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

© 2004, Elsevier Ltd. All Rights Reserved.

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 relatively small amounts of residual lignin, so it is practical to bleach them by removing the lignin. Mechanical pulps, on the other hand, contain so much lignin that to remove it would require large amounts of bleaching chemicals and would be prohibitively expensive. Consequently, mechanical pulps are bleached by decolorizing the lignin instead of removing it. Since it is not feasible to decolorize the lignin completely, bleached mechanical pulps are generally not as bright as bleached chemical pulps. The latter are virtually free of lignin and contain only polysaccharides, which are practically colorless.

In addition to increasing brightness, bleaching simultaneously improves other desirable pulp properties by removing contaminants such as extractives and small particles of bark or incompletely pulped wood. For specialty pulps, such as dissolving pulps, the conditions of the bleaching process can be adjusted to provide for removal of undesirable hemicelluloses. In some applications these other properties are even more important than brightness and the pulp may have to be bleached to a brightness that is higher than needed, to achieve the required levels of contaminant removal.

Lignin removal is accomplished by treating the pulp alternately with oxidizing agents and alkali. Lignin is much more susceptible to oxidation than cellulose and the other polysaccharide components of the pulp, and is selectively removed. Nevertheless, the polysaccharides are not completely resistant to attack and can be damaged if the bleaching process is not carefully selected and controlled. The damage that does occur causes a small amount of the polysaccharide fraction to dissolve and is accompanied by depolymerization of the remainder. Such depolymerization, if it is sufficiently extensive, can result in a loss of pulp strength. Its extent is monitored by dissolving a sample of the pulp in a cellulose solvent and measuring the viscosity of the resulting solution. Some bleaching agents are less likely to damage cellulose than others and are said to be more selective.

Most chemical pulp bleaching sequences use chlorine dioxide to accomplish at least part of the required lignin oxidation. They generate an effluent that contains lignin degradation products and other organic materials, some of which are chlorinated. Since the effluent also contains chloride ion and other chlorinecontaining ions, it cannot be recycled and burned in the mill's chemical recovery system. Consequently, pulp bleaching processes generally have the potential to affect the environment and must be selected and operated with due regard for the environment.

We can summarize the above introduction to pulp bleaching in the form of a working definition. Bleaching is the treatment of pulp to remove or decolorize its lignin component and thereby increase its brightness and other desirable properties while preserving pulp yield and strength, with due regard for potential effects on the environment.

Significance

Bleaching ranks among the most important of the processes used to manufacture pulp and paper. **Table 1** contains estimates of the amounts of the different kinds of pulp that the global pulp and paper industry produced in 2001. World production of bleached chemical pulp amounted to 78.8 million tonnes, or more than 44% of total pulp production. This figure underestimates the total amount of pulp bleached, since it does not account for the bleaching of substantial proportions of other pulp types, such as mechanical, nonwood, and deinked pulps. It would not be unreasonable to assume that nearly two-thirds of global pulp production benefits from some sort of bleaching process.

Kraft Pulp Bleaching Stages and Their Development

Hypochlorite

In the early part of the twentieth century, bleaching was a simple batch process that relied almost exclusively on calcium hypochlorite, made by bubbling chlorine gas into a lime slurry. The hypochlorite (H) stage was begun by adding the chemical to a warm suspension of unbleached pulp at low consistency. The stock was slowly agitated until the desired degree of bleaching had been achieved, after which the pulp was washed free of the spent bleach liquor and reaction products. The next step in the development of the technology was introduction of two-stage (HH) bleaching, in which only part of the hypochlorite was added and allowed to react, after

 Table 1
 Estimated 2001 world pulp production by type (millions of metric tons)

Pulp type	Production
Bleached kraft	76.3
Unbleached kraft	32.4
Bleached sulfite	2.5
Unbleached sulfite	1.1
Semichemical	7.0
Mechanical	34.7
Nonwood	14.3
Unspecified	10.0
Total	178.3

which the pulp was washed and subjected to a second stage, similar to the first. This simple modification of the process had two beneficial effects. First, the removal of dissolved but still oxidizable reaction products after the first stage reduced overall chemical consumption. Second, the reduction in the maximum and time-averaged concentrations of the oxidizing agent reduced its propensity to attack and degrade the cellulose and other polysaccharide components of the pulp. This subtle introduction of stagewise bleaching was a seminal event in the development of today's multistage bleaching sequences.

