonflammable melt when heated that surrounds the paper. Examples include calcium chloride, magnesium chloride, diammonium ethyl phosphate, and mixtures of zinc borates, antimony oxides, and organic halide salts [324] as well as inorganic bromides and oxybromides.

Anticorrosion paper is impregnated or coated with chemicals that inhibit corrosion, e.g.,

sodium nitrite or sodium benzoate. The paper is coated by deposition of the chemicals from the vapor phase. These papers prevent the rusting of iron parts and the tarnishing of silver, aluminum, and copper.

5.2.2. Processing Aids

5.2.2.1. Retention Aids

The term retention refers to the holding back of the papermaking stock on the wire during dewatering. The fibers are retained on the wire fractions and fillers better than the fines, which may be washed through the wire and even through the fiber mat formed. Retention aids increase adsorption of fine particles onto the fibers so that they are retained with the fibers. This adsorption must be able to resist the high shear forces which arise in modern high-speed paper machines. Both cationic and anionic retention aids are used. Although nonionic products are rarely employed, they also produce good effects if their molecular length is sufficiently large. The effect of retention aids is not only dependent on the charge, but is also closely related to the molecular length. However, the particularly effective high molecular products tend to flocculate. The fibers themselves form larger flocks by adsorption resulting in a nonuniform paper. Such a cloudy formation of the paper sheet decreases both the strengths and the printability.

The retention aids usually employed are synthetic polymers, such as poly(ethylene imine) or polyacrylamide, cationic starches, and carboxymethylcelluloses.

5.2.2.2. Defoamers

Foam is a dispersion of air in water and has physical and chemical causes. The violent motion of water during the drainage procedure and in the entire cycle, especially at high paper machine speeds, produces a very stable foam in the presence of surface active agents and colloidal surface active film formers, such as starch and hemicelluloses. The most effective way to prevent and control foam is to determine the cause in each case so that the appropriate defoamer can be employed. Defoamers include mixtures

of higher alcohols, salts of fatty acids, and water-emulsible phosphate esters.

5.2.2.3. Biocides

The large number of organic substances (e.g., starch), which are not only employed for various purposes, but can also originate from the use of coated wastepaper, serve as nutrients for microorganisms, and typical paper-machine temperatures are usually ideal for the growth of these organisms. The nutrients that are important for bacterial growth become enriched due to their low retention in the paper web and the closed paper-machine cycles. To control slime formation, an exact examination of the raw materials and the strains of microorganisms introduced into the cycle is required in order to find a solution which is both economically and environmentally acceptable. Slime control agents include bromine, sulfur, nitrogen, or chlorine compounds, and acetic acid derivatives. Microorganisms can develop resistance to particular biocides, and it is therefore advisable to alternate between different products. With regard to biological wastewater purification, it is important that completely degradable products are used.

5.2.2.4. Dispersing Agents

Dispersing agents are required for both fibers and fillers. They increase the toxicity of slime control agents and, due to their (usually) anionic charge, they disperse resins and other sticky impurities originating from the pulp or wastepaper.

In the dispersion of fillers and coating pigments, dispersing agents prevent secondary agglomeration which would lead to disturbances in the paper sheet. Dispersing agents are also necessary for controlling the viscosity of filler and coating pigment suspensions because without these agents, the solids content of the suspensions required for economic and technological reasons would not be attainable. Dispersants are either added during redissolving after the drying process, where they increase the effect of shear forces of the dispersing machines, or they are added during wet grinding of the filler material. Dispersing agents are used in the transportation and storage of fillers and coating pigments to maintain them in a pumpable slurry form.

5.2.2.5. Complexing Agents

The presence of heavy metals negatively influences many production processes and paper properties. In particular, they interfere with the bleaching of wood pulp by reducing the effect of bleaching chemicals. Complexing agents that contain amino and carboxyl groups mask metal ions effectively. Chemical compounds of this type are nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and hydroxyethylethylenediaminetriacetic acid (HEEDTA), which mask metal ions by chelation. Other complexing agents include the soluble salts of oxalic acid, citric acid, tartaric acid, gluconic acid, amines, and ammonia. From the point of view of environmental protection, the use of these chemicals is controversial because they are only poorly biodegradable.

5.2.2.6. Precipitating and Fixing Agents

Precipitating and fixing agents are used primarily for the precipitation of soluble substances onto the fibers. Acid and direct dyes require cationic fixing agents, and basic dyes require anionic agents. Fixing agents form sparingly soluble complexes with the dyes, and coarse floculates when used in too high a concentration. Therefore a compromise must be made between the need to minimize the turbidity of the coloring and the requirement to maintain the wastewater as clear as possible. Increasing the amount of fixing agent leads to increased dye fixation and clearer wastewater, but also lowers the brilliance of the coloring. Fixing agents are used for tissue coloring to prevent bleeding.

Aluminum sulfate is the most commonly used precipitating agent. Other agents include condensation products of formaldehyde, urea, dicyandiamide, melamine, and condensation products of aromatic sulfonic acids with formaldehyde.

5.2.2.7. Drainage Aids

In the drainage of paper, board, and cardboard made from materials that are difficult to dewater (e.g., highly beaten pulps or wastepaper) the

use of drainage aids is often necessary. Drainage aids are usually ionogenic polymers similar to those used as retention aids. Drainage aids function by binding the fines to the fibers. This prevents their forming flocks which would block the pores between the fibers during formation of the paper web, thus hindering drainage. In order that this process can function smoothly under the high shear forces in modern paper machines, the order of addition of the raw materials and additives must be optimized. The position at which the drainage aids are added to the stock flow is equally important, since this determines the magnitude of the stresses to which the bonds formed by the drainage aids are subjected at various points in the paper machine.

5.2.2.8. Additives for Wastepaper Processing and Deinking

The removal of ink from wastepaper is determined by the type of ink binder and chemicals used. Two separating processes are employed: flotation and washing. The most widely used method in Europe is flotation. The most important chemical is sodium hydroxide, which is used to adjust the pH to 10–11. Saponifiable binders in the ink are saponified. In addition, the fibers swell substantially in this environment, making it easier to detach the dye particles from the fibers. However, sodium hydroxide solution also causes a strong yellowing of wood-containing stocks. In order to prevent this, hydrogen peroxide is used because, apart from its saponifying effect, it also acts as a bleach. In addition, water glass is added to stabilize the hydrogen peroxide. Since hydrogen peroxide is more effective at higher concentrations, the dissolving process is carried out at stock consistencies of 12–15 % (thick stock dissolver or dissolving drums). Soaps and fatty acids are used as dirt collectors and flotation agents. They form calcium soaps with hard water or the calcium carbonate from the coating or filler of the wastepaper. Calcium chloride must be added if the water is not sufficiently hard. For higher quality papers, further bleaching with sodium dithionite and/or hydrogen peroxide may follow. Coated papers can be deinked more easily because the inks are fixed only with the coating. The wastewater sit-

uation can be controlled very well; however, the COD value increases with increasing pH.

The wash deinking process is used in North America. After saponification, the pigments are removed from the stock by washing. Since large amounts of wastewater are produced and the solids losses are high, it is not surprising that the flotation deinking process is also gaining a foothold in North America.

Only pure-grade papers can be used in the deinking process. Newspapers and magazines are used in the largest amounts. Because of the printing inks still present in the finished stock, deinked stocks can be employed only for newsprint (up to approx. 60 %), hygienic papers and improved recycling writing paper (100 %), and in board production.

6. Stock Preparation

Stock preparation denotes the operations that must be undertaken to convert raw stock into finished stock (furnish) for the paper machine. The raw stocks used are the various types of chemical pulp, mechanical pulp, and wastepaper. Raw stock is available in the form of bales, loose material, or, in the case of integrated mills, as suspensions. The finished stock is a suspension of a defined quality as far as the mixture and condition of the fibers, additives, and impurities are concerned. This quality essentially determines the properties of the paper produced [325].

A stock preparation system consists of several process steps that are adapted to one another. These systems differ considerably depending on the raw stock used and on the quality of furnish required. Thus, refining is of central importance in the preparation of virgin pulp, whereas the separation and neutralization of interfering components are the main purposes of wastepaper preparation [326].

6.1. Process Steps

The important steps in stock preparation, their location in the course of the process, and the corresponding machines used are presented in Figure 44. It can be seen that some process steps are required almost throughout the entire process, whereas others are used only at the beginning

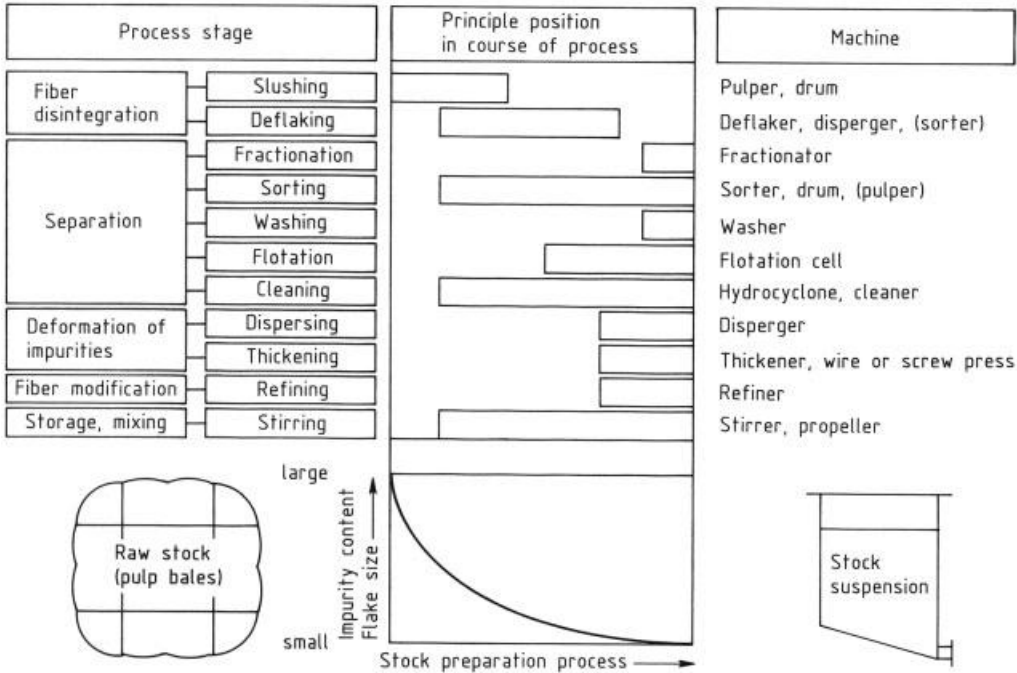


Figure 44. Process stages in stock preparation and the corresponding machines (courtesy of Sulzer Escher Wyss)

and at the end of the process [327]. It is possible to use different machines for a particular process step. In addition, it should be taken into account that most of the machines not only have one effect, but can also exert side effects that may or may not be desirable.

6.1.1. Fiber Disintegration

The fiber networks in raw stock should be broken up as quickly as possible with a minimum of mechanical work and chemicals so as not to alter the fiber properties. In this process, the matrix strength, which results primarily from hydrogen bonds, is reduced greatly by wetting with water. In the case of wet-strength wastepaper, this process is promoted by elevated process temperatures (e.g., $>70^{\circ}\text{C}$) and by the addition of chemicals (acidic or alkaline). The fiber matrix is broken up by the application of tensile stresses. Accelerative forces, shear forces, and holding forces due to mechanical clinging are decisive [328].

Slushing. The first rough disintegration to give a pumpable suspension is carried out in a

pulper or dissolving drum. The pulper (Fig. 45) usually consists of a vessel with a rotor and a perforated plate that is kept free with the help of clearing vanes. The axis of the rotor is arranged vertically, horizontally, or inclined. The fiber consistency in the pulper is 3 – 15 % [329], and the peripheral velocity of the rotors is correspondingly 12 – 24 m/s.

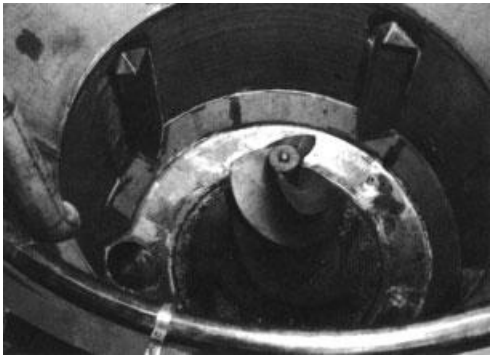


Figure 45. View of an empty pulper drum (courtesy of Sulzer Escher Wyss)

Depending on the raw stock and the type of pulper, the specific energy consumption for

slushing is ca. $10\text{--}40\text{ kW} \cdot \text{h/t}$ and higher for wet-strength papers.

In many cases, the first separation of impurities from the fibers takes place in the pulper. This can occur by means of:

- 1) A ragger, which continuously removes wires and spinnable parts from the pulper tank;
- 2) Periodic removal of the residues retained by the pulper sieve. For this purpose, operation of the pulper is interrupted and the residues are washed out; and/or
- 3) Withdrawal of a partial stream from the pulper which is fed forward into the storage chest after coarse cleaning by a drum screen or coarse pressure screen. Other, older systems return this cleaned partial stream diluted back into the pulper.

High-consistency pulpers are designed increasingly without a perforated plate so that the stock is discharged from the pulper and then coarse screened. Drums are used only for dissolving wastepapers that have very low wet strengths (see Section 6.3).

Formerly, slushing, deflaking, and refining were performed in a single stage in a hollander. However, hollanders do not meet modern production and capacity requirements and are therefore no longer used [330].

Deflaking. The flakes (fiber bundles and pieces of paper) that pass through the pulper screen are separated into individual fibers in a deflaker. A disperging stage may be required in the case of wastepaper with high wet strength. It is more economical to carry out the process of fine disintegration outside the pulper in specially designed machines than in the pulper itself.

The deflaker shown in Figure 46 has a rotor and a stator disk, each of which bears three interlocking slotted rings. As the suspension passes through the slots, accelerative forces, shear forces, and holding forces due to the clinging of the edges break the flakes into individual fibers.

The deflaker operates at stock consistencies of 3–6 %. The peripheral velocity of the disks is up to 30 m/s. The specific energy consumption is $20\text{--}60\text{ kW} \cdot \text{h/t}$ for easily deflakable stocks. Stocks that are more difficult to deflake must be subjected to two or more runs through the deflaker [331].

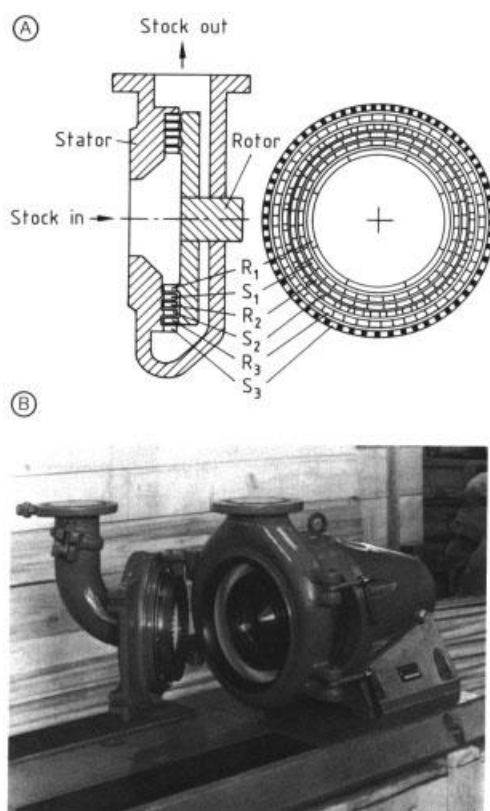


Figure 46. Schematic (A) and photo (B) of a deflaker (courtesy of Sulzer Escher Wyss)

Flakes of high-wet-strength materials can usually be broken down only with a disperger (see Section 6.1.3).

6.1.2. Separation

Separation refers to the processes that are used to separate substances of the same type (fractionation of fibers) or foreign substances (screening, washing, flotation, and cleaning) from fibers in a suspension.

Fractionation. By means of screening, the fibers present in the suspension are divided according to length into a fraction enriched in short fibers and a fraction enriched in long fibers and flakes [332]. These partial streams are then subjected to further treatment separately (deflaking, refining, and disperging) and are used, e.g., for the individual layers of multilayer products such

as board. The fractionating machine usually resembles a pressure screen, but the sieve holes are smaller than those of a pressure screen. Until now, fractionating machines based on other concepts have not been used in the paper industry.

Screening. The objective of screening is the removal of interfering substances from the fiber suspension that differ from the fibers in shape and deformability. The suspension is passed through a screen with apertures in the form of slots or round holes, and the impurities to be separated are rejected by the screen. The screen can be flat or cylindrical and the suspension can be pressurized or pressureless. Clearing devices produce pressure pulsations and thus prevent blocking of the screen. They also aid the transport of the impurities to the overflow.

Rough Screening. The screen apertures of pulpers, secondary pulpers, and drum screens used for rough screening are about 4–25 mm, i.e., they are usually capable of only rough screening.

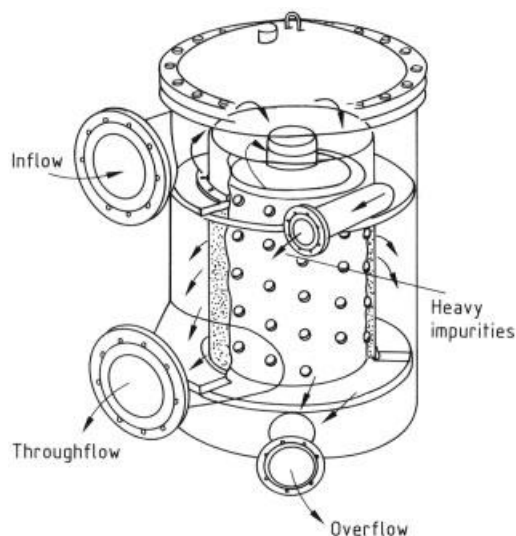


Figure 47. Schematic of a pressure screen with a cylindrical screen basket (Omniscreen) (courtesy of Sulzer Escher Wyss)

Fine Screening. For fine screening with a high screening quality, screens with aperture diameters in the range of ca. 0.8–2.4 mm and slot openings in the range of 0.2–0.8 mm are used.

The screening efficiency depends on the geometry of the screen and the rotor, the direction of flow of the suspension towards the surface of the screen, the volumetric ratio of the overflow to the inflow, and on the specific throughput [333].

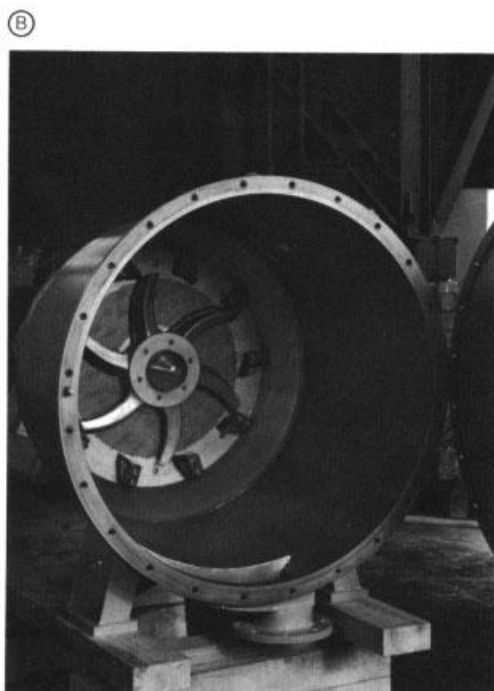
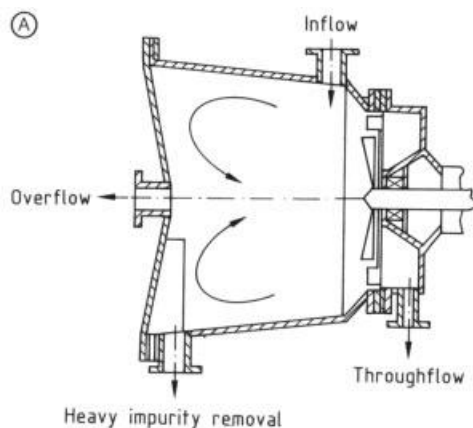


Figure 48. A) Schematic of a flat pressure screen; B) View of flat pressure screen after opening (courtesy of Sulzer Escher Wyss)

A pressure screen with a cylindrical sieve is shown in Figure 47. These screens operate with stock consistencies up to ca. 4 %, and the specific

energy consumption is $5-20 \text{ kW} \cdot \text{h/t}$. Figure 48 shows a flat screen [334], [335]. Flat pressure screens require stock consistencies of $3-4.5\%$ and have a specific energy consumption of $20-40 \text{ kW} \cdot \text{h/t}$. Pressure screens in the approach flow system operate with stock consistencies of ca. 1% .

In the case of pressure screens, the overflow is highly laden with interfering substances and also contains a large number of fibers. These fibers should be recovered in the tail screen without impairing the total screening result. The vibrating screens used in the past as tail screens (cf. Fig. 21) are suitable only for the separation of larger impurities, while the smaller impurities are returned to the cycle in front of the first-stage screening device. Hence, the feeding back of this throughflow with all these impurities leads to a reduction of quality.

A highly effective tail screen is shown in Figure 49 [336]. Similar to the vibrating screen, it has a pressureless mode of operation, and rotors fitted with vanes are used to transport the stock and keep the screen clear. This sorter requires a stock consistency of $1-4\%$, and it has a specific energy requirement of $20-40 \text{ kW} \cdot \text{h/t}$. Screens with aperture diameters in the range of $1.0-4.0 \text{ mm}$ or slot openings of $0.6-1 \text{ mm}$ are used. The rejects accumulate in a form that poses no disposal problems. As a result of the good screening effect, the throughflow contains only a small amount of impurities and can therefore be fed forward into the mainstream production.

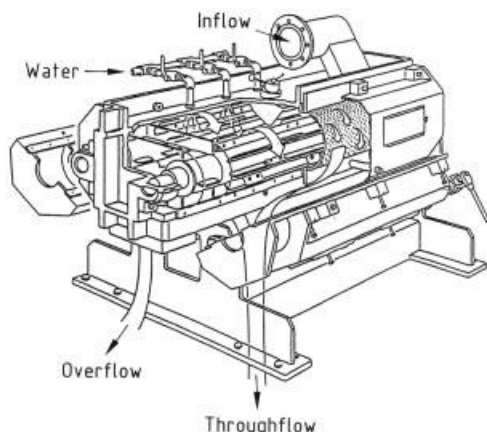


Figure 49. Schematic of a tail screen (reject sorter) (courtesy of Sulzer Escher Wyss)

Washing [337–340] is, in principle, also a screening and fractionating process, in which particles smaller than $30-40 \mu\text{m}$, such as ash, printing inks, and inactive fines, are removed from the suspension. In the washing stage, the suspension is dewatered, and the solids that pass through the screen represent the washing effect. Upright inclined screens, curved screens, round screens, inclined screws, or horizontal presses are used for washing, but they all produce a limited washing effect. An effective washer is represented by the machine shown in Figure 50, which functions in a manner similar to the web-forming part of a paper machine. The suspension emerging from the headbox with a consistency of $0.7-1.4\%$ is dewatered to a stock consistency of $5-12\%$ by a wire running over a central roll. The thickness of the resulting fiber layer, i.e., the dry basis weight, essentially determines the washing effect. The machine is usually operated at a speed of $400-1000 \text{ m/min}$ and $30-40 \text{ g/m}^2$ dry basis weight. The specific energy consumption is $5-10 \text{ kW} \cdot \text{h/t}$.

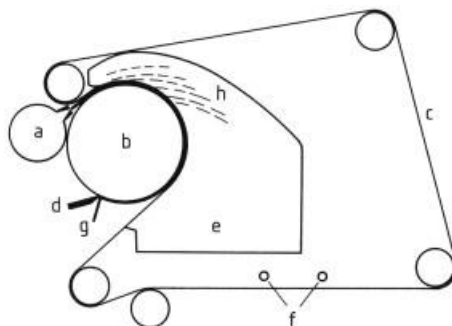


Figure 50. Schematic of a washer for the removal of ash and fines from a fiber suspension (Variosplit) (courtesy of Sulzer Escher Wyss)

a) Distributor; b) Center roll; c) Wire; d) Take-off doctor; e) Filtrate tray; f) Wire cleaning; g) Accepts; h) Filtrate

The washing effect can be further improved by dispersing the printing inks and coating particles contained in the stock in a preceding stage.

Flotation [341–345]. A distinction is made between total flotation, which should remove all the solids from a suspension (e.g., purification of the circulation water) in an expansion flotation step, and selective flotation, in which impurities made hydrophobic are separated from the

fiber suspension by aeration (deinking flotation) [341].

In *total flotation* the solids are flocculated by addition of cationic and anionic chemicals [e.g., poly(aluminum chloride), polyacrylamide, poly(ethylene oxide)]. About a third of the clarified water is saturated with air at a pressure of ca. 0.9 MPa, and is then mixed with the remaining suspension after being expanded. The fine air bubbles formed during expansion adhere to the flocs and cause them to float. The clarified water and the floating sludge are withdrawn separately. A system for the purification of suspensions (e.g., the filtrate from the washing stage) is described in [343], [344] (see also Chap. 8).

Selective flotation is the specific removal of dirt from the suspension. For this purpose, air is mixed thoroughly with the suspension. The air bubbles then become attached to the dirt particles, which have previously been rendered hydrophobic, and carry them to the surface of the suspension. The resulting foam containing the dirt is withdrawn separately from the suspension. Selective flotation is used in wastepaper preparation to remove printing inks from the fiber suspension (deinking, see Section 6.3) [341].

Cleaning is the separation of impurities from a fiber suspension in a centrifugal field. The sinking and floating properties of the impurities to be removed must differ from those of the fibers. Cleaning is carried out in hydrocyclones [346]. A distinction is made between heavy-particle and light-particle cleaners, depending on the purpose of separation, and between cocurrent and countercurrent hydrocyclones, depending on the direction of the main flow. The outward (heavy particles) or inward (light particles) radial velocity of particle motion is determined by the equilibrium between the centrifugal force and the resistance to motion of the impurities. The required rotation of the suspension is usually produced by the entering velocity of the suspension into the hydrocyclone (i.e., by the pump energy), but sometimes by a rotor in the head of the hydrocyclone. The centrifugal acceleration of cleaners operating at low stock consistencies ($\leq$ ca. 1.2 %) is up to 1000 g ($g = 9.81 \text{ m/s}^2$) and that of high consistency cleaners ($\leq$ ca. 6 % stock consistency), up to 40 g .

Three-, four-, and five-way cleaners are used, but the efficiency of the four-way and, above all, the five-way types is much lower than that of the three-way types [347].

Most cleaner plants are multistage systems (up to 5 stages). The overflow from the first stage is fed into the second stage. The material that flows through the second stage is returned to the inflow of the first stage and the overflow is led to the next stage, and so on in a cascade arrangement. Each stage consists of several cleaners operating in parallel because of the high flow rates to be processed [348–350].

6.1.3. Deforming/Dispersing of Impurities

In the dispersing system, impurities should be deformed so that they are separable in a subsequent screening stage and, above all, reduced in size to such an extent that they no longer interfere in the papermaking process or in the paper. In addition, residual fiber flakes from high-wet-strength papers should be disintegrated. Dispersing is carried out with high shear forces at high stock consistencies. A dispersing system has the functions of thickening, heating, and generating shear forces (Fig. 51). In order to apply high shear forces, the viscosity of the suspension is increased by dewatering it to 22–30 % stock consistency. Wire presses, double wire presses, or screw presses, frequently combined with thickeners, are used for this purpose. The stock is heated with steam to ca. 95 °C (pressureless) or up to 130 °C (under steam pressure) in a heating screw to reduce the shear strength of temperature-sensitive impurities such as wax, bitumen, and adhesives [351].

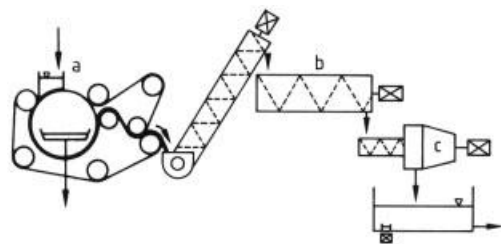


Figure 51. Schematic of a dispersing system (courtesy of Sulzer Escher Wyss)

a) Wire press; b) Heating screw; c) Disperger

The disperger has fittings that consist of a series of toothed rings. The stator and rotor rings are interlocking and leave a very narrow gap. The peripheral velocity is ca. 50–60 m/s. The stock is driven through the gaps between the teeth and is repeatedly subjected to an intense shearing stress due to the high relative velocity between stator and rotor (Fig. 52). The specific energy transferred to the stock depends on the stock, stock consistency, stock throughput, and on the width of the gap, and is in the range 30–120 kW · h/t. The magnitude of the specific energy input determines the quality and strength characteristics of the stock. Dispergers can also be used as mixers, e.g., for mixing bleaching agent with stock in high-consistency secondary fiber bleaching.

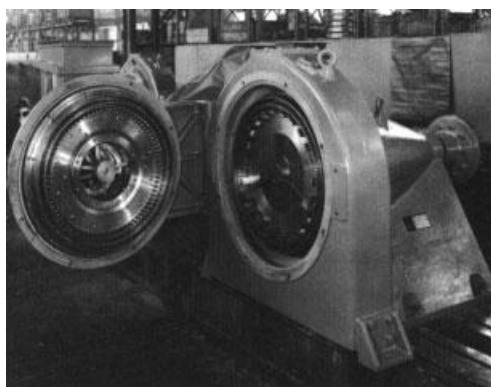


Figure 52. Disperger, with open casing, showing the fillings (courtesy of Sulzer Escher Wyss)

In other systems a slower running kneader (10–20 m/s peripheral velocity) is used instead of the fast running disperger [352], [353].

6.1.4. Refining

Refining is used to improve the bonding ability of the individual fibers of the finished paper as well as the fiber properties with regard to formation quality in paper web forming. The refining process determines the properties of the finished product, e.g., whether an opaque printing paper or a transparent drawing paper has to be formed [354]. Refining is carried out in low and wide-angle conical refiners or disk or double disk refiners. The refiner fillings are equipped with bars and are designed as rotor and stator. The angle

formed by the bars of the rotor and the stator is called the bar or cutting angle. The bars are subjected to wear during operation. The edges of the bars, which run against each other, develop a shape that depends on the bar material and the load applied and has a great influence on the refining result [355].

