fine paper basis weight is expected to continue, leading to increased use of mechanical pulps for their high opacity and bulking attributes. These changes will likely increase the need for strength and brightness of mechanical pulps. This, together with the need to decrease the electrical refining energy, will result in more complex mechanical pulping processes with new pretreatments to decrease energy usage and improve the fiber properties. The strength properties of mechanical pulps will continue to improve, decreasing the need for chemical pulps in nonpermanent printing grades. Recycled fiber, which can be produced with less energy than mechanical pulps and can replace mechanical pulps in many of the current grades, is the principal competition to mechanical pulping. The continual growth of recycled fiber may constrain the growth of mechanical pulps.

See also: Packaging, Recycling and Printing: Packaging Grades. Papermaking: Overview; Paper Grades; Paperboard Grades; The History of Paper and Papermaking; World Paper Industry Overview. Pulping: Fiber Resources.

## **Further Reading**

#### **General Paper Manufacture – Mechanical Pulps**

- Casey JP (1980) Pulp and Paper Chemistry and Chemical Technology. Chapter 4 – Pulping. New York: John Wiley.
- International Mechanical Pulping Conference Proceedings. (1985, 1987, 1991, 1993, 1995, 1997, 1999). Atlanta, GA: TAPPI.
- Kappel J (1999) Mechanical Pulps: From Wood to Bleached Pulp. Atlanta, GA: TAPPI Press.
- Leask RA and Kocurek MJ (1987) Pulp and Paper Manufacture, vol. 2. Mechanical Pulping, Atlanta, GA: TAPPI Press.
- Peel JD (1999) Paper Science and Manufacture. Vancouver, BC, Canada: Angus Wilde.
- Sundholm J (1999) *Papermaking Science and Technology*, vol. 5. *Mechanical Pulping*. Helsinki, Finland: Finnish Paper Engineers' Association and TAPPI.

#### **Color Reversion of Mechanical Pulps**

- Dence CW and Reeve DW (1996) Pulp Bleaching Principles and Practice. Section III: The chemistry of bleaching and brightness reversion. Atlanta, GA: TAPPI.
- Heitner C and Schmidt J (1991) Light-Induced Yellowing of Wood-Containing Papers – A Review of Fifty Years of Research. Proceedings of the 6th International Symposium on Wood and Pulping Chemistry vol. 1, pp. 131–149. Melbourne, Australia.

#### **Bleaching of Mechanical Pulp**

Dence CW and Reeve DW (1996) Pulp Bleaching – Principles and Practice. Section V: The technology of mechanical pulp bleaching. Atlanta, GA: TAPPI.

# **Chemical Pulping**

**R G Aravamuthan**, Western Michigan University, Kalamazoo, MI, USA

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#### Introduction

Pulping processes reduce wood or any other fibrous raw material to a fibrous mass. Chemical pulping essentially dissolves the noncellulosic components in wood, mainly lignin, and thereby liberates the fibers. This process, also known as 'delignification,' centers around the removal of ligneous binding material, but, in the process, certain hemicellulosic as well as cellulosic components are dissolved. Once the pulping process becomes less selective (in the removal of lignin as compared to cellulose and hemicellulose), the process is stopped; further processing of pulp proceeds via extended delignification and bleaching processes. Although the bleaching process is intended to bleach the 'brown' unbleached pulp into bright white pulp, the initial stages in a multistage bleaching process are more aptly called delignification since they essentially contribute to additional and preferential lignin dissolution.

In a chemical pulping process, upwards of 80% of wood lignin is removed with some concomitant carbohydrate (mainly hemicellulose and some cellulose) dissolution. The overall yield of pulp in this stage can be expected to be around 50% of the original wood. Further delignification cannot be effectively carried out by conventional pulping chemicals and is hence left to bleaching chemicals.

Two major chemical pulping processes are sulfite pulping and kraft pulping. Sulfite pulping can be carried out at different pH levels with different bases – calcium at low pH (1–2), magnesium (3–5), and ammonium and sodium over the entire range of pH. The pH levels used in sulfite pulping cover the entire range of 1–13 (1–2, acid sulfite; 3–5, bisulfite; 5–7 neutral sulfite (semichemical) – NSSC; 9–13, alkaline sulfite). On the other hand, kraft pulping is a distinctly alkaline process and works in the range of pH 11–14, using the cooking chemicals of sodium hydroxide and sodium sulfide (the reactive species being the hydroxide and hydrosulfide ions).