Chlorine

The commercial introduction of chlorine gas as a bleaching agent was a similarly significant milestone in the development of modern bleaching technology. The first reported commercial chlorination (C) stage was developed at the Nekoosa-Edwards Paper Co. in 1930 and 1931. It was based on the earlier observation by Cross and Bevan that lignin is rapidly chlorinated and that the chlorinated lignin is soluble in alkali and can be removed in a caustic extraction (E) stage following the C stage. Lignin removal in C and E stages allows final brightening in a subsequent H stage with a much smaller application of hypochlorite than would be necessary to achieve the same result in the single-stage process or in the two-stage HH sequence. In addition, the high selectivity of chlorine and the reduction in the amount of the relatively nonselective hypochlorite applied gave a stronger bleached pulp. Finally, it proved possible to reach higher brightness levels in the multistage CEH process. This development marked the advent of the modern multistage bleaching sequence, in which the early stages remove the bulk of the residual lignin, sometimes without significant brightness increase, and the later stages cause large gains in brightness by removing the last traces of residual lignin.

Chlorine Dioxide

The commercialization of chlorine dioxide use in the early 1940s took all of these advances one step further. WH Rapson, who was at the time an employee of Canadian International Paper Company, pioneered the use of chlorine dioxide in North America. Commercial chlorine dioxide bleaching began at that company's mill in Temiscaming, Quebec in the summer of 1946. Almost simultaneously, two Swedish mills started up similar systems. Chlorine dioxide is a powerful brightening agent and is immeasurably more selective than hypochlorite. Adding a chlorine dioxide (D) stage after the hypochlorite stage to give a CEHD sequence made it possible to achieve much higher brightness levels without compromising pulp strength. In the years following its first full-scale application, chlorine dioxide displaced more and more hypochlorite, and by the 1960s the CEDED sequence had become the standard for the industry.

As well as being an efficient brightening agent for application in the later stages of a bleaching sequence, chlorine dioxide can assume a role similar to that of chlorine, earlier in the sequence. Used in this way, chlorine dioxide oxidizes lignin while it is still present in relatively large amounts and renders it soluble in a subsequent alkali extraction stage. For many years, however, chlorine dioxide was considered too expensive to be used as a complete replacement for chlorine and its use at an early stage in the sequence was restricted to replacing only part of the chlorine in the chlorination stage. This was practiced for either of two reasons - to prevent loss of pulp strength, as indicated by excessive viscosity loss, or to improve delignification efficiency. In the former application, only small fractions of the chlorine were replaced, usually in the neighborhood of 10%. Such a small amount of chlorine dioxide, when added at the same time as the chlorine or shortly afterwards, serves to neutralize free radicals responsible for cellulose degradation during chlorination. When used to improve delignification efficiency, larger fractions of the chlorine were replaced, typically about 50%. This level of substitution results in a significant increase in apparent lignin removal, as measured after the alkali extraction stage that follows the chlorination stage. When used in this way, the chlorine dioxide is added to the pulp before the chlorine. The use of substitution levels much higher than 50% results in a loss of efficiency and 100% substitution usually requires more than the theoretical amount of chlorine dioxide.

In spite of this loss in efficiency, complete replacement of chlorine by chlorine dioxide began in the late 1980s in Sweden and has since become widespread. The practice began in response to new environmental regulations and environment-related market pressures. The potential of bleaching effluents to affect the environment is usually estimated by characterizing them in terms of the results of several different chemical test methods. One of these is a method for determining the effluent's content of adsorbable organic halide, abbreviated as AOX. In effect, AOX is an estimate of the total amount of chlorine in organic compounds found in the effluent. Some organic chlorine compounds are highly toxic, notably chlorinated dibenzodioxins (dioxins), chlorinated dibenzofurans (furans), and highly chlorinated

phenolic compounds. Since it is much easier to measure AOX than to measure amounts of individual toxic compounds, most jurisdictions have adopted AOX as a basis for regulation (in spite of the fact that most of the organic chlorine compounds found in bleaching effluents are not toxic). In general, AOX limits have been set at very low levels by the environmental authorities in pulp-producing countries, effectively forcing the industry to phase out the use of molecular chlorine. Its complete replacement by chlorine dioxide gave rise to the term 'elemental chlorine-free' bleaching, or ECF bleaching. Bleaching with chlorine dioxide generates far less AOX than bleaching with the equivalent amount of chlorine. It also generates no detectable levels of dioxins or highly chlorinated phenolic compounds and usually generates no detectable levels of furans.

