Paper Drying in the Manufacturing Process

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Chapter 7

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Fig. 7.1 View of a modern papermaking machine used to make newsprint.

Although water is central to the papermaking process, it is only when it is almost completely removed that the paper takes on the form we find most useful. The manner in which the water is removed plays an important role in the nature of the structure that is ultimately formed (**Fig. 7.1**). Furthermore, the manner in which paper was dried also influences how it behaves when water is reintroduced to the dry sheet. Most papers remain vulnerable to the reintroduction of moisture, whether it is as liquid water or as water vapour at elevated relative humidity. Increasing the moisture content weakens the hydrogen bonds, causes fibres to swell and become more flexible, and can have a profound effect on the characteristics of the paper.

This chapter considers the removal of water during the papermaking process. It will concentrate on contemporary papermaking in which dilute aqueous suspensions of cellulosic or lignocellulosic fibres and additives are dewatered by filtration, pressed and dried to form a web structure. Understanding contemporary dewatering will also enhance our appreciation of the equivalent historical processes that, although significantly different from modern ones, were governed by comparable mechanisms. Papermaking has always been a cost-intensive industry in which, increasingly, a narrow margin of revenue can only be achieved if product quality is reconciled with processing efficiency. Today, the dewatering mechanisms are tightly controlled to remain economical while achieving properties needed in the product. The focus of this chapter is on the changes in the fibres and web structure that take place during drying. These changes are influenced by many factors, including the fibre species, origin, fibre conditioning by pulping, bleaching, beating and/or refining, reuse after recycling, and the drying process conditions. These factors have a significant influence on the structure and properties of paper, leaving it in a state with the potential for either subtle or pronounced responses to moisture, both during natural ageing or conservation treatments. The discussion of manufacturing drying processes is particularly relevant for understanding the response of paper to conservation treatments involving the removal of water. Thus, the goal of this chapter is to provide the reader with an appreciation of the changes experienced by the fibrous structure of paper as it is dewatered and dried, and the origins of dimensional, structural and chemical properties of paper encountered during conservation.

7.1 Water removal in paper manufacturing

Water serves several essential functions during the papermaking process. When imbibed into the fibres, it provides the flexibility needed to maximize the contact area between fibres. It is the medium through which surface tension forces and hydrogen bonding between the cellulose surfaces takes place and is important as a suspending fluid for the fibres. Copious amounts of water are necessary to disperse and separate fibres, thereby ensuring the uniformity of their distribution within the plane of the sheet, a characteristic known as formation. Kerekes and Schell (1992) introduced the crowding factor as a useful parameter that relates the amount of water needed to suspend fibres with the formation of the paper sheet that is formed. To determine the crowding factor, one need only know the fibre length, the fibre coarseness defined as the mass per unit length, and the mass concentration in the pulp suspension. The crowding factor can be calculated according to the formula:

$$N_C = \frac{5 C l_f^2}{\omega_f} \tag{7.1}$$

where:
N_C = crowding factor (dimensionless)
C = fibre mass concentration in the pulp suspension (mass %)
l_f = fibre length (mm)
ω_f = fibre coarseness (mg/m).

The calculation of the crowding factor allows the determination of the extent of fibre-fibre interaction leading to entanglement and flocculation. If the crowding factor, NC, exceeds 60, then the fibres will tend to flocculate in the pulp suspension and the uniformity of the formed paper, or formation, will be poor. For NC less than 60 the space separating fibres in the pulp suspension is sufficient to reduce the extent of fibre entanglement and flocculation. This results in a uniform formation for the formed sheet. In the following example, typical values for a Douglas-fir softwood pulp suspension at a concentration of 0.5% are used to calculate the crowding factor which falls close to the threshold for flocculation to occur:

$$N_C = \frac{5(0.4\%)(2.7\,\mathrm{mm})^2}{(0.25\,\mathrm{mg/m})} = 58 \tag{7.2}$$

Most papers will therefore begin their passage through the paper machine as a dilute suspension of fibres in water at a solid content of about 0.5%. For each kilogram of fibre, nearly 200 kilograms of water must be removed.

The purpose of the paper machine is to distribute fibres continuously and uniformly within a planar region. All of the water must then be removed and the web consolidated so that adequate bonding occurs between the fibres. The result is a thin, dry, fibrous, layered mat. While contemporary papermaking processes reflect centuries of incremental enhancement in the speed and efficiency in achieving these tasks, the function of each process has remained essentially unchanged. Paper machines of the past 150 years, including those in use today, are divided into two primary areas. The wet end is where as much as 99.5% of the suspension water is removed. In the dry end, the wet web is about one-half water, and is dried to a solid content exceeding 90% (**Fig. 7.2**). In traditional hand papermaking as it was practised since the beginning of papermaking in Europe, the basic procedures equivalent to the wet and dry ends of a paper machine require four separate operations:

- By dipping the mould, the vatman gathers a fibre mat from which is filtered excess water.
- The coucher transfers each freshly formed fibre mat to a wool felt, piling up many of them to accumulate a post.
- The post is pressed so that water is expressed from the fibre mats into the felts, squeezing it out of the post. This causes consolidation of the sheets so that they can be handled without support in subsequent operations. The sheets are separated from their felts and piled on top of each other for a second pressing that removes more water and further densifies the sheet.
- The dry end of a contemporary paper machine has substituted loft drying, which involved hanging small gatherings of sheets (spur) over ropes stretched in tiers across the room. Hanging multiple moist sheets for drying while they were still in close contact with each other improved their planarity. The rate of drying could only be adjusted through shutters that moderated the environmental conditions of the room.

Important surface and strength properties are imparted to paper during drying. We will limit this discussion to how the basic components of the wet end and dry end contribute to the inherent properties of paper (see **Fig. 7.2**). The dewatering, interfibre bonding and fibre shrinkage are modelled in Video 7.1.

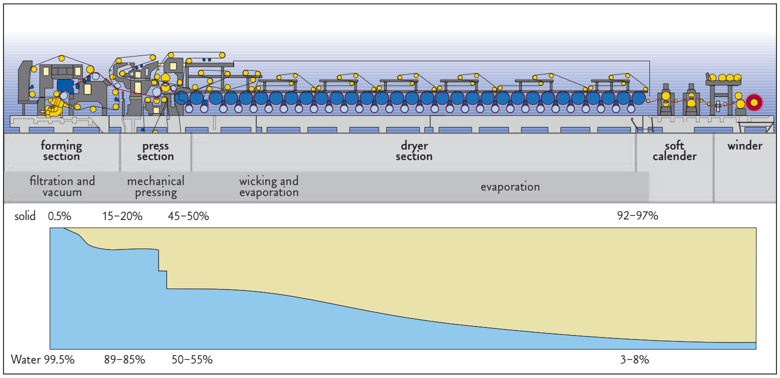

Fig. 7.2 Essential parts of a modern Fourdrinier papermaking machine. The dilute fibre suspension or stock is delivered from the head box on to the moving forming fabric (wire) in the wet end, where forming elements and suction boxes remove most of the free water. The wet web is then consolidated in the press section and dried in the dryer section. The finished paper is collected on the wind-up reel.

7.1.1 Wet end

The wet end includes the headbox, the forming section and the press section. The headbox is designed to convert pipe flow into slit flow in order to distribute fibres uniformly across the width of the machine. This continuously formed fibrous mat that spans the width of the paper machine is known as the web. Modern paper machines are usually more than 4 m wide and may even exceed 10 m. The dilute stock, consisting of the fibre suspension, fillers and chemical additives, is discharged from the headbox on to the moving forming fabric, or 'wire'. The suspension is transported on this continuous mesh through the initial stages of dewatering in the forming section. The design of the headbox, the composition of the dilute stock and the process operating conditions all contribute to the flow dynamics that occur in the forming section as the stock passes through the headbox and impinges on to the moving wire. The result can be a highly uniform sheet, or one that is considered of inferior quality containing streaks or a floccy structure (**Fig. 7.3**). For instance, consider a floc region that has a greater mass of fibres and is thicker than the surrounding regions. As the paper is compressed in the press section and calender, the floc region will be densified to a greater extent. The reduced internal porosity will affect the rate of water absorption and structural swelling when water is reintroduced by printing with water-based inks, humidification, or rewetting methods used in paper conservation. This may cause an increase in print mottle or cockling for papers that have poor formation. While we have used the term 'formation' to describe the uniformity of the fibre distribution in the sheet, the word is also commonly used to describe the transition of the dilute stock into a cohesive wet web that occurs just after the headbox in the wet end, in the forming section.

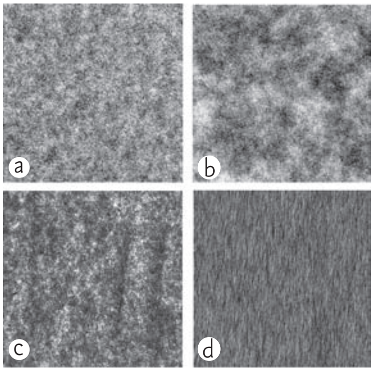

Fig. 7.3 Examples of four machine-made paper sheets showing different formation characteristics. a: well formed, random distribution of fibres in the structure. b: flocculated paper with poor formation. c: paper showing streak defects in commercially made paper. d: highly oriented fibres and flocs as generated on a commercial paper machine (images are 10 cm on a side and were generated by β-radiographic imaging).

Dewatering of the suspension of fibres and fillers to create a cohesive web structure occurs in the forming section. Dissolved and minor suspended pulp additives do not contribute significantly to the mass of the cohesive web structure, although mineral filler content can be as much as 30% in modern office papers. Filtration is the principal mechanism for water removal in the initial part of the forming section. **Fig. 7.2** illustrates a Fourdrinier former that uses a single wire. Modern paper machines may also dewater the stock from two sides as the stock is sprayed between two converging wires moving at essentially the same speed. The dilute stock is squeezed between the forming fabrics under tension and water is expressed from the web. Such formers are referred to as twin wire or gap formers. Whether configured as a single- or twin-wire forming section, the forming fabric is backed with forming elements used to improve dewatering rates and maintain uniform material distribution. In the first part of the forming section, foils or table rolls are used to remove water by a filtration process that leaves the fibres stratified within the fibrous web. The dilute stock exits the headbox at high velocity through a narrow slit that spans the full width of the machine, known as the slice. This jet of dilute stock strikes the forming fabric(s) at a low incident angle. The jet may travel slightly slower or faster relative to the velocity of the moving forming fabric. This causes an inherent orientation of fibre aligned to a greater or lesser extent along the direction of travel of the moving forming fabric, known as the machine direction (MD). The direction perpendicular to the MD, which is also parallel to the slice and the axes of the various rolls on the machine, is referred to as the cross direction or CD. The term in-plane is often used to describe the plane formed by the MD and CD directions. The zed direction or ZD refers to the direction that is perpendicular to the MD-CD plane. This may also be called out-of-plane and refers to the structure or properties through the thickness of the paper. These are the common terms that describe the orientation of machine-made paper (**Fig. 7.4**). The added tensile strength introduced by orienting the fibres preferentially in the MD can be useful for runnability of lightweight papers, such as newsprint, that are printed using continuous web-fed presses. However, excessive orientation may be a disadvantage for high-quality papers, such as office papers printed by sheet-fed processes, since differences in expansion and contraction (dimensional stability) between MD and CD can cause jams, misfeeds and misregistration of imaging. To reduce machine direction orientation, paper machines are sometimes agitated to introduce a lateral shake of the forming fabric. The forming section is oscillated in the cross direction, adding to the turbulence of the pulp suspension on the wire. The significance of fibre orientation will be discussed in the context of anisotropic (not the same in the MD, CD and ZD) shrinkage of the web.

Fig. 7.4 An image of paper on a paper machine illustrating the three perpendicular directions. Machine direction (MD) is aligned parallel with the movement of the web through the paper machine. Cross machine direction (CD) is aligned parallel to the wind-up reel. The zed direction (ZD) is parallel to the thickness direction of the web. It is perpendicular to the principal plane of the web formed by the MD and CD vectors.

Considering the forming of hand-made papers, the dipping action that gathers the fibre from the vat involves a continuous motion in one direction that can cause fibres to remain oriented with slight preference parallel with the short side of the mould. The vatman seeks to overcome this bias by shaking the mould alternating between two perpendicular directions as the water is filtered from the aqueous suspension. Therefore, sheets made by hand usually have little or no perceivable orientation of fibres unless it was intentionally introduced into the sheet by the vatman during drainage. A sheet that has no apparent directionality, either by orientation of fibres or by non-uniform straining or restraint during processing, is said to be isotropic, i.e. having the same properties in any in-plane direction. Papermakers refer to such an ideal sheet as being ‘square’.