During operation, the rotor and the stator are pressed together electrically or pneumatically. This influences the specific refining energy, i.e., the amount of refining energy transferred to a specific amount of stock. Besides the specific refining energy, the specific edge load is also used to assess refining. This is the ratio of the effective refining energy to the edge length per second. The effective refining energy is the difference between the power input and the pumping work of the refiner fillings produced at a rotor peripheral speed of up to 25 m/s [356]. The edge length per second refers to the length formed per second by the edges of the bars as they move past each other.

A distinction is made between shortening refining, which mainly involves cutting of fibers, and fibrillating refining, which involves the splitting of the outer layers of the fiber walls, a process that greatly increases the surface area of the fibers and their bonding ability.

Low cutting angles, sharp bar edges, and high specific edge loads result in more cutting refining. Large cutting angles, rounded bar edges, and lower edge loads have a more fibrillating effect. The beating action of a refiner is assessed by the beating energy required to increase the degree of beating ($\text{kW} \cdot \text{h t}^{-1} \text{ } ^\circ \text{SR}^{-1}$) [357]. This value is influenced by the type of stock processed, the degree of beating, and the type of beating (shortening/fibrillating), and is ca. $0.5\text{--}2 \text{ kW} \cdot \text{h t}^{-1} \text{ } ^\circ \text{SR}^{-1}$.

6.1.5. Storage and Mixing [358]

The storage and mixing of suspensions require different types of agitators. In the former case, the solids should remain suspended, i.e., settling out or floating on the surface should be prevented. In comparison, mixing involves the blending of the different components of the suspension. Agitators of the type shown in Figure 53 are used for storage. This rotating agitator moves automatically in a circular path through

the stock. In this way, a definite part of the contents of the chest is stirred about every 20 seconds. The rate of rotation of the agitator is 60 rpm and the specific power is $0.02 - 0.1 \text{ kW/m}^3$.

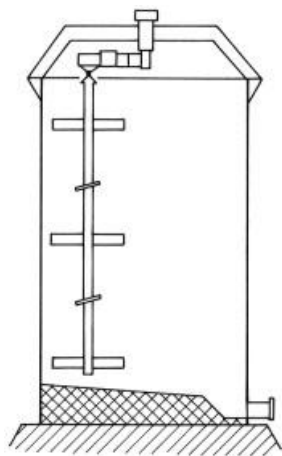


Figure 53. Schematic of a storage chest with rotating agitator to prevent settling out of fibers (Economix; courtesy of Sulzer Escher Wyss)

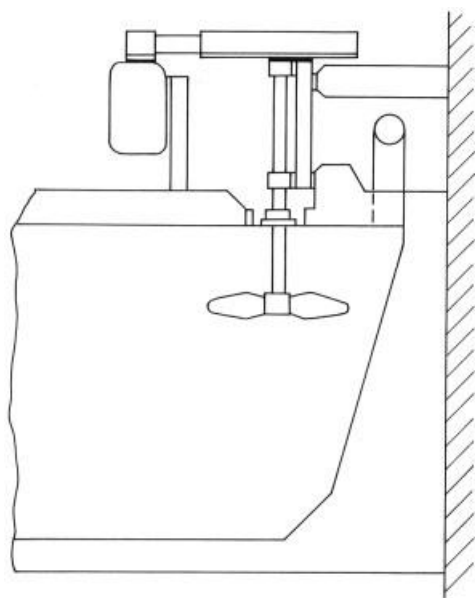


Figure 54. Schematic of a chest propeller for stock mixing (courtesy of Sulzer Escher Wyss)

The chest propeller shown in Figure 54 is used for intensive mixing. This type of agitator requires more energy because the entire con-

tents of the chest are circulated continuously. The chest propeller rotates at ca. 130 rpm, and the specific power is ca. 0.5 kW/m^3 .

6.2. Preparation of Primary Raw Stocks

Complete stock preparation for a paper machine usually consists of several lines, in each of which different raw stocks are prepared. These are then mixed in the mixing chest in proportions appropriate for producing a particular grade of paper. The processing of broke from the paper machine is also a part of this process. The broke is collected in the paper machine in the couch broke chest after the wire part, and in broke chests after the pressing and drying sections. Broke may also come from the reel-slitting machine and the coating machine. Modern stock preparation systems are largely automated, and the preparation varies according to the type of stock. As an example, stock preparation of primary raw stock in bales will be described below.

6.2.1. Preparation of Primary Pulp in Bales

An example of a stock preparation line for primary pulp in bales is shown in Figure 55. Pulp is usually delivered as bales, which must be placed individually on the conveyer belt. The wires holding the bales together are subsequently cut and removed by hand or by machine. The bales reach the pulper via a weighing device, and slushing is started at a calculated stock consistency of 4–6%. The high consistency cleaner that follows is a hydrocyclone operating at a stock consistency of 4–6%; it removes heavy particles to protect the deflaker from damage. The stock is then collected in the dump chest at stock consistencies of 3.5–4.5% and kept in suspension by agitators.

Fiber treatment in the subsequent refining stage depends on the requirements to be met by the final paper. The refined stock is collected in the beating chest and then transferred to the mixing chest in appropriate amounts. The various components are mixed thoroughly with a chest propeller. The stock consistency is then adjusted before transfer to the machine chest. The finished stock is collected in the machine chest, and any slight residual nonuniformity in the stock consistency is smoothened out at this

stage. The mixing and machine chests are the transition to the stock approach flow system (see Chap. 7).

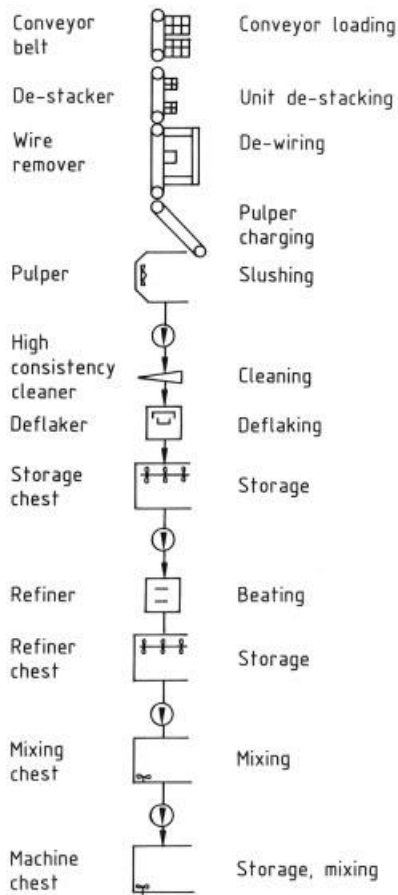


Figure 55. Schematic of a stock preparation line for primary raw stock in bales (courtesy of Sulzer Escher Wyss)

6.2.2. Special Processing Features for Various Primary Raw Stocks

Depending on the raw stock to be prepared, some process steps are of special importance or some of the process steps described above are omitted (Fig. 56). For instance, floc-dried pulp must be subjected to intensive deflaking to prevent the occurrence of “fish eyes” in paper, which are due to non-disintegrated fiber bundles. In the case of pulp being pumped directly from the pulper mill, the slushing, cleaning, and deflaking stages are

omitted. Refining is not required for the various types of mechanical pulp.

6.3. Wastepaper Systems

The wastepaper processing system varies according to the pulp grade to be produced, e.g., pulps for printing, writing, household paper, or linerboard. The systems for the former three consist of a combination of repulping, deinking, screening, cleaning, and bleaching processes. Relatively mild digestion is sometimes carried out as the first stage of the process for household paper production.

6.3.1. Repulping

The wastepapers are put into a pulper together with hot water or white water, and pulped with mechanical agitation. Some chemicals, such as deinking agent, NaOH, etc., are often added as pulping additives. There are three types of pulper: low consistency, high consistency, and drum pulpers.

The *low consistency pulper* (Fig. 57 A) operates at pulp consistencies of 4–6 % and is classified into two types: vertical pulpers, which have a repulping rotor at the bottom of the pulper, and horizontal pulpers, with the rotor on the side wall. Also, there are batch and continuous types. Contaminants are removed during operation by a ragger and dirt trap, in order to avoid the contaminants breaking into small pieces or accumulating in the pulper.

The *high consistency pulper* (Fig. 57 B) operates at pulp consistencies of ca. 15 % by means of a special helical rotor shaped like a screw. The wastepaper is mostly disintegrated by inter-fiber friction, which is very effective and selective for detachment of ink. Therefore, contaminants rarely break into small pieces in spite of excellent pulping and ink detachment abilities.

The *drum pulper* (Fig. 58), also known as a fiber-flow pulper, consists of a high consistency pulping zone and a low consistency screen zone. The wastepapers fall repeatedly after being carried up by lifters on the inside wall of the rotating drum, resulting in their disintegration into flocks. The contaminants and pulp flocks are discharged continuously from the side of

Raw stock	Process step	Slushing	Cleaning	Deflaking	Refining
	sheet	●	●	●	●
Chemical pulp	flocks	●	●	●	●
	suspended				●
Mechanical pulp		●	●	●	
Broke		●	●	●	

Figure 56. Stock preparation process stages required for various raw stocks (courtesy of Sulzer Escher Wyss)

the drum opposite to the inlet and enter the screen zone. Because the pulping is mild, removal of contaminants is successful. Pulping is sometimes preceded by sorting to remove relatively large contaminants, such as polyvinyl films, rags, polypropylene bags, wires, metals, and stones, which cause operational problems. Strainers, raggers, dirt traps, bar screens, drum screens, etc., are usually used.

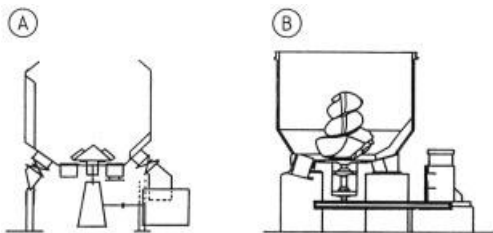


Figure 57. A) Low consistency pulper; B) High consistency pulper

6.3.2. Deinking

The deinking process is composed of detachment and separation stages.

Detachment Stage. The detachment of ink already begins in the repulping stage. The high consistency pulper in particular has a relatively high ability for detachment. In many cases, however, detachment is insufficient, and soaking and

kneading stages are added in order to increase the detachment of inks.

In the soaking process, the repulped and sorted pulps are dewatered to consistencies of ca. 20 %. After the addition of deinking agents, NaOH, and H₂O₂, they are retained in the soaking tower at 40–60 °C. Soaking results in extensive penetration of the chemicals, increases the detachment of inks and contaminants, and decreases the number of undisintegrated pulp flocks. The resulting pulps are deflaked by high speed deflakers which further promote disintegration and detachment of inks.

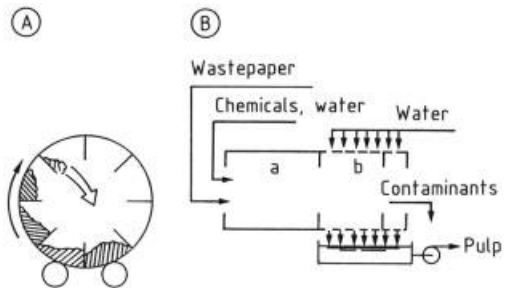


Figure 58. Drum pulper
A) End-view, showing motion of wastepaper;
B) Side view: a) Pulping zone; b) Screen zone

Inks containing large amounts of binders, such as linseed oil and resin, are transformed to nondetachable substances during the aging of

paper. They are difficult to detach from fibers by repulping and soaking alone. In this case, *kneading* is carried out with 30 % pulp consistency at normal or elevated temperature to increase the detachment and dispersion of the inks. Kneading is carried out in, e.g., single- and double-shaft mixers or screw-press pulpers. It is used in the production of high-quality deinked pulp.

Separation Stage. The ink particles liberated from the fiber surfaces and dispersed in the pulp slurry by the detachment process are removed in the separation process by flotation or washing.

In *flotation* the ink particles are rendered hydrophobic, become attached to air bubbles, are floated, and then removed. The flotation mechanism is illustrated in Figure 59. The reject ratio, deinking agent, type of flotator, pulp consistency, and residence time are the factors that influence the ink-removal efficiency. Generally, flotation conditions are: pulp consistencies of 0.8–1.2 %, 7–12 min residence time, and reject ratios of 2–3 %. Effective flotators have a high air-mixing rate and generate small air bubbles.

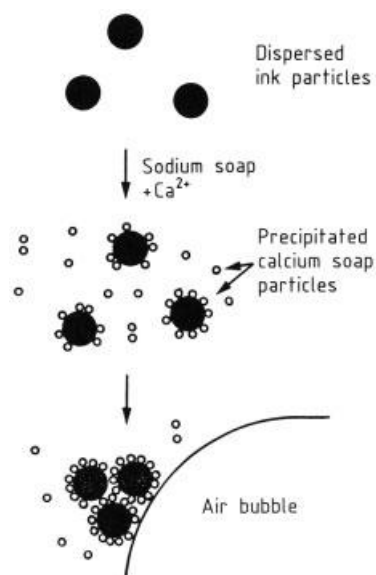


Figure 59. Mechanism for flotation of ink particles

The *washing process*, in which the ink is dispersed and then removed with the liquor in a subsequent dewatering stage, is used mainly in the United States. In other countries it is utilized

as a subprocess of flotation because it is effective for the removal of fine dirt or fillers which are hardly removed by flotation. The washing process is carried out in, for example, a thickener, disk filter, screw press, extractor, or twin wire press.

Deinking agents are formulated with either dispersion- or coagulation-type surfactants. The latter type, which has high aggregative and captive forces for inks, is used in flotation; it consists mainly of fatty acids. Dispersion-type deinking agents contain, anionic and nonionic surfactants and are mostly used in washing.

6.3.3. Screening and Cleaning

Residual contaminants are removed by fine screens and cleaners. Pressurized centrifugal screens are usually used for fine screening. The screen plates have either holes or slotted orifices; the latter are effective for removal of sticky contaminants. Since the stickies are soft and flexible, they readily pass through the screen together with the pulp fibers. Therefore, the slit width of the screen plate must be as small as possible, and may be as narrow as 0.15–0.2 mm. In addition, special wave and profile screens, which have an uneven plate surface, have been developed. Their screening effect and specific throughput differ from those of screens with smooth surfaces.

Conventional cleaners (e.g., forward-flow types) are used to remove large and heavy contaminants such as sand and metal. Since deinked pulp contains large amounts of lightweight contraries, special cleaners have been developed for their removal. These include the reverse cleaner, in which the accept and reject outlets are reversed as compared with the conventional cleaner, and the three-outlet cleaner, which has an extra outlet for lightweight contraries collected at the center of the vortex. They tend to be applied only in the treatment of screen rejects because of their high energy consumption.

Washing, flotation, cleaning, and screening are each effective for the removal of certain sizes of contaminants, as shown in Figure 60. Therefore, a combination of all these units is necessary for the removal of all sizes of contaminants.

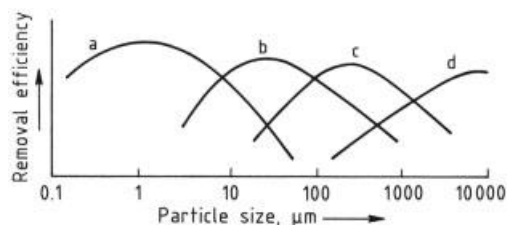


Figure 60. Particle size and contaminant removal efficiency
a) Washing; b) Flotation; c) Cleaning; d) Screening

6.3.4. Bleaching

Since the brightness of wastepaper is often low and decreases further during storage or through the action of alkaline chemicals during processing, bleaching chemicals are added in the pulper, soaking tower, or bleaching tower to maintain or increase the brightness. Hydrogen peroxide and dithionite are usually used. More recently, formamidine sulfinic acid has been introduced as a reducing bleaching agent. Hydrogen peroxide bleaching is carried out in the presence of NaOH, sodium silicate, and chelating agents. Wood-free wastepapers are sometimes bleached with hypochlorite.

6.3.5. Examples of Wastepaper Processing Systems

Since various combinations of the process steps may be important for effective elimination of the contaminants, many processing systems have been proposed. Recent systems pay more attention to the removal of contaminants earlier in the process. Figure 61 shows a deinking system for the production of newspaper-grade pulps, and Figure 62 shows a system for processing corrugated containers into linerboard-grade pulp. The systems for linerboard pulps differ slightly according to the raw materials (for example, old corrugated containers, magazines, and newspapers). Although most of the systems are similar, repulping and deflaking are more important in systems using old corrugated containers because of the difficulty in disintegrating these materials.

7. Paper and Board Manufacturing

7.1. Introduction

The essential steps in the historical, manual papermaking process were sheet forming, pressing, drying, sizing, and calendering. This fundamental process has not changed since the first sheet of paper was produced more than 2000 years ago (Fig. 63).

In sheet forming, the water from a fiber suspension is filtered off on a rotating continuous wire to produce a wet web. The mass distribution in the web should be as uniform as possible. In the press section, the wet web is compressed between rolls and rotating felts by using mechanical pressure, and dewatered mechanically as far as possible. Thus, the strength of the web is increased and energy is saved in the subsequent drying section, in which the residual water, with the exception of a few percent, is evaporated by bringing the web into contact with steam-heated cylinders. In the size press, starch, size, or pigments are transferred onto or into the fiber mat. The calender finally smooths the surface of the paper.

Varying quality requirements have to be met by various types of paper, such as writing and printing paper, tissue paper, packaging paper, board and cardboard. The machines and processes used for the production of the different types of paper and board vary correspondingly.

Modern paper machines are up to 10 m wide, and the fastest machines operate at speeds exceeding 2000 m/min. A single machine for the production of packaging paper can produce over 2000 t/d (Fig. 64).

Paper consists essentially of fibers, either primary or secondary. The quality characteristics of the finished paper sheet are determined by the fiber properties, which in turn depend on the type of fibers and the treatment during stock preparation, the auxiliary agents and additives (e.g., retention agents and defoamers as auxiliary agents; fillers and dyes as additives), and the process conditions on the paper machine. The demands made on the production process have increased considerably, especially because of the use of secondary fibers from wastepaper.

Important quality characteristics of the finished paper sheet are:

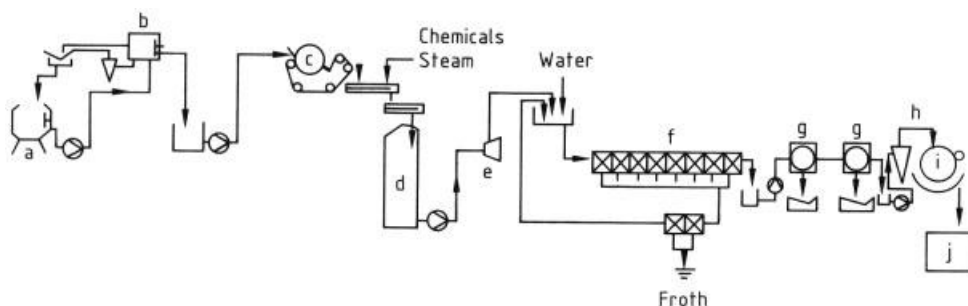


Figure 61. Deinking system for production of newspaper grade pulps

a) Pulper; b) Sorter; c) Thickener; d) Soaking tower; e) Deflaker; f) Flotation; g) Screens; h) Cleaner; i) Washer; j) Chest

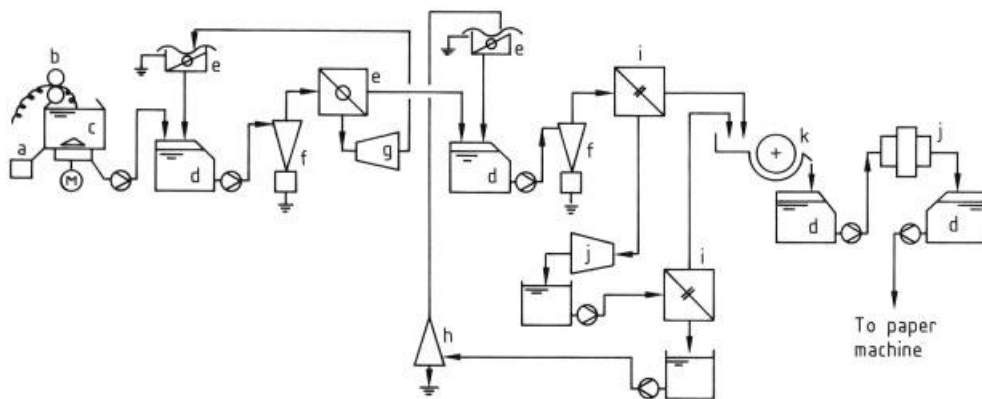
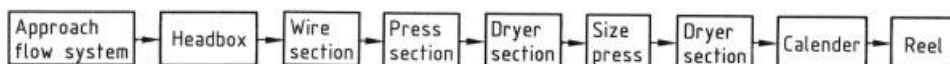


Figure 62. System for processing old corrugated containers

a) Junk box; b) Ragger; c) Pulper; d) Chests; e) Screens (hole); f) Hydrocyclones; g) Deflaker; h) Cleaner (reverse); i) Screens (slotted); j) Refiners; k) Filter

Production stage



Function

Suspension distribution Suspension supply Web forming Web pressing Web drying Web sizing Web drying Paper smoothing Paper reeling

Approximate dry content range, %

0.1-1.5 15-25 35-55 90-98 60-85 90-96

Figure 63. Flow sheet for paper and board manufacturing (courtesy of Sulzer Escher Wyss)

- 1) The mass distribution in the paper, which is discernible as cloudiness when the paper is held up to the light
- 2) The strength properties in the machine direction (MD) and cross machine direction (CD); machine direction/cross machine direction ratio, MD/CD
- 3) The optical properties (brightness, opacity)

- 4) The surface properties (smoothness or roughness)
- 5) The absorptive behavior, which is important for writing and printing
- 6) Behavior in the converting process

These properties must be constant in the longitudinal and cross directions in a given product.

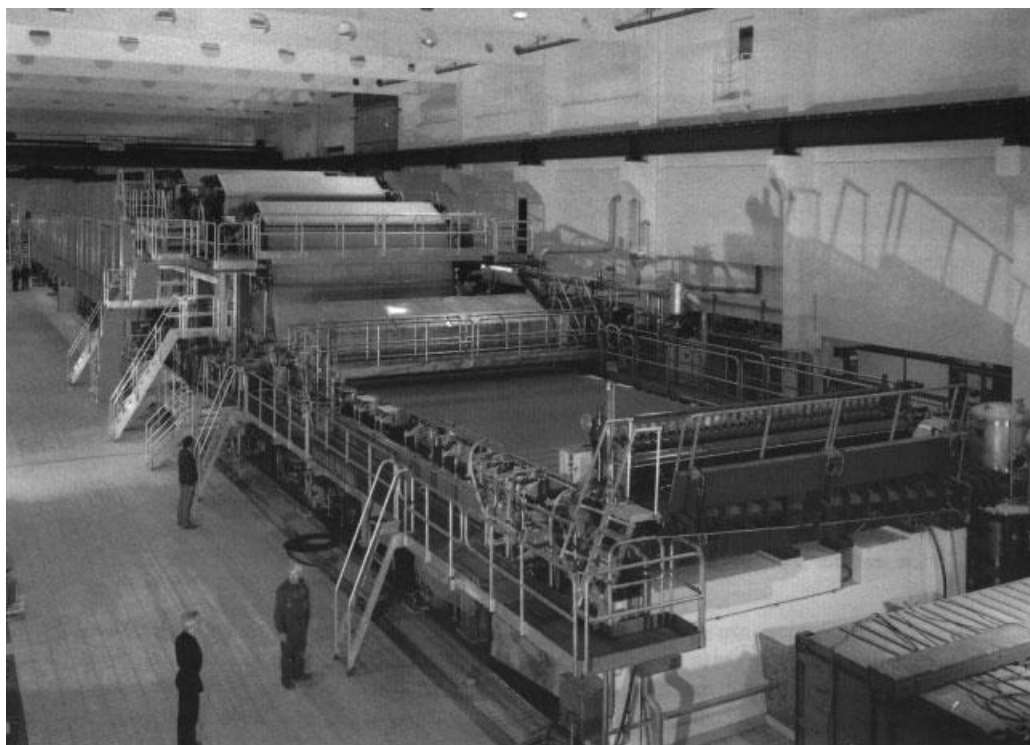


Figure 64. Paper machine, showing (from right to left) the headbox, fourdrinier, press section, and drying section (courtesy of Sulzer Escher Wyss)

The most important working agent in paper-making is water. It is required to provide the individual fibers in the suspension with as much free space as possible for undisturbed movement, slowing down reflocculation, i.e., the agglomeration of fibers to form flocs. Furthermore, water is required to produce strength in paper which is, in turn, the result of the formation of hydrogen bonds between the fibers during the drying process.

7.2. Sheet Forming [363–378]

In the sheet forming stage a uniform sheet with definite properties should be formed continuously. The sheet forming system consists of the stock approach flow system, the headbox, and the wire part.

7.2.1. The Stock Approach Flow System

The stock approach flow system (Fig. 65) is responsible for metering the amount and type of

stock components used, mixing with white water, and for delivering the suspension in the required amount and with the appropriate pressure to the headbox. The suspension delivered must be of constant pressure, quantity, and composition in order to ensure constant, uniform paper quality.

After stock preparation, the various types of stocks are metered and mixed in the mixing chest at a stock consistency of ca. 3–4 %. Variations in the stock consistency are then adjusted by addition of filtrate water; the remaining small variations in consistency are rectified in the machine chest. The stock consistency is now largely constant, and the amount of thick stock is usually dosed via a stock level box and diluted with white water to a stock consistency of 0.1–1.5 %. In simple systems, the suspension is then fed to the headbox through a screen. The screen is intended to protect the headbox and the wire from mechanical damage.

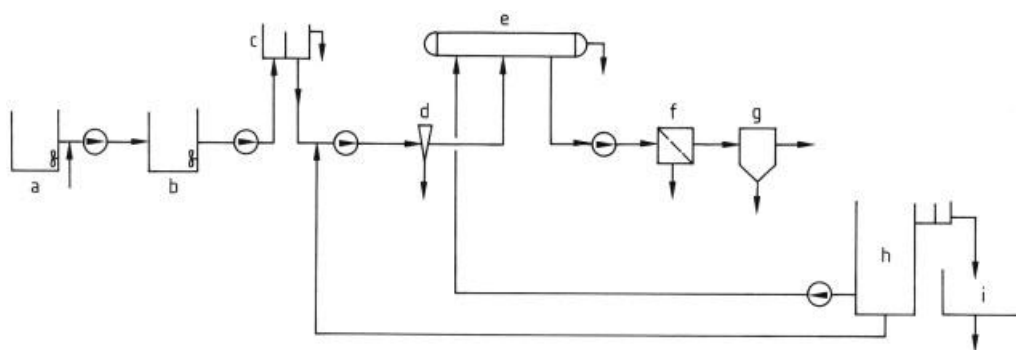


Figure 65. Schematic of the stock approach flow system (courtesy of Sulzer Escher Wyss)

a) Mixing chest; b) Machine chest; c) Level box; d) Cleaner; e) Vacuum tank; f) Pressure screen; g) Pulsation damper; h) White water I tank; i) White water II tank

In more elaborate systems, the quality of the final product is improved still further by removing sand and other heavy or light impurities from the suspension by means of conical hydrocyclones. Other impurities are separated in pressure screens with fine holes or slots. In addition, the suspension is often deaerated under vacuum to improve quality and dewaterability. Sometimes the suspension is fed through a pulsation damper.

To prevent unwanted sedimentation of fillers or the build up of bacterial slime and fiber stringing, the flow rates in the piping of the stock approach flow system must be sufficiently high (at least 1 m/s to more than 2 m/s suspension velocity, depending on the kind of stock) and the surfaces coming into contact with the suspension must be smooth.

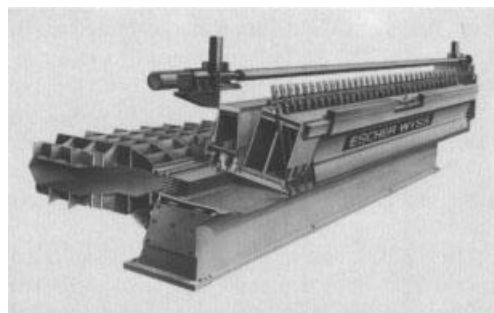


Figure 66. Example of a high-turbulence headbox (courtesy of Sulzer Escher Wyss)

7.2.2. The Headbox

The headbox (Fig. 66) produces a jet of suspension which should have a largely constant velocity, thickness, and direction across the width of the paper machine and be independent of time.

The pumping of the suspension into the headbox and cleaning with pressure screens generates pressure fluctuations, which must be dampened to keep the velocity of the jet constant. For this purpose, pulsation dampers are either used separately or integrated into the headbox.

The suspension, which is delivered through piping that has a round cross section, must be turned and distributed uniformly and with great accuracy across the full width of the headbox. It must then flow out of a narrow slit (normally called a slice, 6–20 mm in height) that is up to 10 m wide. In modern headboxes, this uniform distribution across the width is achieved by passing the suspension through a distributor on the backside of the headbox to a perforated plate. The many individual streams thus produced are reunited to form a single uniform stream in the nozzle, which then provides a constant jet of suspension. The breaking of fiber flocs that have already formed and the prevention of flocculation, at least for a short time until the suspension is transferred to the wire, are essential requirements for good sheet formation. For this purpose, turbulent shear forces are generated in the suspension. The turbulence should have an intensity that can be adjusted to the stock type, but the wavelength (i.e., effective length) should be short. In modern headboxes (high-turbulence headboxes) turbulence is produced by friction

in tubes and channels, or by changes in cross section as carried out in step diffusers.

In the headbox nozzle, the suspension is accelerated to approximately machine speed. The thickness of the jet and, therefore, the amount of suspension is usually adjusted by swinging the upper wall of the nozzle. The slice at the nozzle outlet is limited by a bar, which can be adjusted to an accuracy of ca. 1/1000 mm by means of spindles. This bar is adjusted locally across the width to compensate for deviations in the cross machine weight profile of the web. The direction of the jet with respect to the horizontal is influenced by shifting the upper wall of the nozzle. In this way, the point and angle of impingement of the jet on the wire can be adjusted.