## History

The first commercial sulfite pulp was used in 1874, while the kraft process was commercially used almost a decade later (1885). However, the superior strength properties obtained by kraft pulp came to be recognized early in its development and many soda mills (using only sodium hydroxide) converted to the kraft process to compete with the sulfite mills. Around 1930, with the introduction of the Tomlinson recovery furnace, the kraft process gained favor over the sulfite pulp mills. The one major disadvantage of the alkaline processes (kraft or soda) was overcome with the use of powerful bleaching agents like chlorine, chlorine dioxide, and other chlorine compounds.

Sulfite pulp mills, until 1951, were mainly using calcium base without any efficient chemical recovery system. Sulfite mills, not to be left behind, began to use more powerful bases such as magnesium, sodium, and ammonium that could be used under less acid cooking conditions and were amenable to efficient recovery systems. With the advent of chlorine dioxide as a pulp bleaching agent in the 1950s, the last advantage of sulfite pulps over kraft pulps – specifically, higher brightness and/or better bleachability – was overcome by kraft pulps.

By 1990, the world annual pulp production from sulfite mills was only about 8% and the kraft pulping process had become the leading chemical pulping process. Recent investments in sulfite pulp mills have come in the form of the development of alkaline sulfite processes and the introduction of pulping additives such as anthraquinone, which has been very successfully applied earlier in the alkaline processes – kraft and soda.

On the other hand, in the kraft pulping process, current modifications center on continuous process improvements to improve the yield and selectivity of delignification in the final stages, alleviating the environmental impact of the process, and designing a better recovery system.

## **Sulfite Pulping**

The sulfite pulping liquid is prepared by absorbing sulfur dioxide (prepared by burning sulfur with a controlled excess of oxygen and quickly cooling the product gas to around 200°C to prevent further oxidation to sulfur trioxide) into different bases. The reactions are:

$$SO_2 + H_2O \rightarrow H_2SO_3$$
 (1)

$$CaCO_3 + H_2SO_3 \rightarrow CaSO_3 + CO_2 + H_2O$$
 (2)

$$CaSO_3 + H_2SO_3 \rightarrow Ca(HSO_3)_2 \tag{3}$$

The sulfite pulping terminology can be explained by equation 3.  $H_2SO_3$  is true free  $SO_2$ ; since  $Ca(HSO_3)_2$  leads to one-half  $CaSO_3$  and one-half  $H_2SO_3$ , free

 $SO_2 = H_2SO_3 + 1/2$   $HSO_3^-$  and combined  $SO_2 =$  $SO_3^{\overline{2}-}$  and 1/2 HSO<sub>3</sub><sup>-</sup>. The absorption product is later fortified by additional SO<sub>2</sub> absorption from digester relief gases under higher pressure. A higher percentage of free SO<sub>2</sub> is formed with a calciumbased liquid compound, compared to other bases. The effectiveness of sulfite pulping depends on the diffusion of  $SO_2$  and the base ion into the wood. The diffusion process is helped by monovalent ions like Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup> as well as higher pH. Lack of such diffusion leads to polycondensation and dark pulp ('burnt chips'). Any process that hinders such diffusion, like crushed chips from blunt chipper knives, leads to burnt cooks. The acid sulfite pulp with Ca as the base conducted under low pH is more susceptible to such problems. A slow heating period, relatively long cook time, and a low cooking temperature (130°C) are characteristic of acid sulfite cooks. In addition, the acid sulfite cooks are not amenable to woody materials with resins such as Douglas fir or pines. In the case of monovalent bases, due to more rapid penetration and lower free SO<sub>2</sub>, faster heating times, higher temperatures, and shorter cooking times can be achieved.

Delignification is achieved by the formation of lignosulfonic acids, which become soluble in the presence of base. In addition, the lignosulfonic acid undergoes cleavage into lower-molecular-weight fragments to make them soluble. The process also leads to acid hydrolysis of hemicelluloses, which are then dissolved. This hemicellulose dissolution is sometimes taken advantage of in making hemicellulose-free pulps which are needed for dissolving grades.

To aid in more complete delignification and better hemicellulose retention and/or to increase the species-friendliness of the process, several two-stage sulfite processes have been tried with an acid pH (3-4) in the initial stage followed by neutral (6-6.5)stage (magnefite process) or alkaline pH conditions (pH 9–10 in Sivola process) in the subsequent stage. Complementary processes starting with high pH (5-6) in the initial stage followed by low pH (1.5-2)in two-stage acid and 3–4 in Stora process) in the second stage are also in vogue.