The wet web initially has very low strength that results from fibre entanglement and friction between contacting fibres. In the second part of the forming section, vacuum is applied to the back of the forming wire using wet suction boxes followed by vacuum boxes, and finally by the couch roll. The suction boxes cause the fibres to be drawn towards the wire and compress the wet web structure. When air fully infiltrates the web a situation known as breakthrough occurs, where the rate of dewatering slows and the wet suction boxes no longer effectively drain the water from the wet web. It then becomes necessary to apply a mechanically induced vacuum to draw more volume of the air-water mixture from the fibrous mat. This occurs in the vacuum boxes and the couch roll. A dandy roll that rotates in contact with the top surface of the wet web may also be used to imprint the web with watermarks or ‘laid and chain’ patterns. The movement of the fibres under the dandy roll may also improve formation and water removal, especially on older paper machines. After breakthrough, the presence of air-water interfaces, especially at fibre-fibre crossings where residual water forms menisci, contributes significantly to the web strength. These forces that result from the surface tension of water and the capillary forces within the structure are referred to as Campbell forces (Campbell 1959) (**Fig. 7.5**). Interfibre attraction increases as free water is removed and as the air-fibre-water interface is extended. These consolidating forces are greater for pulps with higher specific surface area, such as those that are more highly refined (beaten) or that have a greater fraction of fine particles. At the end of the forming section, the wet web remains relatively thick and uncompressed. The apparent density (kg/m³) of the structural network at this point is relatively low because the interfibre contacts result only from the small compressive forces induced by Campbell forces and vacuum applied to the bottom side of the forming wire. Fibres do not fully conform to one another and the potential interfibre contact area is not fully developed. The wet web exits the forming section at about 18% solids having nearly 92.5% of the water in the original dilute stock removed.

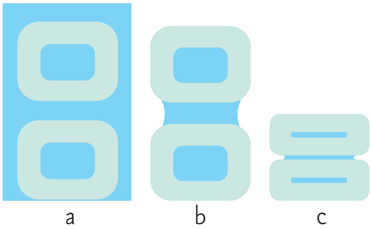

Fig. 7.5 Surface tension and capillary forces acting on the fibre suspension during water removal. Figures (a)–(c) show the increase of fibre-fibre attraction as water drains from the web. Air water surfaces are created after breakthrough in (b), and then reduced with the evaporation of water in (c).

In the press section, the wet web is mechanically compressed to further reduce the water content. More significantly, the fibre network is densified and the fibres conform to one another in close contact. This increases the contact area between fibres, where interfibre bonds can form as more water is removed. As the solid content of the web approaches 25%, the surfaces are brought close enough together for hydrogen bonds to begin to form between the fibre surfaces. Although some hydrogen bonding is expected to occur, the strength of the web is still dominated by surface tension or capillary forces (Campbell forces) that are inversely proportional to the thickness of the water film remaining between fibres. Press sections are designed to affect the greatest amount of mechanical dewatering of the wet web without shearing the network structure or disrupting the fibre cell walls. If the latter does occur, the strength potential of the paper would be seriously compromised. The web exits the press section and the wet end at about 50% solids so that about 99.5% of the water has been removed at this point in the process.

7.1.2 Dry end

The dry end consists of the dryer section, size press, machine calender and winder (see **Fig. 7.2**). The main purpose is to reduce the moisture content of the web to a level where the paper is at equilibrium with ambient humidity conditions, typically 3–7 wt%. Over-drying to lower levels would cause the paper to become brittle and lose the

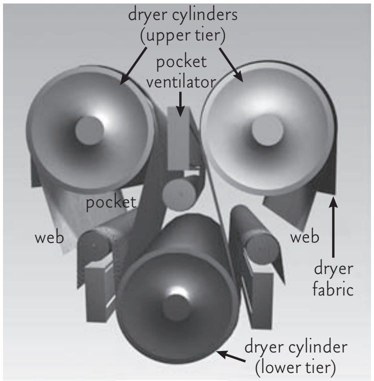

Fig. 7.6 Diagram of a drying section detail showing three cylinders that illustrate the pathway of the paper web.

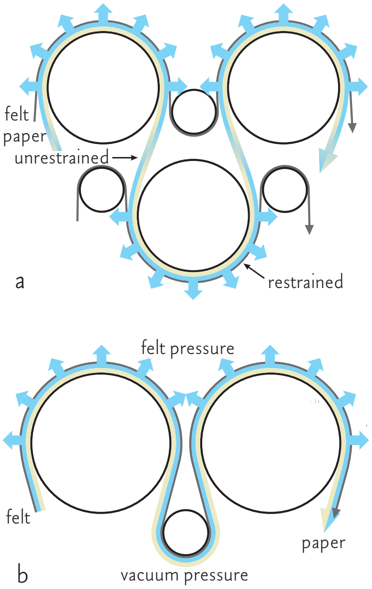

Fig. 7.7 Diagram of two different dryer cylinder configurations: double-tier dryer (top) and single-tier dryer (bottom). The black arrows mark the areas where the paper web is restrained by the dryer fabric that holds it against the heated cylinder surface. The blue arrows indicate the main direction of water removal from the paper contacting the cylinder.
Source: Chance (1994).

flexibility needed for bending and folding. The paper would also become susceptible to severe dimensional deformations such as cockling and curl when water reabsorbs into the paper as it equilibrated to typical humidity conditions. Dry end operations are important for optimizing the mechanical strength and for conditioning the surface properties of paper. The dry end may include sections for surface treatment such as a size press or an on-machine pigmented coating station. The influences these have on the behaviour and properties of paper are beyond the scope of this chapter.

The dryer section of a conventional paper machine used in the manufacture of printing and writing papers consists of a series of large-diameter, steam-filled cylinders. The web enters this section with a solid content approaching 50%. It is conveyed through the dryer section in a serpentine pattern, wrapping around the massive rotating cylinders. In a modern paper machine it is common to have 30–60 dryer cylinders with diameters of 1.5–1.8 m. Transport of the web is facilitated by a permeable dryer fabric, which supports and restrains the web and provides a backing force to hold the paper tightly against the cylinder surfaces. This permits heat energy to be efficiently conducted to the web. Water vapour escapes the web to pass through or condense in the dryer fabric. Water may also evaporate as the web is drawn between rolls in what is called the dryer pocket (**Fig. 7.6**). The figure illustrates how the web is brought into contact with the heated surfaces of the dryer cylinders, alternating exposure from one side to the other. This approach ensures a balanced rate of removal of water from both sides of the paper. This helps prevent a sidedness that could result in a humidity-sensitive curl in the finished paper. As the web passes between the upper and lower tiers of the conventional dryer, it travels in an unsupported open draw where both sides of the paper are fully exposed (**Fig. 7.7**). This permits increased evaporation of water from both sides of the paper. It also introduces a region where machine tension and web shrinkage can have significant effects on the web structure. The development of the single-tier configuration in more recent dryer sections eliminates open draws by fully supporting the web with the dryer fabric and restrain it using vacuum transfer rolls (see **Fig. 7.6**). The benefit this provides, and the importance of web tension and restraint, will be addressed in a later section.

Various methods are used to accelerate the drying process through increased air exchange at the surface of the web, such as pocket ventilation rolls, blow boxes and vacuum rolls. Control of the rate of heating is essential for machine runnability to prevent excessive adhesion of the wet web to cylinders in the early stages of drying that would cause web breaks. It is also important to optimize the drying sequence so that drying at later stages can be maximized when remaining water is more tightly bound to the fibres.

When the wet web enters the dryer section, the fibrous structure is already partially consolidated due to capillary contraction in the forming section and the mechanical compression applied in the press section. The web still contains 45–55% moisture as free water in the voids between the fibres, as imbibed water within the interfibre bonds and fibre cell walls, and as bound water (or adsorbed water) closely associated with the hydroxyl-rich fibre surfaces and fine capillaries (see page 000). The strength of the web is dominated by Campbell forces (Lyne and Gallay 1954, Rance 1954), interfibre entanglement and interfibre friction, which may involve some hydrogen bonding (Baum 1991). While the fibre lumens are partially collapsed, the cell wall thickness remains unchanged from its initial swollen state (Nanko and Ohsawa 1989). As the drying process continues, the fibrous network undergoes significant transformation in structure and properties as bonds strengthen and fibres shrink. The combination of moisture and elevated temperature causes the cellulose to become more pliable under the backing forces of the dryer fabrics. The web is densified, causing even more interfibre bonding to occur.

The rate of drying slows as free and imbibed water are removed by thermal evaporation since more energy is required to liberate the remaining water from fine capillaries and that which is strongly bound to the cellulosic surfaces. The drying process involves three phases that reflect the heating sequence used to efficiently remove water in its various forms while optimizing machine runnability. There is a distinct relationship between the web temperature, moisture content and the drying rate (**Fig. 7.8**). In the initial heat-up period, the sequence of dryer temperatures is kept low to prevent the wet web from sticking excessively to the surface of the drying cylinders. Temperature is incrementally increased in the drying cylinders to raise the web temperature from 40 ± 5°C as it enters, to 70 ± 5°C at about one-third of the way through the dryer section. This marks the beginning of the second phase, called the constant rate period. The web temperature remains constant as free water is evaporated. The web reaches a critical moisture content of about 20 wt% when the free water is fully depleted. The resistance to heat transfer increases as the contact surface between web and cylinder decreases. While the pore structure of the fibres collapses at this moisture content, air and water vapour replace liquid water between fibres and in the cell walls so that heat is transferred by vapour transport rather than by conduction. The rate of transfer depends on how open and tortuous

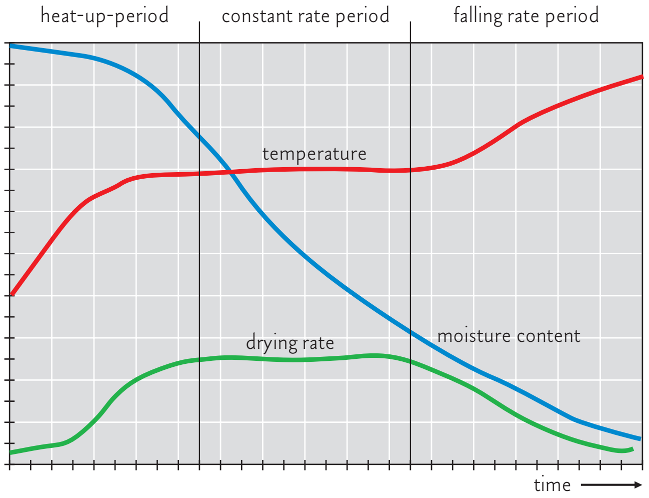

Fig. 7.8 Relationship between the web temperature, moisture content and the drying rate of paper.
Source: Kiiskinen et al. (2002).

the remaining pore network is within the paper structure. This brings on the falling rate period of drying. The temperature of the web increases as the imbibed and adsorbed water is evaporated from the web. Rapid shrinkage of the fibres occurs as the point of critical moisture content is exceeded during drying. Fibre shrinkage causes dimensional changes in the web structure and the introduction of internal stresses that remain in the paper even after it is cooled to room temperature. The response of the wet web to the drying process is significantly dependent on the nature of fibrous structure and the individual fibres.

As the web is conveyed through the drying process it is subjected to a variety of internal and externally imposed forces that strain and restrain the fibrous network as it dries. Tension is applied to the web in the machine direction to pull it away from the dryer cylinders, prevent fluttering and to reduce the occurrence of web breaks. This tension strains or elongates the web in the MD, permanently deforming the network structure and, of course, the fibres contained within. Elaboration on the effect this has on the network and its properties will be provided in a later section. The dryer fabric and adhesion to the dryer cylinders restrains the web, thereby inhibiting shrinkage. However, this is usually not uniform across the width of the paper machine. Thus, it is possible to have paper that has anisotropy of mechanical behaviour that is due solely to the stretching and restraining differences in the dryer section, and not fibre orientation as was pointed out earlier. The shrinkage potential of fibres on drying and the resistance to that shrinkage imposed by other fibres in the network, by drying restraint and by machine tension, can cause stress to be frozen into the structure when the web is cooled and dried to ambient conditions. These residual stresses that remain in the finished product are readily released with the reintroduction of water or water vapour (humidity). Release of internal stress, the breaking of intra- and interfibre bonds, and the swelling of fibres may result in out-of-plane deformation such as cockle or curl, surface roughening, or dimensional changes. Before proceeding to a detailed discussion of how the web structure responded to drying and subsequent rewetting, it is useful to first examine the response of individual fibres to drying.

7.2 Drying of individual lignocellulosic fibres

In their natural state, wood fibres are fully hydrated with water saturating the cell wall. By their chemistry and structure, wood fibres are hygroscopic in that they are easily wet by and absorb water. The porous structure of the fibre is made more porous when lignin and hemicelluloses are removed from the cell wall during the chemical pulping processes. Water remains absorbed between fibres, in the fibre lumen (centre), within the pores of the cell wall and on the fibre surface. As described in earlier chapters, the conditioning of fibres during the pulping and beating or refining processes leaves the fibres in a swollen state with the cell wall delaminated and fibrillated. The extent of swelling depends on the fibre species and origin, and on fibre conditioning.