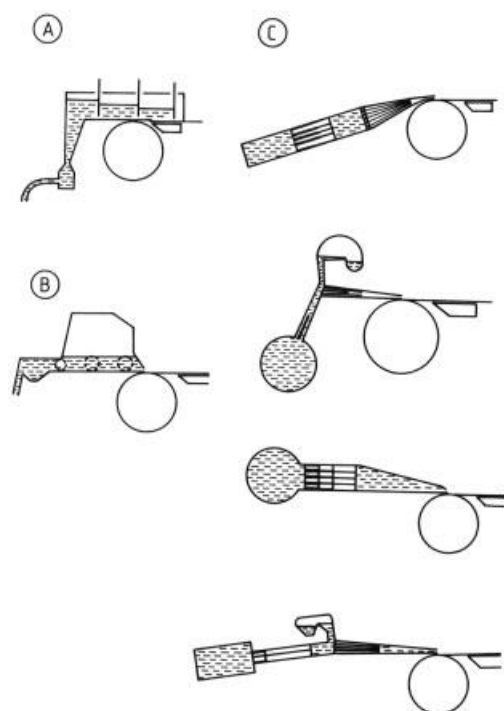


Figure 67. Schematic representation of various headbox types (courtesy of Sulzer Escher Wyss)
A) Pond slice headbox; B) Evener roll headbox; C) Various high-turbulence headboxes

In addition to modern high turbulence headboxes, there are also evener roll headboxes and antiquated pond slice headboxes (Fig. 67). The high-turbulence headboxes (also called hy-

draulic headboxes) have, as described above, a closed suspension guidance without a free surface. The essential functional element for distribution and dispersion in evener roll headboxes are the perforated rolls that rotate in the suspension. The suspension passes through these rolls, thereby generating shear forces. These headboxes possess a large free surface and are more suited to lower throughputs and machine speeds. The air cushion above the suspension is usually under pressure (air cushion headboxes). As an open headbox, the pond slice headbox no longer meets the most modern demands on throughput and speed.

7.2.3. The Wire Section

In the wire section, a fiber web is formed from the suspension. Three objectives are of primary importance:

- 1) Extensive separation of fibers from water
- 2) Prevention of fiber flocculation
- 3) Well-ordered deposition of the fibers on the wire

The separation of the fibers from water is a filtration process. The driving force for dewatering can be:

- 1) The height of the suspension above the wire
- 2) A vacuum behind the wire, produced by the action of dewatering elements
- 3) The pressure generated by tension in the wire over a curved surface

The forming and dewatering elements used in the wire section are (Fig. 68):

- 1) The forming board, which is a dewatering element at the beginning of the fourdrinier wire where the stock jet impinges. It consists of several blades or bars arranged closely together. Thus, it performs gentle, initial drainage of water from the suspension.
- 2) Table rolls, used in the fourdrinier section for drainage and to generate turbulence. Pressure is developed in the upstream wedge and in the region of contact between the wire and roll, and a vacuum is induced in the downstream nip.

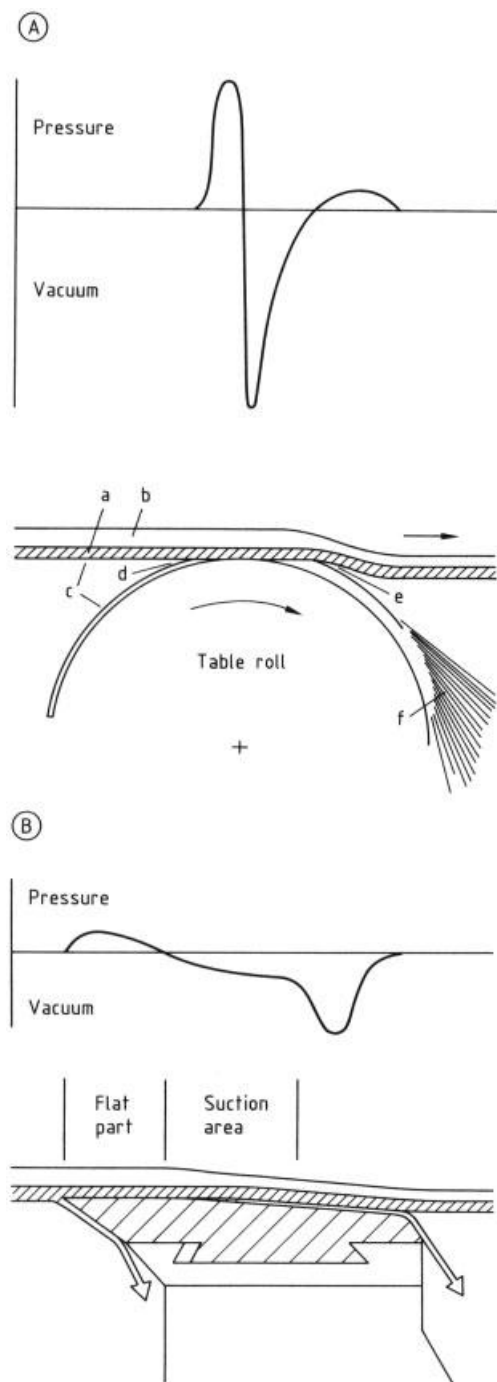


Figure 68. Schematic and mode of operation of dewatering elements (courtesy of Sulzer Escher Wyss)

A) Table roll; B) Foil

a) Wire; b) Fiber suspension; c) Water film; d) Overpressure; e) Suction; f) Discharged water

- 3) Dewatering foils, used with both the fourdrinier wire and twin wire formers. They have an acute-angled leading edge to doctor off the water hanging under the wire and a slope on the downstream side (foil angle of $0-3^\circ$) which induces a vacuum for drainage. Apart from wedge shaped foils, step foils can also be used.
- 4) Foil boxes which combine several foils in a unit. In addition, the foil box can operate under vacuum (vacuum foil box).
- 5) Wet suction boxes, which are dewatering elements that are located in front of the water line. They operate under vacuum and, in contrast to suction boxes, they drain mainly white water. The water line is a line on the fourdrinier wire that is discernible by light reflection and beyond which no free water is present on the surface of the freshly formed web.
- 6) Suction boxes, which are dewatering elements that are generally located behind the water line. They operate under vacuum and, in contrast to wet suction boxes, also suck air through the paper web.
- 7) Suction rolls, which have an open shell; sometimes vacuum is applied through the interior. They are used in sheet formation as suction breast rolls, suction formers, suction forming rolls, or suction rolls. Suction rolls accelerate drainage and increase the dry content in sheet formation.

Drainage is opposed by the resistance to filtration, which depends on the degree of beating, chemical treatment, and type of stock, and on the amount of fines and fillers present. The drainage resistance is increased by drainage that is too intensive at the beginning of the filtration process. The dry content after the wire section is 15–25 %.

The water removed in the filtration process (white water) carries away fibers, fines and fillers. The solids content retained, also called retention, can be increased by the addition of retention aids. The white water is reused to dilute the thick stock in the stock approach flow system.

The short-wave turbulence (micro-turbulence), generated in the suspension in the headbox to maintain fiber deflocculation, dissipates rapidly. For this reason, good formation

requires that either the fiber web be fixed very quickly or additional turbulence be generated in the suspension to be dewatered. This can be achieved by means of pressure and vacuum impulses from table rolls and foils. However, impulses that are too strong are harmful. Hence, table rolls are no longer used at higher machine speeds (above ca. 500 m/min) because their pressure pulses strongly increase with increasing machine speed.

Formation on fourdriniers is sometimes improved by agitating the wire. A shaker vibrates the fourdrinier wire with a frequency of 2–7 Hz and an amplitude of up to 10 mm in the horizontal direction.

The difference between the velocity of the jet and the wire is decisive for the controlled deposition of the fibers on the wire. If the jet and the wire have the same velocity, the fibers are deposited with random orientation or according to a possible preorientation in the headbox nozzle. If the jet is slower or faster than the wire, more fibers are aligned in the machine direction. The highest value for the tensile strength of paper is observed in the direction of the main fiber orientation. The relationship between the properties in the longitudinal and cross directions is often important in the processing and use of paper. If the jet is not directed exactly in the machine direction, this angular deflection is magnified on the wire many times over. The main fiber orientation is then no longer in the machine direction, which can lead to problems (diagonal sheet stress) in certain types of paper (e.g., copying paper).

The nature of the wire, which acts as a filtering auxiliary layer, influences the surface properties of the web (wire mark), fiber orientation, retention, dewatering velocity, and machine operation. Important parameters are the topography of the wire surface, resistance to fluid flow, free volume, cross stability (so that the wire remains level), and the wear properties of the wire. Today, single layer or multilayer woven wires are used. The material employed is predominantly plastic, but bronze is still used occasionally.

During the forming process, the suspension is guided between the wire and air (fourdrinier wire), between the wire and a solid wall (former), or between two wires (twin wire formers). Drainage can occur on one or both sides of the web. Two-sided drainage produces a more sym-

metrical paper. The different principles involved in sheet formation are shown schematically in Figure 69.

The Fourdrinier Wire. The fourdrinier wire (see Fig. 69 D) is the classical method of sheet formation. Today, speeds exceeding 1200 m/min are achieved with the fourdrinier. Normally, the fourdrinier is fitted with a wire table, foils and/or table rolls, suction boxes, wet suction boxes, and suction rolls. Drainage proceeds in the direction of gravity. A dandy roll is often used just in front of the water line to improve formation. This is a wire-covered open roll, with a honeycomb structure, which dips into the suspension and distributes the fibers in the web more uniformly. The dandy roll is also used to produce watermarks in the web through displacement and compression of fibers. These marks are visible in the finished paper in transmitted light. They are generated by a raised pattern soldered onto the roll.

Cylinder Formers. In the cylinder former (see Fig. 69 A), web formation occurs on a wire-covered, water-permeable cylinder. The uni-flow and contra-flow former with an immersed mold represents the oldest design. These were later replaced by the nonimmersed mold former and finally by the suction former. In suction formers, drainage is further increased by reduced pressure in the interior of the forming cylinder. The suspension is led between the wire cylinder and a solid wall (lip, former box). Suction formers are employed in the making of the single layers of board at lower speeds. Higher speeds (up to 1500 m/min) are only achieved with the suction breast roll former in the production of tissue.

Twin Wire Formers. In twin wire formers, (Fig. 69 F), the suspension is led between two wires operating at the same speed, and is drained through one or both sides. One of the driving forces in twin wire dewatering is the drainage force due to wire tension, which counteracts the centrifugal force of the suspension. Open rolls, suction rolls, forming blades, and vacuum shoes are used to increase drainage capacity and improve formation. In the twin wire former, the jet is injected directly into the gap between the two wires (gap former). The first section of the hy-

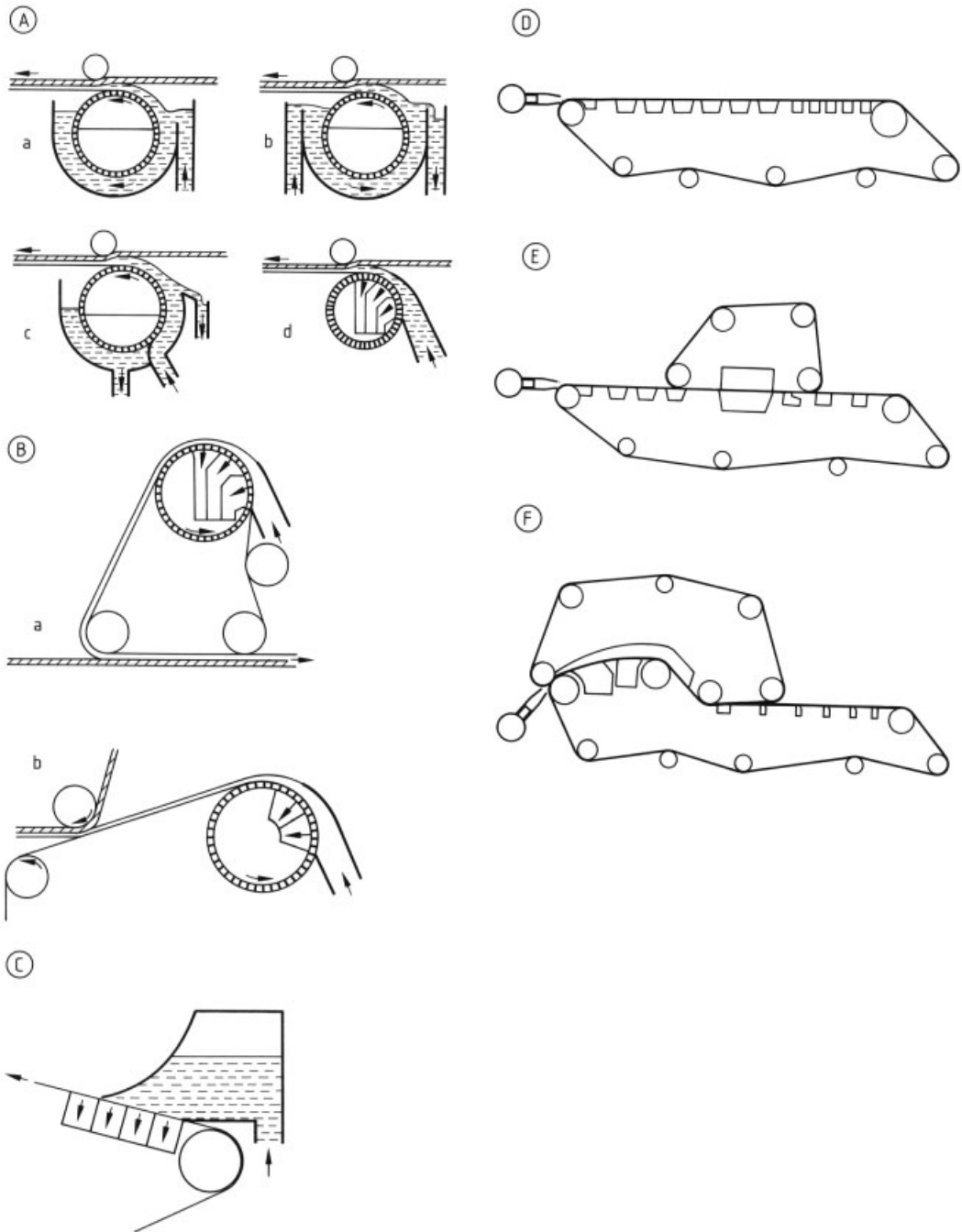


Figure 69. The various principles of web formation (courtesy of Sulzer Escher Wyss)

A) Cylinder formers: a) Contra-flow former; b) Uni-flow former; c) Nonimmersed mold former; d) Suction former
 B) Suction former with rotating wire: a) Former isolated on fourdrinier; b) Suction breast roll
 C) Inclined wire; D) Fourdrinier; E) Hybrid former; F) Twin wire (gap) former

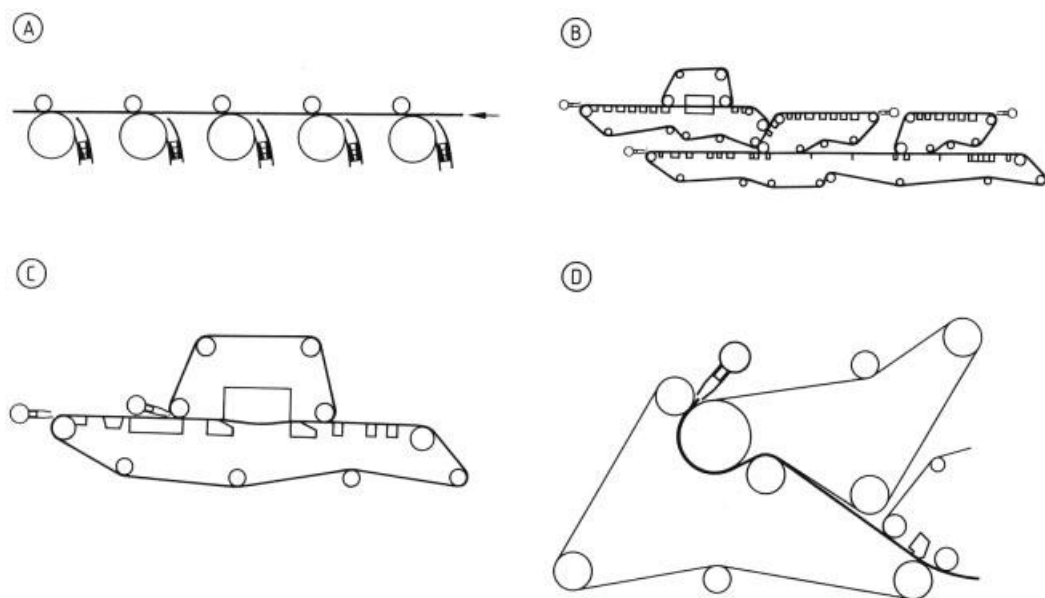


Figure 70. Various methods for the production of multilayer products (courtesy of Sulzer Escher Wyss)

A) Suction forming section; B) Fourdrinier coupled with fourdriniers and a hybrid former; C) Hybrid former with secondary headbox; D) Tissue former with double-layer headbox

brid former consists of a fourdrinier, which is followed by a twin wire section in which dewatering also occurs through the top wire.

7.2.4. Systems for the Production of Multilayer Products

Multilayer products such as board are produced by forming the individual layers separately in several web-forming units and then couching them together in the wet state (multi-former). This process gives the entire web improved uniformity compared with a single layer web. Since the cross section of the web can be tailored to suit its intended purpose, and different materials can be used to form the individual layers, increased functional value and improved economy can be achieved. The latter applies also to products that are formed on a single web-forming unit in which the headbox delivers a jet having two or three layers of varying stock composition (multi-layer headbox). Here, dewatering is usually carried out in a twin wire former. The use of a secondary headbox allows the application of a further layer of suspension to a web that has already been formed on a fourdrinier wire.

Dewatering then occurs through the web downwards or in a hybrid former to the top (Fig. 70).

7.3. Press Section [379–388]

The purpose of the press section is to increase the dry content of the paper web by dewatering and to increase the strength of the web by compression before the web enters the subsequent dryer section.

The press section usually consists of several successive press nips, formed between two rolls (Fig. 71). The rolls are pressed with linear forces of 20–150 N/mm and up to 1000 N/mm in some special designs. Today, the dry content after the press section reaches 55 % and more, depending on the product and the raw material used. Because of these high dry contents, less thermal energy is required in the dryer section, and the increased web strength results in fewer breaks.

In modern press sections, the web is transported between one or two felts through the nip. The water removed from the web is stored and carried away in the felt and, in the case of high water extraction, also in grooves or perforations in the surfaces of the rolls. With suction press

rolls, the storage and transportation of water are improved and rewetting of the paper web is reduced. The most important properties of the felt are the storage capacity under pressure, the water retention behavior on leaving the nip, which, in turn, prevents rewetting of the web, and the smoothest possible surface in the nip for uniform pressure transfer to the web. To meet these requirements, the felts are equipped with a coarser, frequently multilayered, base fabric and a fine, surface layer made of synthetic and natural fibers needled into the base layer. The dewatering of the felts is performed with suction pipes. In order to maximize the working life of the felt, it is constantly or intermittently treated with a fine, high-pressure water jet and/or wetting facilities (felt conditioning) to keep the felt clean.

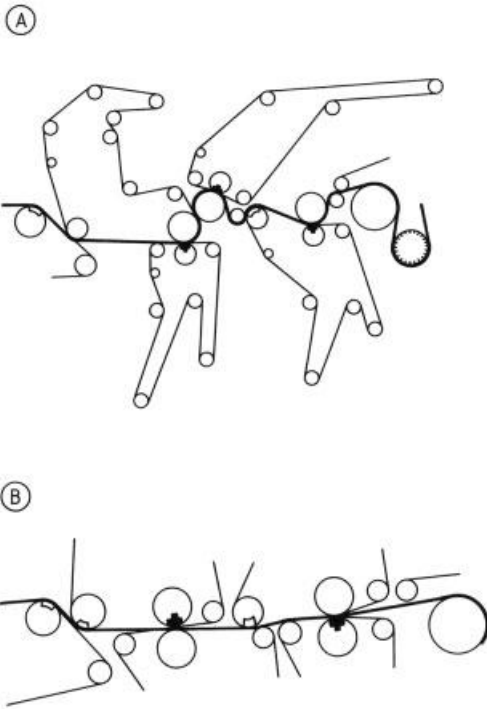


Figure 71. Schematic of two press sections (courtesy of Sulzer Escher Wyss)

A) Press section of a newsprint machine with rolls for line force control across the machine width; B) Press section of a packaging paper machine with two wide-nip rolls

The magnitude of the pressure applied and the time in which it acts depend mainly on the diameter of the roll, the elastic properties of the surface of the roll or the roll coatings (rubber,

plastic, steel, or bronze; grooved/perforated) and on the felts, and less on the elastic properties of the web. The applied pressure must first overcome the structural resistance of the web before it can generate the hydraulic pressure required for web dewatering. The higher the hydraulic pressure and the time of action, the higher the dewatering performance. The pressure is increased from nip to nip, corresponding to the decreasing water content. If the hydraulic pressure is too high, however, the paper web can be damaged (crushing).

The dewatering pressure is counteracted by the structural strength of the web and the flow resistance of the water in the web, which is determined by the type of stock, the fiber treatment, and the amount of fines and filler. Increasing the web temperature by steam or infrared heating facilitates dewatering by lowering the viscosity of the water and the structural strength of the web.

The time during which the pressure acts on the web can be prolonged almost tenfold by using wide nip pressing. In this process, a concave hydrostatically or hydrodynamically supported shoe presses a flexible revolving plastic sleeve or a plastic belt against the other press roll.

A closed web guidance system is important to prevent web breaks, especially at high machine speeds, low basis weights, and low dry contents of the web. Indeed, in modern paper machines the web is not conveyed freely, but it is nearly always supported by a felt or the surface of a roll.

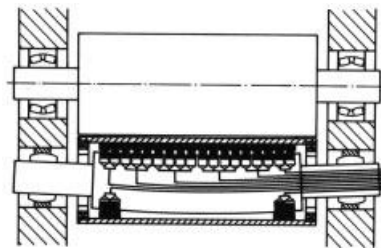


Figure 72. Example of a press roll with which the line force can be varied locally across the width (courtesy of Sulzer Escher Wyss)

A uniform moisture profile in the cross machine direction on the reel is very important for reasons of quality and economy. Press rolls which can vary the line force selectively across

the width (Fig. 72) and sectioned steam boxes which heat the web to varying extents across the width are suitable for cross machine moisture profile correction.

7.4. Dryer Section [389–393]

In the dryer section, water is removed by heating, whereby fiber–fiber bonding via hydrogen bonds is effected and the web strength is increased. The dry content of the web after the dryer section is 90–98 %.

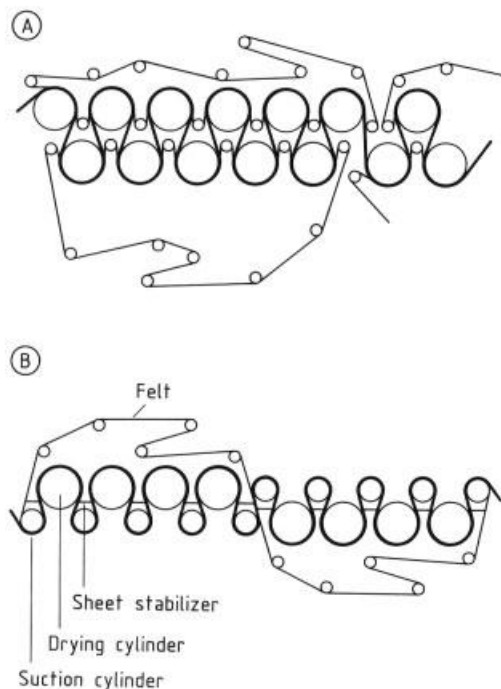


Figure 73. A) Schematic of a multiple cylinder dryer section; B) Schematic of a multiple cylinder dryer section for high speeds and for minimizing paper shrinkage in the cross machine direction (courtesy of Sulzer Escher Wyss)

In the multiple-cylinder dryer section, the web is transported in a slalom course over a number of steam-heated cylinders (contact drying). Dryer felts or dryer fabrics press the web against the drying cylinder for better heat transfer (Fig. 73). The dryer felts are, in turn, freed of water by means of felt dryers (steam-heated cylinders, blowpipes, blow boxes). The dryer section is aerated with hot air (pocket ventilation) to carry off the water vapor generated and

to increase the drying efficiency. The entire dryer section is enclosed in a drying hood.

Apart from contact drying, which is the most commonly used process, forced convection drying and infrared drying are also used in the paper industry, usually in combination with contact drying.

The paper web shrinks during drying. The extent of shrinkage depends on the type of stock, degree of beating, the fiber orientation, and on forces applied that counteract shrinkage. The shrinkage in the longitudinal direction can be controlled by stretching the paper between the individual drying groups. Shrinkage across the width is nonuniform and is higher at the sides than in the center of the web. Attempts have been made to influence the shrinkage across the width by using a special web guidance system. In this system, the web in one row of cylinders is pressed against the drying cylinders by the drying fabric, and in the other row, it is held by reduced pressure in suction rolls and partly by web stabilizing elements on the drying fabric (see Fig. 73).

7.5. Size Press [394], [395]

In the size press, starch, size, or pigments are applied to the fiber matrix to increase the strength of the paper web and to modify the surface properties with respect to liquid uptake during writing, printing, or coating.

In sizing, the web is passed through the sizing liquor pond, which is located above a roll nip. As a result of capillary action in the pond and hydraulic pressure in the roll nip, the paper web absorbs the sizing liquor. Some modern size presses for high machine speeds no longer have a pond. A thin layer of size is applied to the rolls and is subsequently transferred to the paper web in the nip (Fig. 74).

The amount of size taken up depends on the dry content of the web. To guarantee uniform size uptake across the width, the web must be pressed uniformly across the width in the nip and must exhibit a constant moisture content. The dry contents before the size press are high and can reach 98 %.

The water applied in the size press is evaporated in the after-dryer section. The first cylinder

in particular must be protected against the formation of coatings.

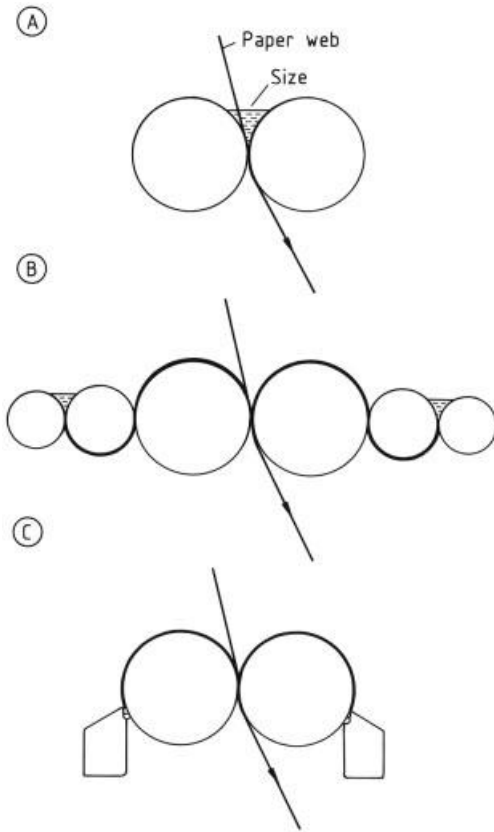


Figure 74. Size presses (courtesy of Sulzer Escher Wyss)
A) Size press; B) Gate roll; C) Speed sizer

7.6. Calendering [396–402]

The objective of calendering is to produce a smooth paper surface which meets the printing and writing requirements for the intended use. Not only must smoothness and gloss be produced, but thickness reduction is also important in some cases. However, the increase in smoothness and gloss must frequently be as high as possible, but thickness reduction of the web must be as low as possible. Apart from thickness, the opacity, tear strength, and absorptivity of the paper are reduced to a certain extent by calendering.

In calendering, the web is fed through counteracting press rolls and in this process the sur-

face roughness of the web is leveled by the action of pressure and sometimes temperature. Calenders consist of two or four to eight cast-iron rolls with very smooth surfaces that are arranged one on top of the other. The web is passed through the press nips of these rolls (hard nips). Calenders that are being increasingly used today have a heated cast iron roll and a mating roll with a “soft” plastic cover (soft nip). Two or more of these are arranged one behind the other. The rolls are heated externally by induction or internally with hot water, steam, or heating oil (Fig. 75).

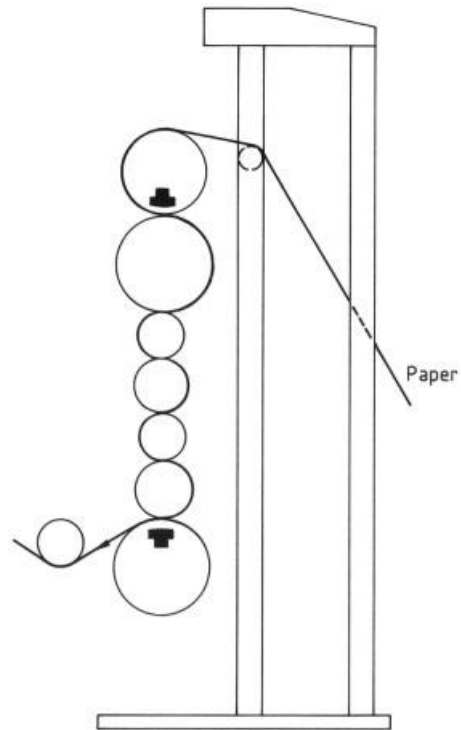


Figure 75. Example of a seven-roll calender (courtesy of Sulzer Escher Wyss)

The level of smoothness that can be attained is greatly influenced by the type of stock, the moisture content and temperature of the paper web, the pressure applied, the retention time in the nip, and the surface temperature of the roll.

On entering the nip, irregularities in the web with regard to thickness, web weight, moisture and temperature, and local differences in the pressure applied have a negative effect on calendering and on the product. This can be cor-

rected by using rolls which can specifically adjust the linear force locally across the width (cf. Fig. 72). Moreover, the rolls can be heated or cooled locally across the width with blow jets, by which the diameter of the rolls is changed locally. The roll diameter is also changed locally by induction heating that is controllable across the machine width. In some cases, the web is specifically steamed before calendering.