As explained earlier, the future of the sulfite process on a large scale does not seem bright, though special sulfite pulping systems like NSSC (high-yield pulp), sulfite treatment in chemithermomechanical pulping (CTMP), sulfite-AQ process or alkaline sulfite with anthraquinone and methanol (ASAM) may hold their own in specific niche markets.

Sulfite pulps find their market in bond and writing or reproducing papers that require good formation but only moderate strength and in tissues where softness, bulk, and absorbency are the main characteristics. Sulfite pulps are also used to produce grades such as greaseproof and glassine that need pulps with high hemicellulose content due to its relative ease of delignification.

## Kraft pulping

The kraft process uses the cooking chemicals of NaOH and Na<sub>2</sub>S and an excellent chemical recovery process. The make-up chemical is provided in the form of sodium sulfate (hence the name sulfate process) or salt cake. The sodium sulfate is reduced in the chemical recovery furnace to Na<sub>2</sub>S and the other sodium components are converted to Na<sub>2</sub>CO<sub>3</sub>. The Na<sub>2</sub>CO<sub>3</sub> is converted in the causticizing cycle to NaOH by the use of lime. The lime itself is regenerated by calcining the CaCO<sub>3</sub> formed in the causticizing reaction. The various reactions are as given below:

$$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO (reduction - furnace)$$
 (4)

$$Na_2CO_3+CaO + H_2O \rightarrow CaCO_3+2NaOH (causticizer)$$
(5)

$$CaCO_3 \rightarrow CaO + CO_2$$
 (lime kiln) (6)

The cooking liquid thus consists of NaOH, Na<sub>2</sub>S, and other inerts (Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>3</sub>, etc.) as well as unconverted Na<sub>2</sub>CO<sub>3</sub>. The effective cooking species is not Na<sub>2</sub>S but NaHS, generated as follows:

$$Na_2S + H_2O \rightarrow NaHS + NaOH$$
 (7)

Hence, in the cooking liquor, NaOH + one-half Na<sub>2</sub>S is known as effective alkali and NaOH + Na<sub>2</sub>S is known as active alkali. Other terms that are used in kraft cooking are causticity (NaOH/NaOH + Na<sub>2</sub>CO<sub>3</sub>) and sulfidity (Na<sub>2</sub>S/Na<sub>2</sub>S + NaOH). Sulfidity has an important role to play in kraft cooking in that HS<sup>-</sup> helps in breaking specific lignin bonds and hence in delignification. The extent of sulfidity is also found to influence the transition point between bulk and residual phases of delignification. Higher sulfidities also help to preserve cellulose viscosity during cooking.

### **Process Cycles**

On the whole, the kraft pulping process consists of two cycles (Figure 1): (1) pulping/cooking liquor cycle, and (2) causticizing and lime cycle. The pulping of wood chips is done with white liquor containing the active chemicals (NaOH and Na<sub>2</sub>S). The residual black liquor, consisting of reaction



Figure 1 The kraft process.

products of lignin and solubilized carbohydrate moieties, is then evaporated and burnt in the recovery furnace. The inorganic smelt (Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>S), dissolved in water or weak white liquor and called green liquor, is then causticized to convert the Na<sub>2</sub>CO<sub>3</sub> to NaOH to reform the white liquor. The causticizing and lime cycle, as explained earlier, uses quick lime to convert Na<sub>2</sub>CO<sub>3</sub> to NaOH, which generates calcium carbonate (lime mud). The lime mud is washed, filtered, and pressed, and then burnt in a lime kiln to regenerate CaO to be used in the causticizing cycle.

### **Batch and Continuous Processes**

The kraft cooking process is conducted either in batch or continuous digesters, with some small process variations. In batch cooking, the digester is packed with wood chips and liquor, and the contents are heated up according to a predetermined schedule with direct or indirect steam, usually with forced circulation through the aid of liquor circulation pumps that can turn over the liquid contents of the digester about once every 10 min. The maximum temperature in a kraft cooker is between 160 and 175°C and the cooking time is adjusted to obtain a particular yield or delignification. Cooking time is also adjusted for any variations in the actual process temperature. After cooking, the pulp is discharged into a blow tank wherefrom the blow vapors are passed on to heat recovery systems via accumulator and heat exchangers. The heatingup period in the bath digester allows for impregnation, which is aided by the alkaline nature of the cooking liquor. The capillary penetration of chemicals in a longitudinal direction is six times that of diffusion of chemicals in a radial direction (across the fiber wall).