Beating and refining result in an increase of the cell wall surface area, water absorption and swelling. The shrinkage that fibres exhibit when they are dried directly result from changes in the internal structure of the cell wall. Stone and Scallan (1966) studied the effects of drying on the porous structure of the fibres using nitrogen adsorption surface area measurements. They found that the lamellae in the water-swollen secondary wall S2 layer (see page 000) are drawn together in progressively thicker aggregations that result in a decrease in the total pore volume (**Fig. 7.9**). The pore volume that remains once the

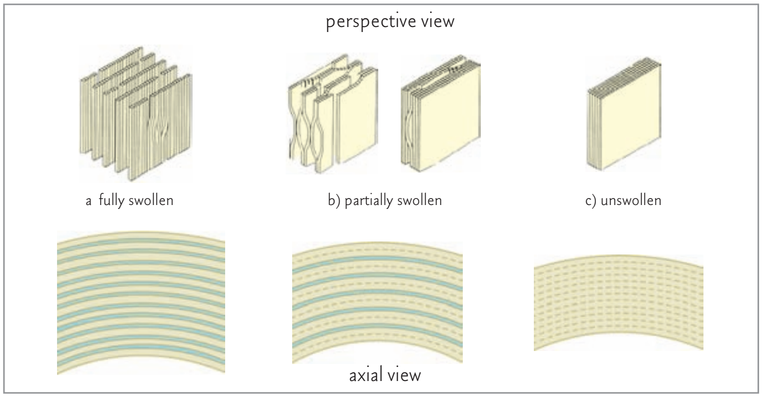

Fig. 7.9 Lamellae (consisting of macrofibrils) drawing together in thicker aggregations as a fibre dries. In the upper row, a perspective view shows lamellae from wet (a) to dry (c). The bottom row shows lamellae in the same process in cross-section (axial view).
Source: Stone et al. (1966).

fibre is dried is negligible compared to the original swollen state. The microfibrils that comprise the S2 layer are principally oriented along the fibre axis, mostly less than 30° off axis, referred to as the microfibril angle. This explains the response of the fibre as water is removed from the cell wall, where shrinkage across the width, called transverse or lateral shrinkage, is much greater than shrinkage along the length, referred to as axial or longitudinal shrinkage. This model also addresses the dependence on fibre conditioning in which increased delamination of the cell wall causes greater initial cell wall thickness and thus greater shrinkage as the S2 layer collapses with the removal of water.

Stone and Scallan (1966) also found that as much as 80% of the water contained in the cell wall is molecularly associated with the cellulose. This occurs in spaces within the microfibrils that compose the lamellae, the so-called microreticular pores. Molecular mechanisms to explain the changes in mechanical and viscoelastic properties encountered as single fibres are dried under tension have been suggested by a number of investigators. Hudson (1963) proposed that the changes occurred as a result of conformational changes of the cellulose in the cell wall for more favourable molecular alignment and the elimination of microcompressions. Microcompressions appear as creping or wrinkling of the fibres when they undergo unrestrained shrinkage along the principal axis, or when fibres are subjected to external compression, for example at fibre crossings in a network structure (**Fig. 7.10**). The shrinkage potential of a fibre is defined as the amount it would shrink if dried unrestrained with no applied external forces.

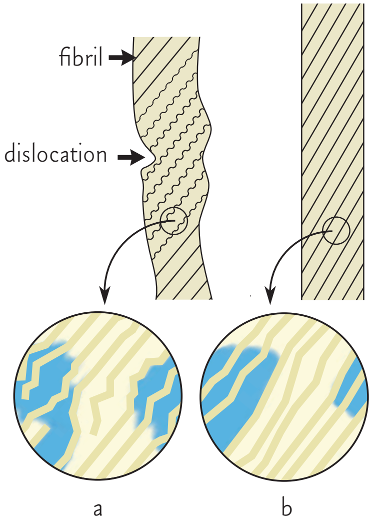

Fig. 7.10 Structural configuration of a fibre interior free air-dried (left) and dried under tension (right). Drying under tension results in fibre stiffening due to the increased alignment of fibrils within the fibre cell wall.
Source: Retulainen et al. (1998).

Jentzen (1964) and others (Spiegelberg 1966, Hill 1967) observed that fibres dried under external axial load showed increased tensile strength and elastic modulus and reduced strain-to-failure or elongation. The tensile strength is the maximum load per unit area where the fibre breaks. The elastic modulus is the resistance to elastic stretching. Kallmes and Perez (1966) found that the increase in tensile strength and decrease in strain-to-failure were proportional up to twice the values for fibres dried unrestrained. Thus the drying of fibres under tension will have considerable significance for the final strength properties of the network they form. Jentzen attributed the increase in fibre stiffening and tensile strength to the increased orientation of the crystallite regions of the cellulose, and more uniform distribution of stress among the fibrils. The effect was greater for fibres with low-yield chemical pulps, for pulps with a higher content of hemicelluloses or for those that were more heavily beaten or refined. Either of these conditions enables the cell wall elements to rearrange more easily under the tensile load (see **Fig. 7.9**). Kim et al. (1975) divided the effects of drying on single fibres into two mechanisms. For fibres with low microfibril angle (<10°), kinks and other distinct dislocations generated in pulping and refining are removed by drying tension and the fibre strength is restored. For fibres with high fibril angles, strength is also imparted by a reduction of the fibril angle. None of these phenomena can occur without the presence of water. A more comprehensive explanation of prevailing mechanisms forwarded by Salmén et al. (1987) emphasizes the importance of the plasticizing action of water in softening the hemicelluloses surrounding the crystalline and amorphous regions of cellulose. Under the right conditions of temperature and humidity, the hemicelluloses are softened and deform so that external forces are able to align crystallites and orient the disordered zones (**Fig. 7.11**). When the fibres are dried and cooled, the result is the increased stiffness and load-bearing capacity (tensile strength) of the fibres.

When fibres are dried, transverse, axial and thickness shrinkage and collapse of the lumen change the fibre dimensions (**Fig. 7.12**).

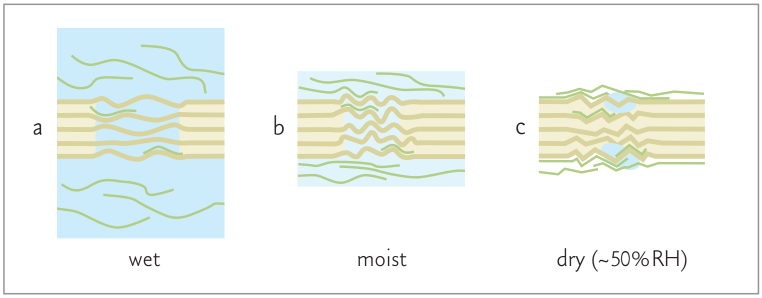

Fig. 7.11 Fibril section showing the configuration of the crystalline and amorphous regions of cellulose (beige lines) and hemicellulose (green lines) during drying. The fibre in wet condition is fully relaxed (a). Axial restraint tensions the fibril during initial drying stages (b). Drying causes hemicellulose surrounding the fibril to be aligned with the direction of fibril restraint (c).
Source: Salmén et al. (1987, Waterhouse 2002).

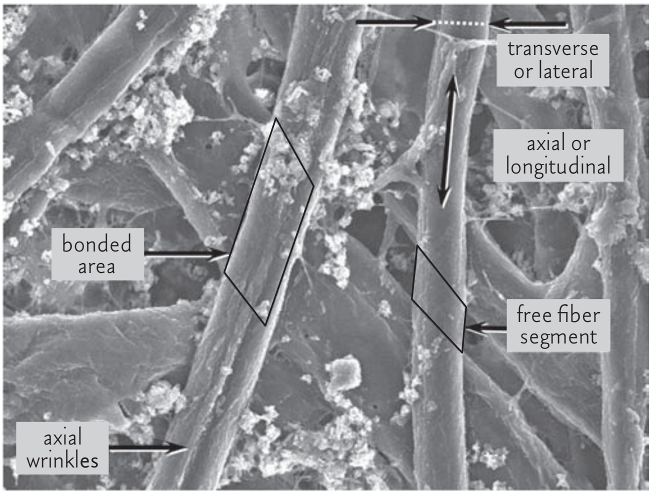

Fig. 7.12 SEM photograph of a paper surface indicating areas where the fibre experiences transvere, axial and longitudinal shrinkage during drying. At ×400, the bottom edges represents 250 μm.

The transverse shrinkage of individual, unrestrained fibres was first measured by Page and Tydeman using soft X-ray micro-radiography[1] (Page and Tydeman 1963, Tydeman et al. 1966). For chemically pulped softwood fibres, they reported the average shrinkage in width to be 18% for unbeaten and 29% for beaten fibres. The average thickness shrinkage was 60% for unbeaten and 75% for beaten fibres. These values are significantly larger than those for the axial (lengthwise) shrinkage of individual unrestrained fibres that is typically of the order of 1–2% (Nanko and Wu 1995).

More recently, Nanko et al. studied the shrinkage of individual kraft chemically pulped fibres and thermomechanically pulped (TMP) fibres in web structures as a function of moisture content using confocal scanning laser microscopy[2] (Nanko and Ohsawa 1989, Nanko et al. 1991). They studied the transverse shrinkage in unrestrained, free fibre segments and also in segments restrained by bonding at fibre crossings (**Fig. 7.13, Videos 7.2** and **7.3**). Nanko and Ohsawa (1989) suggested that the fibre morphology (form and structure) passes through five stages from the saturated state through dryness (**Fig. 7.14**). The stages are as follows:

- For solid contents up to 50–55%, the morphology of the fibres remains relatively unchanged as free water and water at the surface (terms; see previous comment) evaporate.
- As solid content increases from above 50% to above 60%, water evaporates from the lumen and increased capillary forces cause

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[1] Soft X-ray microradiography is a non-standard method that measures the attenuation of low-energy (0-5 keV) X-rays as they pass through the specimen. The mass of the material in the path of the beam causes a reduction of transmitted X-rays to reach the detector, which for Page and Tydeman was X-ray film. The procedure is similar to transmission electron microscopy, although instead of a lower energy electron beam, the higher energy of the X-rays permits thicker or denser samples to be imaged.

[2] Confocal laser scanning microscopy (CLSM) is a method used to map the surface of opaque samples and the subsurface, three-dimensional structure of transparent and semi-transparent materials, such as paper. In the CLSM, a laser light beam is focused through a beam splitter and objective lens on to the specimen, which has been treated with a fluorescent dye. The light from the focal spot passes back through the lens and the beam splitter to a photodetector. A confocal aperture (pinhole) is positioned in front of the photodetector to filter out all of the light emitted from the focal planes above or below the focal plane at a certain depth within the specimen. A two-dimensional (X-Y in-plane) image of a narrow focal range (Z-thickness), called an optical section, is obtained by raster scanning the sample underneath the sensor. The microscope sensor is then moved slightly closer or further away from the sample and a new optical section is acquired. For semi-transparent materials such as paper, optical sections can be obtained from several fibre thicknesses beneath the top surface. A three-dimensional reconstruction of the fibrous structure can be obtained by stacking two-dimensional optical sections.

the fibre to collapse. Compression at the fibre crossings begins to occur.

- For solid contents above 60% to above 70%, water begins to evaporate from the cell wall and axial or longitudinal wrinkles that are aligned along the principal axis of the fibre begin to form.
- At solid contents from above 70% to above 80%, transverse shrinkage of the fibres in unbonded segments begins to occur and fibres continue to flatten. Significant web shrinkage coincides with the onset of transverse fibre shrinkage at the fibre crossing regions.
- For solid contents greater than about 80%, substantial transverse shrinkage of fibre begins to occur at fibre crossing regions. Shrinkage of the fibres in the unbonded regions continues, and axial wrinkles, aligned along the principal axis of the fibre, become more distinctive. This region includes the fibre collapse point (FCP).
- For solid contents greater than about 90%, only a small amount of dimensional change is seen to occur up to the final solid content of the product paper.

Nanko found fibre shrinkage to be minimal up to a specific solid content, called the fibre collapse point (FCP), which for the pulps in his study was close to 86 wt% solids in stage five above. Fibre shrinkage increased dramatically when fibres were dried further. Other investigators observed a similar increase in fibre shrinkage around this solid content for different fibres (Rance 1954, Tydeman et al. 1966).The point at which rapid increase in shrinkage begins was attributed to the depletion of free or imbibed (capillary) water up to the FCP. At that critical point, the water that is strongly associated with the cellulose (Zeronian 1985) either by being adsorbed on the fibre surface, or which fills the fine porous structure within the cell wall, begins to evaporate. This causes collapse of the pores, significant contraction of the cell wall and transverse shrinkage of the fibre. The extent of shrinkage at the FCP has significant influence on shrinkage of the fibrous network observed when the wet web dries to this solid content in the dryer section. This will be discussed in more detail in the next section.