7.7. Supercalendering [403–406]

The paper or board web that has been presmoothed in the calender is often subjected to a further finishing treatment called supercalendering. A uniform, high surface smoothness is produced in this process, which is carried out independently of the paper machine, usually in supercalenders and sometimes with gloss and glassy calenders. This treatment also improves the gloss. Supercalendering increases printability, e.g., in the case of picture printing. Before supercalendering, the web is frequently checked in rewinders for possible defects. Defective parts are eliminated and the ends of the web are spliced together again. Supercalenders usually process the web in its full width as it comes off the paper machine or the coating machine. The system consists of the reel-off stand, the actual supercalender, and the reel-up stand (Fig. 76). The supercalender is more than 10 m high, the working width up to 10 m, and the maximum working speed ca. 1000 m/min. The roller stack usually consists of 12 (or more) rolls, half of which are cast-iron rolls of a high surface quality (the diameter of the top or bottom roll is up to 1000 mm and that of the other rolls is up to 560 mm) that are sometimes internally heated, while the other half are paper rolls (called filled rolls, diameter up to 800 mm), which have shells composed of paper rings that consist of pure cotton or a mixture of cotton and wool or soda paper, depending on the desired property (e.g., hardness). These rings are threaded onto a steel core and are pressed together axially under a high pressure. This stack is then turned and ground. The hardness of the cover is ca. 82–90 Shore D. The cast-iron rolls and the softer paper rolls are installed alternatingly. At about the middle of the calender, the sequence of the rolls is reversed so that both sides of the web come in contact with

the paper rolls. The hard roll presses into the soft roll on loading. The resultant relative movements between the two rolls confer smoothness and gloss on the paper web as it passes through the roll nip. After each nip, the web is led over paper guide rolls to compensate for width increases of the web produced by the supercalendering process in the nip, and to prevent curling.

In modern supercalenders, the top and the bottom roll are deflection control rolls, which can be used to adjust nip forces locally across the width. This system permits a uniform loading of the web across the width in all the nips over a wide range of linear forces. Sometimes the entire roll stack floats, in which case very uniform loads across the width are achieved.

In the case of web breaks or other disturbances, the roll stack is opened quickly so that the sensitive paper rolls are not damaged. To save the threading time for each new roll of paper, the beginning of the new roll is sometimes stuck (flying splice) to the end of web of the old roll at low speeds (max. 40 m/min). Subsequently, the machine is quickly switched to normal operating speeds.

The result of supercalendering depends not only on the linear forces, speed, and surface temperature of the roll, but also on the paper properties, especially on the type of fibers, coatings, and on the moisture content and temperature of the paper web.

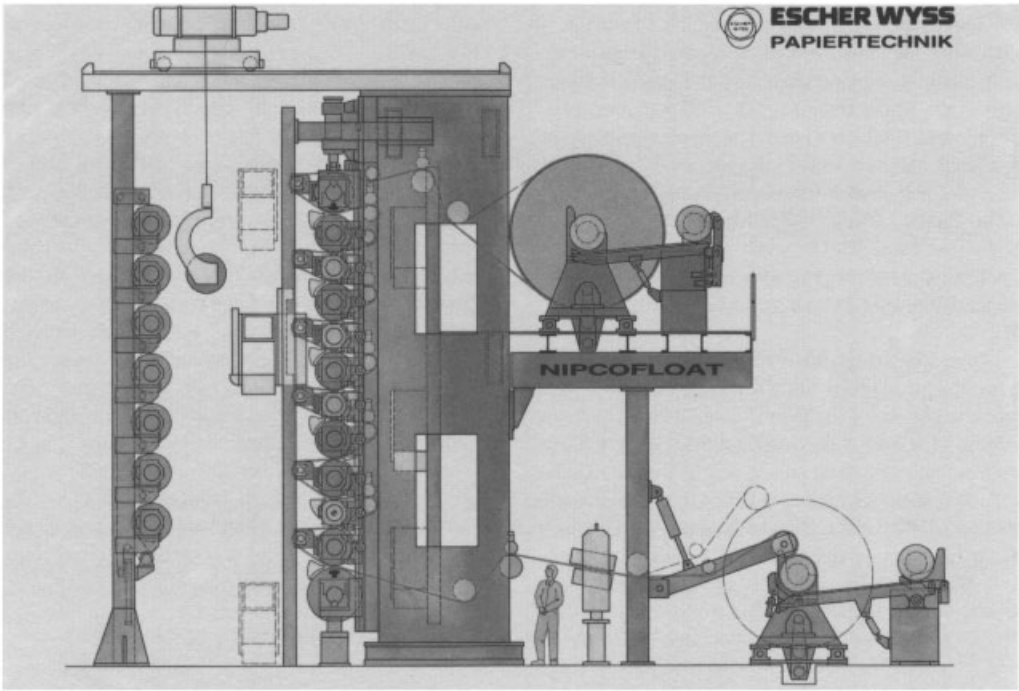
Other calender types which are less important are as follows:

- 1) Calibrating calenders that calibrate the thickness of the web (usually with cardboard)
- 2) Embossing calenders that transfer a pattern onto the surface of the web (usually with cardboard)
- 3) Friction calenders that utilize the friction between separately driven rolls of a roll pair to smooth the web
- 4) Sheet calenders that are used for heavy grades (above ca. 300 g/m²) and are especially gentle in bending the thick product.

7.8. Reel-Slitting Machine

In the reel-slitting machine, the paper web is cut to the width required for further processing.

(A)



(B)



Figure 76. Schematic (A) and photo (B) of a supercalender (courtesy of Sulzer Escher Wyss)

Reel-slitting machines process web widths of up to 10 m, working speeds exceed 2500 m/min, and diameters of individual rolls reach 1500 mm and sometimes 2400 mm. The functions of a reel-slitting machine (Fig. 77) include

- 1) Unreeling the roll present in the full paper machine width
- 2) Cutting to the desired web width
- 3) Reeling the individual rolls on to separate cores

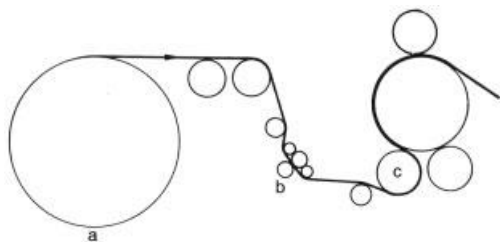


Figure 77. Schematic of a reel-slitting machine (courtesy of Sulzer Escher Wyss)

a) Machine-width roll; b) Rotating circular knives; c) Wind-up drum

The web is cut with rotating circular knives of high-alloy tool steel, hard metal, or ceramic. At a defined contact pressure, the disk-shaped upper knives penetrate into the groove of the lower knives. The positioning of the knives and, consequently, the adjustment of roll width is performed manually or automatically.

Roll changing is automated, and changing times of less than 40 s have been achieved. In the reeling up of the individual rolls, the reel hardness is important for further use. Apart from paper tension, the reel hardness is essentially determined by the linear force of the load roll, which can be controlled for this reason.

The most important requirements to be met by the cut rolls with regard to further processing (printing, cross cutting) are uniform reel hardness across the width of the roll and in the diameter, straight front surfaces, and absence of roll defects and roll damage.

8. Water Circuits and Effluent Treatment

8.1. Introduction

Papermaking is a branch of industry that requires large amounts of water. However, the fresh water demand and, consequently, the wastewater emission can be reduced substantially by the realization of almost closed water circuits and the reuse of process water. The water is recycled either directly or via clarifiers (save-alls). Fibers and fillers are removed from process water by sedimentation, flotation, or filtration. The resulting clarified water is reused in production and replaces fresh water at many points in the production process. The separated solids are also reused. Hence, the closure of water circuits is favored from the viewpoint of environmental protection, the saving of resources, and economy of operation.

8.2. Fresh Water

Primarily surface water and to some extent groundwater are used to meet the water demand of the paper industry. The essential criteria for the choice of sources of water are sufficient availability and the local conditions. A combined utilization of water sources is common. Irrespective of its source, fresh water should neither reduce the quality of the paper nor cause disturbances in the papermaking process (e.g., score breaks, lime precipitation, corrosion). Surface water frequently does not meet these requirements and must be treated before use.

Sedimentation processes (with chemical flocculation) and/or gravel filter processes are principally used for conditioning fresh-water treatment. In the production of specialty papers (e.g., photographic base paper, filter paper, cigarette tissue, capacitor tissue), fresh water is also deionized, demanganized, softened, and desalinated (ion exchanger). Boiler feed water for power plants within the mill is always softened and/or desalinated.

Fresh water is chiefly used:

- 1) As cleaning water for the paper machine (wire and felt cleaning)
- 2) As sealing water and confining water in stuffing boxes, suction boxes, and cleaners

- 3) As a solvent and dispersant for fillers and additives

Fresh water used as cooling water is sometimes introduced into the process in a separate pipeline and removed after use. However, it is usually also employed as process water. In calculating the specific fresh water consumption, cooling water is not taken into account provided that it had no contact with fibrous materials and additives.

8.3. Water Circuits

There are three process water circuits in a paper mill [407], [408] (Fig. 78): the primary circuit, the secondary circuit, and the tertiary circuit. In the primary circuit, the fiber-rich water obtained in the sheet-forming zone of the wire section (white water I) is recycled for stock dilution in the stock approach flow system. The primary circuit is maintained as closed as possible. It is the most important circuit in terms of the amounts of water and stock.

Excess water from the sheet-forming section, suction and press water, as well as cleaning water is called white water II and is circulated in the secondary circuit. A save-all is generally installed in this system. Fibers and filler materials are largely removed from the circulating water by sedimentation, flotation, and filtration. The resulting clarified water is returned to the process circuit, where it replaces fresh water at several points. The separated solids, a concentrate containing fibers and fillers (3–10 % consistency), is used for suspension and dilution in stock preparation.

The tertiary circuit, also called the outer cycle, contains excess water from the secondary circuit and, in addition, all other process water which is not, or is not directly, reusable because of its degree of contamination. The water in this circuit represents the wastewater of a paper mill; it is treated in chemomechanical and/or biological wastewater purification plants. Purified water can be either completely (closed water circuit) or partially (tertiary circuit) returned to the production process.

Residual substances are obtained as sludges in wastewater purification. These can either be dewatered and disposed of or reused in production. In particular, fiber-containing sludges

from chemomechanical clarification plants are returned to the process. In some cases (e.g., in board production [409]), sludges from biological wastewater treatment plants are also reused. However, these sludges are usually disposed of in dumps or by incineration or used as raw materials in the production of other products, especially in the brick industry.

The specific amounts of wastewater listed in Table 17 can be used to classify the closure of water circuits within the mill [410]. The specific wastewater is the ratio of the amount of wastewater to the gross production of the mill. It is 1–2 L/kg less than the specific fresh water consumption because evaporation losses occur in the dryer section of the paper machine. Almost closed water circuits are used in the production of packaging papers from wastepaper (corrugating medium, screenings). The reusability of process water and therefore the extent to which the water circuits can be closed are limited by, for example, buildup of salt loading, enrichment of dissolved organic substances, increase in temperature, slime formation, corrosion phenomena, and odors. Causes and remedial measures are described in [411–414].

Table 17. Classification of paper mill water circuits [410]

Water circuit	Specific effluent volume, L effluent/kg paper
Open	> 100
Less closed	10–100
Almost closed	< 10
Completely closed	0

8.4. Closed Water Circuits

A closed water circuit is achieved when no wastewater leaves the paper mill. The process water is then utilized to almost 100 %. Only evaporation and vaporization losses, and the water content in the paper and in the residual matter must be replaced by fresh water (1–2 L/kg).

A closed water circuit is shown schematically in Figure 79. The essential requirement for reusing circulating water in the tertiary circuit is adequate save-all clarification. The quality of the clarified water must be suitable for the operation of sensitive systems (e.g., showers,

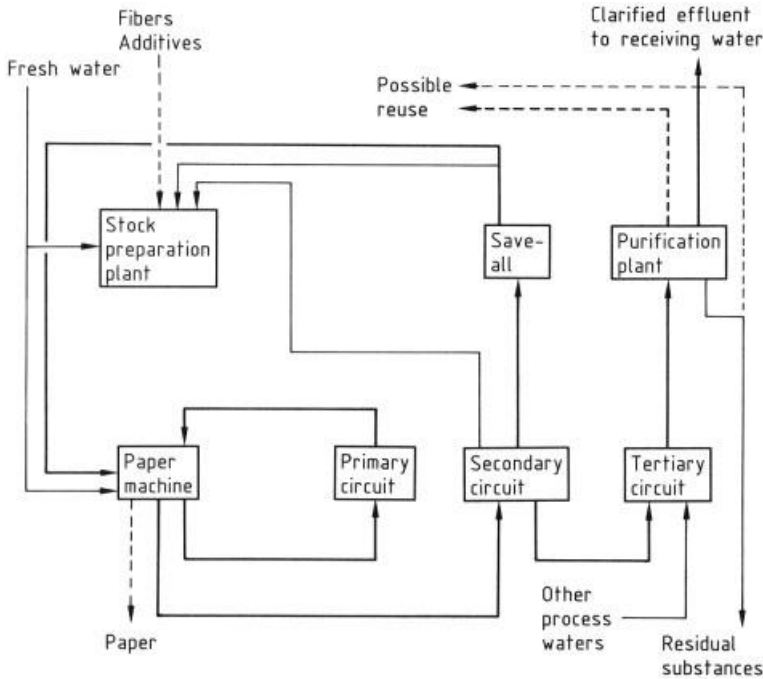


Figure 78. Scheme of the water circuits in a paper mill [407]

trim showers). There must be enough storage capacity to compensate for variations in quantity caused by disturbances and interruptions in production. Until now, closed circuits have been realized only in paper mills processing wastepaper. Measures and operating experiences are described in [415–417].

8.5. Save-Alls

Save-alls have a dual function: stock recovery and water clarification. The save-alls used almost exclusively in the paper industry are based on sedimentation, flotation, and filtration. The requirement for optimal solids recovery efficiency is the flocculation of the fibers and fillers to form larger agglomerates. High-molecular, water-soluble polymers (e.g., polyacrylamides, polyamines, polyethyleneimines) or inorganic electrolytes (iron(III) chloride, aluminum sulfate, calcium hydroxide) are used as flocculants.

Apart from economic factors, the choice of the save-all system depends on the solid composition (fiber and filler components), space requirement, reliability of operation, energy con-

sumption, and chemicals consumption. The advantages and disadvantages of the individual systems are presented in Table 18.

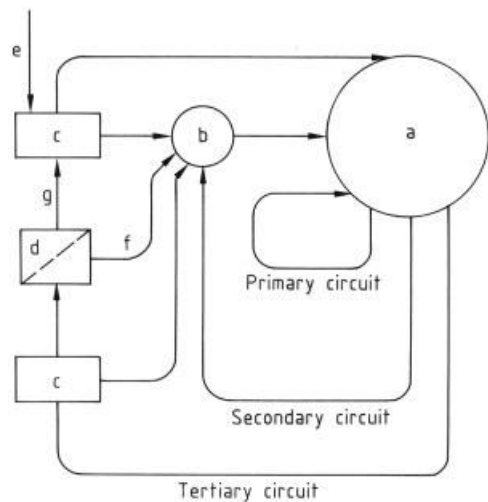


Figure 79. Scheme of a closed water circuit
a) Paper machine; b) Stock preparation plant; c) Storage;
d) Save-all; e) Fresh water; f) High density stock; g) Clarified water

Table 18. Advantages and disadvantages of various save-all systems [408]

	Sedimentation	Filtration	Flotation
Space requirement	large	very low	low
Holding time	long	very short	short
Buffer efficiency	moderate	none	slight
Sensitivity to load variations	low	low	somewhat higher
Control and maintenance requirement	low	low	higher
Sensitivity to disturbances	low	low	somewhat higher
Solids removal efficiency			
with long fibers	good	very good	very good
with short fibers	good	moderate	good
with fillers	very good	moderate	moderate
Undissolved substances in clarified water, mg/L	10–100	10–300	10–50
Thickening efficiency	low	very high	high
High density stock concentration, %	1–2.5	8–30	1–15
Investment costs, specific	low	high	moderate
Operating costs	low	moderate	high
Energy consumption	very low	low	moderate
Chemicals consumption	low	low	higher

Sedimentation plants (rectangular scraper save-alls, round clarifiers, and cone save-alls) are suitable for the clarification of filler-loaded process water; the solids removal efficiency is greater than 90 %. However, the consistency of the stock is relatively low (1–2.5 %). A further disadvantage of sedimentation plants is the long retention time of the water to be clarified in the clarifying basins. This necessitates large volumes and therefore a large space requirement.

The flotation plants employed in the paper industry are either open or closed. Both full stream and partial stream aeration processes are used. In the former, the entire wastewater is aerated under pressure (up to 800 kPa), while in the latter, only a partial stream of either wastewater or circulated clarified water is aerated. Figure 80 shows an open flotation plant with partial stream clarified water aeration. The plant consists of a clarifying basin with sludge removal, aeration equipment for a partial stream of clarified water, and a dosing plant for the flotation chemicals.

Flocculation chemicals are added to the process water to be purified before it is fed into the clarifying basin. At the same time, compressed air is dissolved under pressure in a partial stream of clarified water. This partial stream is introduced into the stream of process water via an expansion valve, whereby a part of the dissolved air is degassed into very fine bubbles. The water, containing air bubbles and flocculation chemicals, enters into the clarifying basin,

where the flocculation and flotation occur. The floated solids form a floating layer of sludge, which is removed by reamers. The consistency of the floatate is between 7 and 15 % and the efficiency of solids removal is often almost 100 %. Computers and flotation simulators have been used to obtain a low flocculant consumption and a stable operation with process water of varying solids content. Computerized flotation plants are described in [418], [419].

Filtration save-alls (disk filters and drum filters) have the lowest space requirement compared with other save-all systems. The retention time of the water to be clarified in the aggregates is very small. Filtration save-alls are mainly installed in paper mills where the grade of paper produced is frequently changed. They are also often used in mills with large, high-speed paper machines. Solids removal efficiencies of up to 90–95 % are obtained for fiber-containing process water. The efficiency decreases with increasing concentration of filler. Better efficiencies are attained by using fibrous filter aids (chemical pulp, groundwood, and paper stock), which form a layer of fibers on the screen that can retain the smaller filler particles and fines. Of all save-all systems, filtration produces stocks of the highest consistency (10–30 %). A disk filter that uses fibrous filter aids is shown in Figure 81.

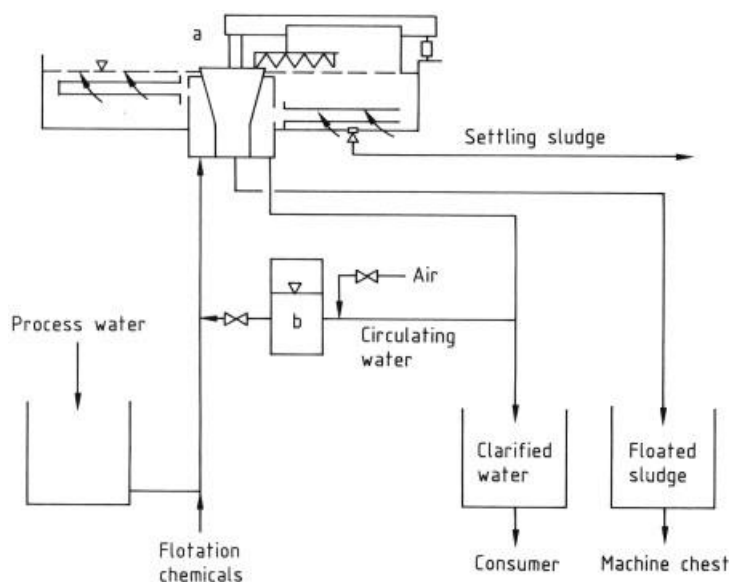


Figure 80. Scheme of a flotation plant with partial current clarified water aeration
a) Clarifying basin; b) Air saturation tank

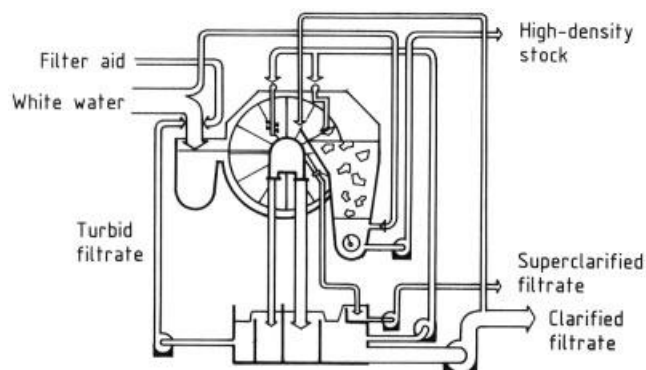


Figure 81. Scheme of a disk filter

8.6. Wastewater Pollution

The pollution in the wastewater of a paper mill depends on the type of raw material, the type and amount of fillers and additives applied, and on the degree of circuit closure. Effluents from mills that largely or exclusively process chemical pulps have a lower degree of pollution than those from mills in which mechanical pulp or wastepaper is employed. The use of starch or other organic additives results in a marked increase of the oxidizable effluent components, measured as BOD₅ or COD. Dyes and fillers can lead to discoloration and/or turbidity of ef-

fluents. Effluents from paper mills have a low content of nitrogen and phosphorus compounds. For this reason, these elements must be added as nutrient salts (e.g., urea and phosphoric acid) to feed microorganisms during treatment in biological purification plants. The closure of the water circuit within the mill results in an increase in the concentrations of the effluent components. On the other hand, the inorganic and organic load is reduced owing to its partial elimination via the paper produced. For this reason, the specific load in kg per tonne of paper (specific load = concentration $\times$ specific amount of effluent) is a more suitable parameter for quantifying the

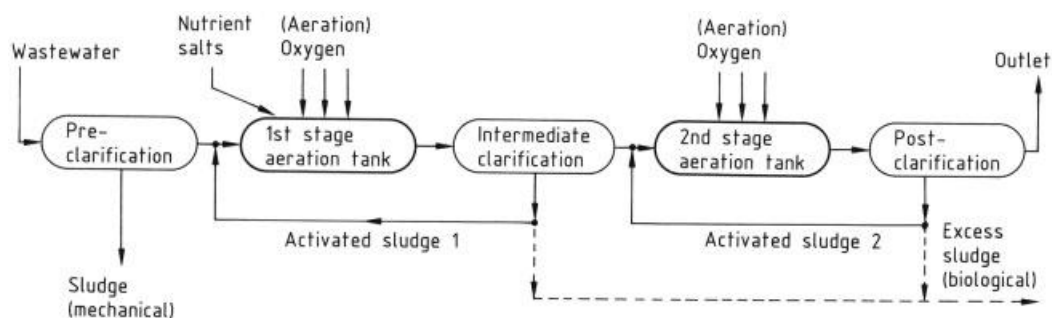


Figure 82. Scheme of biological effluent treatment with a two-stage activated sludge process [408]

effluent pollution. Information on the specific COD and BOD₅ loads, classified according to product groups, is given in [420].

8.7. Effluent Treatment Plants

Effluents from paper mills contain solids and dissolved substances. Solids (fibers, fillers) are mostly removed from the effluent in a chemomechanical clarification process by the use of flocculants. The degradation of dissolved organic substances is performed in aerobic and anaerobic biological treatment plants.

Chemomechanical clarification of effluents is carried out almost exclusively in sedimentation plants (round and rectangular basin with bottom sludge removal). Only in a few cases, is it necessary to neutralize the effluents. Rakes for the separation of coarse material and sand traps are seldom used. The clarifying efficiency of sedimentation plants is increased considerably by the use of flocculants. Undissolved substances are removed with an efficiency exceeding 90 %. Primarily activated sludge processes and, less often, trickling filter processes are employed for aerobic biological treatment. In North America and Northern Europe, effluent purification is frequently carried out in aerated oxidation ponds [421], [422]. Anaerobic treatment has also become established, especially in paper mills processing wastepaper.

The activated sludge processes applied are single-stage processes, systems with recycled sludge aeration, cascade systems, and two-stage processes. Atmospheric oxygen transfer is employed, using surface aerators (roll aerator, gyratory aerator) or pressure aerators. Pure-oxygen

processes with pressure aeration are also used occasionally [423]. It is possible to improve the purification efficiency of activated sludge plants by using pulverized brown coal [424] or foamed plastic carriers [425] in the activated sludge tank. Biological treatment with a two-stage activated sludge process is shown schematically in Figure 82. The trickling filter system is usually operated in combination with an activated sludge process. The trickling filter can be either the first stage (in high-load operation) or the second stage (in low-load operation). Combination processes also include activated sludge processes with fixed-bed internals and submerged disk filters. Activated sludge plants and trickling filter plants are almost exclusively fed with mechanically preclarified wastewater. The addition of nitrogen and phosphorus compounds is required.

Anaerobic processes have been employed recently for the treatment of more highly polluted effluents (COD > 2000 mg/L). Above all, effluents from paper mills processing wastepaper are treated in anaerobic contact systems with sludge recycling and in USAB (upflow anaerobic sludge blanket) reactors. Information on plants installed up to now and on operational experience is given in [426], [427]. Fixed-bed reactors, fluidized-bed reactors, and other reactor concepts are still being tested. Anaerobic effluent purification is almost exclusively operated as a preliminary step to the aerobic treatment. The BOD₅ efficiency attainable with activated sludge processes is usually in the range 90–98 %, and the COD efficiency between 80 and 95 % [428].

For final clarification after the aeration tank, horizontal (rectangular and round basin) or vertical-flow (hopper basin) sedimentation

basins are preferred. Biofilters are occasionally employed as a further purification stage [429]. Third-stage purification processes for the elimination of nitrogen and phosphorus compounds are not required.

The sludges generated in effluent treatment must be dewatered and disposed of if they cannot be returned to the papermaking process. Screen belt presses, chamber presses, vacuum filters, or centrifuges are used for dewatering. The dewatering behavior can be improved by the addition of chemicals (polymers, trivalent metal salts, lime). Machines and plants for sludge treatment and their dewatering efficiencies are described in [430].

Most dewatered sludges (solid content 20–60 %) are disposed of in landfills. Thermal utilization (combustion) is becoming increasingly important. The sludges also can be composted together with bark, applied to agricultural land, and used as a porousing agent in the production of bricks, as additives for fiberboard, and in making cat litter.

9. Coating of Paper and Board

Paper, composed of individual fibers, has a rough surface and pores whose size corresponds approximately to the fiber dimensions. Since this roughness has a negative effect on printing, a large amount of paper and board is coated in order to impart a smooth surface for printing. Coating is a process by which a mixture of water, white pigments, binder, and various additives are applied to one or both sides of a paper sheet. The resulting covering and smoothening of the surface of the paper improves its glaze, gloss, brightness, and above all, its printability in all conventional printing processes.

Economic Importance. In spite of the higher costs of coated papers, the proportion of the total production of paper and board that is coated has increased steadily in the last 25 years because of the quality advantages described above. Current (1988) prognoses assume that this development will continue up to the year 2000 (see Table 19). Of the 57×10^6 t of paper produced in Europe in 1988, 12.7×10^6 t (22.3 %) were coated. However, as shown in Table 20, this percentage varies greatly from coun-

try to country depending on the structure of the paper industry in each case.

Table 19. Estimated development of the world consumption of paper and of coated grades between 1988 and 2000

Paper grade	Consumption, 10^6 t		Increase, %/a
	1988	2000*	
All grades	227	289	2
Coated grades			
Paper	20	32	
Board	12	15	
Total	32	47	3.2
% Coated	14.1	16.3	

*estimated

The largest producer of coated paper and board in Europe is Germany, followed by Finland and Italy. About 39 % of the 5.2×10^6 t of graphic paper produced in Germany is coated, ca. 50 % of which is wood-containing, and the remainder wood-free. About 45 % (1.4×10^6 t) of the board employed for packaging (folding boxboard, liquid packaging) is coated.

Table 21 shows that between 1986 and 1988 the proportion of coated papers increased continuously both in Germany and in the United States. It should be taken into account that in the same period of time, the export of coated papers from Europe into the United States also increased and has now reached ca. $600\text{--}800 \times 10^3$ t. The paper manufactures in Europe are concerned about the fact that many producers have already made or are planning considerable investments because of the favorable prognosis. The production capacity for wood-containing coated papers will increase by about 800×10^3 t and that for wood-free coated papers by 2.4×10^6 t from 1990 to 1992. It is questionable whether this drastically increased supply will meet with an equally high demand. The enormous capital required for these new investments—a new paper machine and coating machine cost about 255×10^6 €—has previously led to the closing down of companies, even in Europe.

Coated Paper and Board Grades. The classification of coated grades has not yet been standardized. However, certain terms are recognized throughout Europe.

Table 20. Coated production as a percentage of the total production in some Western European countries in 1988

Country	Total production, 10 ⁶ t	Coated production, 10 ³ t			
		Board	Paper	Total	% of total production
Western Europe	57.0	3 870	8 840	12 710	22.3
Germany	10.6	683	2 044	2 727	25.7
Sweden	8.2	592	476	1 068	13.0
France	6.3	281	1 193	1 474	23.4
Finland	8.7	602	1 621	2 223	25.6
Italy	5.4	589	1 279	1 868	34.6
United Kingdom	4.3	236	353	589	13.7

Art Paper. This term refers to wood-free or slightly wood-containing paper that is coated on both sides. The weight of the coating exceeds 20 g/m² per side, resulting in the complete disappearance of the fiber structure of the raw paper. These papers can be either dull or glossy. Up to three coats are applied to each side to obtain the high quality required. Art paper is used for high quality printed products.

Table 21. Coated papers as a percentage of the total graphic papers in Germany and the United States, 1986–1988 (in 10³ t)

	1986	1987	1988
<i>Germany</i>			
Graphic papers	4565	4828	5185
Coated	1657	1786	2044
%	36.3	37.0	39.4
<i>United States</i>			
Graphic papers	22 666	23 897	24 950
Coated	5710	6230	6700
%	25.2	26.1	26.9

Chromopapers. Chromopaper is coated only on one side. However, the weight and quality of the coating correspond to that of art paper. Much of this paper is employed for packaging purposes.