In a continuous digester, the chips are first passed through a steaming vessel where air and other noncondensables are purged. This helps give better penetration of chemicals into chips. Hence, chip thickness is also an important variable in kraft pulping and leads to fewer screen rejects. However, it is not as critical as in sulfite pulping. The preheated chips and the liquor then enter the continuous digester where they move through different zones – impregnation, heating, cooking, and washing. Each of these zones is maintained at different temperatures and finally the pulp is discharged at the bottom of the digester at a comparatively cooler temperature of around 80°C.

The auxiliary components required for a continuous digester, although more complex than those for the batch digesters, are of lower capacity due to constant leading. The equipment itself is more compact and requires less space. Also, there is better energy recovery and reuse, leading to less steam requirement. However, one major advantage of the batch system is that it offers greater operating flexibility and ease of start-up and shutdown. Also, more efficient turpentine recovery is achieved from batch digesters due to the scheduled relief gas flows throughout the cooking cycle. Grade change or species change in a continuous digester should be planned ahead to reduce variations in product quality. Some of the recent improvements in batch digester systems, such as rapid displacement heating, lead to better heat recovery and reuse in bath systems. The computer control systems that are available for batch digesters have reduced the fluctuations in steam demand from batch units ('resource leveling').

### **Lignin Reactions**

The chemicals that penetrate into fiber lumens and diffuse into fiber walls react with lignin through OH<sup>-</sup> and HS<sup>-</sup> and break major lignin bonds. The fragmented lignin is then dissolved. In the latter parts of the cooker, the lignin fragments in solution can take part in condensation reactions and be readsorbed on the fiber surfaces, resulting in dark cooks. HS<sup>-</sup> reduces the possibility of such condensation reactions by blocking some reactive groups. Along with lignin, some of the carbohydrate is removed during the cooking process. The carbohydrates are susceptible to primary and secondary alkaline 'peeling' and alkaline hydrolysis reactions. In a typical kraft cook, about 80% of lignin, 50% of hemicelluloses, and about 10% of cellulose can be brought into solution.

The delignification reactions proceed in three distinct phases — initial, bulk, and residual. Kraft cooks are typically terminated at the end of the bulk delignification phase, since delignification slows down in the residual phase and condensation reactions increase. Also, during the residual phase, the carbohydrate reactions continue, leading to the loss of viscosity and strength in pulp. The effective result is a dark and hard-to-bleach pulp with lower strength properties. The delignification rate reactions in the three phases can be represented by the following equation:

$$-dL/dt = kL^{a}[OH^{-}]^{b}[HS^{-}]^{c}$$
(8)

Thus, the delignification rate depends on the extent of the remaining lignin and the activities of the reactive species. The delignification kinetics is of first order with respect to lignin (a = 1); the values of *b* and *c* vary with the phases of delignification (Table 1).

Thus, the initial phase of delignification, in which there is rapid lignin removal, is independent of  $HS^-$  and  $OH^-$  and is characterized as an extraction process. This phase is diffusion-controlled with low activation energy of 40 KJ mol<sup>-1</sup>. This stage removes approximately 20% of the lignin, while the bulk stage removes upwards of 60% of the lignin – mostly after major lignin bonds are broken. Delignification in the bulk stage depends on both  $OH^-$  and  $HS^-$ , while the residual-stage delignification depends only on  $OH^-$ . However, in the residual stage,  $OH^-$  is bound to be low and cooking is hence stopped at this point to avoid the effects of condensation previously mentioned.

The bulk stage of delignification has been extensively studied and it has been found that the reaction rate constant k follows the Arrhenius equation,  $k = k_0 e^{-E/RT}$ , where the activation energy E is about  $135 \text{ kJ mol}^{-1}$ . The kraft cooker is often controlled on the basis of H-factor, which is the relative reaction rate integrated over time. The relative reaction rate is defined as  $k/k_{100}$  and by an arbitrary assignment of a value of 1 for  $k_{100}$ . Under these conditions, the relative reaction rate is given by exp (43.2 – 16.113/T) where T is the temperature in Kelvin scale. Extensive relative reaction rates have been tabulated for temperatures spanning the heating

Table 1Values of b and c

	Initial phase	Bulk phase	Residual phase	
b	0	0.7	0.7	
С	0	0.4	0	

and cooking range and the *H*-factor for any cooker is calculated on the basis of the measured temperature– time profile of a kraft cooker. The variance in relative reaction rates with temperature is a measure of relative delignification rates at a specified concentration (activity) of the reactive species.