Hydrogen Peroxide

Hydrogen peroxide is similar to chlorine dioxide, in that it can be applied at a later stage in the bleach sequence to attain high brightness. Though not as highly selective as chlorine dioxide, a hydrogen peroxide (P) stage does not adversely affect pulp strength if the bleaching conditions are appropriately chosen. Both hydrogen peroxide and chlorine dioxide found wide application, but the generally greater costeffectiveness and selectivity of chlorine dioxide resulted in its being more widely adopted. Although, as noted above, the CEDED sequence had become the standard for the industry by the 1960s, hybrid sequences such as CEHD and CEDP were still in common use. More recently, technologies have been developed for using peroxide to remove significant amounts of lignin earlier in the bleaching sequence while simultaneously brightening the pulp. These methods employ forcing conditions of high temperature and pressure to accelerate the normally sluggish reaction of hydrogen peroxide with lignin. The use of such forcing conditions is only feasible if the pulp is pretreated to remove traces of transition metal ions, which would otherwise catalyze decomposition of the peroxide. This is achieved by inserting a chelating agent (Q) stage ahead of the peroxide stage. A chelating agent commonly used for this purpose is diethylenetriaminepentaacetic acid (DTPA). Peroxide may also be used to enhance the effectiveness of alkali extraction stages and oxygen stages. Conversely, oxygen may be added under pressure to give a pressurized peroxide (PO) stage as part of a strategy to impose forcing conditions in the peroxide stage. The advent of this practice during the 1990s has blurred the distinction between peroxide and oxygen stages.

Oxygen

During the period of chlorine dioxide's ascent, research was being conducted on two other promising bleaching agents - oxygen and ozone. Oxygen, when applied together with alkali in an oxygen delignification (O) stage, is capable of removing much of the residual lignin in a kraft pulp, but its low solubility and its tendency to be nonselective (especially in the presence of trace amounts of one or more transition metal ions, notably iron, manganese, or copper) slowed the development of oxygen delignification processes. Ozone is even more reactive toward lignin than oxygen but its tendency to be nonselective similarly hindered its commercialization. Oxygen was the first of the two to achieve the status of a commercially viable bleaching agent, owing in part to the discovery of a cellulose 'protector' by Robert and coworkers in France in the early 1960s. They found that adding a small amount of magnesium ion to the pulp before oxygen bleaching deactivated trace metal ions and allowed about half of the residual lignin to be removed without affecting pulp strength. Soon after this, in 1970, a mill in Enstra, South Africa, started up the first commercial oxygen delignification system. The significance of this development lay in its potential for decreasing the environmental impact of the bleach plant. Unlike the effluents from C stages or stages following C stages, oxygen-stage effluents do not contain significant amounts of chloride ion, so they can be recycled to the mill's chemical recovery system and ultimately destroyed by burning in the recovery furnace. The quantities of materials discharged to the environment are roughly proportional to the amount of lignin in the pulp entering the bleach plant. Consequently, removal of, for example, 50% of the lignin in an oxygen stage before conventional bleaching (such as in an OCED sequence) can result in a roughly 50% reduction in bleach plant discharges.

In addition to being used to reduce the lignin content of the pulp entering the bleach plant, oxygen can be used in the bleach plant itself. The earliest such application appeared in about 1980 and consisted of reinforcement of the first caustic extraction stage. Oxygen is dispersed in the pulp after addition of alkali, transforming the E stage into an (EO) stage. The result is more efficient removal of lignin that has been solubilized by the preceding oxidative stage (then C, now D). The benefit can be realized either in the form of reduced cost for bleaching agents in the succeeding stages of the sequence or reduced AOX, by decreasing the application of chemical in the stage preceding the (EO) stage. Adding both oxygen and hydrogen peroxide to the extraction stage has an even greater effect than adding oxygen alone. The result is an (EPO) stage. A related but more recently developed use of oxygen in the bleach plant combines it, under pressure, with hydrogen peroxide, giving a (PO) stage.

Ozone

Ozone has even greater potential than oxygen for lessening the effects of bleaching on the environment because its greater reactivity, at least in principle, allows it to remove nearly all of the lignin in a form that is recyclable to the recovery system. That same reactivity, however, can lead to cellulose degradation and loss of pulp strength if the ozone is not applied uniformly and in controlled amounts, under appropriately selected conditions. Because of these demanding requirements, the commercial application of ozone took a long time after the initial discovery of its bleaching power. In 1992, however, Union Camp Corporation announced that it had successfully developed a viable ozone (Z) stage capable of selectively delignifying kraft pulp. That company started up a 1000-ton per day bleach plant incorporating both ozone and chlorine dioxide stages, the sequence being OZED. Since then, many other commercial ozone stages have been put into operation, though not all of them are placed in such a way that their effluents can be recycled to the recovery system.