Machine-Coated Papers. This term was previously used only for papers coated on-machine. Today, it is also applied to papers which are coated off-machine and have a similar coating weight and appropriate quality. It includes both wood-free and wood-containing papers with a coat weight of up to 18 g/m² per side. Higher weights are often obtained by applying a double coat. The coating formulations are normally simpler than those for art paper. The covering of the fiber structure depends on the particular coating weight and the roughness of the base pa-

per. Machine-coated papers are used chiefly for printing.

Lightweight Coated (LWC) Papers. The English term is used internationally for this grade of paper. These papers are highly wood-containing and generally have coat weights in the range 5–12 g/m² per side. They are mass papers and are used for the production of catalogs, magazines, advertising pamphlets etc. The fiber structure can still be discerned in most cases. Either web offset or rotogravure printing is used for LWC paper. The total weight of LWC papers varies between 51 and about 71 g/m². From about 1982 the weight range has been extended below (ULWC or LLWC) and increasingly also above (MWC = medium-weight coated and HWC = high-weight coated) these limits. Today, the heavy grades are often provided with a double coat and are, consequently, grouped with machine-coated grades.

Cast coated papers are specialty paper and board grades. The mirror-like gloss is obtained by a process called cast coating, in which the still moist or remoistened coating surface is brought in contact with a highly polished cylinder and dried. Only one side is coated in most cases.

Folding Boxboard and Chromoboard. In these grades of board, the white topline, which is usually made of pulp, is coated on the board machine. The remaining layers of board can consist of bleached or unbleached pulp or of wastepaper. However, the use of wastepaper for the topline is also rapidly gaining acceptance. The coating weight is in the range 12–25 g/m² and the coat is normally comprised of a precoat and a topcoat. Three coating layers have also been applied. The board is rarely coated on the reverse and if it is, it is mainly to improve the flatness and to reduce

dust deposition. High-gloss board is produced by using a brush finishing system or a gloss calender.

9.1. Requirements of Coated Papers

The composition of the coating color is largely determined by the demands made on the surface of the paper by the particular printing process. Offset and letterpress printing require an especially well bound coat because considerable tensile forces are exerted by the highly viscous inks at the high printing speeds used today. At the same time, the coating must be sufficiently porous to permit fast, controlled removal of the printing ink vehicle without reducing the gloss of the ink. For offset printing, the surface of the coating must have not only an especially high water resistance, but also the ability to absorb sufficiently quickly the fountain solution applied in the printing machine. In general, coatings must have adequate stiffness, good brightness, low yellowing tendency, and good aging resistance.

In rotogravure printing, the tensile forces between the printing cylinder and the surface of the paper are very small because of the low viscosity, solvent-containing inks that are used. For this reason, the amount of binder required should only be sufficient to bind the pigment particles to each other and the paper surface so that picking of the coating is prevented during the further processing of the coated rotogravure paper. Important criteria for coated papers that are to be used for rotogravure printing are good compressibility, a high degree of smoothness, and adequate receptivity for the ink solvent.

Apart from the optical and printing properties, there are other criteria that are important for paper and board used for packing purposes. These include low odor, flexibility, glueability, and crease resistance. Coated specialty papers require specific properties, such as alkali resistance (labels), washability (wallpaper), and solvent resistance (silicone release paper).

9.2. Properties and Components of Coating Colors

Apart from water, the main components of a coating color are coating pigments and binders.

In addition, a variety of auxiliary agents, such as dispersing agents for the pigments, additives to reduce wet abrasion, products for the control of viscosity and water retention, foam control agents, shading dyes, optical brighteners, and lubricants to improve paper calendering, are employed.

Coating colors, which are almost without exception all water-based, are fairly complicated multicomponent systems. Nowadays, paper is coated on high speed coating machines that are either a part of the paper machine or separate from it (on- or off-machine coaters). Coating colors are classified according to their solids content:

- 1) Low-concentration coating colors, solids content 35–45 %; Newtonian flow behavior; viscosity (Brookfield method) 100–500 mPa · s (at 100 rpm, 20 °C); coating process or equipment: a) air knife, b) bar coater (for low coating weights)
- 2) High-concentration coating colors, solids content 55–70 %; occasionally Newtonian, mostly pseudoplastic-thixotropic flow behavior; viscosity (Brookfield) 600–2500 mPa · s (at 100 rpm, 20 °C); coating process or equipment: a) roll coater, b) blade coater, e.g., inverted blade, billblade, c) roller blade
- 3) Coating colors of moderate concentration, solids content 45–55 %, Newtonian to slightly pseudoplastic flow behavior at greatly varying viscosity; coating process or equipment: a) roller blade (for intermediate coating weights), b) roll coater (gate roll coater, size press), c) blade coater

The properties of the coating colors must be adapted to the coating process and the intended use of the coated paper. The *solids content* greatly influences the runnability of the coating color in the coating machine. It basically influences the viscosity of the color and its flow behavior at varying shear stresses in the coating machine. The various components of the coating color determine the solids content attainable at a given viscosity. The highest possible solids content is aimed for to save drying energy. Another important property of the coating color which greatly influences its workability is the pH. Most coatings are processed in the pH

range 7.5–11.5. The alkaline range is preferred because most of the color components have an anionic character and, from a colloidal chemical viewpoint, form considerably more stable systems at higher pH values than at low pH values. In addition, the drying time of the mostly oxidatively drying offset inks is greatly reduced with increasing pH.

For most coating processes, the water retention capacity of the coating color is also important; i.e., the ability of the coating color to retain water in spite of the sucking action of the coating base paper. If the water retention capacity of a coating color is too low, it may be too strongly dewatered between application and leveling.

9.2.1. Pigments

Pigments form the actual “body” of paper coatings. They usually account for at least 80 % of the total dry coating weight. Thus, pigments largely determine the quality and cost of the coating. White pigments are used almost exclusively in the coating plant, the most important being clay, ground and precipitated calcium carbonate, calcium sulfoaluminate (satin white), titanium dioxide, talc, and occasionally barium sulfate. Calcium sulfate (gypsum) has also been used in exceptional cases. For special applications, calcined and delaminated clays and synthetic pigments based on aluminum silicate are employed (cf. Table 16). The pigment most often used is coating clay. It is especially well suited to the production of a smooth coating surface because of its platelike structure. Furthermore, the large number of types makes it possible to take into account all the requirements of the coating and of the processing machines. Most of the coating clay used in Europe comes from England. However, North and South American clays are being used in European coating plants to an increasing extent. American clays are normally a little yellower than the English varieties and also have a different area-to-thickness ratio (shape factor). This, in turn, results in a lower viscosity and a somewhat lower water retention capacity of the coating color.

Apart from clay, finely ground grades of calcium carbonate have become particularly important, and the amounts used are now comparable to clay. Typical grades of calcium carbonate

have a particle fineness of 90–95 % $< 2 \mu$ and a brightness of 93–95 %. They permit the production of highly concentrated coating colors which can still give a very smooth and glossy coating. Calcium carbonate normally increases the microporosity and brightness of the coating, but the ground form can give lower opacity.

Satin white is still of some importance in paper coating. This pigment has very fine particles; it is extra white, and has a low density. It increases ink absorption and gloss. The disadvantages of satin white are its sensitivity to increases in temperature and decreases in pH, and its high adhesive demand.

In spite of the high price and limited availability of titanium dioxide, it is employed especially in the United States to compensate for the yellowish U.S. clay. As a result of its high refractive index, this pigment greatly increases the opacity of coated paper, even in the wet state. For this reason, it is used in Europe mainly for specialty papers (e.g., labels).

9.2.2. Dispersing Agents

The first stage in the production of coating colors is the conversion of the coating pigments, which are usually supplied in the dry state, into a flowable and pumpable aqueous slurry. This dispersion process consists of two steps: the mechanical dispersion of the coarse pigment agglomerates in an aqueous medium and the chemical stabilization of the slurry towards reagglomeration. The second step requires dispersing agents.

Suitable dispersing agents are polyanions, e.g., salts of polyphosphoric acids (pyrophosphates, hexametaphosphates) or poly(acrylic acids). These products permit the production of stable, highly concentrated pigment slurries that are still flowable. Coating colors with concentrations of 70 % and more can be produced. Today, ready-for-use pigment slurries are often available from pigment suppliers. The specific requirement of dispersing agents for the individual pigments varies greatly. English clays, for instance, require ca. 0.3 % and American clays ca. 0.1 % of dispersing agents. Calcium carbonates need 0.4–0.8 %, depending on the fineness and the pretreatment, and satin white requires 2–3 %. The protective colloid action

of organic dispersing agents stabilizes the rheological properties of the coating color, especially in the case of satin white.

9.2.3. Binders

The function of the binder or adhesive is to bind the pigment particles to each other and to fix the coat to the base paper. In spite of their low proportion by weight in the coating color (generally 5–25 % based on the pigment), binders have a large influence on the coating and processing properties of the coating color.

Binders from Natural Raw Materials.

The natural binders all have hydrophilic properties. The most widely employed binders of this type are starch and its derivatives, cellulose ethers such as carboxymethyl cellulose, and in the United States, hydroxyethyl cellulose, soybean protein, and to a very small extent casein and alginates.

Natural binders act as protective colloids that prevent the flocculation of the pigments; they increase the viscosity and water retention of coating colors and give the coat a higher stiffness. In general, natural binders are used as additives for synthetic polymer binders.

Starch derivatives are intended to lend the coating color good rheological properties at high shearing forces. They should have a good pigment-binding power and ensure good adhesion of the coating to the paper. In order to meet these and other requirements, mixtures with other binders, and variation in type of derivatives are used. For example, oxidized starches are usually employed together with polymer dispersions. Hydrolyzed starches exhibit high stability in solution, good binding power, and good flow behavior. Hydrolyzed, esterified starches exhibit good stability in solution, high binding power, and increased reactivity towards wet-strength additives such as urea–formaldehyde resins. Hydrolyzed, etherified starches exhibit the same properties as the esterified derivatives. However, in contrast to the esterified derivatives, they can be used at pH values above 8 without the risk of saponification. Starch derivatives that contain phosphate and amino groups are compatible with cationogenic substances such as satin white. The phosphate groups react with

multivalent metal ions, such as aluminum ions, which in turn leads to a certain degree of water resistance. The amino groups react with aldehydes, which in turn enhances the activity of wet-strength additives.

Cellulose Ethers. The sodium salt of carboxymethyl cellulose (CMC) is the principal cellulose ether used as a binder in papermaking. Pure CMC coats of 0.5–3 g/m² increase the grease resistance and printability of paper. Depending on the use, various mixtures of low- and high-viscosity CMC are employed. Pigment-containing CMC coats, which can be applied on the size press, contain up to 10 % semitechnical, low-viscosity CMC or salt-free, purified CMC. CMC is usually processed together with other natural or synthetic binders. Above all, CMC increases the water retention of the coating mixture. However, the water retention is so high that the addition of other binders that promote water retention in the coat to a lesser extent is necessary. In general, the amounts of CMC employed are 0.3–1.5 % based on the pigment, and very low viscosity types are preferred. This gives an adequate coating color viscosity, even if the solids content of the coating color is high. Types of CMC that are soluble in cold water are rapidly becoming established because they do not require dissolving at elevated temperature. The presence of satin white pigment can cause strongly interfering coagulations in the coating color.

Casein must be present in the dissolved state. It is dissolved by the addition of alkali (e.g., ammonia, sodium hydroxide, borax, or sodium carbonate) either separately in a cooker (up to 70 °C) or with the pigment in a kneader. The casein concentration is limited to ca. 20 % by its high viscosity. The limit of processability is shifted to ca. 33 % by the addition of urea or dicyanodiamide, which reduces the viscosity and increases the storage stability of casein solutions. The mixing of casein solutions with pigments, especially China Clay, can cause a “shock” phenomenon (a rapid increase of viscosity).

Soybean protein has properties very similar to those of casein. Isolated soybean proteins are hydrolyzed, isoelectric proteins. They are used in the form of alpha and delta proteins with four different viscosities (extra low, low, medium, and high). The viscosity refers to the

dissolved soybean protein, the solvent of choice being aqueous ammonia (26 Bé). Proteins dissolved in this way exhibit very low sensitivity to water after drying. Like casein, soybean protein is mostly used as a mixture with polymer dispersions. This combination permits the preparation of coating colors with high solids content and a relatively low viscosity. Solids contents of ca. 60 %, suitable for blade coaters, can be achieved.

Synthetic Binders. In the initial phases of paper coating, natural binders were used exclusively. However, in the 1940s in the United States and in 1950s in Germany, the demand for synthetic binders in the form of polymer dispersions started increasing. These products made it possible for the first time to attain a high solids content at low viscosities, a prerequisite for modern high-speed coating machines. In addition, polymer dispersions give the coat a higher water resistance, better flexibility, higher gloss, and better printability. They are aqueous dispersions of polymers, usually stabilized with anionic emulsifiers. The solids content of the dispersions is generally 45–50 %. In most cases, the polymers are copolymers of several monomers, e.g., styrene, butadiene, acrylic ester, vinyl acetate, and acrylonitrile. Apart from these components—the so-called main monomers—small amounts of auxiliary monomers, such as acrylamide, acrylic acid, maleic acid, and methacrylamine are added to modify the dispersion properties.

The styrene–butadiene dispersions are most widely used worldwide. Products of varying film hardness are obtained, depending on the proportion of styrene used. The compatibility of these highly hydrophobic polymers with the other coating components can be improved considerably by carboxylation, i.e., by incorporating small amounts of unsaturated carboxylic acids such as acrylic acid. Approximately equal proportions of styrene and butadiene give binders which provide a relatively soft film and a very good pigment binding capacity. However, the odor of the dispersion and the tendency of the films to yellow when exposed to light are disadvantages.

Acrylate dispersions are of comparable importance in Europe. These are copolymers of butyl acrylate with styrene or vinyl acetate. The ratio of the soft component (butyl acrylate) to the

hard one (styrene or vinyl acetate) determines the application characteristics of the dispersion. In general, acrylate dispersions have an excellent ageing resistance and are less odorous. Apart from these two most important groups of polymer dispersions, vinyl acetate homo- or copolymers have gained entry into paper coating plants, especially in the United States. These products generally have a lower binding power, but provide very hard and porous coats, and have an excellent ageing resistance. Polymer dispersions based on methacrylates and copolymers of vinyl acetate and ethylene are less important in paper coating.

The above-mentioned products are low-viscosity aqueous dispersions which usually do not influence properties such as viscosity and water retention that are important for the flow behavior of the coating. For this reason, only in a few cases are these “multipurpose dispersions” used alone. They are usually mixed with cobinders, which are responsible for adjusting the flow properties of the coating color. In general, these cobinders are naturally occurring products, such as starch, casein, CMC, and alginate.

Products based on acrylate esters have also been used as cobinders. Due to their high degree of carboxylation, these dispersions turn into colloidal dispersions upon addition of alkali. Thus the laborious and energy consuming dissolution and preparation processes involved in the use of natural binders are avoided. Another synthetic cobinder that has long been known is polyvinyl alcohol. Although its binding power exceeds that of all other binders used in paper coating, it has gained only limited acceptance. This is mainly due to the fact that the application of large amounts of polyvinyl alcohol leads to rheological problems on the coating machine during processing.

Apart from these two-component systems, synthetic sole binders which do not require a cobinder have been available since the early 1960s. On addition of alkali, these products develop the required viscosity and water retention, but retain their dispersion form. Special binders of this type have become popular, especially for illustration paper that is produced in large amounts and printed by the rotogravure or web offset process. Table 22 lists the various binder systems, their influence on the produc-

Table 22. Comparison of various binder systems

Binder system	Production	Rheological behavior	Coating properties
Polymer dispersion alone (rarely used)	simple mixing process	usually unfavorable	variable via type of dispersion; waterproof, glossy coat attainable; no activation of optical brighteners
Polymer dispersion + watersoluble cobinder, e.g., casein, starch, CMC (very frequent)	mixing and dissolving processes, sometimes separately with heating	largely controllable via cobinder	variable via single components; limited water resistance and gloss; full activation of optical brighteners
Polymer dispersion + synthetic cobinder (frequent)	integrated mixing/dissolving processes, no heating	controllable via cobinder	limited variability; waterproof and glossy coat attainable; full activation of optical brighteners
Polymer dispersion + viscosity regulating additives (in special cases)	integrated mixing/dissolving processes, no heating	limited controllability	variable only via type of dispersion; good water resistance and gloss, no activation of optical brighteners
Special dispersion (for publication papers)	integrated dissolving/mixing processes, no heating	slight controllability	limited variability; improved water resistance with additives; good gloss attainable; optical brighteners can be activated only via auxiliary components

tion of coating colors, the rheological properties of the coating color, and the coating properties.

9.2.4. Other Additives

In many coated papers and boards, the coating must be resistant to water. For instance, offset papers are exposed to the fountain solution in the printing machine, labels should not disintegrate when wet, and some wallpapers must be resistant to cleaning with detergents.

Good waterproofing of coatings can be achieved by using water-insoluble polymer dispersions. However, additional auxiliary agents are required to harden the coating since a water-soluble cobinder is used in most cases, which renders the coat sensitive to water to some extent. Three main classes of products are employed as hardening agents: melamine–formaldehyde resins, urea–formaldehyde resins and bifunctional aldehydes such as glyoxal, which is added only to coatings containing starch. The other two resins are used in various binder combinations. High proportions of natural binders require the addition of 10–15 % of hardening agents, based on the natural binder. For sole-binder coatings or coatings with only very small

amounts of cobinder, 0.8–1 % is used, based on the pigment.

The waterproofing of the coating is due to a cross-linking reaction between the resin and the binder, with elimination of water. The rate and degree of cross-linking depend on the pH and the temperature. The desired effect increases with decreasing pH of the coating color and intensity of drying. The worldwide discussion on formaldehyde being a possible carcinogen has led to an intensified search for other cross-linking systems. For instance, products based on ammonium zirconium carbonate or epoxides are being used in some cases.

Foam-control agents (→ Foams and Foam Control) are another important class of additives. Most coating colors contain considerable amounts of products that act as foam producers or stabilizers (e.g., emulsifiers, protective colloids). Due to the constant motion of the coating color, air is easily introduced into it. The resulting foam causes an increase in viscosity and processing problems. However, the more serious problems are flaws in the finished coat such as craters and longitudinal streaks caused by the bursting of foam bubbles. The foaming tendency

decreases with increasing solids content and is, therefore of minor importance for modern high-solids coatings. The use of appropriate systems that minimize the ingress of air during preparation and circulation of coating color is the principal measure taken to prevent foam. However, in many cases this is not sufficient and chemical defoamers must be added.

A distinction is made between agents that prevent foam formation (foam inhibitors) and those that destroy foams (defoaming agents). Coating color defoamers must not only be easily emulsifiable, but should also be worked into the coating color under an appropriately high shear gradient. Otherwise, or if too much is used, agglomerates of defoamers are formed in the coating and these in turn lead to spots of low surface energy where printing ink will not adhere (fish eyes). In practice, the amounts of foam inhibitors used vary from 0.02 to 0.05 %, based on the pigment. Defoamers are usually diluted with water and added to the coating mixture dropwise. Amounts ranging from 0.01 to 0.05 vol % are usually sufficient.

In many cases, the yellowish color of the coating clay does not satisfy market requirements. Apart from the addition of pigments such as titanium dioxide which increase brightness, blue-violet dyes (*shading dyes*) are often used at a concentration of about 2 g per 100 kg of pigment to attain a bluish white coating surface which appears brighter to the eye. Not only basic dyes, but also the considerably more light-fast pigments may be used. If the brightness required is very high, *optical brighteners* are added in addition (→ Optical Brighteners). In order to be effective, most optical brighteners need a substance to which they can be attached. Substances of this type are polyvinyl alcohol, carboxymethyl cellulose, casein, starch, and some synthetic cobinders. Polymer dispersions do not have this property.

So-called *lubricants* such as calcium or ammonium stearate are used in many illustration papers to reduce dusting on the calender and produce a higher paper gloss.

9.2.5. Coating Color Formulations

The coating color formulations presented below are examples of formulations commonly used in Europe at present. However, they must usually

be adapted to suit the particular conditions in the individual mills.

LCW Rotogravure Paper. A coating color based on a special sole binder is usually used for this paper, which is produced on very large machines ($150-250 \times 10^3$ t/a). Composition (in parts):

Clay	100
Dispersing agent	0.1–0.3
Sole binder	4.8–5.5
Sodium hydroxide solution added until pH 8.5 is reached	
Calcium (ammonium) stearate	0.7
Solids content	45–60 %
Viscosity (Broofield; for blade coater)	400–2500 mPa · s at 100 rpm

LWC web offset paper (in parts):

Pigment (clay + CaCO ₃)	100
Dispersing agent (as required)	
Multipurpose dispersion	9–12
Natural or synthetic cobinder	0.5–4
Hardening agent	0.5–1
Calcium (ammonium) stearate	up to 1
Solids content (for blade application)	58–70 %

This is an example of a large number of different compositions. Today, great importance is attached in many cases to the stiffness of the paper. Consequently, the binders should form very stiff films.

Sheet offset paper (in parts):

Pigment (clay + CaCO ₃)	100
Dispersing agent (as required)	
Multipurpose dispersion (see above)	10–14
Natural or synthetic cobinder	0.5–4
Hardening agent	0.5–1
Solids content (for blade application)	57–70 %

A wide variety of coating formulations are available.

Board (in parts):

Pigment (clay + CaCO ₃)	100
Dispersing agent (as required)	
Multipurpose dispersion, e.g., based on acrylate	12–20
Natural or synthetic cobinder	1–6
Hardening agent	1

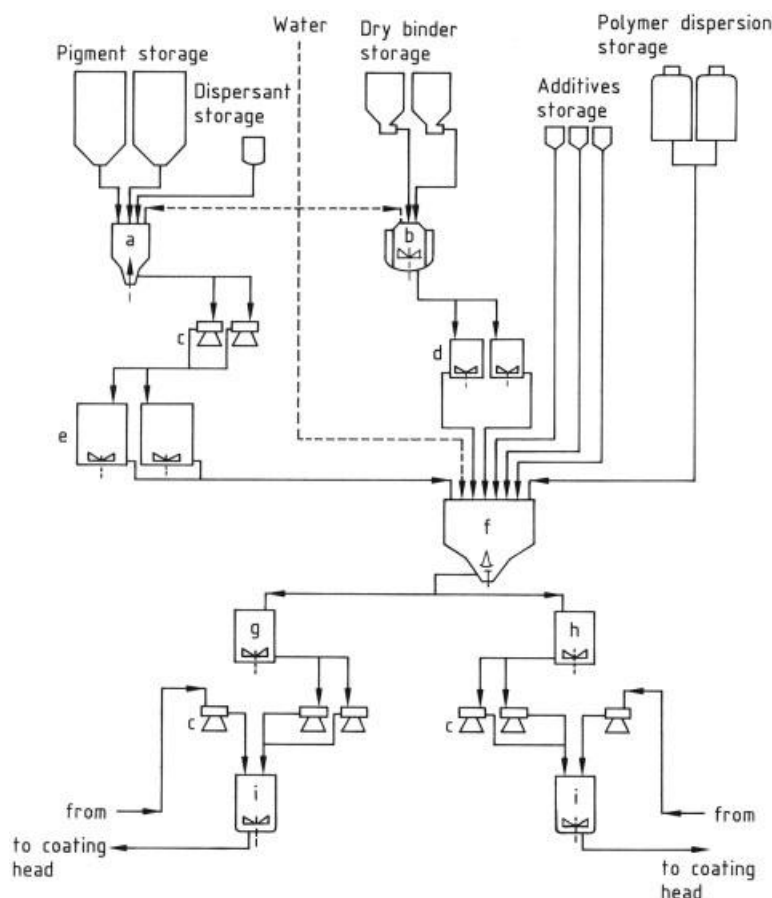


Figure 83. Production of coating colors

a) Disperser; b) Dissolving vessel; c) Filters; d) Vessels for dissolved binder; e) Containers for pigment slurry; f) Coating mixer; g) Reservoir for coating 1; h) Reservoir for coating 2; i) Working vessels

Starch is used only rarely in the topcoat. CMC or a synthetic acrylate based cobinder is preferred for board.

9.3. Coating Color Preparation

A flow sheet for the batch production of coating colors is shown in Figure 83. These, or similar plants that permit adaptation to a very variable coating program, are used in practice in by far the most cases.

Water, dispersing agent and, when required, alkali are fed to the dispersing machine and the dry pigments are then added. While kneaders were used previously for dispersion, high-speed mixers with rotor–stator systems have

now gained acceptance. These turbomixers permit the production of a completely dispersed pigment slurry in 5–60 min, depending on the amount of pigment. The next step is either the intermediate storage of the slurry or the immediate preparation of the coating color in the turbomixer, depending on the size of the plant. Dispersion requires the highest rate of rotation, but the speed is reduced when binding and auxiliary agents are added. Natural binders such as protein or starch are dissolved in advance by heating in a separate vessel.

When adding the binding and auxiliary agents, the amount of water required to give the desired final solids content is added to the pigment slurry first. The natural cobinders are then added with constant stirring, followed by

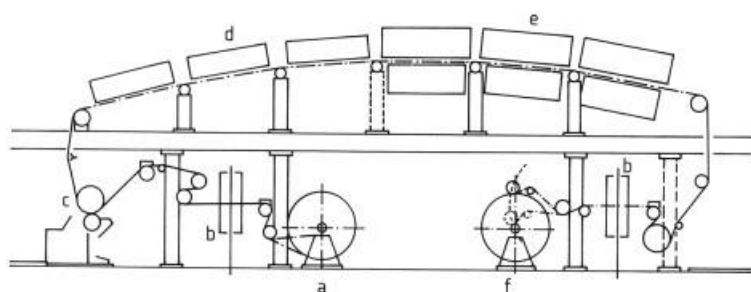


Figure 84. Schematic of coating plant

a) Unwind station; b) Moisture and coating weight measurement; c) Coating station; d) Infrared dryer; e) Hot-air dryer; f) Rewind station

the polymer dispersion, and finally the auxiliary agents, such as hardeners, shading dyes, optical brighteners, and lubricants. This is followed by the final adjustment of the pH, viscosity, and solids content, and pumping the mixture into the storage vessel.

The pigment slurry and also the finished coating color are screened at least once before they enter the coating machine. The use of a screen in the coating color return flow is also recommended to remove particles torn off the paper. Pressure or disk filters or vibrating screens are used for the filtration of the coating color. The mesh size of the screens is 5000–10 000 apertures/cm². Coarser screens with mesh sizes of 2500–3500 apertures/cm² are required for clay. Apart from batch plants, continuous plants also exist and they have the advantage of requiring less space, and the amount and composition of coating color can be more easily changed. The precondition for a continuous plant is that all the components of the coating color are present in the liquid state. They are then transferred to the dispersion apparatus by dosing pumps. After passing through the shearing zone the finished coating color leaves the closed system.

9.4. Coating Machines

The first coating machines imitated the process of painting in that the coating was leveled with oscillating brushes. The brushes were then replaced by distributor rollers, and finally by systems such as the air knife or trailing blade. Modern coaters (see Fig. 84) consist of the unwind

station, coating head, a dryer, and the rewind station. Paper may be coated either on equipment that is an integral part of the paper machine (on-machine) or on separate coating equipment (off-machine). A compromise is frequently made between the two types, the coater being installed directly after the paper machine (in-line). In this case, the coater can be used when required.

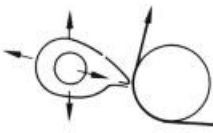
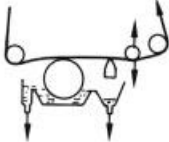
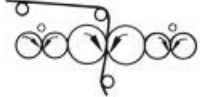
The most important part of the coating machine is the coating application unit. It has three functions: transferring the coating color onto the web, metering of the excess, and leveling of the remaining coating. The most important coating equipment is listed in Table 23.

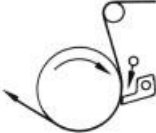
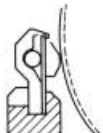
The air knife is widely used in Europe. Metering and leveling are achieved with a thin jet of air. This contact-free doctoring off permits the use of almost all coating raw materials and an almost unsurpassed range of coat weights. The air brush is also used as an intermediate coating aggregate for triple-coated board.

The coating equipment most often used for on-machine coating is the size press. It is used almost exclusively for the precoat, and the application weight is relatively limited.

The blade coating processes have rapidly gained tremendous importance due to their simple operating principle, which permits the attainment of speeds exceeding 1400 m/min. The blade is usually made of flexible steel of 0.3–0.4 mm thickness. It is used to remove excess coating color from the paper. Especially in the case of the inverted blade, coating weights of 4–26 g/m² can be achieved. Blade coatings have a particularly high smoothness. This system has the advantage of requiring a lower drying energy because coating colors of high solids

Table 23. Survey of the most widely used coating equipment

				
	Air knife	Bar coater	Size press	Film press
Usual mode of operation	separate and board machine	board machine	paper and board machine	paper machine
Application	one-sided	one-sided	two-sided	two-sided
Use for multilayer coatings	topcoat, intermediate coat	precoat, topcoat	precoat	
Working speed (max.), m/min	500	300	800	400
Coating weight (per side), g/m ²	10–30	4–10	4–8	8–15
Solids content of coating, %	35–50	40–50	25–45	50–60
Viscosity (Brookfield, 100 rpm), mPa·s	100–300	100–300	100–300	1000–3000
Types of paper usually coated	Art paper, chromopaper, specialty paper, wallpaper, packaging paper, board	board	graphic	graphic

					
	Trailing blade	Bill blade	Inverted blade	SDTA	Roller blade
Usual mode of operation	separate	paper machine	separate and paper machine	separate and paper machine	board machine
Application	one-sided	two-sided	one-sided	one-sided	one-sided
Use for multilayer coatings	topcoat	precoat, topcoat	precoat, topcoat	precoat, topcoat	topcoat
Working speed (max.), m/min	1200	1000	1500		1000
Coating weight (per side), g/m ²	6–15	6–12	4–25	4–25	6–12
Solids content of coating, %	55–62	50–65	45–70	45–70	50–65
Viscosity (Brookfield, 100 rpm), mPa·s	500–1500	300–1000	500–2000	400–1000	500–1500
Types of paper usually coated	graphic, LWC	graphic	graphic, LWC, art paper, specialty paper, board	LWC, board	board

content (70 %) can be processed in blade coating plants. Apart from the usual application with a roll, the short dwell or short dwell time applicator (SDTA) system has been used increasingly in the past years. In the SDTA, the coating color is in a chamber under pressure directly in front

of the blade. The distance between coating and blade, which is about 80 cm in normal roll applicator coaters, is reduced to 3–30 cm. Thus, the time in which the coating color is in contact with the base paper before blade metering is reduced substantially. A relatively new system used in

paper machines is the bill blade, which simultaneously coats both sides of the paper, and the roller blade, which has a rotating bar instead of the rigid blade placed on the running paper web.