#### **Carbohydrate Reactions**

Similar reaction rates have been determined for carbohydrate reactions in kraft cooking with two main differences: (1) activation eenergy of cellullose chain cleavage is  $179 \text{ kJ mol}^{-1}$  (42.78 kcal mol<sup>-1</sup>); and (2) cellulose chain cleavage in all three phases only depends on OH<sup>-</sup>

$$-(\mathrm{d}c/\mathrm{d}t) = kc^{a}[\mathrm{OH}^{-}]^{b} c \text{ where } a, b = 1$$
(9)

throughout the cook. A factor similar to H-factor, defined for cellulose cleavage, is G-factor. The relative effect of temperature on the G-factor is much higher than in the case of the H-factor. That is the major reason why there is a limit on the maximum temperature of a kraft cooker. Recent modifications in kraft cooking have sought to reduce the cooking temperature as far as possible (Table 2).

The carbohydrates (cellulose and hemicellulose) are susceptible to peeling (removal of one end-unit at a time) and alkaline hydrolysis (a random cleavage of the polymer molecule) followed by secondary peeling. The hemicellulose content is significantly reduced by these reactions while there is relatively low loss of cellulose – about 10% – due to the low accessibility of cellulose chains by virtue of their crystallinity. The acidic products of such reactions also consume the alkali in the cooking liquor. The reactions involving carbohydrates and the neutralization of acidic components start rather early in the cooking process. To determine the extent of the loss of cooking chemicals in such reactions, online cooking liquor analysis is carried out in digester operations and the sampling point is determined on the basis of the accumulated G-factor. The cooking time is then controlled for a calculated H-factor which depends on the targeted lignin removal and the cooking liquor strength  $(OH^- + HS^- \text{ activities})$ . About 90% of the extractives (fatty and resin acids) are removed during the

**Table 2** Ratio of temperature in cellulose and lignin

	Temperature		
	160° F	170°C	Ratio
Cellulose – G-factor	3960	9100	3.1
Lignin – H-factor	398	921	2.3
Ratio	7.4	9.9	

initial phase of the cook and the sodium salts can later be removed from the black liquor by acidulation in the form of 'tall oil.' Volatile turpentine is recovered from the vapor relief during cooking.

The kraft process is also characterized by redeposition of xylans from liquor on to fibers in the later stages of cooking. The kraft pulp consists of these five carbon sugars (pentosans), which are not conducive to producing dissolving grade pulp. In such a case, the kraft cooking process is preceded by an acid prehydrolysis stage in which the wood chips are exposed to direct steaming for about 2 h and the natural wood acids present are allowed to hydrolyze the hemicellulose to soluble sugars at high temperatures (170°C). This, of course, reduces the pulp yield by 5–7%, compared to normal kraft cooking.

#### **Extended Delignification**

Extended delignification is practiced in many commercial kraft pulping operations to reduce the bleach chemical cost and bleach plant pollution loads. This seeks to fine-tune the kraft process to achieve additional delignification without the deleterious efffects of a residual delignification phase. The extended delignification involves maintaining high sulfidity, leveling out the alkali concentration profile throughout the cook, decreasing dissolved lignin concentration, cooking at a low temperature, and cold blow. This has resulted in the multistage addition of cooking liquor, removal of spent liquors at various stages, and low temperature/longer-duration cooks, and extensive equipment modifications to achieve all of the above.

The other type of extended delignification is oxygen delignification, which is compatible with the kraft process and is a subsequent process step. The oxygen-stage effluent can be added to black liquor and processed through the traditional kraft recovery cycle, thereby reducing the bleach plant pollution loads.