The total water contained within the cell wall, indicative of the porous structure accessible to the water, determines how much the fibres will shrink during drying when the pore structure collapses. It is also related to the ability of the fibres to reabsorb water once they have been dried beyond the FCP. An indirect method of quantifying the amount of water contained within the cell wall, known as the water retention value (WRV), was introduced by Jayme (1944). A wet pad of pulp is centrifuged and the moisture content of the sediment

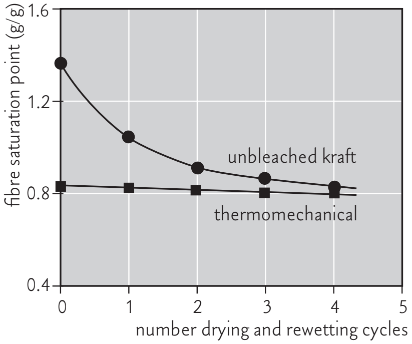

Fig. 7.15 Change of water sorption capacity (fibre saturation point or FSP) of different types of pulps after repeated drying cycles. The unbleached kraft pulp fibre responds to repeated wetting and drying with a significantly reduced FSP due to fibre cell wall collapse. The thermomechanical pulp fibre is prevented from collapsing by the presence of lignin. Source: Laivins and Scallan (1993).

pulp is determined. Since the amount of retained water was found to be proportional to the extent of beating and other properties associated with the swelling of the cell wall, the WRV has been considered an indicator of the imbibed and bound water associated with the cell wall structure. Jayme applied this method to examine the irreversible stiffening of fibres, called hornification, which will be discussed in detail in a later section.

Stone et al. (1968) used the solute exclusion method[3] for measuring the internal pore structure of the water-swollen fibre walls, thereby determining the amount of water contained within the cell wall, termed the fibre saturation point (FSP). For example, a high FSP value indicates that the cell wall is open and porous and contains a substantial amount of water. Multiple drying and rewetting of mechanical and chemical pulps alters the FSP (**Fig. 7.15**). For the thermomechanical pulp fibres, the lignin and hemicelluloses that are present within the cell wall limit swelling and the subsequent collapse of the layered structure during the drying. Therefore, little change in the FSP is observed. The FSP for never-dried pulp increases with decreasing yield as lignin and hemicelluloses are extracted from the cell wall, leaving an open porous structure (**Fig. 7.16**). Upon drying, the pore structure of the cell wall collapses. With rewetting, the pore space within the fibre is never fully restored to its original state. This is evident from the lower FSP values. While it is of little consequence in conservation treatment that beating/refining can reopen the pore structure through mechanical action and restore the FSP of recycled chemical pulps to a state close to that of never-dried virgin fibres, two important conclusions may be drawn. First, shrinkage is much more pronounced for chemical pulp fibres. This should result in more pronounced internal stress in the formed sheets as fibres move and change dimension. Thus, when they are rewet in use or during conservation treatment, the dimensional changes in the fibres and fibrous network will occur as the fibres swell and internal stresses are

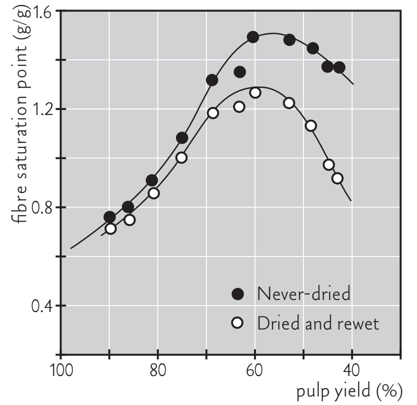

Fig. 7.16 The water sorption capacity (fibre saturation point or FSP) of never-dried pulps of different composition. Pulps of high lignin content or high yield absorb less water than pulps freed of their lignin content. The effect of lignin removal on the FSP is especially prominent after pulps were dried and then are rewetted, as pulps of low lignin underwent permanent loss of pore volume during drying which causes them to absorb less water when rewet (see also **Fig. 5.14**). Source: Laivins and Scallan (1993).

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[3] The solute exclusion technique seeks to determine the size and volume of the pore structure of a water-swollen material such as the fibre cell wall. The method quantifies the amount of penetration of a series of probe molecules of a range of molecular sizes (diameters). The probes are inert with regard to the pore surfaces of the specimen. The fibres are immersed in an aqueous solution of known concentration of the probe. For small-diameter probes that penetrate the water-swollen structure, the volume of water displaced from the pores contributes to the dilution of the solution. The change in probe concentration reflects of the volume of the pores accessible to that size probe for pores of the probe size or larger. Incrementally larger probes are tested so that a plot of the distribution of pore sizes can be generated. The fibre saturation point (FSP) was formally defined by Stone et al. (1968) as the volume attributed to pores with a diameter of 56 nm or less.

released. Mechanical pulps will be more resistant to shrinkage as the lignin-hemicellulose gel within the cell wall limits internal hydrogen bonding. These fibres will also be subject to swelling and the release of stress when rewet, although to a lesser extent as compared to chemical pulps. Secondly, rewetting of chemical fibres in conservation treatments will never fully recover the internal pore structure that they once had when first used to form the paper. Such fibres are said to undergo ‘hornification’ during the drying process, a term that will be discussed in more detail below. The dimensional changes of the fibres can result in significant changes to the fibrous structure, a subject that will now be considered.

7.3 Drying of the fibrous network

The characteristics of a fibrous network as it dries are only partially determined by the nature of the fibres that comprise it. There are a number of other factors that significantly influence the rate of drying and the properties of the dried structure that forms once the drying process is completed. Since the fibres are distributed randomly (stochastically) in the web, all papers have some in-plane variability of mass, viewed as flocs or, in some situations, streaks. The rates of drying may be quite different for floccy and lightweight regions. Stresses build as the regions and fibres contained within shrink at different rates (Corte and Herdman 1975). This results in competing strains and the build-up of internal stresses over a range of dimensions. With no restraining, the web will likely undergo out-of-plane deformation appearing as cockle or curl. The anisotropic drying behaviour of individual fibres can cause directionality in the web shrinkage if the fibres are preferentially oriented in the machine direction during formation, either in the paper machine wet end or by the hands of the vatman. We will see that this directionality (anisotropy) can influence the shrinkage patterns of the fibrous network that result in out-of-plane deformations such as curl or waviness. While formation and orientation are determined by the manner in which the fibres are distributed in-plane when the paper is formed, other factors such as the externally applied stresses of web tension and drying restraint will have a key role in the development of the properties of the network. These will be discussed in the sections that follow. It is first important to understand how individual fibre shrinkage is transferred to the shrinkage of the web structure.

7.4 Network shrinkage from fiber shrinkage

Page and Tydeman (1962) advanced a model describing the mechanisms for shrinkage of the fibrous network based on the shrinkage behaviour of individual fibres and the transferral of fibre contraction through the fibre-fibre bonds. Their key observation was that interfifibre bonds form before significant shrinkage of the fibres occurs. This is the so-called ‘adhesion before shrinkage’ concept. Thus the positions of fibre crossings along the swollen fibre axes are preserved by hydrogen bonding in the contacting areas where they cross (**Fig. 7.17**).

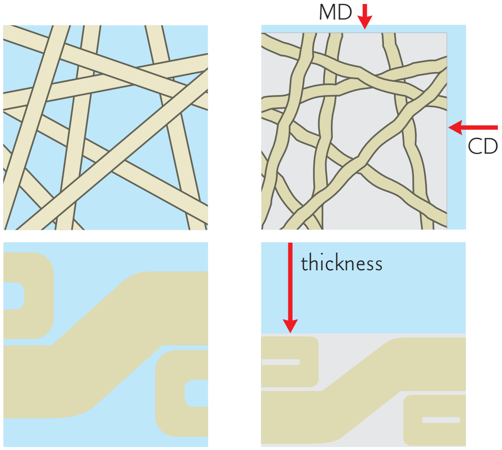

Fig. 7.17 Adhesion before shrinkage concept according to Page and Tydeman. The interfibre hydrogen bonding develops before shrinkage of the fibres occurs during drying of the web. The position of the fibre crossings established in wet web (a) are preserved in the contacting areas during drying while the sheet shrinks to its final dimensions (b).
Source: Page and Tydeman (1962).

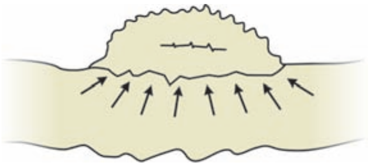

Fig. 7.18 The cross-sectional (transverse) shrinkage of the fibre is much greater than its axial (longitudinal) shrinkage. This causes microcompressions in axial direction on crossing fibres.
Source: Baum (1991).

As described in a previous section, the transverse shrinkage of a fibre is considerably larger than its axial shrinkage. This transverse shrinkage is passed on to the crossed fibre through contraction of the bonded area (**Fig. 7.18**). The compressive forces exerted on the crossed fibre are opposed by the axial stiffness of that fibre so that shear stresses arise in the bond area that result in fibre deformation. Since the compressive forces are acting on only one side of the fibre, bending strain is expected if the fibre is not sufficiently restrained by the fibrous network (Rance 1954). When the crossed fibre has many bonding sites on the top and bottom sides and only a small amount of free fibre length, then the restraint imposed by the network will cause axial compression in the bonded area. Microcompressions or fine scale buckling of the cell wall may occur in the crossed fibre. This causes a measurable shrinkage along the fibre axis (axial shrinkage). The shear stresses may also delaminate the cell wall structure and pucker the lamellae in addition to axial compression (see **Fig. 7.18**). Considering all of the crossings that occur along a fibre located in a fibrous structure, the potential for axial shrinkage is the summed shrinkage at all of the crossings. Most printing papers have sufficient grammages (basis weights) and density so that most fibres are bonded on the top/and or bottom sides over nearly all of their length (see **Fig. 7.12**). Therefore, axial shrinkage of a fully bonded fibre can theoretically approach the transverse shrinkage of about 20%. The presence of neighbouring fibres in the network adds to the complexity of simple shrinkage analysis since each fibre may experience similar contractions that oppose or redirect the strains. If no external restraining forces are applied to the network, a nominal shrinkage of about 12% could be expected in drying. As the compression of the fibre occurs at bond sites, the site first pivots to align parallel to the principal plane of the web. The contraction then exerts a stress on the adjacent free fibre segments. This strains (stretches) segments, thereby removing dislocations, kinks and wrinkles. As discussed in the previous section, fibres that are dried under restraint or axial load exhibit increased tensile stiffness and strength. This, combined with the increased stiffness of the densified bonded sites, confers the strength and stiffness to the entire network structure of paper. Additional restraint of the network imposed by external forces will further add to network strength and stiffness. This subject will be addressed in section 7.8.

7.5 Structural factors that control shrinkage

In work by Nanko et al. (1991), the shrinkage behaviour in bonded and unbonded regions was directly measured using confocal laser scanning microscopy. As with single fibres discussed in the previous section, the transverse shrinkage increased significantly as the fibre collapse point (FCP) of about 85wt% solid content was approached. The unbonded regions were observed to shrink first as they are not subject to the transverse restraining forces of a contacting fibre. When the bonded regions were observed to shrink, they did so to a lesser extent due to the axial compression resistance of the crossed fibre. The theory of Page and Tydeman (1962) identifies the major structural factors that control shrinkage in the fibrous network as:

- The intrinsic potential shrinkage of the fibres
- The resistance of the fibres to axial compression during shrinkages
- The strength (of the network) during shrinkage and the extent of fibre-fibre bonding
- Fibrillation, the presence of which has shrinkage forces associated with it.

The shrinkage potential of fibres (factor 1) depends on the fibre composition determined by species and origin and the extent of pulp conditioning, i.e. chemical pulping and beating or refining that affects swelling of individual fibres. The shrinkage potential of a wet web increases with decreasing pulp yield as the removal of lignin opens the porous structure of the cell wall for increased swelling. Pulps with higher content of hemicelluloses, such as those composed of flax fibres, also have a greater shrinkage potential since hemicelluloses are associated with the amorphous (non-crystalline) regions of the microfibrils. The hydrophilic nature of most hemicelluloses causes the rapid sorption of water. Beating and/or refining delaminate and fibrillate the cell wall, which also promotes swelling and increases the shrinkage potential of fibres. This increased water in the cell wall is commonly quantified indirectly by measuring the water retention value (WRV).