Drying. The coat must be dried after leveling in the coater. The drying facilities vary greatly. The festoon drying system, in which the web was dried on slowly moving rods in a long tunnel, is now obsolete. Hot-air hoods and drying cylinders are used on the paper machine. The latter are often coated with teflon or a similar substance to prevent the sticking of the moist coating. In off-machine coaters hot air tunnels are often used, through which the paper web is transported. The paper is supported by rolls when only one side is coated and by a hot air cushion when both sides are coated. Air foils are a modern version of this process, involving air-cushion drying with the paper web being supported and dried on both sides by hot air rapidly streaming out of narrow jets. In addition, infrared dryers are usually used in combination with the above mentioned drying facilities. These IR dryers immediately fix the coating after it leaves the coater, preventing migration of binder in the paper.

The drying facilities not only determine to a large extent the coating speed and the maximum application weight, but they also greatly influence the quality of the coat.

10. Paper Dyeing [431–440]

Colored papers are obtained by dyeing the paper stock or the paper surface (size press, paper coating, printing). Optically brightened papers can be produced in the same manner. Dip dyeing is used only for special purposes. Anionic direct, cationic direct, and basic dyes are the most important dyes employed for paper coloring, and are now frequently available as liquid formulations. Acid dyes are used in individual cases and pigments only in special grades.

10.1. Dyeing Processes

Stock dyeing is the most widely used type of paper dyeing. Dyes, pigments, and optical brighteners are added either batchwise in the

pulper or mixing chest or introduced continuously into the stock flow.

The choice of dye and the fixing and dyeing conditions largely depend on the raw material used in papermaking (recycled fibers, groundwood, unbleached pulp, bleached pulp, CTMP, TMP) and on the pH of the dyeing system. In continuous dyeing, the point of addition is also determined by these two factors (low consistency dyeing at a stock consistency of ca. 0.8 % and high consistency dyeing at a stock consistency of 3–4 %). In general, there is a trend towards dyeing processes in the neutral pH range. The higher the degree of beating of the pulp, the deeper the coloring.

Fillers increase the dye requirement because they absorb dyes and, at the same time, reduce the coloration owing to their covering power and brightness. The addition of aluminum sulfate usually promotes the absorption of dyes and yields less colored effluent. The two stock dyeing processes have the following advantages and disadvantages.

Batch addition has the advantage of thorough mixing of all additives with the paper stock, optimal fixation due to longer contact time between fiber and dye, as well as easy handling. The disadvantage is that the time required for color correction and color change is long.

Continuous addition has the advantage of a shorter zone in the stock line that must be cleaned when the color is changed, and of less broke because the desired shade is attained more quickly. However, a lower color yield (low contact time) is obtained for intensely colored papers, and the more complex equipment required for this dyeing process must also be taken into consideration. For example, the shade of a production is controlled by continuous color measurements in the paper machine, and the feeding pumps can be adjusted automatically to carry out the required corrections.

Surface Coloring in the Size Press. In this process, dissolved dyes are added to the size press liquor. Optical brighteners and other additives have long been applied in this way. An essential prerequisite for uniform dyeing is adequate and, above all, uniform absorbency of the paper.

The advantages of this process are: quick changeover of shades, absence of dyes in the wa-

ter circuit, and, in the case of papers with higher basis weights ($> 80 \text{ g/m}^2$), the saving of dye. Nevertheless, compared with stock dyeing – the classical dyeing process – surface dyeing has gained acceptance only in individual cases because uniform dyeing of the paper is difficult to achieve. It is occasionally advisable to combine the stock and surface dyeing processes, e.g., to correct two-sidedness. The bleed fastness of surface dyed papers is generally lower, compared to internal addition.

Dip Dyeing. A small group of specialty papers, called effect papers (flower crepe paper, tissue paper), is noted for its intensive and brilliant shades. The paper is passed through a dipping bath containing an aqueous solution of the dye. The excess dye liquor is pressed off between two rolls and the wet paper is creped, if required, before drying. Acid dyes are usually used because they have high solubility and bright shades. The low affinity of these dyes for plant fibers results in uniform dyeing, even in the case of papers with greatly varying fiber composition. The bleed fastness of dip dyed paper is poor, corresponding to that of surface-colored paper.

Surface Coloring by Coating. In normal coating, the surface of the paper or board is covered with a pigment coating (see Chap. 9). In the case of colored coatings, the starting material is the white coating mixture, and the desired shade is attained by adding a dispersion of an organic or inorganic pigment. Water-soluble dyes can be used only to a limited extent because, even with the use of fixatives, they cannot be rendered bleed fast in the coat (danger of migration into the base paper). Also, the inadequate lightfastness compared to pigments limits the use of these dyes.

10.2. Fastness, Dyes, Pigments

Depending on the intended purpose of the paper, the following types of fastness are required of paper dyeing [432]:

Lightfastness is required for all kinds of fine paper, especially document paper, photographic paper, laminate base paper, and wood-free writing and printing paper. Organic and inorganic

pigments and direct dyes are suitable for this purpose.

Bleed fastness is required for paper and board that are used for food-packaging and tissue papers. Organic and inorganic pigments and direct dyes are suitable for this purpose.

Rub fastness is required for album and wrapping paper and for cover board. Direct dyes are suitable for this purpose.

Acid fastness is required for parchment and vulcanized fiber base paper, writing, and printing paper. Organic and inorganic pigments, selected representatives of all colorant groups, are suitable for this purpose.

Solvent resistance is required for labeling paper (packaging of perfumes, medicines, and spirits). Special pigments are suitable for this purpose.

Heat resistance is required for cable and core paper and laminate paper. Organic and inorganic pigments are suitable for this purpose.

Basic Dyes (Cationic Dyes). The affinity of basic dyes is extremely good on lignin-containing fibrous materials (e.g., groundwood) and unbleached pulps, which are negatively charged. Salt formation gives rise to very stable color lakes that are insoluble in water.

Anionic fixatives, e.g., Mesitol (Bayer) or Tamol (BASF), also form color lakes of this type with cationic dyes, and can therefore be used to improve the fixation of basic dyes on bleached pulps that contain only small amounts of lignin. Better dye fixation always results in richer colors, improved bleed fastness, and less effluent staining.

Advantages: brilliant and tinctorially strong dyes, which result in good fastness to water and steam on groundwood-containing furnishes.

Disadvantages: poor substantivity on bleached furnishes, mottling tendency (i.e., parts of the paper stock or stock mixture are dyed more deeply than others), and poor lightfastness.

Applications: low-quality paper, packing paper, kraft paper, cartridge and cheap wrapping paper, dip dyeing, and surface coloring.

Direct dyes, compared with basic dyes, have a high affinity for wood-free, bleached pulps. Cationic fixatives are not required to increase the dye yield of direct dyes, unless deep shades with

good bleed fastness are required (e.g., deeply colored napkins).

Advantages: high affinity for wood-free bleached stocks. The lightfastness is often superior to that obtained with basic dyes.

Disadvantages: direct dyes are less suitable for the dyeing of unbleached furnishes (groundwood) because the shades obtained are not as brilliant as those produced by basic and acid dyes. Mottling tendency is occasionally observed with stock mixtures (cellulose – groundwood).

Applications: text and cover paper, cable paper, quality writing paper, bookkeeping and carbon paper, punch and filing cards, all unsized papers such as blotting paper and hygienic papers (e.g., serviettes, handkerchieves, toilet paper).

Cationic direct dyes are moderately absorbed on bleached and wood-containing stocks, and even in the case of deep shades, alum or a fixative is not required. These dyes produce fairly good bleed fastness. Combination dyeing with anionic direct dyes can be carried out to reduce the contamination of the wastewater and to improve bleed fastness.

Acid dyes have little affinity for natural plant fibers. Although the dye molecules penetrate well into the capillaries of the fibers, they must be fixed with aluminum sulfate (pH ca. 4.5) and cationic fixing agents, e.g., Levogen (Bayer) or Tinofix (Ciba-Geigy), in order to achieve a satisfactory dye yield.

Advantages: good solubility, no tendency to mottle on stock mixtures, and very well suited to dip dyeing.

Disadvantages: no affinity for plant fibers, suitable only for sized papers when aluminum sulfate and fixatives are added, colored effluent, and poor bleed fastness.

Applications: certain writing and printing papers, decorative crepe paper, and carbon paper.

The importance of acid dyes for pulp dyeing has decreased tremendously because they pose wastewater problems.

Pigments. Inorganic pigments (iron oxides and chromium oxides), organic pigments (e.g., azo and phthalocyanine types), and carbon black are used for paper dyeing. The retention of pigments on paper fibers is based on the following phenomena:

- 1) Filtration, i.e., the fibers on the wire of the paper machine act like a filter. The retaining power of the stock is directly proportional to the degree of beating to which it has been subjected.
- 2) Absorption (van der Waals forces and electrostatic effects).
- 3) Occlusion, i.e., the pigment particles are enveloped by other substances (colloidal components of the paper stock, aluminum hydroxide hydrate, resin precipitate).
- 4) Flocculation, i.e., improvement of retention by the addition of agents such as cationic retention or wet-strength additives, which bind the pigment to the fibers.

Advantages: excellent fastness and no risk of mottling.

Disadvantages: no affinity for fibrous materials, two-sidedness in the case of pulp dyeing (the wire side of the paper is less strongly colored), and low tinctorial strength.

Applications: lightfast writing and printing papers, bookkeeping and label papers, document and laminate base papers.

Blueing. This type of paper dyeing basically consists of counteracting the slight yellow tinge of all paper stocks by adding “violet”. Pure blue and brilliant red dyes, which together give violet, or violet dyes are used for blueing.

The highest degree of whiteness is obtained with *fluorescent whitening agents*, which, like direct dyes, are absorbed directly on the fiber. This method is mainly applied to paper stock and to paper surfaces (size press, coating). The presence of optical brighteners in paper can be detected by the characteristic fluorescence under a UV lamp.

Dyeing of Specialty Papers.

Veined paper is made from a mixture of bleed fast dyed fibers (cellulose, cotton fibers, wool, or synthetic fibers) and pulp that is either dyed differently or undyed.

Effect papers (see the Section on page 121)

Laminate base papers for the production of high quality laminate materials, e.g., for the furniture industry, are obtained by pigment dyeing.

Bronze-glazed paper: the color bearing component of the coating color is aluminum or

brass powder, which produces a silver or gold effect or, in combination with dyes, a metallic effect.

Security papers are treated with dyes or chemicals that change color under the influence of reducing or oxidizing agents, alkali, or acids and thus make forgeries more difficult.

11. Types of Paper, Cardboard, and Board

Paper is a product made from plant fibers that have been mechanically or chemically digested. The fibers are bonded together in an aqueous suspension and processed into sheets with the addition of auxiliary agents.

Accordingly, paper is defined as a planar material made essentially from fibers that are mostly of plant origin. It is formed by draining a fiber suspension through a sieve. The resulting fiber web is subsequently compacted and dried to give a basis weight of $< 225 \text{ g/m}^2$ [441], [442].

There are approximately 3000 kinds of paper products [443]. These can be divided into four main groups:

- 1) Graphic papers
- 2) Packaging papers
- 3) Hygienic papers
- 4) Specialty papers

This classification has also been largely adopted by the Statistisches Bundesamt (Federal Statistical Office) of Germany in Chapter 48 of the “commodity index for foreign trade statistics” [444]. The basis of this systematology is a “harmonized system for the marking and coding of merchandise” of the “council for tariff cooperation”.

11.1. Graphic Papers

The term graphic papers refers to a large range of different papers that are suitable for printing.

Printing and Press Papers [445]. Printing and press papers are divided into the following four groups:

- 1) Newsprint
- 2) Wood-containing natural printing papers
- 3) Wood-free natural printing papers
- 4) Coated printing papers

Newsprint represents an important subgroup. It consists primarily of a mixture of primary and secondary fibers. The primary fibers include groundwood and small amounts of pulp, which are used to increase strength. “Improved” newsprint, which has a high filler content and is calendered (closed surface), also belongs to this group. As a result of the good runnability in the printing machine, the main field of application is newspaper production. Other uses are, e.g., paperbacks, calculating-machine rolls, telex rolls, and interleaving paper.

Newsprint has a basis weight of $40 - 56 \text{ g/m}^2$. It is machine-finished or supercalendered. Standard newsprint should have an ISO brightness of $57 - 60 \%$.

Improved newsprint is used, e.g., for book and offset printing. The ISO brightness should not be less than 63% .

Wood-Containing Natural Printing Papers. This is another important group of printing and press papers. The term wood-containing indicates that these printing papers consist mainly of groundwood along with pulp, while “natural” refers to the fact that they are not coated. Fillers, e.g., kaolin or calcium carbonate, are used to produce high smoothness and good opacity. These natural papers include gravure printing paper, also called SC paper (supercalendered).

Natural magazine papers have high lignin content, and are filled and highly supercalendered. Their main use is the production of magazines and other products of the press.

Gravure papers (SC gravure) have the same properties as natural magazine paper, but are specially suited to gravure printing. ISO brightness $> 67 \%$.

Newsprint, improved for gravure printing has the same properties as natural magazine paper; ISO brightness $< 67 \%$.

SC offset paper has the same properties as natural magazine paper. The ISO brightness ($> 67 \%$) is optimized for offset printing.

Wood-containing thin printing papers have a basis weight of $\leq 45 \text{ g/m}^2$. They are used

for telephone, railroad timetable, and address books.

Book papers are used in the production of books. They have a groundwood content of 5–20 %. The filler content depends on the desired volume.

Voluminous book papers are produced with ≥ 1.4 -fold volume.

Supercalendered Writing Papers. These woodcontaining natural papers are sized and supercalendered. They can also be made from wastepaper.

Machine-finished offset papers are supplied in sheets or rolls.

Wood-Containing Coating Base Papers and Boards. Coating base papers are papers that are intended to be further processed into coated papers or boards.

Wood-Free Natural Printing Papers.

Wood-free natural printing papers consist almost exclusively of pulp. The proportion of fibers from mechanical pulp should not exceed 5 %. Wood-free printing papers do not yellow to any appreciable extent and have a high strength. This is the main difference between these papers and the wood-containing grades described above. The papers are uncoated and normally leave the paper machine in a machine-finished state. These papers are calendered on a supercalender for certain printing processes. This group of papers includes:

Wood-Free, Machine-Finished Natural Printing Papers. Basis weight:

Group 1	$\leq 80 \text{ g/m}^2$
Group 2	$81 - 149 \text{ g/m}^2$
Group 3	$> 150 \text{ g/m}^2$

Wood-free, Supercalendered Natural Printing Papers. The classification of the basis weights is as described for machine-finished papers.

Letterpress printing papers are voluminous and are particularly suitable for books (volume ≥ 1.4 fold).

Wood-free Bible and thin printing papers can be rag-containing or rag-free. They are highly filled to give good opacity. The basis weight is in the range below 40 g/m^2 to above 50 g/m^2 .

Coating Base Papers for Printing Papers and Boards. Coating base papers and boards are materials that are intended to be further processed into coated papers or boards.

Coated printing papers represent the largest group within the printing and press papers. In the case of these printing papers, the base paper is finished by the application of a layer of coating color to both sides of the paper web, which imparts a closed surface to the printing papers (see Chap. 9). These papers are supercalendered and supplied with a dull or glossy surface and are described as wood-containing or wood-free, depending on the raw materials used. The wood-containing, coated printing papers represent the largest part and the LWC papers (light weight coated), in turn, make up the main part of this subgroup. Examples include:

Wood-Containing, Two-Sided Coated Papers. The minimum coating application is 5 g/m^2 per side. Main areas of application: magazines, catalogs, and job printing.

Wood-containing LWC paper is coated on both sides; basis weight $\leq 72 \text{ g/m}^2$. It is suitable for gravure printing and roller offset printing.

Wood-containing consumer papers, coated on both sides must have a minimum groundwood content of 50 %.

Wood-Free, Two-Sided Coated Papers. The coating application is 5 g/m^2 per side and the fields of application are the same as for the corresponding wood-containing papers.

Wood-free LWC paper is coated on both sides and has a basis weight of $\leq 72 \text{ g/m}^2$.

Art papers (picture printing papers) have a minimum coat application of 20 g/m^2 per side and are usually wood-free letterpress printing papers with a surface suitable for multicolor printing and printing from blocks with fine screens.

Pigmented papers have a coat application of less than 5 g/m^2 per side. Wood-containing or wood-free coating base paper can be used for their manufacture.

11.2. Office and Administration Papers

These papers offer a wide spectrum for very different areas of use, e.g., writing papers, papers for data printing, papers for forms, copy

and duplicating papers, envelope paper, postcard board, self printing papers, refined papers for offset printing, blueprint papers, work drawing paper, bank notes, documents, and map paper. These printing and writing papers and the corresponding base papers are the papers that are used predominantly in offices, administration, and schools. Examples are:

Data papers and boards are used for the manual, mechanical, electronic, and magnetic recording of data and its input and output.

Bookkeeping transparent paper is highly beaten and is therefore transparent.

Account book paper or paper for bookkeeping machines is wood-free, highly supercalendered, and fully sized.

Punched tape paper is vegetable parchment or other specialty papers for use in tape instruments.

Perforated tape board, magnetic tape board is wood-free kraft board, also semibleached, with high dimensional stability and rigidity.

Optical character recognition must comply with the requirements in DIN 6723 and 6724 [446], [447], which guarantees that the exchange of machine-readable vouchers between companies, e.g., in automated data exchange, proceeds without problems. The papers are uncoated.

Paper for continuous forms is wood-containing or wood-free, usually machine-finished reeled paper, including recycled paper.

Index board is wood-containing or wood-free, supercalendered, single-layered board that can also contain wastepaper.

Writing papers are used almost exclusively for manual writing. They are supercalendered and can also be made with varying amounts of rags. This group also includes handmade papers, moldmade papers, bond, and air mail papers.

School writing paper is a machine-finished, highly sized paper with a basis weight of 60–80 g/m².

Typewriting, copy, duplicating, and photocopy papers are wood-containing or wood-free papers that may also be made from wastepaper. They are machine finished or supercalendered, sometimes voluminous, and have a basis weight of up to 100 g/m². They can also be used as transfer paper or for copying.

Air mail paper is light-weight, wood-free, often rag-containing paper with high opacity.

Carbon copy paper is well sized, has a basis weight between 23 and 30 g/m² and is used in the copying of letters and manuscripts.

Carbonless copy papers contain color forming reagents, which produce a contour-true copy when subjected to pressure (exerted on underlying sheets).

Correspondence envelope paper can be made from a wide range of stocks, from wastepaper to pulp. This paper is used exclusively in the production of envelopes and mailing bags.

Kraft paper is used to make envelopes and mailing bags and is made from unbleached or bleached kraft pulp.

Envelope lining tissue is an intensely colored, sometimes dip dyed, wood-free tissue paper with a basis weight of 22–30 g/m². It is used for the lining of expensive envelopes.

Base paper for diazotype is wood-free, has a basis weight of 55 to > 200 g/m² and is used in the making of blueprint papers.

Copy base papers are wood-free. As a result of special properties, they can be finished to give various coated copy papers, e.g., zinc oxide paper, thermocopy, and photocopy papers.

Base papers for offset films are predominantly wood-free papers that are used for making paper offset plates.

Carbonizing base papers are carrier papers for a wax-bearing color mass. They are used for the production of carbon and blue papers.

One-time carbon (OTC) base paper is used in the production of one-time carbon paper.

Multiple carbon base papers are used in the production of multiple carbon or blue papers.

Base papers for nonimpact printing processes are predominantly wood-free and are specially suitable for nonimpact printing processes (thermosensitive, electrosensitive, thermostatic papers).

Blotting papers are wood-containing or wood-free, white or colored, and sometimes have veined fibers. They possess a very high absorbency and wettability.

Security, banknote, and archival papers are wood-free and/or rag-containing or linters-containing. These heavy duty, nonaging papers are suitable for color printing and can be made resistant to forgery, e.g., by means of a watermark.

Map and nautical chart papers are wood-free, dimensionally stable, and are used for the printing of maps and sea charts.

Letter board is wood-containing or wood-free and may contain wastepaper. It has a basis weight of $>150 \text{ g/m}^2$ and a supercalendered surface.

Picture postcard board is wood-containing or wood-free and is used in the production of picture postcards.

Letter File Cardboard. This solid fiber board used in the production of files is multilayered, vat-lined or unlined and has a basis weight of $1000\text{--}2000 \text{ g/m}^2$. Special properties: exactly planar, and precisely maintained moisture level.

Filing board is a special, tough board which is usually colored and supercalendered.

Ticket board is wood-containing or wood-free and often colored. It is used, e.g., for street-car tickets, entrance and weighing tickets. Ticket board is produced in accordance with regulations issued by the railroad authorities.

Fancy cardboard can be pasted or unpasted and is often wood-free, e.g., ivory, Bristol, and opaline board. It is used in the production of visiting cards, invitations etc.

11.3. Paper, Board, and Cardboard for Packaging

A large number of grades of paper, board, and cardboard are available for packaging and are employed for many different purposes. These include:

Folding Boxboard. This product is ideally suited for the production of folding boxes because of its properties, such as good scorability, creasing ability, groovability, and printability. This board can be coated or uncoated; the former gives a better printed format.

Machine-made board (also solid fiber board) is produced almost exclusively from wastepaper and is processed primarily into mailing boxes. Pressed rolled board is also used for this purpose.

A great variety of papers are used for packaging. These range from simple WP wrapping paper (made from mixed wastepaper) to kraft paper, which is made predominantly in rolls from various pulps (sulfite/kraft pulp) or from mixtures of pulp and wastepaper. These grades are employed in the production of bags, beer mats, carrier bags, gift wrapping paper, etc.

For the foodstuff sector, special types of paper and board are produced which must fulfil the requirements of the food laws (see also $\rightarrow$ Foods, 4. Food Packaging). These papers are also widely used in the nonfood sector, e.g., as coating papers. The possibilities of combination with each other and with other materials (plastics) are numerous. In this way, special packing materials can be produced for most packaging.

Greaseproof papers are used for the packaging of butter, margarine, meat, and sausage. These papers include vegetable parchment and glassyne, which were provided with barrier polymers.

Depending on their intended purpose (for the smooth surface or the corrugated inner layer of corrugated board), corrugated papers are produced with varying strength, rigidity, wet strength, and printability. The normal designations, which are all used for the production of corrugated board, are kraft liner, test liner, covering stock, and corrugated stock.

For most of the papers, boards, and cardboards described above, the stock is adjusted to meet the requirements in each case. Examples are:

Kraft Papers. In order to exhibit the high strength properties required, these papers consist of primary or primary and secondary fibers of kraft pulp. They are used predominantly for packaging purposes.

Kraft sack paper, bleached and unbleached, includes kraft bag asphalt base paper which is used in the production of asphalt paper.

Extensible kraft sack paper (clupack) corresponds to the kraft sack papers, but it has a higher extension ($>6\%$) in the longitudinal direction. It can also be used as base paper for plastic coating.

Secondary kraft sack paper is made from at least 50 % unbleached kraft primary fibers.

Kraft packing papers, slightly bleached, unbleached, or bleached must contain 80 % of primary fibers.

Kraft tissue, bleached or unbleached, has a basis weight of $<30 \text{ g/m}^2$. It is a one-sided smooth or fluted kraft paper that is employed for wrapping glass or metal goods; it is also suitable for packing fruit, e.g., oranges.

Sulfite Wrapping Paper (ZP). The stock composition of this paper is on average 70 % of primary fiber pulp and not more than 30 % of fibers from sulfite or kraft wastepaper. The basis weight is $>30 \text{ g/m}^2$.

ZP 1:	made from knotted pulp, 30 % secondary fibers permitted
ZP 2:	inferior sulfite pulp, up to 30 % higher quality secondary fibers permitted
ZP 3:	100 % inferior sulfite pulp, up to 30 % groundwood or higher quality secondary fibers permitted
ZP 4:	65 % sulfite pulp, up to 35 % groundwood permitted
ZP 5:	made from 100 % unbleached or bleached sulfite pulp

WP packing papers consist of mixed wastepapers of varying composition; they may also contain pulp.

Crepe packing material is a highly sized and creped packing paper of any stock composition.

Mixed soda pulp-paper is made predominantly from secondary fibers of kraft pulp.

Glassyne is a highly supercalendered paper made from strongly beaten pulp. It is largely greaseproof, but not water resistant. The high transparency is achieved by intensive supercalendering. It is frequently colored. This paper is used, e.g., as wrapping paper for chocolates, covering paper in photograph albums, for dust jackets, envelope windows, and for packing high-quality preserves.

Supercalendered base paper for waxing is designed to be waxed and frequently contains titanium dioxide as filler. The waxed paper is often used as wrapping paper for candies.

Silicon base paper is a supercalendered paper to be used for siliconization.

Greaseproof paper is made resistant to grease primarily by using a special beating process (high fibrillation) and by the addition of auxiliary agents. In comparison with vegetable parchment, this paper is neither waterproof nor boil-proof.

Parchment base paper is unsized, highly absorptive and is made of 100 % pulp fibers. It contains no chemical auxiliary agents and is employed in the production of parchment paper.

Vegetable parchment [448] is a highly waterproof, greaseproof, boilproof paper product of high purity. It is used in the packing of fats, also in combination with aluminum foil or with a plastic coating. Silicon-coated parchment pa-

per has a wide range of applications, e.g., baking paper, antiadhesive papers, etc.

Coated papers are often coated on one side and are suitable for offset and gravure printing. They can be painted, bronzed, and punched. They are waterproof and alkali resistant to prevent the detachment of labels in washing machines. They are used, e.g., as wrapping paper for chocolates, cigarettes, soap, and as dust jackets for books and records.

Coated Packaging Papers. These bleached kraft papers have a one-sided dull or glossy coat and are suited to the production of bags and carrier bags.

Corrugated Papers. These papers include:

Kraft Liner. This covering paper is made of at least 80 % kraft pulp, bleached or unbleached, and has a bursting strength per basis weight of $3.43 \text{ kPa} \cdot \text{m}^2 \text{ g}^{-1}$.

Kraft-Faced Liner. This covering paper does not have a specified stock composition, but it has guaranteed strength properties.

Two-layer paper is a double-layered covering paper.

Semichemical paper is corrugated paper made of at least 65 % semichemical pulp.

Fluting Medium Paper. The corrugated paper used for the production of corrugated board has no specified stock composition; however, definite strength properties are required.

Board and cardboard are planar materials consisting mainly of fibers of plant origin. In terms of basis weight, these materials can be included in both the paper sector and the board sector (250 to $> 600 \text{ g/m}^2$).

1) Folding Boxboard. The following board types are included in this group:

Coated pulp board is made from bleached pulp.

Cast coated pulp board is used for high-grade packaging and for folding boxes, fine pasteboard boxes, paperback covers, etc.

Chromo board, chromo duplex board, chromo triplex board have very different stock compositions, depending on the intended purpose.

Artificial Chromo Board, Triplex Board. A gray core can also be used in this case.

2) Machine-Made Boards. This group includes the following board types:

Mechanical pulp board has a light or gray core. It is used, e.g., in the production of paper plates and round cheese boxes.

Brown mechanical pulp board is made predominantly from wastepaper and has a brown colored cover and reverse. It is used for the production of mailing boxes.

Chipboard consists predominantly of wastepaper and is employed for the production of mailing boxes, box lining, etc.

Pasted board consists of two or more layers of mill board that have been pasted together in the dry state.

Sheet-lined board is made from mill board. It may also be pasted, is lined on one or both sides with paper, and is used for high-grade packaging.

Mill board is made by winding one or several fiber webs on a press roll. Thus, high basis weights and the production of especially stable packaging material are possible.

Cartridge papers and boards are usually made from wastepaper and are used in the production of cartridges, special cartridges, cardboard tubes, and containers such as detergent drums.

Board for cups is a single layered hard board consisting of bleached pulp and is used for the production of drinking cups, etc.

11.4. Hygienic Papers

The major component of all hygienic papers is tissue. Tissue is a high-grade, fine paper with a closed structure. Tissue is usually used in multiple layers because of its low basis weight. Cellulose wadding and crepe paper also belong to this group.

Cellulose wadding is a loosely structured, highly absorbent fiber product. Its uses include the production of sanitary towels, surgical artificial cotton, patients' sheets, and packing cotton.

Soft tissue is made entirely or predominantly of pulp fibers, with fine, soft creping and closed formation. It is especially absorbent and is employed in the production of toilet paper, handkerchiefs, kitchen towels, hand and face towels, serviettes, and for covering diapers and sanitary towels. The basis weight is $<27 \text{ g/m}^2$.

Crepe paper is a single-layered, highly absorbent hygienic paper made from groundwood and/or secondary fibers from wastepaper. The basis weight is $>27 \text{ g/m}^2$. The most important uses are toilet paper, paper handkerchiefs, and cleaning rolls.

11.5. Papers and Boards for Technical and Specialty Uses

This group of papers and boards covers a wide range of grades. The most important subgroups comprise base papers for decor, priming and barrier foils, body, coating and soakage base papers and base papers for wallpaper, papers for electrotechnical purposes, drawing paper, photographic base paper, cigarette paper, filters and filter layers and special cardboards for the various branches of industry, e.g., presspahn, car body and shoe cardboard. All these papers and boards have a common requirement; they must exactly fulfil defined quality criteria. This group includes:

Chromatography papers are porous, absorbent special papers made from linters without the addition of sizing or filling agents. They are often acid washed and contain silicon compounds to render them hydrophobic.

Reagent and indicator papers are high-grade special papers used for impregnation with test reagents and indicator dyes.