#### **Pulping Additives**

Another disadvantage of the kraft pulping process – the low yield from wood due to carbohydrate degradation – is overcome by using pulping additives such as polysulfide, borohydride, and anthraquinone. While all of these protect carbohydrates from the peeling reaction by oxidizing (polysulfide, anthraquinone) or reducing (borohydride) the end groups of carbohydrate chains, anthraquinone is the only reagent which has a redox cycle of its own. In the oxidation cycle, it protects the cellulose chain, and in the reduction cycle it leads to lignin fragmentation. Use of small levels of anthraquinone (about 1 lb t<sup>-1</sup>)

of pulp) increases the yield (2-3%) and lowers the effective alkali requirement as well as increasing the delignification rate. The other two compounds have not found favor with the industry either because of the cost or because of the associated pollution problem due to sulfur compounds.

## **Control Parameter**

A major control parameter in kraft pulp is a target kappa number (which directly relates the percentage of lignin left in pulp). Thus, a lower kappa number indicates a higher level of delignification. The higher the H-factor and/or active alkali, the lower will be the kappa number. The target kappa number is based on one or more of the following: (1) maximum pulp strength; (2) limitations on recovery loading; (3) maximum screened unbleached pulp yield; and (4) maximum bleached pulp yield. The cooking is essentially controlled by using the H-factor as a primary variable based on a desired kappa number and the cooking liquor strength from online analyzers. The desired H-factor is maintained in the batch digester by adjusting time and/or temperature, while in the continuous digester it is done by manipulating the temperature.

## **Pulp Properties**

Softwood kraft pulps produce the strongest papers and are used in wrapping, sack, and liner papers. Bleached kraft pulps are used, along with high-yield pulps, in magazine-grade or newsprint furnish to provide additional strength and runnability on high-speed machines. Bleached grades are also used for toweling and boards. Unbleached grades for packaging applications are cooked to a higher kappa number to maximize the screened unbleached pulp yield while the bleached grades for writing, printing, and tissue applications are cooked to a lower kappa number.

# **Pulp Processing**

Chemical pulps, as they come out of the blow tank, are fiberized enough to pass through knotters that can remove irregularly shaped reaction wood pieces, overthick chips, and other uncooked chips. Knots are generally defined as the pulp that is retained on 3/8 in. perforated plate. The removed knots can be recycled to a digester for recooking. The knotters can be atmospheric vibrating knotters or pressure screen knotters. The former have been superseded by the latter due to the fact that the open-type design generates foam and liquor splashing and the foam generated hinders the subsequent washing operation. The major disadvantage of the pressure knotter is that the knotter rejects should be processed through a secondary screen to recover the good fiber rejected along with the knots.

The pulp is then washed in multiple stages to remove the residual liquor from the pulp. This helps to reduce the costs of further processing and to recover the maximum amount of spent chemicals. The aim is to do so using a minimum amount of wash water, thereby reducing the dilution and consequent evaporation costs. Washing is done using any of the following: a battery of countercurrent rotary vacuum washers, rotary pressure washers, atmospheric or pressurized diffusion washers, or horizontal belt washer or dilution/extraction equipment.

Washing can be characterized either as displacement or diffusion washing. In displacement washing, a thick layer of pulp is built on a screen and wash water is applied to displace the liquor in the sheet and the displaced liquor is drained either by vacuum or forced out by pressure. Three or four stages are generally used to achieve an overall removal of about 99%, since the displacement for a single stage rarely exceeds 80% and can vary from stage to stage depending upon factors such as fiber mat drainage characteristics, air entrainment, pulp temperature, and pulp hardness and freeness.

Pulp slurry feed to a washer is prepared by mixing the filtrate of a particular stage with the exiting stock from a previous stage. In addition, the filtrate from a particular stage is also used as wash liquor in the previous stage. A countercurrent operation is maintained by balancing the liquor flows throughout the system, with fresh wash water being added to the final washer. The fresh water flow rate is controlled by monitoring the dissolved solids concentration in the exit stock from the final washer.

Diffusion washing is marked by a relatively long period of contact between the pulp and the wash liquor which allows the liquor solids to diffuse from the fiber structure. The diffusion rate depends on the temperature, concentration gradient, and fiber structure. Since the fibers are submerged, there is no air entrainment. The time of contact can vary between 10 min per stage in a multistage diffusion washer to about 2–4 h at the bottom of a Kamyr continuous digester.

Rotary pressure washers are similar to vacuum washers, but have some advantages: (1) a single washer can be operated with two or three displacement stages; (2) due to the high pressure, a hightemperature wash liquor can be used without the fear of fluffing the pulp; and (3) the closed vapor circulation system helps to prevent pollution.