The third factor addresses bond strength, which is influenced by the fibre surface chemistry. The cellulosic surfaces of low-yield chemical pulps will hydrogen bond more readily than the high-yield mechanical pulps that have lignin and extractives contaminating the exposed surfaces. The strength of the bond will be enhanced by strength promoters such as starch or carboxymethyl cellulose. Additives such as mineral fillers or rosin size particles tend to interfere with hydrogen bonding and reduce bond strength. Byrd (1974) demonstrated that web contraction decreased when debonding agent was added to chemically pulped handsheets. The strain-to-failure of the dried sheets also decreased as bonds were weakened. Byrd found the opposite trends occurred when bonds were fortified with highly beaten pulp gel.

It is also important to appreciate that the transfer of the transverse shrinkage from one fibre into the axial shrinkage of another is directly dependent on the bonded area as quantified in paper science as the relative bonded area (RBA). Relative bonded area is a dimensionless expression of the average degree of bonding of the network, defined as the ratio of the bonded surface of fibres and their total external surface area. For papers that have low interfibre bonding area or where the bonding in the region is modified with additives that promote or interfere with hydrogen bonding, the transfer of shrinkage from one fibre to another will be affected. This directly affects the shrinkage of the network as well. The bonded area may be influenced by fibre stiffness and dimension as well as beating and wet pressing. Thus it is not merely the shrinkage potential of the fibres that is important, but also the ability of the bonding of the network to transfer individual fibre shrinkage to other fibres within the network.

The degree of beating/refining and wet pressing both increase the shrinkage potential of the web because they both increase the interfibre bonding area. Beating and refining cause an increased flexibility of the fibres so that they conform to the contours of other fibres within the network, increasing the RBA. The swelling of fibres also reduces the compressive modulus (stiffness) so that the crossed fibres will deform more easily under axial compression. Pressing provides increased densification of the network so that more fibres are brought into contact and the areas of contact are increased. Considering the importance of the shrinkage associated with fibre crossings, more fibre bonding will contribute to the shrinkage potential of a pulp.

7.5.1 Fibre orientation

In machine-made papers, fibres preferentially align along the machine direction (MD) as a result of the forming process in the wet end. For publication grades such as newsprint, the fibres may have 1.5–2.5 times the probability of ordering in the MD as compared to the CD. This creates anisotropy of shrinkage and mechanical strength properties of the paper. Gates and Kenworthy (1963) studied this aspect of drying shrinkage for chemical pulps. They found that shrinkage in the cross machine direction was generally greater than that in the machine direction (**Fig. 7.19**). The strain-to-failure, or the amount the paper stretched to the point of breaking, was also greater in the CD, although tensile strength was observed to be greater in the MD (**Fig. 7.20**). This behaviour is explained using the so-called 'adhesion before shrinkage' model of Page and Tydeman (1962) discussed above. One can easily conceptualize that the fibres aligned in the cross machine direction will have a statistically greater number of fibre crossings along their length than those aligned in the MD. When fibre shrinkage occurs, fibres aligned in the CD will experience more sites where axial compression can occur. This causes more overall shrinkage of the network in the cross machine direction unless external forces, such as drying restraint (**Fig. 7.19**), interfere. In the dried network, the fibres in the CD will have more regions of creping and microcompressions as compared to the MD fibres. When the paper is strained in the CD the compressed bonded regions will stretch so

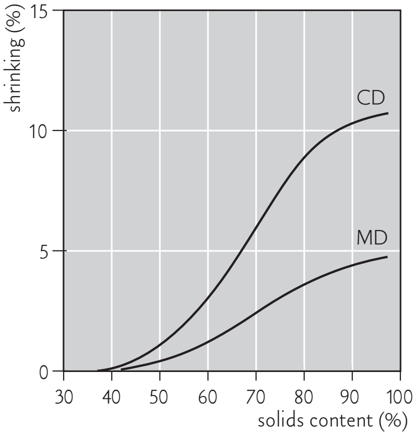

Fig. 7.19 Relationship between solids content of pulp and web shrinkage in machine (MD) and cross machine (CD) directions. The shrinkage in the cross direction is generally greater in CD than MD for machine-made paper.
Source: Hansson et al. (1989).

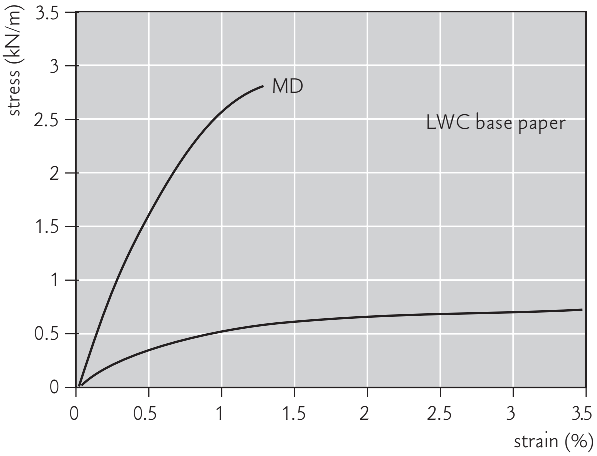

Fig. 7.20 Relationship between strain-to-failure – that is, the force required to break the tensioned paper – and the shrinkage experienced by the paper during its drying on the paper machine. In the MD, the paper has a higher tensile strength because more fibres are more oriented in that direction.
Source: Kajanto and Niskanen (1998).

that a greater strain-to-failure of the paper will occur. Gates and Kenworthy (1963) found the strain-to-failure (extension at break) is linearly related to the percent shrinkage (**Fig. 7.21**). Essentially the shrinkage (negative strain) that occurs during drying is recovered under tensile loading. Lower tensile strength is observed in the CD since paper derives a significant amount of strength from the tensile strength of individual fibres and fewer fibres are oriented in the CD to bear the load (**Fig. 7.20**). The MD tension of the paper machine also imposes directionality on the network, which will influence the mechanical properties. This will be discussed in more detail below.

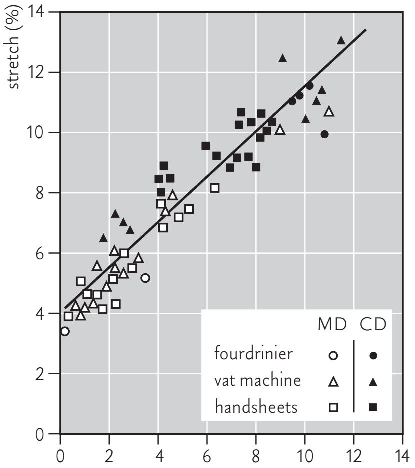

Fig. 7.21 Relationship between stretch and shrinkage of machine-made paper comparing the MD and CD directions. The more the paper web is allowed to shrink during drying, the more it will be extended before it ruptures when tensioned. The extension at break is linearly related to percent shrinkage.
Source: Gates and Kenworthy (1963).

7.5.2 Development of residual stresses

As fibres shrink during the drying process, their straining (movement) exerts stresses (forces/area) on the network through all of the fibres that they cross and form bonds with. The fibres become increasingly rigid as their cell walls collapse, hydrogen bonds form and the water that once imparted flexibility is evaporated. Hemicelluloses or dry strengthening agents such as starch will solidify and reinforce contact points between fibres, microfibrils or fillers that may be present. A significant distribution of internal stress will still remain. Additional stresses may be induced if the web is mechanically restrained from shrinkage or if it is stretched in the MD by the tension of the paper machine. The finished paper will therefore contain ‘frozen-in’ stresses (Ivarsson and Steenberg 1947) that are a function of the characteristics of the fibres contained in the network, the drying conditions and any external forces that may have been imposed on the network during drying. In his review of the subject, Waterhouse (2002) described a body with residual stresses to be ‘… in a state of stress even though it has no external forces or constraints acting on its boundary’. Based on this widely accepted perspective, residual stress is distributed at various structural levels encompassing stress at the molecular level, within microfibrils and fibres, at fibre-fibre bond sites, and between flocs in the fibrous network.

When a wet web is dried with no external forces, referred to as unrestrained drying (also free drying), many of the residual stresses are relieved by the deformation of the network either by dimensional shrinkage or as out-of-plane deformation (cockling or curling). The total shrinkage that occurs in this situation is referred to as the potential shrinkage (or free shrinkage). This is dependent on the shrinkage potential of the fibres and the other factors that influence shrinkage and drying stress discussed in the previous section. Paper made on a paper machine or by hand typically have imposed external forces that oppose the shrinkage, or may even elongate the web during drying. The shrinkage that actually occurs during the drying process is referred to as the drying shrinkage (also allowed shrinkage). Smith (1950) first defined the difference between potential shrinkage and allowed shrinkage as the dried-in strain. This is a useful parameter for predicting the tensile strain-to-failure. Smith also found that the hygroexpansion of paper is inversely proportional to the dried-in strain. In general increasing dried-in strain, as in the case of a fully restrained sheet, will increase dimensional stability and reduce the strain-to-failure.

If the wet web is restrained during drying by holding the edges stationary to maintain the in-plane dimensions, the net stress within the network will increase as moisture content decreases. This stress, which acts in opposition to the shrinkage of the web, can be measured at the sample edges. The final stress measured when drying is complete is defined as the drying stress. An example of the development of drying stress is shown in **Fig. 7.22** for bleached softwood kraft pulp (Htun and de Ruvo 1977). The drying stress is first detected at a solid content of about 40%. Drying stress increases slowly until about 85% solid, which coincides with the fibre collapse point (FCP). The drying stress then increases rapidly as more shrinkage of the fibers within the network occurs. In that same study, Htun and co-workers also found that tensile strength, elastic modulus (tensile stiffness) and compressive strength were all linearly related to the drying stress of paper for situations where the paper was fully restrained from shrinkage during drying.

From numerous investigations it can be inferred that the four structural factors that control shrinkage, as identified by Page and Tydeman (1962) and discussed above, will directly affect drying stresses. Ivarsson (1954) and others (Brecht and Pothmann 1955, Brecht et al. 1956, Byrd 1974) studied the drying stresses of papers and found them to be dependent on the level of beating and also the shrinkage observed during unrestrained drying. Hansson et al. (1989) showed a direct relationship between the swelling of fibres, as measured by the water retention value, and the drying stress (**Fig. 7.23**). Ivarsson (1954) showed that drying stress was almost proportional to the grammage (basis weight) of a paper. Byrd (1974) demonstrated that the drying stresses were directly affected by the strengthening or

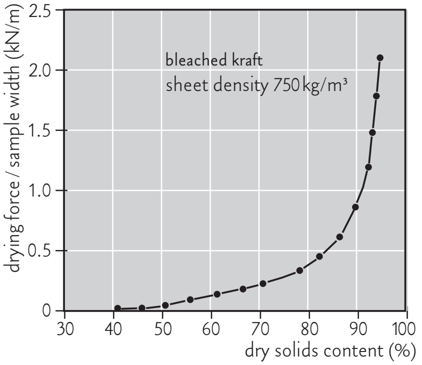

Fig. 7.22 Relationship between drying force versus solid content during the drying of the paper web restrained along its edges. The drying force, which is a measure for the stress exerted upon the restrained paper sheet during drying, increases as the solids content of the web increases.
Source: Htun and de Ruvo (1977).

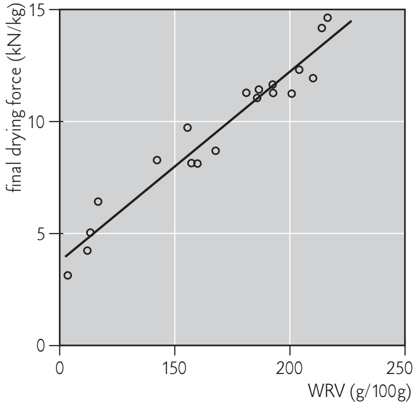

Fig. 7.23 Relationship between the drying force versus the degree of swelling of fibres as measured by their ability to hold water (water retention value or WRV). The WRV is dependent on the degree of beating. The drying force is a measure for the stress exerted upon the restrained fibre during drying.
Source: Hansson et al. (1989).

weakening of the interfibre bonds using chemical additives. Since drying stress appears to be directly related to the network shrinkage, one might assume for webs with significant fibre orientation that increased shrinkage in the CD would cause greater drying stress in the CD than in the MD. On the contrary, the opposite is observed. This results from the greater number of fibres oriented in the MD, and the axial stiffness of a fibre is greater than the transverse stiffness (Hansson et al. 1989).

Another approach used to characterize the in-plane internal stresses was introduced by Kubát and co-workers (Johanson and Kubát 1964, Johanson et al. 1967), and reviewed by Htun (1986a). The Kubát internal stress level is determined by generating a series plots from stress relaxation experiments where the change in stress is measured as the sample is held at constant strain. The measured stress level increases with beating, pressing, and by drying under restraint or tension. The Kubát internal stress is zero for sheets dried unrestrained. Htun and de Ruvo (1977) further asserted that the Kubát internal stress is essentially equal to the drying stress for paper samples, regardless of conditions of refining, wet pressing and sheet structure. This equivalency is useful for simplifying the relationships between drying and the mechanical properties of the paper.