Household filter papers are wood-free special papers that give a defined rate of filtration. They must comply with food laws. They are used, e.g., for coffee filters. The rate of filtration and the separating ability depend on the degree of fiber beating.

Analytical and industrial filter papers are usually made from cotton, dissolving pulps, and glass microfibers. They possess a uniform stock distribution and, thus, a homogeneous pore size. Analytical filters are acid washed and are made without paper making additives. Filter layers with a basis weight of up to ca. 750 g/m^2 are produced to withstand special stress, e.g., in the beverage industry. Filter layers of this type, that are

also used for sterilization filtration, must comply with food laws. For industrial use, the paper and filter layers may also be impregnated with melamine–urea resins or similar compounds.

Filter mass is made from soft-cooked, highly bleached pulps or from rags or linters and is used in the form of flocks for industrial filtration.

Cable and condenser paper (capacitor tissue paper) is stiff, nonporous paper made from pulp and is usually impregnated with artificial resins. These papers contain neither fillers, metal impurities, nor salts. The absence of pores is achieved by fine beating of the pulp fibers and by supercalendering. Cable paper must exhibit high strength in the longitudinal direction. The thickness of condenser paper is 0.006–0.012 mm and the basis weight is 6–7 g/m². These papers must meet IEC regulations [449].

Presspahn is a single-layered, highly rigid product that is made from pure pulp and couched in the wet state. When used in the electrical industry, the pulp must be produced with a high degree of electrochemical purity.

Building Papers and Boards.

Roofing Felt Base. This wool–felt board (reclaimed wool) is impregnated with tar/bitumen and used to produce roofing sheets.

Felt and wool–felt board consist of waste-paper and rags. They are used as the base material for textile floor coverings and as insulating material in various fields, predominantly in the automobile industry. They are also employed as separating layers on flat roofs that are covered with a plastic foil.

Gypsum liner board is used for the production of gypsum plates (building plates).

Covering Papers and Cardboards. This general term describes various papers and cardboards that are used as protective coverings. These single-layered or multilayered materials can be made from various raw materials. They are used, e.g., as covering papers in road construction.

Substrate Papers, Saturating Base Papers, and Coating Base Papers.

Substrate papers are used in many different technical systems as manufacturing aids. They are frequently removed from the finished product at the end of the production process, rewound and reused in the same process.

Coating base papers must be moisture resistant and stable to organic solvents. One or both sides of the paper are treated with various solutions or dispersions, which represent the requirement for the desired coating.

Saturating base papers must be absorbent and have wet strength and often also resistance to organic solvents.

Raw Material for Artificial Leather. This tough kraft paper is not dyed and is usually moisture resistant. It forms the web base for the production of artificial leather.

Base Paper of Vulcanized Fiber. This absorbent, voluminous paper is made from cotton rags, cotton linters, and refined pulps.

Photographic Base Paper. A suitable base paper for the production of photographic paper is a moisture resistant, dimensionally stable, chemically neutral pulp paper that is free from traces of iron or copper. Today, papers coated with a thin polyethylene foil on both sides have replaced barite paper. This paper is used for the uptake of light-sensitive emulsions.

Saturating base paper (overlay paper) is made from special pulp and has basis weights of 15–40 g/m². It is highly porous, free of dirt, and protects the underlying decor in the production of laminated products.

Decor base paper is a soakage base paper made from bleached or unbleached kraft pulp; it is used for resin absorption in the production of laminated plates.

Base papers for abrasive papers are tough, sized papers made from kraft pulp and are coated with an abrasive.

Calender bowl paper is strong, compressible, heat-resistant paper used for the manufacture of calender bowls.

Technical Drawing Paper. This group includes the following:

Opaque drawing papers are fine look-through papers made from pulp and have good sizing and hardness. Exacting demands are made on the erasability.

Translucent Drawing Paper. A distinction is made between natural transparent paper and paper made transparent by chemical treatment. Natural transparent papers are made from pulp, linters, or mixtures of the two by intensive beating of the fibers. They are well sized and exhibit good surface smoothness and look-through. Opaque papers are rendered transparent by soaking them in a solution of synthetic resin.

Sketching papers are wood-containing or wood-free, machine finished, sized natural papers with a basis weight $\geq 80 \text{ g/m}^2$.

Art drawing papers and board are suited to special drawing and painting techniques, e.g., watercolor paper. The latter has a rough surface which accepts water colors but does not allow their penetration. This material also has good erasability.

Base Paper and Board for Wallpaper.

This is the general name for papers and boards that are suitable for the production of wallpaper [450]. They can be single- or multilayered, couched or pasted, wood-containing or wood-free, coated or uncoated. They may contain wastepaper or have a woodchip coat. Strip-off wallpapers or pregglued wallpapers can also be produced.

Papers for Tobacco Products.

Imitation cork paper is a brownish yellow colored paper used for the production of cigarette tips. It has an imitation cork imprint and joins the filter to the tobacco stick.

Filter encasing paper is used for the production of acetate and/or cellulose filters.

Cigarette paper has a high filler content and a basis weight of $18\text{--}28 \text{ g/m}^2$. To control the smoking properties, this paper has a porosity that is suited to the type of tobacco and contains additives that regulate burning.

Cigar or cigarillo casing paper holds the chopped tobacco together and serves as the inner casing.

Long-fiber paper is used for tea bags and artificial sausage skin and is made from fibers having an average length $>3 \text{ mm}$. The addition of synthetic fibers is permitted.

Binding papers are tough, wood-free papers that are frequently embossed.

Cover paper and board is tough, elastic, durable, wood-free white paper or board that has a linen finish and is specially suited to the production of covers for brochures, paperbacks or similar products.

Bookbinding board is press rolled or mill cardboard that is pasted or unpasted and has high rigidity, dimensional stability, and perfect lining ability.

Car body cardboard is a hard cardboard used predominantly as shaped parts in automobile manufacture; it is usually capable of being cupped.

Leather fiberboard is an especially tough hard cardboard that is flexible and resistant to moisture.

Suitcase board is an embossed hard cardboard used in the production of luggage.

Jacquard cardboard is a tough, dimensionally stable cardboard used in the production of perforated cards for the control of textile machines.

Flong. This coated cardboard (solid board) is made from very high-grade stocks (rags). It is processed with fillers and is completely knot-free and can be subjected to hot embossing. It is used to produce the matrices for high-pressure dry stereotyping.

Cardboard for beer mats is a highly absorbent groundwood cardboard that may be pulp covered. It can be punched, embossed, and printed.

Base papers for chart paper have a basis weight of $30\text{--}130 \text{ g/m}^2$ and are usually filled and sized. They have a refined surface and good dimensional stability.

Gardener, Flower, and Decoration Crepe.

Gardener's crepe is a white or colored, highly expandable paper that has longitudinal grooves and serves as decorative flowerpot wrappers.

Flower crepe paper is wood-free and is used in the making of artificial flowers.

Decoration crepe paper is flameproofed by impregnation with chemicals and is used for decorations of various types.

Board for playing cards is made of two or three layers pasted together. It is coated on both sides, has a supercalendered surface, and is sometimes linenized. The basis weight is 280–340 g/m².

Album Board. Board for photograph, stamp, and other albums is often wood-free and voluminous.

Hot setting paper and hot sealing paper are coated on one side, become sticky on heating and can consequently be fixed to another material.

Insect resistant or insecticide paper is resistant to insects. It can kill insects by means of volatile components or by contact.

Antitarnish Paper. This impregnated or coated paper protects other materials against corrosion by releasing substances in the vapor phase or by direct contact.

Photographic protective wrapping (black photo paper) is lightproof, black-dyed, chemically neutral paper that can be folded without breaking and is suitable for wrapping photographic film.

Sterilization paper is a wood-free paper that, even when coated, can tolerate sterilization processes and is used for packing sterilized materials.

12. Book and Paper Preservation

12.1. Introduction

Most modern paper lacks the durability and permanence that has characterized its use since its

earliest application to chronicle the history of man and his civilization. Although fundamental papermaking techniques have changed little in nearly 2000 years, two 19th century innovations, namely: 1) the use of alum as a component of size and 2) the replacement of cotton fiber by wood pulp, are responsible for this predicament. Papermaker's alum readily forms sulfuric acid on exposure to water in air; this acid in turn readily catalyzes the depolymerization of cellulose. Further, cellulose from wood pulp is more susceptible to this attack than linen- or cotton-derived fiber. The inherent acidity of such papers accounts for 85–90 % of the destruction in book papers, resulting in a half-life for fold endurance of an estimated 7.5 years [451].

One of the first to detail the problem and correctly identify the cause was WILLIAM BARROW at the Virginia State Library [452] beginning in the 1930s. Prior to his work, book and paper conservators relied as much on art as science. While highly skilled, these practitioners often selected materials and treatment without adequate consideration of the long-term consequences.

Today mass deacidification of books and archives materials has become a commercial reality. The Wei T'o process, which employs methyl magnesium carbonate in a nonaqueous liquid-phase process, operates at the National Archives of Canada, while a variation on it treats books for the Bibliothèque Nationale in France. The Diethyl Zinc process invented by the Library of Congress now treats library materials in a United States facility owned by Akzo. There are four additional processes in various stages of development, including two that are marketed for their ability to also impart strength, that are of general interest to the preservation community.

12.2. Paper and Deacidification Chemistry

Paper nearly universally involves cellulose, although its source and methods of processing have evolved steadily throughout the centuries. As production costs dropped significantly, the application of paper dramatically expanded so that its traditional applications, particularly its use in books and official records, were dwarfed by other functions. Such widespread use of paper reduced the emphasis on permanence.

The sizing of paper continues to be the predominant cause of paper deterioration. In the early 1800s, about the time of ROBERT's invention of the fourdrinier machine for continuous paper manufacture, gelatin sizing was abandoned in favor of alum or alum-rosin blends. Papermaker's alum, $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$, is readily hydrolyzed by water to form sulfuric acid. Acid-catalyzed hydrolytic attack causes degradation of cellulose by random scission of the hemiacetal links, leading to breakage of chain linkages (Fig. 85). Even a few scissions per molecule cause a substantial loss in physical properties [453].

In 1851, the discovery of the soda process for separating cellulose from wood added a further dimension to the problem since paper derived from wood pulp is more susceptible to acid attack than the cotton cellulose obtained from linen and rags.

The lack of paper permanence is attributable to both internal and external influences [454]. In addition to sizing materials, internal factors include the type of fiber, coatings, and the presence of acidic and metallic compounds. External variables are the conditions during storage and use. Heat and humidity accelerate the deterioration of paper, and atmospheric pollution is frequently the source of external acid attack. A comparison of identical volumes stored in the New York Public Library and the Royal Library in The Hague attest to the importance of proper storage as the New York books were found to be in a far more advanced stage of deterioration [455].

It wasn't until 1926, when GOSTA HALL of Sweden developed a satisfactory method for accelerated aging [456], that researchers had a means for simulating the effects of the natural aging process. Although EDWIN SUTERMEISTER of the S. D. Warren Company recognized as early as 1901 that stable paper should contain an alkaline filler, it was left to WILLIAM BARROW of the Virginia State Library to pull the disparate elements of early researchers together in a scientific analysis of the problem [457].

As acid-catalyzed hydrolysis of cellulose is responsible for up to 90 % of paper's loss of permanence, researchers have concentrated on deacidification as the primary solution to the impermanence of modern papers. Paper deacidification involves introduction of a strong base

to convert acid species to their corresponding neutral salts, and the establishment of a neutral buffer to protect against future acid-catalyzed damage. The first recorded attempt to neutralize paper was advanced by ARTHUR CHURCH at the Victoria and Albert Museum in London who in 1891 advocated immersion of paper in a methanolic solution of barium hydroxide [458].

Subsequent attempts to develop effective deacidification focused on aqueous techniques, which offered the additional benefit of modest strengthening through reestablishment of hydrogen bonding. OTTO SCHIERHOLZ, working for the Ontario Research Foundation in Toronto, secured a patent in 1936 for his work which involved dipping paper in a solution of alkaline earth bicarbonates [459]. In 1943 BARROW described a two-step process, involving immersion in a calcium hydroxide bath and subsequent treatment with calcium bicarbonate. Commentators differ as to whether BARROW was aware of the earlier Canadian work.

Further refinement of the technique included the 1957 development by JAMES GEAR et al. at the United States National Archives of a one-step process involving magnesium bicarbonate, and the use of the more soluble magnesium hydroxide by scientists at the Library of Congress in 1978. While effective and proven, these techniques involve painstaking care as they are applied to single sheets.

12.3. Development of Mass Deacidification Processes

Mass preservation is designed to meet the needs of national and major research libraries and archive groups. With a mean collection deterioration rate of 4.7 % [460] and limited resources, a treatment based on painstaking manual work is inconsistent with the need. Further, emphasis has focused on nonaqueous and gas phase deacidification techniques to offset some of the intrinsic limitations of aqueous methods.

Nonaqueous deacidification systems contain a deacidification agent and an organic solvent that serves as the carrier. The solvents offer the advantage of rapid penetration and drying. The latter is particularly important in minimizing the obvious appearance of treatment, most notably cockling. Liquid techniques can function eco-

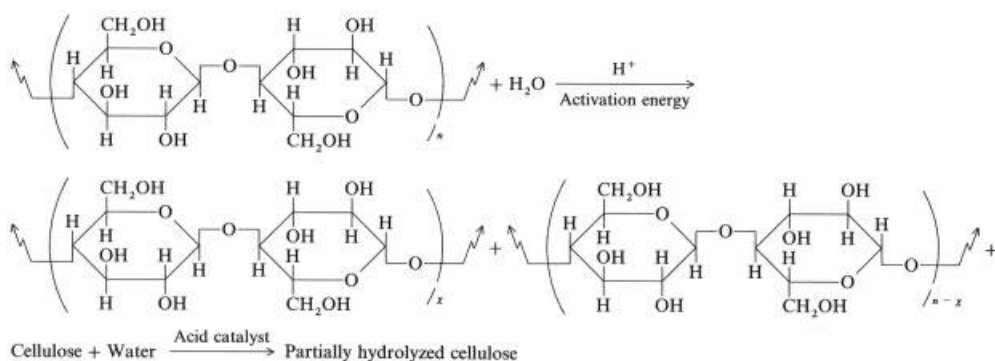


Figure 85. Acid-catalyzed hydrolysis of cellulose

nomically over a broad treatment range. The late 19th century approach of CHURCH was updated by A. D. BAYNES-COPE in the mid-1960s [461]. This followed the 1961 experimentation by BAYNES-COPE with a magnesium methoxide solution which, while quite effective, was impractical in terms of preparation and storage. Independently, RICHARD SMITH at the University of Chicago developed a process that utilized a magnesium methoxide compound solubilized in a mixture of methanol and chlorofluorocarbons (CFC) [462]. This overcame many of the problems associated with earlier approaches regarding stability and ease of use.

In contrast, a vapor-phase approach offers prospects for minimal preselection and maintenance of document integrity because no solvents are involved. At least one researcher likened this approach to a “fountain of youth” among deacidification methods [463]. Gas-phase processes work best at substantial scale because the facilities characteristically have high capital intensity.

Early attempts at gaseous deacidification included work reported in 1962 by Y. P. KATHPALIA at the Nehru Library in New Delhi, involving exposure of books to high concentrations of ammonia [464]. The compound proved to be too weak a base to completely neutralize strong acid and the ammonia buffer was highly impermanent. At about the same time, BARROW working in the United States and BAYNES-COPE in England combined ammonia and short-chain amines, including butylamine, diethylamine and piperidine, but observed sim-

ilar results—a short term alkalization that was reversed as the amine left the treated paper.

A more promising approach was advanced by WILLIAM LANGWELL who placed cyclohexylamine carbamate impregnated sheets in books [465]. The active compound diffuses into the book paper to neutralize acidity, but no alkaline reserve is established and the neutralization is reversible. Finally, morpholine treatment was promoted by KUSTERER and others working at the Barrow Laboratory in 1977. Besides the lack of permanence, significant discoloration was observed in the paper of treated books.

GEORGE KELLY and JOHN WILLIAMS at the Library of Congress designed a mass deacidification process in 1977 that utilizes diethylzinc (DEZ) [466]. The compound easily diffuses between the pages of closed books, neutralizing the acidity and establishing a uniform, controllable reserve of zinc oxide.

12.4. Commercial Mass Deacidification Processes

Today mass deacidification is a routine undertaking with prospects for substantial use by libraries and archives. The national libraries of France, England, Austria, and the United States have developed preservation processes, and the private sector has advanced additional techniques. Table 24 describes the processes that are under development to treat the broad range of materials that exist in library and archive collections. Three of the processes use chlorofluorocarbons as the solvent or as part of the solvent

Table 24. Mass deacidification processes

	BPA	DEZ	Wei T'o	Bookkeeper	British Library	Lithco
Developer	BPA	Library of Congress	Wei T'o	Koppers	British Library	Lithco
Type	gas	gas	liquid	liquid	liquid	liquid
Neutralizing agent	amine complex	diethylzinc	methoxy Mg methyl carbonate	MgO	amine complex	magnesium butoxytriglycolate
Carrier	none	none	Freon	Freon	none	Freon
Cycle time, h	24	60	24	5	< 15	3–5
Preselection *	minimal	minimal	some	minimal	minimal	minimal
pH of treated paper *	6.5–9.0	7.0–7.5	8.0–9.5	8.0–9.0	7.0–9.0	8.0–9.5
Alkaline reserve, % *	up to 1.0	1.0–2.0	0.7–0.8	up to 2.0	up to 1.0	1.5–2.5
Commercial status	yes	yes	yes	pilot	pilot	pilot
Strengthening *	some	no	no	no	yes	yes

* Most process results have minimal third party verification.

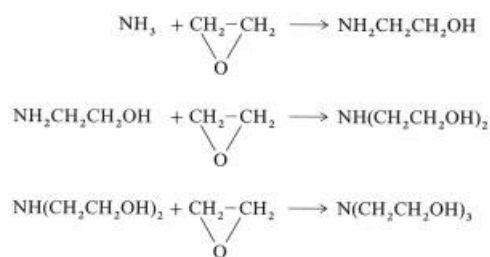
system. Additional development work is underway based on 1) operation in a closed system to preclude loss of CFC's and/or 2) operation with CFC replacements and subsequent paper testing.

BPA Process. Book Preservation Associates (BPA) was formed in 1988 as a wholly owned subsidiary of ETO Sterilization, a processor of spices, medical products, and cosmetics. Books or other library materials are placed in unopened boxes in a vacuum chamber. The pressure is reduced and the books are exposed to ammonia for 6 h. The chamber is then purged and reevacuated. Ethylene oxide is introduced and the materials are held for 12 h at nearly atmospheric pressure. The chamber is alternately purged and evacuated up to 25 times before treated materials are removed. The total cycle time is 24 h [467]. Books are placed in an aeration room for two days to permit off-gasing of the ethylene oxide before being returned to libraries.

The process was designed to create high molecular mass primary, secondary, and tertiary amines within the cellulose matrix of the book paper. The in situ generation of amines, together with free ethylene oxide, neutralizes acidity and establishes an alkaline reserve of ca. 1 %. Ethanolamine generation during treatment is described as follows. (see right column)

Developers of the process report that the mono-, di-, and triethanolamines are formed in approximately equal amounts, with a modest dominance by the monoethanolamine. The reaction is dependent upon the ratio between reactants and is adjusted intentionally.

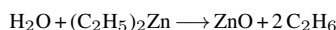
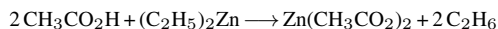
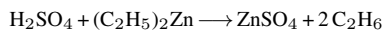
BPA personnel report that the pH drops approximately 1.5 points in the two months following treatment. As the company has readily available capacity for deacidification, commercial activity has been initiated.



The DEZ Process. The DEZ Process was developed by the Library of Congress over more than 15 years, progressing from simple laboratory experiments to an operating small-scale commercial unit. Much of the latter work was in conjunction with Texas Alkyls, one of three major producers of compounds such as diethylzinc (DEZ). Akzo secured an exclusive license for the DEZ Process and is presently commercializing the technology.

As strong alkylating agents, metal alkyls react readily with acids to form the corresponding neutral salts. DEZ also reacts with residual water in the paper to form a stable, permanent buffer of zinc oxide. Unlike most other processes, the neutralization of existing acidity is independent of the formation of the alkaline reserve. Thus both highly acidic and neutral paper are both

provided with an optimum alkaline reserve. Key reactions are summarized below [468]:



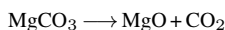
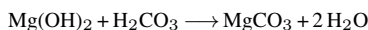
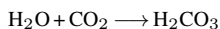
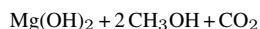
The buffer established by the DEZ process is more nearly neutral (saturated solution pH of 7.3–7.5) than that of magnesium or calcium salts used in other deacidification methods.

The process has three steps: pretreatment, permeation, and postconditioning; the total cycle time is 55–60 h. Akzo operates a treatment facility near Houston, Texas with capacity for ca. 40 000 books per year. Owing to its high reactivity, liquid DEZ is dangerous if mishandled. Poor design and operating procedures on the part of an earlier contractor threatened to halt further development of the process because of the inoperative first pilot plant. The issue of safe handling was fully resolved in the second facility.

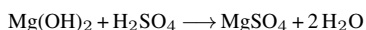
The Wei T'o Process. Wei T'o Associates, developers of a nonaqueous liquid deacidification process, derives its name from an ancient Chinese god regarded as a protector of books. The National Archives of Canada operates a treatment facility in Ottawa with capacity for ca. 40 000 books per year. The process is based on work conducted by RICHARD D. SMITH, a graduate student at the University of Chicago in the mid-1960s. In 1989, Union Carbide acquired exclusive rights to the process and intends to market the technique as part of a paper preservation services unit.

The deacidification agent is methoxymagnesium methyl carbonate carried in a solvent system composed of methanol, trichlorotrifluoroethane (Freon 113), and dichlorodifluoromethane (Freon 12). Books are placed in wire baskets and dried to a moisture content of 0.5%. The pretreated materials are immersed in the treatment solution for 1 h under modest pressure. Drying is initiated by evacuating the chamber and recovering the solvents. Final drying is performed under vacuum. It is during this stage that the deposition of the magnesium compounds occurs. Careful control of pressure regulates the evenness of deposition [469].

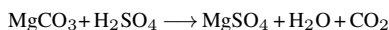
Following deposition, the active agent reacts with water from the air to form a mixture of intermediate magnesium compounds [458]:



These magnesium compounds react with strong acids to form the corresponding neutral salts. For example, magnesium hydroxide converts sulfuric acid to magnesium sulfate.



Magnesium sulfate is also generated by the reaction of magnesium carbonate with acid:



Residual magnesium hydroxide, carbonate, and oxide form the alkaline buffer that protects paper from subsequent acid attack.

Similar chemistry is practiced by the Bibliothèque Nationale at its treatment facility in Sable sur Sarthe. The unit has annual capacity for 60 000 volumes. However, the French process employs ethoxymagnesium carbonate as the deacidification agent.

The Bookkeeper Process is a liquid, nonaqueous process that employs a Freon 113 carrier to deposit a submicron dispersion of magnesium oxide. No alcohol is involved and a surfactant is employed to keep the neutralization agent evenly distributed in the fluorocarbon solvent. The technique was developed by Koppers Chemical Company in 1981, who transferred the rights to the process to RICHARD SPATZ in 1987. Book Preservation Technologies, in which SPATZ is a principal, continues the development of the method.

Books are placed open on a supporting grate which is loaded into a treatment chamber. No predrying is required. The chamber is flooded with the treatment solution and the grate is mechanically agitated so that the pages are exposed and completely wetted. Books are subsequently removed from the chamber and placed

in an air dryer, from which the solvent is condensed and recycled [470]. Total process time is 5 h or less. The process can be operated in batch or continuous mode.

The Bookkeeper Process relies on the migration of paper acid to the magnesium oxide for neutralization to occur. To date the method has only been operated on a modest scale and there has been no known commercial application.

The British Library Process. The British Library has achieved promising results in its effort to deacidify and strengthen book paper in a bulk process that has been under development since 1980. The method involves graft copolymerization techniques initiated by low-intensity γ -radiation. Work has been conducted by the Industrial Chemistry Group of the University of Surrey under British Library supervision and sponsorship.

Short-chain monomers, in particular ethyl acrylate and methyl methacrylate in a volume ratio of 5:1, are introduced in liquid form without solvents in a closed system. Low-intensity γ -radiation polymerizes the monomers under ambient conditions. Additionally, the liquid monomer mixture has been modified to include an amine-substituted alkyl methacrylate to neutralize acidity and establish a buffer against future acid-catalyzed hydrolysis [471]. The presence of a small amount of a diacrylate leads to cross-linking and hence strengthening of the paper.

Paper strength, as measured by fold endurance, is enhanced by a factor of 5 to 10 and a weight gain of 15–20 % occurs. No dimensional changes in treated books have been observed. Researchers have concluded that the polymer is deposited within the cellulose network of the paper as well as on and between the fiber surfaces. Treated books retain their original appearance and pages do not stick together at the prescribed polymer deposition levels. Future development will include operation on a pilot-plant scale to permit refinement of the monomer mixture and processing details.

The Lithco Process. Lithco began development of a nonaqueous deacidification technique in 1988. Magnesium butoxytriglycolate, the active ingredient, is solubilized in Freon 113 as a ca. 10 % solution. The company markets the

process for its ability to both deacidify and strengthen book paper.

The process consists of three steps: preconditioning, impregnation, and postconditioning. Books or other library materials are dried rapidly by dielectric heating to a moisture content of ca. 2 %. The documents are immersed in a pressurized Freon solution for deposition of the neutralization agent. Finally, excess solution is drained, excess chemicals are rinsed out, the solvent is removed under vacuum, and the books are removed. Total cycle time is less than 5 h.

The butoxytriglycolate ligands are intended to interact with cellulose to strengthen paper through hydrogen bonding. Similar chemistry based on zinc compounds has also been explored by Lithco on a more limited basis. Additionally, the company utilizes dielectric heating to speed the drying during both the first and last steps [472].

Early work was conducted in a demonstration unit capable of processing 20 standard bound volumes per batch. Lithco commissioned a larger pilot unit with capacity for 1000 books per day in May 1990.

Other Processes. Additionally, there are several other deacidification or strengthening techniques that have been commercialized and applied selectively to portions of a research library or archives collection. For instance, several such processes are utilized routinely to treat newspapers to neutralize acidity and restore strength. Newspaper is typically made of groundwood pulp to which cellulose fiber is added in processing. The resulting paper exhibits very low permanence, and represents a particular challenge for a research or national library.

The Austrian National Library Process. Work on an effective deacidification process for bound newspapers began in the Austrian Library in 1973. The technique, which has been in regular operation in Vienna since 1987, involves immersion in an aqueous solution of calcium hydroxide and methyl cellulose.

Process steps include: preparation, treatment, drying, and rebinding. Covers are removed from bound newspapers, and the materials are placed in a vacuum chamber. Following immersion in the treatment solution, the paper is shock frozen at -30°C to prevent the formation of large crys-

tals that would damage the paper web. Final drying consists of freeze-drying to avoid pages sticking together. Treated papers experience no significant change in dimensions, permitting use of the original covers [473].

Although testing and preselection is required, the Library has successfully applied the technique to various other archival materials. Capacity is 3000 bound volumes per year.

Leipzig Paper Splitting Technique. Since 1980, the Deutsche Bücherei in Leipzig has successfully operated a process that splits heavily mechanically damaged paper and introduces a new paper carrier composed of cotton linters. Developers intend to follow the mechanical treatment with an aqueous liquid-phase introduction of calcium hydroxide to neutralize the paper. Mechanization is under development.

German State Archives in Bückeburg. Pioneering work conducted in Bückeburg focuses on the fixation by cationic and anionic active agents prior to aqueous liquid phase impregnation with a solution of magnesium hydrogencarbonate for neutralization and carboxymethyl cellulose for strengthening. Successful pretreatment to fix dyes and inks would minimize the preselection characteristically required before the use of liquid-phase processes [474].

Strengthening without Deacidification. The most commonly discussed method to accomplish strengthening alone involves the gas-phase deposition of poly-*p*-xylylene. Paralyne is the generic name for the various members of the polymer series of *p*-xylylenes developed by the Nova Tran Corporation. The technique is capable of establishing a thin, durable coating of the polymer on the paper. No deacidification is accomplished, however, and the high cost of treatment has discouraged widespread use.

12.5. Commercial Prospects

The most compelling evidence for the need for mass deacidification is the substantial involvement of national libraries in the development of treatment methods. Research libraries and archives groups universally seek a low-cost option that will permit preservation of collection materials in their original form. Current deacidification techniques represent a viable and cost effective preservation solution to the problem of

acid paper. Although it is presently difficult to define costs in order to make meaningful comparisons among processes, mass deacidification is unquestionably far less costly than reformatting options such as microform. In addition, users of research library and archives collections continue to prefer original format materials.

More than one mass deacidification method will be adopted by the library and archives community. The problem is so great and the needs are so diverse that a single institution may well elect to pursue multiple treatment options.