The horizontal belt washer resembles a Fourdrinier paper machine in that the pulp suspension is distributed on a moving filter belt from a headbox to form a thick mat. The displaced filtrate is collected at the bottom and the filtrate from one section is used as wash liquor in the previous section in a classic countercurrent system. Unlike the rotary washer system, there is no mixing and reforming of pulp between stages.

The dilution/extraction system consists of diluting a pulp slurry with a weaker liquor and rethickening. Modern extraction presses which can thicken the pulp to a consistency of 30–40% have made such a system, operated in multistages, comparable with regular washers.

The diverse washing systems are often compared in terms of a single efficiency factor, viz., Norden efficiency factor, defined as the number of mixing stages that will give the same result as the washing equipment under consideration when operated at the same wash liquor ratio. From the computed cumulative Norden factor of the proposed equipment system and the dilution factor proposed, the anticipated washing efficiency of the system can be predicted from literature data.

The washed pulp is then screened through pressurized contrifugal screens with either centrifugal (outward) or centripetal (inward) flow or both. The screen perforations can be either taper-drilled holes or slots with relief on the accept side. Slots are oriented perpendicular to the direction of rotation so that the long dimension of the debris is presented to slot width. Slots, with their widths normally smaller than hole diameter, are more effective in removing smaller cubical debris. However, with screen open areas in the 3-7% range, compared to 10% for screens with holes, slotted screens have lower throughputs. The screen cleanliness efficiency is defined as  $1 - (S_a/S_i)$ , where  $S_a$  and  $S_i$  are weight fractions of debris in the accepts and inlet flow, respectively. The cleanliness efficiency depends on the perforation size and type, and percentage reject rate.

The screened pulp may then be centricleaned by employing centrifugal force (density differences) and fluid shear (particle shape). The stock enters tangentially and is rotated by inlet guides. As the stock flows inward, the velocity increases, resulting in high centrifugal force near the center which carries the dense particles outwards and away from the accepted pulp. The dirt (which is heavier) held in the downward current continues toward the tip under increasing force (due to narrowing diameter). The smaller the debris size to be removed, the smaller should be the diameter of the cleaners to be employed. The contracleaning system is normally operated in three stages in a cascade sequence (with the rejects of the primary being fed to the secondary, and the secondary accept being fed to the primary, and so on) so that the overall rejected fiber is usually less than 1% while a reject rate of 10–20% is maintained in each stage to ensure good cleaning efficiency.

The cleaned pulp is then thickened using various filters (10-15% consistency), gravity thickener (4-8%), screw extractor, or various presses (>20%) before being stored in high-density chests/towers. Integrated pulp mills often store the pulp at 10–15% consistency. Nonintegrated operations can deliver pulp in wet laps (40-45%) or dry laps (80-85%) oven dry) using equipment similar to the paper machine. Besides steam cylinder drying of pulp laps, pulp can be dried in air float dryers or flash-dried after prefluffing the pulp, using hot air as a drying medium.

See also: **Papermaking**: The History of Paper and Papermaking; World Paper Industry Overview. **Pulping**: Chip Preparation; Fiber Resources; Physical Properties.

## **Further Reading**

- Biermann CJ (1996) Handbook of Pulping and Papermaking, 2nd edn. Chapters 3 and 4. San Diego, CA: Academic Press.
- Gullichsen J and Paulapuro H (2000) Papermaking Science and Technology – Books 6A and 6B – Chemical Pulping. Helsinki, Finland: Fapet Oy.
- Kocurek JJ (1985/1989) *Pulp and Paper Manufacture*, vols 4 and 5, 3rd edn. The Joint Textbook Committee of the Paper Industry, TAPPI/CPPA.
- Sjostrom E (1993) Wood Chemistry Fundamentals and Applications, 2nd edn. Chapter 7. San Diego, CA: Academic Press.
- Smook GA (1992) Handbook for Pulp and Paper Technologists, 2nd edn. Chapters 4–10. Bellingham, WA: Angul Wild.

# **Bleaching of Pulp**

**T J McDonough**, Institute of Paper Science and Technology, Atlanta, GA, USA

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## Introduction

The term 'bleaching,' when used in reference to wood pulp, means chemical treatment of the pulp to increase its ability to reflect visible light or, in other words, its brightness. The color of unbleached pulp is practically all due to the lignin it contains, so bleaching necessarily implies that the lignin is either decolorized or removed. Chemical pulps contain