7.6 Drying of the web in papermaking

The previous sections have shown that when a web is unrestrained during drying, and allowed to shrink, a relatively extensible paper is formed with strength that is less than optimal. Historical handmade papers were often subjected to restraint of some form in order to improve the paper properties, especially planarity, stiffness, strength and dimensional stability. In contemporary machine papermaking, the design of web transport and drying strategies are also used to control and optimize these properties. The paper machine also introduces artefacts such as fibre orientation, web tension and fabric patterning that are integral parts of the process and are difficult to eliminate entirely. In this section, those aspects of the process that apply external forces to change the web structure during drying will be discussed. A drying load is an external force that acts in opposition to the drying stress. It may originate from the adhesion forces between the wet web and the drying surface that restrain the web from shrinkage. Drying load may also be imposed by tension forces of the dryer fabric that compress the web against the dryer cylinder that adds to the in-plane restraint of the fibrous network. The tension of the web as it is drawn through the paper machine will introduces a machine directional (MD) load that may restrain dry or even stretch (strain) the web in the MD.

7.6.1 Wet straining and draws

Tension applied to the web is important for maintaining runnability during the papermaking process. It is especially important as the unsupported web passes in the spaces between machine components, known as open draws. The force applied to the web in the machine direction will stretch or draw the web. This will actually cause subtle acceleration of the web as it travels from the couch roll to the reel. Machine direction tension is closely controlled by varying the rotational speeds of the machine rolls and dryer cylinders. In general, faster machines require greater tensions to maintain stability of the unsupported web. Wet straining of the web may occur as it leaves the forming section at the couch roll to enter the press section (as on older machines) or more commonly between the press section and the dryer section. Stretching at the latter can be as much as 2.5–3.0% (Kiiskinen et al. 2002). The solid content of the web is typically less than 50% when it leaves the press section. In this hydrated state, the fibre structure is deformable and local separation or slippage of the internal structure can occur. Straining of the fibrous network tends to move, straighten and align fibres with the risk of separating contacting fibres that are in contact. In fact, the thickness of the web increases, causing the density to decrease. Schultz (1961) and Parsons (1972) observed that wet straining of more than 3% causes the light scattering coefficient of dried paper to increase, which is an indication that the relative bonded area (RBA) has decreased. Since only a small amount of hydrogen bonding has occurred at that low solid content, the straightening and separation of fibres in wet straining reduced the potential for bonding that was developed in the press section. The loss of internal bond strength of the dried paper was observed when the wet stretch exceeded 1% in the open draw in pilot trials conducted by Juppi and Kaihovirta (2003). However, the tensile strength, tensile stiffness and compressive strength in the machine direction will also increase, by as much as 20% with wet straining of a web at 50% solids (Htun 1986b, Hansson et al. 1989). Silvy (1971) found that MD web strength increased when the web was wet strained up to about 2%, above which no strength gain is realized. Schultz (1961) found a similar relationship where a maximum for tensile strength was observed at 4% wet straining. This added strength is an obvious benefit for the papermaker since strength of the web in MD is sought for runnability in web-fed printing processes. This is especially beneficial for publication paper grades made at lower basis weights and from mechanical fibres that form weaker networks, such as newsprint, lightweight coated and supercalendered paper grades. Wet straining reduces the extensibility or strain-to-failure of the papers. The CD strength properties will also be reduced.

7.6.2 MD drying restraint

In a conventional dryer section, the web is drawn in the machine direction as it passes from the upper to the lower tiers of dryer cylinders. The web is pressed to the surface of the cylinder by the dryer fabric as it passes around the cylinders (see **Fig. 8.6a**). However, there is an open draw between the tiers where the web is unsupported. Sufficient machine tension must be applied to pull the web away from the cylinder surface, where in the early stages of drying the web may experience some adhesion. Also, at high machine speeds the velocity of the web and the air currents surrounding the fast-moving web may cause it to flutter. Fluttering can be the source of web breaks unless adequate tension is applied to the web in the MD. For faster machine speeds, additional tension must be applied, which adds to web stretching in the open draws. To maintain tension, the rotational speed of cylinders is increased. This is done in groups, with 6–10 groups in the dryer section, with each successive group operating at slightly increased rotational rate. The stretching, or draw, experienced between each group is typically 0.2–0.3% (Kiiskinen et al. 2002). This small amount of MD straining results from the applied drying load (web tension) that slightly exceeds the drying stress that is characteristic of the fibrous structure of the web. This straining is effectively uniform across the paper machine, as demonstrated by Rutland (1992). The MD shrinkage is a function of the position across the paper machine, labelled as 'MD Allowed' (**Fig. 7.24**). Using the rewet web as an approximation of the dimensions of the web in the pre-dried state, the shrinkage that occurred during the drying process is estimated. The near zero values for 'MD Allowed' indicate that when this sample is rewet, for instance during conservation processes, very little hygroexpansion (expansion of the dried web on exposure to humidity or water) will occur. Restraining the MD shrinkage to near zero or even stretching the web causes the MD tensile

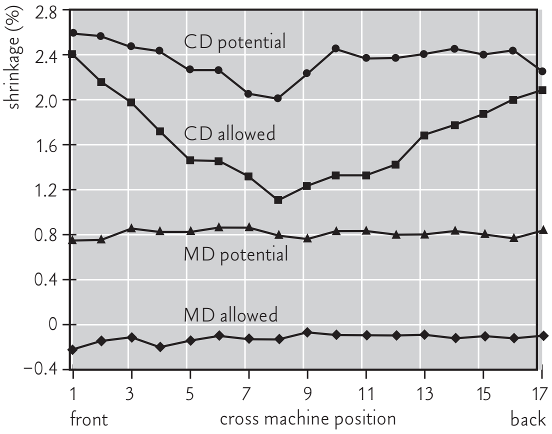

Fig. 7.24 Shrinkage across the width of the paper web on the paper machine. Shrinkage is greater in the cross direction (CD) than in the machine direction (MD). In CD, shrinkage is smaller in the centre of the sheet than along the edges. Source: Rutland (1992).

strength to increase.The 'MD Potential' represents the potential shrinkage that would occur if the wet web was dried unrestrained. The potential shrinkage of the web is a function of many variables discussed in preceding sections. The difference between the plots is the dried-in strain. With the high dried-in strain, the MD extensibility will be low. The results for the cross machine will be discussed in a section below.

It was shown in a preceding section that the preferential alignment of the fibres in the machine direction that occurs in the forming section contributes significantly to the anisotropy of papers. The differences in the MD and CD properties could be related to the anisotropy of individual fibres and the strength and shrinkage of the network they form when fibres are preferentially oriented. The MD uniaxial stress applied to the web by paper machine tension also contributes significantly to the anisotropy of paper, referred to as internal stress orientation. Setterholm and Kuenzi (1970) and Htun and Fellers (1986) observed that tensile strength was influenced more by the orientation of the fibres, while the tensile stiffness (elastic modulus) and strain-to-failure were influenced more by the internal stress orientation induced by directional restraint in drying. Therefore, the science of making paper relies on the control of these two variables, fibre orientation and internal stress orientation, to obtain a sheet with the desired level of directionality. Unfortunately, these two parameters also have a complex role in the dimensional stability of papers and their response to rewetting.

7.6.3 Drying strategies

The drying strategy that determines the rate of drying and when restraint is applied to the web in the drying sequence is critical for developing properties that are important for end use, such as strength, elasticity and extensibility. Compromises may need to be made in order to optimize the properties important to a specific grade of paper. For instance, cross machine strength may be sacrificed to improve strength in the machine direction, or the load-bearing strength may be developed at the expense of elasticity and toughness. While detailing the various strategies used to manufacture paper is beyond the scope of this chapter, it may be of use to the conservator to appreciate that additional control is possible by applying a specific drying strategy. Up to this point, only a comparison between unrestrained and various levels of restraint has been considered. However, drying strategies may include the application or omission of restraint depending on the solid content the web is dried to. Htun and de Ruvo (1983) investigated this aspect of paper drying in the simplest cases, where full restraint was initially applied and then removed at a specific solid content, and where the paper was dried unrestrained to a solid content and then restraint applied. The extensibility, expressed as strain-to-failure, can be controlled by changing the drying strategy (**Fig. 7.25**). In the case of 'restrained then free' (RF) drying, the longer that restraint is maintained through the drying process, the less extensible the paper becomes. In contrast, the sooner restraint is applied in 'free then restrained' (FR) drying, the lower the extensibility. While these observations are consistent with what has already been described for the unrestrained and restrained drying situations, it should be noted that the relationships are not linear with solid content. More complex strategies that combine restrained and free shrinkage with wet straining were investigated by Htun (1986b).

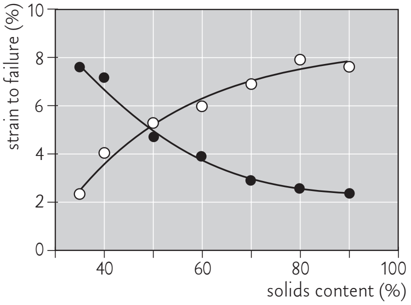

Fig. 7.25 Relationship between different restraint strategies for paper webs during drying and the subsequent response of paper to tensile stress, expressed as strain-to-failure. The two curves can be read as follows: the upper curve, labelled 'free-restrained', illustrates paper webs that were first allowed to dry to specific solids content without restraint, and then were restrained for final drying stages. The sooner restraint is applied during drying, the lower the extensibility of the sheet. The lower curve, labelled 'restrained-free', illustrates paper webs that were first restrained during drying to specific solids content, and were released for the final stages of drying. The longer restraint was maintained during drying, the lower the extensibility of the sheet. Source: Htun and de Ruvo (1983).

The sequence of drying temperatures can also be used to control paper properties. Castellan et al. (1985) studied how changing the rate of temperature increase of the web influences the strength and strain-to-failure properties of chemically pulped papers. They found that the most rapid increase in temperature gave the lowest strength and elasticity, although the strength properties depended very little on the temperature programme. A gradual increase in temperature was found to the extensibility of the paper.

7.6.4 CD shrinkage

While the web is fully restrained in the machine direction as it passes through a conventional cylinder dryer section, the shrinkage in the cross machine direction remains essentially uncontrolled. As the web winds between the upper and lower tiers of the dryer section (see **Fig. 8.6a**), there is no external force preventing shrinkage in the CD in the open draws. Since there is no drying load applied in the cross machine, shrinkage will proceed unopposed from the edges toward the centre of the web. This directional shrinkage becomes less as the drying stress is dissipated in the network structure and the structure itself imparts restraint from further directional shrinkage. Structural restraint never approaches full restraint so, regardless of the distance from the edge, the CD shrinkage is always greater than the MD shrinkage for papers made using conventional cylinder drying sections. A typical cross machine profile showing the actual CD shrinkage realized at each position is shown in **Fig. 7.23** as 'CD Allowed'. This pattern in the CD shaped as a 'smile' is observed for all commercial papers. The CD strain-to-failure shows a similar pattern, as shrinkage is recovered in tensile loading, while the CD tensile strength is essentially uniform across the width of the machine (Chance 1994). The 'CD Potential' plotted in **Fig. 7.24** shows that the unrestrained shrinkage is greater than the MD restrained, although greater shrinkage still occurs at the edges. This is attributed to the effects of fibre orientation causing greater CD shrinkage, as discussed in a previous section.

The greater shrinkage at the edges causes a cascade of artefacts to occur that create a non-uniformity of the paper when taken from various positions across the web. Since the web shrinks more at the edges, the grammage (weight per unit area) of the paper is observed to be higher at the same positions. To compensate for this, the slice may be narrowed at the edges so that less fibrous suspension, hence less fibre, would be distributed to the edges. The result was a uniform profile of the grammage across the machine. However, by narrowing the slice, flow patterns of the suspension changed so that the fibre orientation is no longer oriented exactly along the MD, but rather off axis at an angle. The front and back sides of the machine are at opposite angles and the centre remains aligned in the MD. The hygroexpansivity of the paper reflects these subtle differences in fibre orientation. To overcome this problem, most contemporary paper machines are designed so that the fibrous suspension is diluted at the edges, or wherever grammage is too high, so that the flow patterns are not disrupted while the amount of fibres in a given position are controlled.

Single-tier dryer sections were developed in order to address the shrinkage profile, and to introduce restraint of CD shrinkage (see **Fig. 7.7b**).In such systems the open draws between the upper and lower tiers are eliminated. The web is continuously supported by the dryer fabric as it passes around the vacuum roll. The vacuum roll offers additional restraint while sweeping water vapor from the web. Chance (1994) showed that the shrinkage of the web could be reduced from 3.3% in a conventional dryer to 1.3% shrinkage using the single-tiered configuration. Support of the web enables the paper machine to be operated at faster speeds without increasing the web tension and the internal stress orientation. This results in better control over the web properties.