Table 25. Comparison of selected properties of wood and paper

Property	Wood	Paper
Density, g/cm ³	0.3–0.5	0.5–1.5
Young's modulus, GPa	1.3	1.8–4.3
Tensile strength, MPa	90–200	20–200
Breaking length, km	7–30	1–8
Strain to rupture, %	0.6–0.8	0.8–4
Fiber alignment	ordered	random

13. Properties and Testing

13.1. The Material Paper: A Survey

13.1.1. Introduction

The term paper refers to sheet material that is made essentially from fibers of plant origin. The characteristic feature of this nonhomogeneous material is its fiber network, which is usually arranged in layers containing pores of varying size. The properties of paper differ substantially from those of the fiber resources. These differences are illustrated in Table 25, which shows some selected material properties of wood, as the most important fiber source, in comparison with paper. As a result of the physical and chemical properties and the highly ordered state of wood fibers, wood is unsuitable for direct production of sheet material which could serve as writing material. The construction of paper, i.e., sheet material with properties that are optimal for writing or printing, is possible only after the breakdown of wood into its elemental fiber building blocks, their modification in the pulping process, and their controlled bonding in the papermaking process. Paper can be made with an

Table 26. Selected properties of some grades of paper and board

Property ^a		LWC paper	Newsprint	Wood-free offset printing paper	Bag paper	Creped bag paper	Boxboard
Basis weight, g/m ² ^b		55.2	53.5	81.4	69.7	91.7	286
Caliper, μm ^c		52	79	110	106	248	453
Density, g/cm ³ ^c		1.05	0.68	0.74	0.66	0.37	0.63
Specific volume, cm ³ /g ^c		0.95	1.48	1.35	1.52	2.70	1.59
Tensile strength, N ^d	MD	40.9	26.5	64.5	78.5	65.0	245.5
	CD	14.6	12.6	25.1	53.5	55.0	80.5
Elongation, % ^d	MD	1.0	0.8	1.6	2.8	8.4	2.0
	CD	1.6	1.8	3.0	6.2	6.6	3.2
Breaking length, km							
	MD	4.95	3.30	5.25	7.50	4.70	5.75
	CD	1.75	1.55	2.05	5.15	4.00	1.85
Tear growth resistance, mNm/m ^e	MD	180	120	340	640	910	1200
	CD	250	170	410	630	1110	2440
Bursting strength (Mullen), kPa ^f		100	50	150	350	450	550
Smoothness (Bekk) ^g	fs	633	71.4	18.2	6.1	< 1	22.9
	ws	600	63.4	8.6	4.4	< 1	2.9
Roughness (Bendtsen), mL/min ^h	fs	22	90	273	702	> 500	113
	ws	20	114	469	838	> 500	> 500
Specific bending stiffness, Nmm ⁱ	MD	0.06	0.12	0.37	0.39	0.39	37.8
	CD	0.03	0.04	0.19	0.18	0.54	13.1
Brightness, % ^j	fs	73.1	55.9	84.6			81.5
	ws	72.3	56.3	84.6			
Opacity, % ^k		92.7	96.5	90.5			

^a = machine direction; CD = cross machine direction; fs = felt side; ws = wire side. ^b ISO 536. ^c ISO 543. ^d ISO 1924. ^e DIN SCAN/P 11:64. ^f ISO 2758. ^g ISO 5672. ^h ISO 2494. ⁱ ISO 5629. ^j ISO 2470. ^k ISO 2471.

extremely wide spectrum of properties by varying the construction parameters: type of wood, pulping process, fiber preparation, and paper-making process. This is illustrated in Table 26.

The wide range of product properties that result from the construction parameters mentioned above can be increased still further by the use of additives such as mineral and chemical aids. For instance, the smoothness and brightness of printing paper can be increased by addition of inorganic pigments (fillers) [475].

Many special demands made on paper can be met by using suitable chemical additives, e.g., wet strength by using wet-strength additives or printability by using sizing agents [476]. However, paper produced with all these aids will never meet all conceivable requirements at a time. In each case only a few paper properties that are particularly important for the intended purpose can be optimized. As far as the other

properties are concerned, concessions must be made.

13.1.2. Material Properties

The specific characteristic features of paper vary widely, depending on the type of paper. Nevertheless, there are a number of properties that are characteristic of all papers. These are inhomogeneity, hygroscopicity, anisotropy, and viscoelasticity.

Paper is an inhomogeneous material made from the homogeneous elements: fibers, fillers, and air-filled pores. The homogeneous regions extend over a few micrometers (a few millimeters in the longitudinal fiber direction), corresponding to the characteristic dimensions of these elements.

A sheet of paper also exhibits other inhomogeneities, which can have characteristic di-

mensions of a few millimeters or centimeters. These are known as the cloud effect and result from undesired fiber flocculation in the sheet forming process [477]. In this way, variations in caliper and density develop, and this leads to corresponding variations in transparency, the "clouds". Finally, the production process can also give rise to inhomogeneities, e.g., due to stock pulsations in the headbox and in the sheet forming section [478]. The existence of inhomogeneities must be taken into account in paper testing, e.g., by choosing the appropriate size of sample.

The most important characteristic of paper is its hygroscopicity, i.e., its ability to absorb or release moisture, depending on the ambient climate, until an equilibrium is reached. It is significant whether the state of equilibrium is established by absorption or desorption of water [479]. The moisture content of some types of paper at various levels of relative humidity is listed in Table 27.

As a result of the hygroscopicity of paper, physical paper properties, such as sheet dimensions, basis weight, tensile strength, strain to rupture, folding strength, bending stiffness, etc., are dependent on the ambient conditions [480]. With a change in the ambient climate, the attainment of a new equilibrium moisture content of paper is a slow process which takes several hours. However, the change in the physical properties of the paper occurs almost without delay. For this reason, paper should be processed in rooms in which the climatic conditions are favorable for the particular paper property required. The paper must be in equilibrium with the climate in the room and the climatic conditions must be kept largely constant. The testing of paper requires the establishment of testing climatic conditions (standard climate: 23 °C, 50 % relative humidity, cf. Section 13.2.1).

Paper is an anisotropic material with regard to many physical properties. This anisotropy is due to the anisotropic properties of the individual fibers, which result from the fibrillated microstructure of the fiber rather than the fiber shape [481]. As a result of the fibrillated structure, the fiber can accept, for example, high tensile forces in the direction of the fiber axis with low elongation; however, even small tensile forces acting perpendicular to the fiber axis cause high elongations. During drying in the

paper machine the fiber shrinks in the axial direction by only a few percent. In comparison, shrinkage in the direction perpendicular to the fiber axis reaches 40 %. If the fiber orientation were completely random, however, the anisotropy of the fibers would cancel out and the paper properties would be isotropic. Thus, the observed anisotropy is due to the production process. First, the fibers are not aligned randomly in the sheet-forming process because the machine direction is preferred (anisotropy of fiber orientation), and second the fiber mat is passed through the paper machine under tension, which prevents free shrinkage of the fibers during drying. This inhibition of shrinkage is only effective in the machine direction and is essentially responsible for the anisotropy of the moisture expansion of finished paper, which is generally far lower in the machine direction than in the cross-machine direction. The inhibition of shrinkage during drying also affects the load – deformation properties of paper, which are therefore also anisotropic (cf. Table 26).

Many papers exhibit a further anisotropy with respect to their composition in the normal direction (z-direction). The process technology of production on the wire is responsible for this phenomenon. On the wire side, substances that can pass through the wire are washed out, while on the other side, they are retained by the fiber mat. This results in different smoothness properties on the two sides of the paper, also known as the two-sidedness of paper.

As a result of the in-plane anisotropy of the sheet, the machine direction must be considered when taking samples for testing anisotropic properties, such as strength. Two-sidedness is important in the testing of printability, for example.

Finally, paper has viscoelastic properties [482], [483], i.e., it can be elastic like a solid or viscous like a thick liquid. The viscoelasticity is also a result of the superimposition of the properties of the individual fibers and those of the fiber network. The viscous flow of the individual fibers is caused by the sliding of fibrils at high tensile loads. The individual fibers exhibit elastic behavior at low tensile loads. In the fiber structure of paper, the sliding of fibers at fiber intersections results in a flow effect and the paper undergoes plastic deformation.

A characteristic feature of viscoelasticity is the dependence of the onset of flow on the load-

Table 27. Moisture content of selected types of paper in equilibrium with various levels of humidity at 23 °C

Type of paper	Basis weight, g/m ²	Relative humidity, %		
		20	50	75
Newsprint	50	6.5	8.5	10.0
Gravure printing	65	6.0	8.0	9.2
Offset, mechanical	80	5.2	6.4	7.9
Offset, wood-free	80	5.0	6.3	7.5
Art paper, mechanical	120	4.1	5.7	6.9
Art paper, wood-free	120	3.8	5.3	6.5

ing rate. Small loads acting over long periods of time result in flow, whereas large intermittently acting loads cause only elastic deformation. Therefore, in the determination of the tensile strength of paper, the time is fixed within which the tensile stress applied causes the paper to break.

13.1.3. Summary

The material paper has essentially four characteristic features: inhomogeneity, hygroscopicity, anisotropy, and viscoelasticity. These features must be taken into consideration in the testing of paper (cf. Table 28).

Table 28. Characteristic material properties and their effect on testing conditions

Property	Effect
Inhomogeneity	sample dimensions, number of measurements
Anisotropy	testing direction
Two-sidedness	tested side
Hygroscopicity	relative humidity, temperature
Viscoelasticity	duration of test

The magnitude of these features depends on the type of fiber, the fiber raw material, the pulping process, and on the process techniques used in stock preparation and papermaking. Consequently, there are a large number of variables in papermaking and many degrees of freedom are involved in the adjustment of the desired paper properties. Therefore, several different paths can usually be pursued to obtain papers with comparable technical properties. This is of importance in the standardization of paper properties. Only the technical characteristics may be stipulated

in each case, but not the process used to realize these characteristics. Otherwise, there would be the danger of excluding new technologies and impeding technical progress.

13.2. Paper Testing [484–486]

13.2.1. Preliminary Measures

A direct consequence of the paper properties described above is the necessity of having available sufficient sample material that can be tested. Sampling must be carried out correctly because the test results obtained with a sample should be representative for all of the paper from which the sample was taken. A straightforward process for cut-size and reel paper is described in ISO 186 (1988).

As a result of its hygroscopic properties, paper must be tested under standard climatic conditions and the samples must be conditioned in this climate before testing (sample conditioning). In ISO 187 (1977), the preferred climate for paper testing is specified as 23 °C and 50 % relative humidity.

13.2.2. Basic Properties

The basic properties of paper include the dimensions and the mass. In the case of sheet material such as paper, the basis weight m_A is determined in accordance with ISO 536 (1976). The value m_A is the ratio of the mass m to the area A of a sample. If m is measured in grams and A in square centimeters, then

$$m_A = \frac{m}{A} \cdot 10000 \text{ g/m}^2$$

Another basic property of paper is the caliper. The caliper of paper must be defined in terms

of the measuring instrument. ISO 534 (1988) specifies an instrument with two parallel planar measuring surfaces of 200 mm^2 which act on the sample with a surface pressure of 100 kPa. The resulting distance between the surfaces is the caliper D of the paper.

The ratio of the basis weight to the caliper is the density of paper. The reciprocal density is the specific volume.

The moisture expansion of paper, i.e., the change in dimensions with changing ambient climate, is also a basic property. According to DIN 53 130, the moisture expansion (ME) is the ratio of the length L of a sample paper strip, resulting from a change in the ambient climate from $23^\circ\text{C}/45\%$ relative humidity to $23^\circ\text{C}/83\%$ relative humidity, to the original length L_0 . The temperature can also be 20°C in each case.

$$\text{ME} = \frac{L}{L_0} \cdot 100\%$$

The moisture expansion test is also standardized in ISO 8226-1 (1985).

13.2.3. Composition and Chemical Paper Testing

The fiber composition of paper is determined with a light microscope (fiber microscopy). Due to the varying fiber morphology, both the fiber raw material and the pulping process can be determined. Chemical dyeing methods are used for contrast enhancement.

The term moisture content refers to the amount of water in the paper in equilibrium with a defined ambient climate. It is determined gravimetrically in accordance with ISO 287 (1985). A dry sample is produced by drying the paper to constant weight at 105°C . The moisture content is expressed in percent, based on the moist sample.

Chemical testing is used to determine the components of paper. Moreover, it is of significance in papermaking for quality control and process control. Another important field of chemical paper testing is the control of papers for the packaging of food.

The entire spectrum of analytical methods used for the chemical testing of paper ranges

from gravimetric methods to spectroscopy, electrochemical and enzymatic methods, as well as sensors and microbiological processes.

Only in exceptional cases can the components of paper be determined nondestructively. In general, the components to be determined must be extracted out with water or organic solvents. For example, the resin content of paper is determined gravimetrically in the extraction residue by using an organic solvent as an extracting agent.

The inorganic fillers contained in paper are determined as residue on ignition (ash content). In accordance with ISO 2144 (1987), the sample is ignited at 900°C until no change in weight is observed. The ignition residue is then determined gravimetrically and expressed as a percentage of the original weight of the sample. Other ignition temperatures are used for chemical pulp (575°C) and filter papers (800°C). X-ray microanalysis is employed for the quantitative determination of the types and amounts of fillers. Elements such as calcium, magnesium, and metals in trace amounts can be analyzed by atomic absorption spectroscopy. For the determination of organic substances in paper extracts, IR spectrophotometric and chromatographic methods are applied, e.g., gas chromatography for volatile components and high performance liquid chromatography for thermally sensitive constituents.

Other chromatographic methods are used for the determination of chlorides, nitrates, and sulfates, or for the differentiation and characterization of dyes and optical brighteners.

Apart from the analytical methods mentioned above, the sum parameters are of special importance. These include the ash content, pH (ISO 6588, 1981), electrical conductivity of aqueous extracts (ISO 6587, 1983), and the resin content of paper.

Apart from the ISO standards mentioned above, other standards for chemical testing of paper are, e.g., the ZELLCHEMING, SCAN, and TAPPI test methods.

13.2.4. Strength Properties

In the tensile strength test, the tensile strength and the strain at rupture are determined as values characteristic of paper strength (ISO 1924,

1981). The tensile strength together with the sample width gives the tensile strength per unit width, measured in N/m, which together with the sample thickness gives the tensile strength, measured in kPa.

In paper technology, the breaking length is also of some importance as a relative measure of strength. This is the length of a freely suspended paper strip of any constant width and thickness that breaks at the point of suspension due to its own weight.

The breaking length L in kilometers is then calculated from the tensile strength force F_B of the paper measured in N, the basis weight m_A in g/m², the width of the strip w in mm, and the gravitational constant $g = 9.81 \text{ m/s}^2$.

$$L = 10^3 \cdot \frac{F_B}{m_A w g}$$

The bursting strength is important in the characterization of packaging papers. The bursting strength of paper is determined in accordance with ISO 2758 (1983) and that of board in accordance with ISO 2759 (1983). In the testing instrument, the free area of the sample stretched in a circular frame is exposed to increasing pressures until it ruptures.

Packing materials are also characterized by their bursting strength. For instance, set values are stipulated in DIN 55 468 Part 1 for the strength of corrugated boards, and are used for classification. The same standard specifies set values for the puncture resistance. This strength property is determined, mainly for cardboard and corrugated board, by measuring the resistance offered by a sample to the penetration of a pyramidal body (ISO 3036, 1975).

To determine the tear resistance (Elmendorf), a sample is torn with the help of a pendulum device starting from a predetermined cut, and the work required for a tear of a given length is measured. The test is described in ISO 1974 (1990).

The plybond strength (DIN 54 516) is a measure of the matrix strength of multi-ply papers and boards. It is determined by measuring the maximum force per unit sample width required to split the sample.

The crush resistance of paper under compressive stress is measured as the short span compression strength. To prevent the sample kinking, the free span length must be very small (typically 0.7 mm). The resistance measured accord-

ing to DIN 54 518 gives the ultimate crushing load per unit width.

The flat crush resistance (ISO 3035, 1982) and the edge crush resistance (ISO 3037, 1982) are used to characterize the strength of corrugated board. In the former test, a circular sample of corrugated board is exposed to increasing pressures between two parallel planar plates until the corrugation collapses, and the maximum load is measured. In the second test, the load is applied in the direction of corrugation starting from the edge of the sample. The edge crush resistance is used in DIN 55 468 Part 1 for the classification of corrugated boards.

The folding strength is an important property of both packaging and graphic papers. It can be determined either as described in ISO 5626 (1978) as the Schopper double fold value, or as described in SCAN P 17 (1977) as the Köhler–Molin folding endurance value. The sample is subjected to specified tension in both cases. The Brecht–Wesp pressure folder functions without tension. A sharp fold in the sample is produced between two rolls and is repeated up to fifty times in the same position. The ratio of the tensile strength of the folded sample to that of the unfolded sample is the folding strength.

13.2.5. Load–Deformation Properties

Not only can the strength properties, tensile strength and strain to rupture be determined in the tensile strength test (ISO 1924, 1983), but also the tensile energy absorption, TEA, which is especially important for bag paper. The TEA value represents the nonelastic portion of the deformation energy and thus that portion of dissipated energy which should be high in the case of bag paper.

The resistance to flexural stress is measured as the bending stiffness under approximately pure elastic deformation as defined in DIN 53 121. This test is usually performed with a two-point beam method. To guarantee elastic deformation, maximum bending angles, which depend on the span length and the sample thickness, are specified. This may be circumvented by the resonance length method (ISO 5629, 1983) in which the resonance length of a free sample strip is measured. Resonance is generated via a clamp vibrating at 25 Hz.

Deformations in board and cardboard can also be produced by creasing. Testing the properties of creases requires defined production processes, e.g., DIN 55 437 Part 1. In Parts 2 and 3 of this standard, methods are described for the manual folding of the creases and for the visual evaluation of the folding or the technical evaluation of the creases with a folding-moment tester.

13.2.6. Surface Properties

A large number of methods are available for evaluating the topography of paper surfaces. The Bekk smoothness is determined according to ISO 5627 (1984) as follows. At a defined pressure difference, the time in seconds is measured which a specified amount of air requires to flow radially inwards between the paper surface and a ring-shaped glass plate and on into a vacuum chamber. The smoother the surface of the paper, the longer the pressure equalization takes. The determination of roughness according to Bendtsen (ISO 2494, 1974) is related to the Bekk method for the determination of smoothness. In this case, however, the direction of the air flow is reversed and the magnitude of the air flow is measured. The air escapes under defined conditions between the measuring ring of the measuring head and the paper surface under constant overpressure.

Another surface property of paper is the abrasion resistance. The mechanical abrasion resistance of surfaces is determined in the friction wheel process (DIN 53 109). In this process, the amount of abrasion is measured which is obtained by abrading the conditioned or wet sample with an abrasion wheel of defined quality under defined conditions.

13.2.7. Optical Properties

An object, e.g., a paper surface, is termed white when the illumination intensity and the absorption capacity of the surface are independent of the wavelength. Deviations confer a more or less pronounced color shade on the surface.

In the paper industry, a special process is used to characterize the brightness because this is one of the most important optical properties of paper. The determination of the reflectance factor (ISO brightness) is based on ISO 2470 (1977).

For this test, a filter is used which has an intensity maximum at a wavelength of 457 nm. The reflectance (blue component) measured in a reflectometer under specified conditions is known as brightness. It is expressed as a percentage of the brightness of a white standard.

Another optical property of paper is its transparency, i.e., a measure of its light transmittance. It is calculated from the reflectance factors R_0 , R_w , and $R_{(w)}$, which are determined in accordance with DIN 53 145 Part 1 or Part 2. The reflectance factor of the individual sheet on a completely black background is R_0 , R_w is the reflectance factor of the individual sheet on a white background, and $R_{(w)}$ is the reflectance factor of the white base.

The opacity is a measure of light-tightness. It is defined in ISO 2471 (1977) as the ratio of the reflectance factor R_0 to the reflectance factor R_∞ . Both reflectance factors are determined in accordance with DIN 53 145. R_0 is measured as the reflectance factor of an individual sheet on a completely black background and R_∞ as the reflectance factor of an "infinitely" thick stack of the same paper.

13.2.8. Printing Properties

The printing properties of paper result from complex interactions between printing ink, printing process, and paper. Practice-oriented printability tests must be performed to evaluate these properties. Test printers are also suitable for this purpose. Instruments for offset printing, gravure printing, and flexographic printing can be used with standard printing inks under laboratory conditions to test the dry pick resistance or the wet pick resistance of papers. Mottling and ink penetration properties can also be tested. Conversely, the behavior of various printing inks towards standard papers can also be evaluated.

Furthermore, defined proof copies produced with the test printers can be used to test full ink coverage, color density, color gloss, shade, abrasion resistance, stacking ability, and contact yellowing.

13.2.9. Behavior Towards Liquids

The behavior of liquids towards paper is characterized by the processes of wetting and pene-

tration. In both cases, the characteristic physical property is the surface tension. This value can be measured directly and tensiometrically in the case of liquids and indirectly, via the contact angle of test liquid droplets, in the case of solids such as paper. A liquid wets the surface of paper only if its surface tension is lower than that of the paper. The same holds for the wetting of the capillary walls upon penetration of liquids into the capillaries of the paper.

If the wetting and the penetrating capacity of liquids are to be changed, the surface tension of the paper must also be changed. This is achieved, for instance, by sizing the paper, a process which must fulfill the requirements regarding printability with aqueous inks. According to DIN 53 126, paper is considered to be printable if an ink line drawn with a normally adjusted drawing pen has neither run nor penetrated into the paper after 24 h.

The water absorption W_A (Cobb) (ISO 535, 1976) refers to the amount of water that is absorbed by a certain area of paper on one-sided contact for a specified exposure time. The time of exposure to water must be chosen such that a sufficient amount of water enters into the fiber matrix, but does not penetrate to the opposite side of the sample.

In the determination of grease permeability (DIN 53 116), red-colored palm kernel oil is used as the testing agent. The passage of fat through the sample under specified conditions is then evaluated.

13.2.10. Exclusion of Gases and Vapors

As a rule, papers have only a limited ability to exclude gases and vapors. Of particular importance are the air permeability (e.g., for filtration properties) and the water-vapor permeability.

There are two standardized test methods available for the determination of the mean air permeability: the Bendsen method (ISO 5636-2, 1984) and the Schopper method (ISO 5636-3, 1984).

A gravimetric method for the determination of water-vapor permeability is described in ISO 535 (1976). This method is not suitable for very dense or coated papers. In these cases, the use of electrolysis described in DIN 53 122 Part 2 is recommended.

14. Economic Aspects

In 1988 world production of paper and board was ca. 228×10^6 t. Although paper and board are used in some form or other in all parts of the world which are inhabited by people, the production is left to a limited number of countries. More than 4000 paper machines are responsible for production in 95 of the approximately 200 countries in the world, whereby the 15 largest producer countries alone account for 85 % of total world production (Table 29).

Table 29. World paper and board production according to countries (1988)

Country	Production, 10^6 t	Share, %
United States	71.0	31
Japan	24.6	11
Canada	16.6	7
China	12.6	6
Soviet Union	10.7	5
FRG	10.5	5
Finland	8.6	4
Sweden	8.1	4
France	6.3	3
Italy	5.3	2
Brazil	4.6	2
UK	4.2	2
South Korea	3.6	2
Spain	3.4	1
Taiwan	2.9	1
80 other countries	34.1	15
World total	227.8	100

The various requirements for the production of paper are not met everywhere. For instance, suitable raw materials must be available, including water, energy, and trained personnel. Furthermore, the construction of paper mills requires a very high investment, and a sufficiently large market and a favorable location are both essential prerequisites for papermaking. For these reasons, the modern paper industry is based mainly in the coniferous forest zone of the Northern Hemisphere, with centers in Northern and Western Europe, North America, as well as in Eastern Europe and Japan.

World paper production has increased more than fivefold since 1950, when production was ca. 44×10^6 t (Table 30). During this time, the regions which did not belong to the classical paper

Table 30. World production of paper and board (10^6 t)

	1950	1960	1970	1980	1988
Europe	13.194	25.826	45.377	59.495	75.934
East	2.840	5.765	10.560	14.103	16.480
West	10.354	20.061	34.817	45.392	59.454
North America	28.286	39.393	56.323	71.179	87.638
United States	22.108	31.255	45.186	57.789	71.000
Canada	6.178	8.138	11.137	13.390	16.638
Japan	0.873	4.513	12.973	18.087	24.624
Others	1.387	5.193	15.014	23.357	39.650
World	43.740	74.925	129.687	172.118	227.846

Table 31. Regional shares of world production of paper and board (%)

Region	1950	1960	1970	1980	1988
Europe	30.1	34.5	35.0	34.6	33.3
East	6.5	7.7	8.1	8.2	7.2
West	23.6	26.8	26.9	26.4	26.1
North America	64.7	52.6	43.4	41.3	38.5
United States	50.5	41.7	34.8	33.6	31.2
Canada	14.2	10.9	8.6	7.7	7.3
Japan	2.0	6.0	10.0	10.5	10.8
Others	3.2	6.9	11.6	13.6	17.4
World	100	100	100	100	100

countries have come to the fore, and their share of world production has grown from ca. 3 % in 1950 to 17 % in 1988. At the same time, the circle of paper producing countries has widened considerably from 61 to 95 and now includes a large number of developing countries. In these countries, the tendency towards self sufficiency is influenced by national economic considerations and the need to save foreign exchange for paper imports.

In 1988, Europe, North America, and Japan still produced 83 % of the total world production (Table 31). However, the development in these regions has varied considerably. In Japan, the paper industry has developed from a low during the postwar years to become the second largest paper producer in the world. In the last three decades, Western Europe has more or less been able to maintain its share of world production. North America has had to accept large losses of its share of production, which has, however, been increasing relatively constantly.

In 1988 graphic papers accounted for more than 40 % of total paper production. This included newsprint (31.7×10^6 t) and other printing and writing papers (62.4×10^6 t). The production of packaging papers was 95.8×10^6 t, and that of the remaining papers and boards was 37.9×10^6 t (Table 32).

Table 32. World production of paper and board, arranged according to main types (1988)

Paper and board type	Production, 10^6 t	Share, %
Newsprint	32	14
Other printing and writing papers	62	27
Packaging papers and boards	96	42
Other papers and boards	38	17
Total	228	100

At present, a little more than one-fifth of the world production of paper and board is sold across borders. In 1988 exports and imports accounted for about 50×10^6 t.

The net imports to the United States, i.e., imports minus exports, amount to 7.1×10^6 t, which corresponds to a quota of 9 % (based on the consumption). In contrast, Canada, with its comparatively low population, has net exports amounting to 10.5×10^6 t, which is 63 % of its own paper production. The predominant part of Canadian exports go to the United States.

In Western Europe, the foreign trade situation within the EC and EFTA also varies greatly. The EC, with 12.4×10^6 t, a quota of 26 %, is a net importer. The EFTA with 15.6×10^6 t or 70 % (based on the internal production) is a net exporter. The EC as a whole has more than 320×10^6 consumers and is the largest market in

the world. As a customer, it plays a paramount role for the paper industries of the EFTA countries.

In Japan the amounts imported and exported balance out at ca. 10^6 t each.

Of all the remaining regions, the countries in Africa and Asia are the largest net importers with 0.8×10^6 t and 4×10^6 t, respectively. The imports and exports of South and Central America are roughly balanced. World consumption of paper and board in 1988 was 226×10^6 t. The United States has by far the highest consumption, followed by Japan and China. Germany is the fourth largest consumer, before the Soviet Union (Table 33).

Table 33. World paper and board consumption according to countries (1988)

Country	Consumption, 10^6 t	Share, %
United States	78.0	35
Japan	25.0	11
China	13.2	6
FRG	12.3	5
Soviet Union	10.0	4
UK	9.3	4
France	7.9	3
Italy	6.2	3
Canada	6.1	3
Spain	3.9	2
Brazil	3.8	2
South Korea	3.4	2
Taiwan	3.0	1
The Netherlands	2.8	1
Australia	2.5	1
188 other countries	38.0	17
World total	226.2	100

Looking at the world paper consumption from a geographical point in view, it is apparent that the industrial countries of Europe and North America, and Japan not only produce, but also consume the bulk of the paper (Table 34).

There is also a relatively rapid increase in the consumption of paper in the remaining regions, especially in Asian countries such as South Korea and Taiwan, which are becoming increasingly important for the international paper market. In the past 30 years, countries in South and Central America as well as in Eastern Europe and Africa have increased their share of world paper consumption annually. Improvements in the living conditions in these regions are accompanied by a corresponding increase in the consumption of paper. The rise in both the standard of living and the individual income is as impor-

tant a prerequisite as the spread of literacy for the consumption of writing paper and printing products. Another important factor is the building up of export and consumer industries with their demand for packaging materials.

The amount of paper consumed, however, is not an adequate measure of the standard of living of a country. Only the relative per capita consumption can give a very rough indication of the living standard, because other factors such as the average income, way of life, and consumer patterns must also be taken into consideration. The United States has the highest per capita consumption per year (1988) with 311 kg, followed by Sweden (247 kg), Canada (236 kg), Switzerland (207 kg), Japan and Finland (204 kg each), Denmark (202 kg), and Germany (201 kg). In terms of paper consumption, the countries can be grouped according to their per capita consumption. For example, while the average consumption in Western Europe is 152 kg and in North America 304 kg, the per capita consumption in Eastern European countries is 40 kg, in Latin America 25 kg, and in Africa only 5 kg. Paper consumption per inhabitant is less than 1 kg in about 30 developing countries.

A comparison between population and paper consumption in different regions shows that Asia, which represents 60 % of the world population, accounted for only 24 % of world paper consumption. Conversely, North America has 5 % of the world's population but a consumption of 37 % (Table 35). An important indicator for the development of paper consumption is not only the gross national product but also the population growth.

World population has doubled from 2.5×10^9 in 1950 to 5.1×10^9 in 1988. The per capita consumption of paper worldwide was 18 kg in 1950 and 44 kg in 1988, an increase of 144 %. Thus the relative consumption of paper per capita has increased considerably faster than the world population. It is obvious that these average global values do not reflect the substantial regional differences.

In summary, the largest growth percentage potential for paper consumption is in the Third World countries, especially in Asia, while industrialized countries such as the United States, Japan, and the EC countries have relatively low growth rates, but still represent in absolute terms a considerable market potential.

Table 34. Regional shares of world paper and board consumption (%)

Region	1950	1960	1970	1980	1988
Europe	27.3	33.6	34.7	33.9	31.8
East	6.3	7.7	8.3	8.5	7.1
West	21.0	25.9	26.4	25.4	24.7
North America	64.2	50.9	43.4	38.4	37.2
USA	60.6	47.7	40.7	35.8	34.5
Canada	3.6	3.2	2.7	2.6	2.7
Japan	2.0	5.8	9.8	10.5	11.1
Others	6.5	9.7	12.1	17.2	19.9
World	100	100	100	100	100

Table 35. Population and paper consumption (1988)

Region	Population		Paper consumption	
	× 10 ⁶	Share, %	10 ⁶ t	Share, %
Europe	750	14	72	32
Africa	610	12	3	1
North America	273	5	84	37
Central and South America	429	8	11	5
Asia	3 069	60	53	24
Australia/Oceania	26	1	3	1
World	5 112	100	226	100

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Paraformaldehyde → **Formaldehyde**
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Parasite Infections → **Veterinary Drugs**