7.6.5 Development of surface properties

The preceding sections have focused on how drying affects the mechanical behaviour of paper. The surface properties are substantially influenced by the manner in which the web is dried. Lindem (1991) investigated the relationships between surface roughness and gloss and shrinkage allowed during drying. The roughness was found to monotonically increase with allowed shrinkage. The Parker Print Surf roughness used in this test is based on the passage of air under a ring in contact with the paper surface. This is referred to as an air leak method. The gloss was found to decrease linearly as a function of shrinkage. Restrained drying causes the bonds to align and the fibre segments between bonds to stretch and straighten under the tension of web shrinkage. The paper surfaces are also plasticized at high moisture and temperature early in the drying sequence. When the web is brought into contact with the smooth heated surface of the dryer cylinder, the fibres in the structure conform to the planar surface, levelling out peaks and out-of-plane deformation. By drying the web unrestrained, the fibres and fibre flocs freely strain and bend under the drying stresses, causing large-scale out-of-plane deformation, as curling and cockling. It will also occur on a finer scale as twisting and bending of fibres and microfibrils occurs. This will appear as roughening of the surfaces, which changes both appearance and tactilility.

7.7 Historical drying of paper

The mechanisms that cause shrinkage and the development of the mechanical properties of the fibrous network as it dries also apply to the drying of papers made by hand throughout history. It is beyond the intent of this chapter to provide the details of historical drying and the specific effects that may be caused in papers dried by the various methods. However, it may be useful to examine some examples of the more common methods, and how they may enhance the properties. Loft drying was widely used in Europe and North America before the introduction of cylinder drying on the paper machine in 1821. The use of restraint in drying and moulding the paper on to a smooth surface are universal techniques to enhance the paper quality.

7.7.1 Loft drying

Pressing establishes hydrogen bonding before sheet shrinkage occurs during loft drying. In loft drying spurs of four or five sheets are draped over ropes or wooden poles suspended in the drying loft (**Fig. 7.26**). Loft drying allows free shrinkage of the paper, which then is free of dried-in strain. The only potential restraint in traditional loft drying is caused by the rope on which the paper was suspended along its centre, and areas of contact it has with other sheets lying adjacent in the

Fig. 7.26 Loft drying in a Western hand paper mill. Damp sheets are hung in gatherings or spurs on ropes extending across the loft.

spur. In the moistened state the sheets in the spur adhere due to the surface tension forces of the Campbell effect. The additional thickness of the consolidated spur restrains the sheets from out-of-plane buckling that produces cockling or curling. As the solid content of the sheets exceeds 50%, the sheets no longer adhere to each other and free shrinkage similar to that shown in **Fig. 7.22** will occur. The potential restraint of handmade sheets resulting from these factors is negligible compared to the restraining forces exerted on the web by the paper machine. Finishing the loft-dried handmade paper with a glazing hammer, platen press or calender roll is necessary to improve planarity and smoothness.

7.7.2 Contact restraint drying

Drying methods for handmade papers used in Asia (China, Japan, Korea and India) rely on contact with a rigid surface to restrain dry the paper (Hunter 1947). The simplest method is to dry the paper on the mould on which it was formed. The paper adheres to the mould by surface tension forces, or by the penetration of the fibres into the woven or laid pattern. While this may provide added mechanical restraint of the paper, the imprinted pattern and fibre pull-off that occurs on the wire side yields a roughened surface requiring finishing to improve smoothness. The paper may be spread or 'pasted' against smooth boards, masonry wall or metal plates exposed to the sun. This will provide restraint at some point in the drying process where the adhesion between the paper and the surface no longer resists the

drying stress. The smooth surface may act as a cast for the softened fibres on the paper surface so that, when dried, the paper surface becomes smoother as well. In Japanese papermaking, formed papers were brushed on to a wall that was heated by fire on the reverse side (**Fig. 7.27**). Although contact restraint improved planarity and in some cases smoothness on one side, the drying restraint needed to attain the high strength properties of machine-made paper was absent.

Fig. 7.27 Drying single sheets of handmade paper in Japan. Damp sheets are brushed into contact with boards that are exposed to sun to accelerate the drying process.

7.8 Rewetting and humidity response of paper

Paper that is composed of lignocellulosic fibres is extremely hygroscopic, in that it readily absorbs water. However, in the manufacture of printing and writing grades, it is usually the practice to include additives that change the paper's response to water. These additives could slow the penetration of water into the structure, such as sizing agents, or may even reinforce the structure from degradation that occurs when exposed to water, such as strengthening aids. Although the hygroscopic cell walls were once swollen with water when the wet web was first formed, the drying process causes the collapse and contraction of the cell wall so that much of the pore structure is rendered inaccessible or disappears entirely. Therefore, the water sorption characteristics of paper are usually quite different than the pulps from which they were formed.

This section will focus on how the drying conditions affect the response of the paper to the reintroduction of water, as humidity or by wetting. Of specific interest is the hygroexpansivity of the paper, which is the dimensional change that the paper undergoes as a function of absorbed moisture. It is these dimensional changes and the release of residual stress that cause deformation defects such as cockling, curling or surface roughening.

In the discussion of the drying of paper provided in the preceding sections, no mention was made of the chemical additives, such as sizing agents and wet and dry strengthening agents that significantly affect the interactions of paper and water as it is reintroduced. While an adequate treatment of these additives could take up a separate chapter, it is important for the reader to understand the important functions these additives provide. The hydrogen bonds that formed between fibres can be easily broken if water penetrates the bond either at the edges or through the cell wall as the fibre re-imbibes water. Sizing agent is usually added to slow the flow of water into the structure and may thereby protect the bond from softening and failure. Sizing may be applied as an additive to the pulp water suspension, known as an internal sizing, or directly on to the paper as a surface sizing. Internal sizing agents treat the fibre and bond surfaces, making it more difficult for water to wet the surfaces. This slows the rate of water penetration and can protect the fibres and bonds from swelling. Surface sizes fill some of the pore structure on the surface and may also increase the surface's hydrophobicity (lower tendency to be wet by water). Usually neither sizing method renders the paper fully waterproof. Rather, these treatments slow the rate of wetting so that water is absorbed into the paper over the course of minutes or hours. The drying conditions that influenced drying stress and shrinkage will then affect how the paper responds. It is the reversibility of the dried-in strain and the release of residual stresses that are the subject of this section.

Salmén et al. (1985) observed that the conditions of drying restraint did not affect the moisture sorption characteristics of paper. This was determined from the water sorption isotherms, where paper moisture content is plotted as a function of relative humidity at a fixed temperature. The isotherms for the restrained and unrestrained samples are superimposed, even though the hygroexpansion of the two samples differed substantially. This indicates that the access of the structure to the penetration of water vapour was unaffected by straining the samples during drying.

7.8.1 Cockling

Cockling is an out-of-plane defect that usually occurs in random positions in the paper. It occurs when regions of 5-50 mm in diameter undergo hygroexpansion and the network structure cannot accommodate the expansion within the principal plane. The non-uniformity in dried-in stresses, possibly resulting from the structural unevenness of the paper formation, are satisfied by local buckling of the sheet, resulting in out-of-plane deformation. Cockling tends to decrease with increased grammage since the increased bending stiffness of the sheet resists the out-of-plane buckling (Kajanto and Niskanen 1998). **Fig. 7.28** shows the artificially generated cockles created by restraining the surrounding region and permitting the centre region to expand. Conversely, the centre region may be restrained from expansion while the surrounding region expands (Brecht 1958).

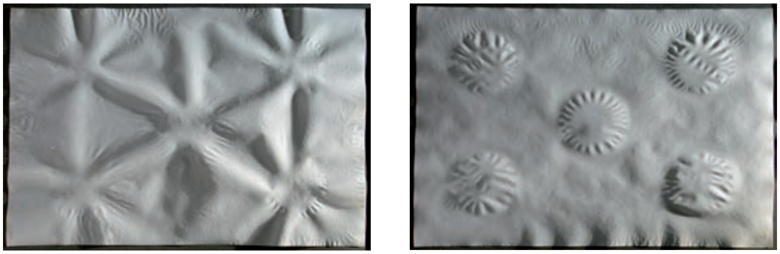

Fig. 7.28 Demonstrations after Brecht (1958) of the influence of non-uniform drying on the planar dimensions of the sheet. Areas of the paper that were allowed to dry first were restrained by the still expanded wet areas that were kept damp. The first-dried areas remained partially expanded. The last-dried areas were able to shrink fully and force the first-dried areas out of plane. In (a), the area within the circles was dried first, in (b) the area around the circles was dried first. Source: Buchschuster (2007).

7.8.2 Dimensional stability

Dimensional stability of paper refers to the resistance of paper to hygroexpansivity, the change in dimension, or strain, associated with a change in water content, or thermoexpansivity, which is the dimensional change that accompanies a change in temperature. In this section we will only consider the hygroexpansivity of paper. Uesaka (2002) provided a comprehensive review of dimensional stability as it pertains to paper. Soon after paper is made it reaches equilibrium with its surrounding relative humidity. The final moisture content of the paper determined in the dryer section was selected so that only a small change in moisture content would be required for that equilibrium to be met. If, at some point in time, the relative humidity surrounding the paper changes, the paper will either gain or lose moisture content. A plot of these two variables is the water sorption isotherm (see page 000). If the paper gains moisture, the fibres and the fibrous structure should swell, resulting in an increase in the linear dimensions of the sheet. The increased moisture may also weaken bonds and relieve residual stress. So in the situation where the sheet was stretched during drying, there is a chance the shrinkage will initially occur as the residual stress is relieved. Thereafter, increased sheet expansion will be proportional to sheet moisture content (**Fig. 7.29**) (Uesaka et al. 1992). The irreversible shrinkage that appears in that plot results directly from the dried-in strain introduced by MD tension during the papermaking process. After the drying strain is recovered, the sheet then swells and contracts directly with moisture content in subsequent cycles. A similar plot for the hygroexpansion in the cross machine shows no initial decrease in strain (**Fig. 7.30**) (Uesaka et al. 1992). Since the web is effectively unrestrained in the CD, there is no dried-in strain to recover. Thus, the expansion and con-

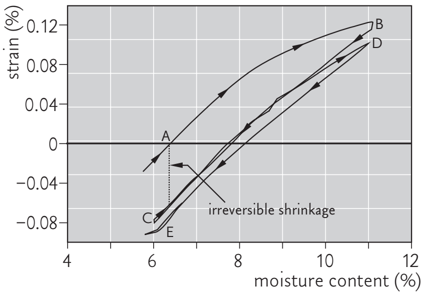

Fig. 7.29 Dimensional stability of paper in MD under changing climatic conditions plotted as the relationship between the percentage strain and the moisture content of the paper. Strain is taken as a measure for change in dimension or hygroexpansivity. The uppermost curve shows the initial expansion of the humidified paper and its subsequent shrinkage during drying, at which point dried-in strain imparted to the paper during manufacture is released. This shrinkage of the paper is irreversible (see also **Fig. 13.12**). The lower curve shows that during a subsequent humidification and drying cycle, sheet swells and contracts directly with its moisture content. Source: Uesaka et al. (1992).

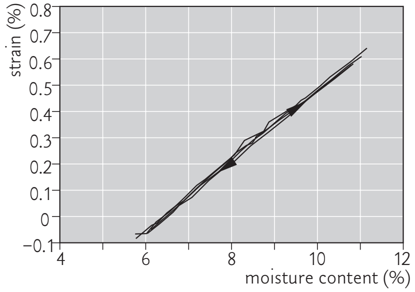

Fig. 7.30 Dimensional stability of paper in CD under changing climatic conditions plotted as the relationship between the percentage strain and the moisture content of the paper. In the cross direction, there is no dried-in strain to recover and therefore the expansion and contraction of the paper relates directly to its moisture content.
Source: Uesaka et al. (1992).

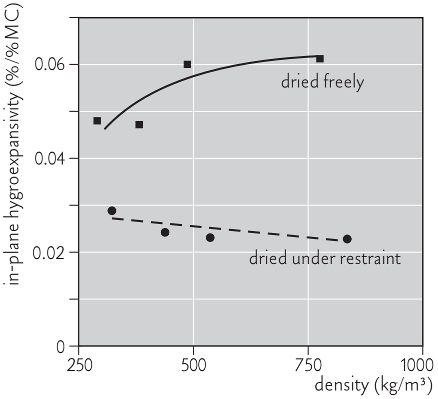

Fig. 7.31 Relationship between the density of isotropic paper (handsheet, no directionality) and its in-plane hygroexpansivity (lateral expansion of the sheet dimensions). The paper dried freely is more labile to hygroexpansion than the paper dried under restraint.
Source: Salmén et al. (1985).

traction appear to be superimposed with no irreversible shrinkage. The hygroexpansion coefficients are the slopes of the lines, defined as the change in dimension divided by the change in humidity. The hygroexpansion coefficient for the MD shown in **Fig. 7.29** is 0.036%/% RH. The CD hygroexpansion coefficient from **Fig 7.30** is 0.140%/% RH. The reasons for the difference are attributed to those structural factors that control shrinkage discussed in the context of network shrinkage (section 7.4). In this case the increased transverse hygroexpansion of the fibres expands the bonded regions that experienced microcompression during drying shrinkage. This results in increased CD expansion. Salmén et al. (1985) found that for oriented sheets with a restrained tensile strength ratio MD/CD of 2.5, the hygroexpansion coefficients were six times greater in the CD than in the MD.

The in-plane hygroexpansivity of isotropic handsheets dried freely is more than twice that of the same handsheets dried under restraint (**Fig. 7.31**). This graph shows the effect of increasing density, an indication of interfibre bonding, on the hygroexpansivity. The unrestrained sheet, freely dried, shows a slight increase in hygroexpansivity with density, suggesting the increased bonding caused more drying shrinkage and more hygroexpansivity in the paper.

The hygroexpansivity of machine-made papers changes as a function of density (**Fig. 7.32**). For the sheet dried without restraint, the differences in MD and CD hygroexpansivity are clearly shown. These are attributed to the free shrinkage that occurs in the CD, which allows a greater expansion to occur as water is reintroduced into the structure. Since the MD was restrained, its hygroexpansivity is much lower. The axial stiffness of the fibres, preferentially oriented in the MD, along with the MD machine tension that restrained initial shrinkage would also contribute to the dimensional stability in the MD. Additives such as fillers, that are dimensionally stable, or debonding agents, that reduce shrinkage by interfering with bond strength, will also improve the dimensional stability of papers. However, in both cases the strength of the paper is reduced, a compromise that may not be acceptable for the papermaker.

The Z-direction (ZD) hygroexpansivity is always much greater than the in-plane (MD or CD) values. This change in the structure has significant influence on several paper properties. First, bending stiffness is highly dependent on thickness, increasing by the cubed power. The decreased interfibre bonding, associated with a thickness increase, will increase the scattering coefficient (opacity). Increase in thickness will also cause the Z-directional strength to decrease so that the paper is more subject to delamination.

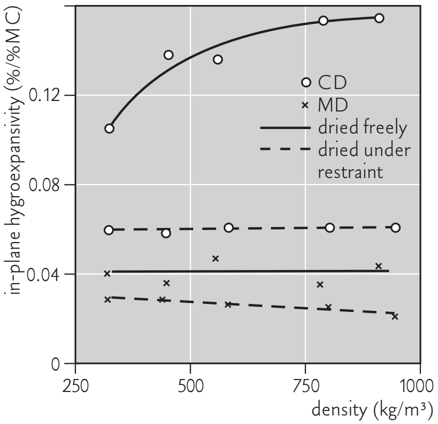

Fig. 7.32 Relationship between the density of anisotropic paper (machine-made paper with directionality) and its in-plane hygroexpansivity (lateral expansion of the sheet dimensions). The graph shows that there is a marked difference in the MD and CD hygroexpansion of the paper that was dried without restraint.
Source: Salmén et al. (1985).

Fig. 7.33 shows the out-of-plane (ZD) hygroexpansivity as a function of sheet density, i.e. bonding, for the same papers shown in Figs 7.29 and 7.30 (Salmén et al. 1985). The values for the ZD dried freely increase with density, showing the effect of the swelling of the fibre cell walls transferred directly to expansion of the web structure. ZD hygroexpansivity is about 10 times greater than the in-plane average hygroexpansivity. For restrain-dried sheets, this factor is 30 times greater for the ZD, showing not only the effects of fibre swelling, but also the release of internal stress that breaks bonds and allows more out-of-plane deformation of the fibres.

Sung et al. (2005) investigated the Z-directional hygroexpansivity of printing papers by mapping the change in thickness as a function of relative humidity from 50% to 80% RH, then from 80% to 90% RH. In the study of newsprint and copy paper, they found that machine-calendered or super-calendered papers exhibited a hysteresis when subjected to an increase then decrease in moisture content (**Fig. 7.34**). This irreversibility of hygroexpansion was attributed to release of the extreme stress imparted by the calendar densification. It is also a recovery of the collapsed lumen and recovery of the fibres to more tubular shape as demonstrated by Forseth and Helle (1997). Newsprint has significant initial expansion (0.58%/% RH). This expansion is not fully reversed and the thickness remains 10% greater than initially. The copy paper has a hygroexpansivity of 0.16%/%RH, and only a small amount of irreversible swelling. One would expect this since this sample had 20% mineral matter, one benefit of which is that it adds dimensional stability to the paper. While in-plane dimensional instability is easily perceived, by the appearance of cockles or change in length dimensions, out-of-plane (Z-directional) expansion that accompanies reintroduction of water can be difficult to

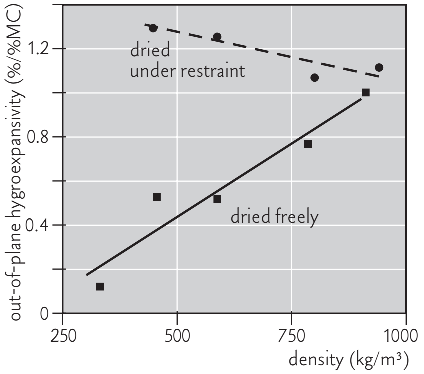

Fig. 7.33 Relationship between the density of oriented machine-made paper and its out-of-plane (Z-directional) hygroexpansivity (thickness expansion of the sheet). The graph shows the direct relationship between hygroexpansivity and bonding for papers dried without restraint.
Source: Salmén et al. (1985).

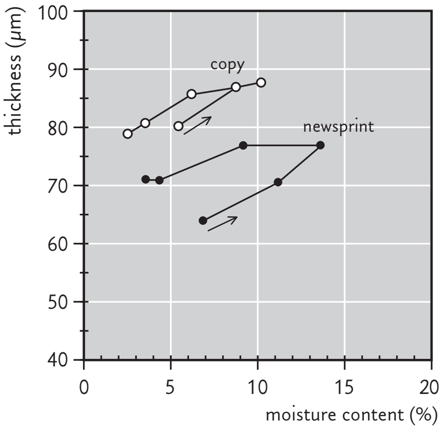

Fig. 7.34 The thickness of copy paper and newsprint as a function of the moisture content as controlled by changing the relative humidity. The irreversible expansion of both papers is evident in the plot. Thickness was measured at 250,000 locations within a 12 mm square region of the paper using opposing laser profilometers. The method is non-contacting and has a precision of 1 μm in three dimensions.
Source: Sung et al. (2005).

detect. However, the profound influence it will have on the paper's properties, such as opacity, bending stiffness and mechanical strength, can be easily measured.

7.8.3 Hornification

Jayme (1944) introduced the term 'irreversible hornification' to describe the loss of rewettability and swellability of low-yield chemical pulps once they have been dried. Minor (1994) and Laivins and Scallan (1993) provided reviews of the subject. This phenomenon originates in the changes in the cell wall and microstructure of the fibre that were discussed in section 7.2. The collapse of the pore structure within the cell wall, the formation of hydrogen bonds between lamellae and increased crystallization of the cellulose molecules cause the fibres to stiffen. The rate of water absorption into the fibre also slowed substantially. This has important consequences for papermakers as they select the raw materials for their process. Pulps used for papermaking are most commonly derived from one of three categories: never-dried pulps, dried pulp lap, or recycled fibres. Never-dried pulps, as the name implies, remain wet from the tree, through the pulping and bleaching process and into stock preparation. The pulp may be obtained directly from a pulp mill in the vicinity of the paper machine. The pulp may also be received as wet pulp lap, which is received as bales of wet pulp sheets. In both cases, the fibres remain swollen and flexible, which provides good bonding and sheet strength. Such pulps will have high shrinkage potential for reasons discussed in section 7.2. Shipping costs may be reduced if the pulps are first dried. The fibres contained in dried pulp lap will be hornified. It is necessary to refine or beat the fibres in order to condition the cell wall to promote swelling, flexibility and improved bonding associated with more hydrated fibres. Recycled fibres will also be hornified and may also require conditioning to promote bonding for sheet strength. The fibre saturation point (water contained within the cell wall) for never-dried pulp is higher than that for pulp which was dried and rewet (see **Fig. 7.16**).

Hornification has implications for the conservators for at least two reasons. First, the furnish used to make a paper, whether it is never dried or from dried fibres that have been rewet, will influence the strength properties of the paper. Consideration of the source fibres may allow a better understanding of how a paper will respond to conservation treatments that require exposure to water. It may also elucidate the strength and stiffness properties observed for a given specimen. Secondly, in rehydration of paper during conservation treatments, the fibres never fully absorb water to their original state. Thus the releases of internal stress, the swelling of fibres and the breaking of all hydrogen bonds may take extensive amounts of time to fully achieve. Therefore, the length of time that a paper is exposed to water will influence the extent to which the rehydration proceeds. Other variables will influence this, including the fibre types, the pulping process and the extent of refining or beating. Sizing agents, surface treatments and web density will also play a significant role in the rate of rehydration. Thus, hornification describes fibres that, once dried below the fibre collapse point, never fully recover the properties they had in never-dried pulps.

Summary

This chapter has focused on the hidden forces that are frozen into the paper when it is manufactured. These forces, referred to as internal stresses, are responsible for many of the mechanical characteristics of paper that give it valuable end-use properties. The introduction of water or heat usually disrupts these forces, causing an imbalance that produces dimensional changes at small and large scales. The result is irreversible contortion of the structure so that the smooth planar form that it had when first made is lost. In order for the paper conservator to consider solutions to the treatment of paper exposed to wet or humid conditions, or before using water in conservation methods, a familiarity of the conditions that give rise to internal stresses and the result of their release is important.

In discussing the manufacturing process, a justification for the copious amounts of water required to obtain a uniform distribution of the fibres is given. This sets the stage for the manner in which fibres are organized in the fibrous structure. The relative non-uniformity of the fibrous structure is typical of all papers, although excessive flocculation of fibres is considered a disadvantage. The fibres are deposited stochastically in stratified layers, giving rise to a difference in the properties within the plane of the web (MD-CD) and through the thickness (ZD). Fibres also tend to align preferential along the machine direction, or direction of flow, of the papermaking web, causing significant differences in the machine direction and cross machine direction properties. The small- and large-scale positioning of the fibres has a dramatic influence on the shrinkage that occurs when water is removed and the expansion when it is reintroduced. This chapter has discussed how the dewatering processes change along the paper machine, from removing large quantities of water from the fibrous suspension in the wet end, to the final conditioning of the web in the dry end, to bring it close to a state that will be at equilibrium with typical humidity conditions. Superimposed on this discussion are the structural changes, mostly shrinkage that the web undergoes as it goes from the wet to the dry state. The influence of the processes that act in opposition to web shrinkage, notably machine tension and the dryer fabric, is also discussed. Analogies between machine-made paper and historical handmade papers are provided, since all of the underlying mechanisms that control shrinkage are the same for both.

The elongated shape, complex microstructure and hygroscopicity of papermaking fibres cause characteristic dimensional changes when water is removed and reintroduced. Upon drying, hollow fibres collapse into ribbon structures and shrink many times more in the transverse direction (across the fibres) than axial (along the length). When fibres are bonded into the web structure, this shrinkage affects the entire structure by causing large-scale shrinkage, and fine scale internal stress as shrinkage is restrained. Preconditioning of fibres through pulping and refining or beating causes fibres to accept more water during the early stages of the papermaking process in order to improve bonding. However, during drying, this water is yielded so that fibres shrink more. This in turn significantly affects the dimension changes in the fibrous structure, as well as the internal stresses that build within. The intrinsic potential shrinkage of the papermaking fibres is an important parameter when considering the dimensional response of papers. During manufacturing, the fibres in the web collapse and dry, increase their stiffness and strengthen, known as hornification. Although still hygroscopic, this process is not fully reversible, and so the original state of swelling and flexibility that the fibres once exhibited in the papermaking dilute stock fed to the headbox. Conservators must consider that water does cause fibres to swell, and internal stress to be released, but it is not possible for fibres to attain the original state of hydration while still locked in the fibrous structure of paper.

Finally, a discussion of the dimensional changes that a sheet exhibits when rewet by water is given. The release of stress and the softening of interfibre bonds cause the web to expand to greater and lesser extents at different locations. When the web cannot accommodate this swelling within the structure, buckling occurs. The web experiences out-of-plane deformation, most often known as cockling. The paper is left in a state much different than what it was in when first manufactured. The only recourse for a conservator is to re-enact the papermaking process by rewetting the sheet and drying the paper under similar restraint to that which was done originally. However, because of hornification of the fibres, this re-enactment will never be as convincing as the real process.

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