Ozone may be used in close combination with chlorine dioxide by sequentially adding the two chemicals in the same stage. The resulting stage may be designated (DZ), (ZD), (D/Z) or (Z/D), depending on the order of addition and the time that is allowed to elapse between additions of the two chemicals.

Hemicellulose-Degrading Enzymes

In 1987, Finnish researchers proposed the idea of using hemicellulose-degrading enzymes as pulp-pretreating agents to facilitate subsequent bleaching. Although they do not themselves remove lignin from the pulp, xylanases were shown to be capable of rendering the lignin in unbleached pulp to be more readily removed by subsequent treatment with chlorine dioxide and alkali. The xylanase (X) stage typically results in reductions in chlorine dioxide requirements of approximately 5 kg per ton of pulp. The technology has been commercialized in a significant number of bleached kraft mills.

Prehydrolysis

Another significant discovery emerged from Finnish research laboratories during the 1990s. This was the finding that a significant fraction of the oxidizable material (as measured by the kappa number, a test designed to estimate the amount of residual lignin in pulp) is not lignin. This material, hexenuronic acid, is formed from xylan during kraft pulping, and consumes chlorine dioxide during bleaching. Since hexenuronic acid is also susceptible to removal by acid hydrolysis, this discovery led to the development of an acid hydrolysis (A) stage that can be used as a pretreatment to reduce the requirement for chlorine dioxide significantly during subsequent bleaching. Since hardwoods contain much more xylan than softwoods, hardwood pulps contain more hexenuronic acid than softwood pulps. The prehydrolysis process has been commercialized in hardwood pulp bleach plants at several mills.

Bleaching Sequences

Successive incremental additions of any bleaching chemical result in progressively smaller incremental effect, regardless of whether the effect in question is lignin content reduction, brightness increase, or some other property change. Furthermore, an asymptotic limit is approached that usually falls far short of the desired target level and high total chemical charges are needed to approach the limit. On the other hand, if chemical addition is stopped at some economical level and the pulp is washed before the same chemical is again incrementally added, the incremental increases in effect are initially larger than if the washing step had been omitted. To illustrate, a DD sequence requires less chlorine dioxide than a single D stage to reach a given brightness and is capable of reaching a higher brightness. Furthermore, if the bleaching chemical in question is an acidic oxidant, such as chlorine dioxide, the effect is strongly enhanced by intermediate alkali extraction. Thus, a DED sequence requires much less chemical to reach a given brightness and is capable of reaching a much higher brightness. By extension, a DEDED sequence requires still less chemical and is capable of reaching an even higher brightness.

Notation

As is already apparent from the preceding paragraphs, a system of shorthand notation has evolved for designating the individual stages that make up a bleaching sequence. The uppercase letters appearing in parentheses are used to represent the stages to which they refer. A single uppercase letter represents a bleaching stage that consists of a mixer, a retention vessel (usually a tower), and a washer. A stage to which two chemicals are added sequentially without intermediate washing is represented by an ordered combination of letters within parentheses, with or without an intermediate '/,' depending on whether the time elapsed between the two chemical additions is greater or less than 1 min. Simultaneous addition is indicated by using a '+' instead of a '/.' Examples are D, (ZD), (D/Z), and (C+D). A bleaching sequence is then represented by an ordered combination of stage designators, D(EPO)DED, for example. Numerical subscripts are sometimes used to denote the position of a stage within the sequence, for example, $D_0(EPO)D_1ED_2$.

Partial Bleaching Sequences

One may consider a chemical pulp bleaching sequence to be made up of two partial sequences, a delignifying partial sequence and a brightening partial sequence. The purpose of the former is primarily to remove lignin, rather than to increase brightness. The purpose of the latter is primarily to increase brightness by removing the small amount of remaining lignin and perhaps decolorizing traces of lignin that remain with the bleached pulp. Table 2 provides lists of delignifying and brightening partial sequences. Any one of the former can be combined with any one of the latter to create a full bleaching sequence, capable of bleaching softwood kraft pulp to brightness values in the range 80-90, depending on the particular sequence. Note that the partial sequences listed in the table are only examples; many more could have been included.

ECF and TCF Sequences

As already noted, sequences based on the use of chlorine dioxide without any use of molecular chlorine are termed elemental chlorine-free (ECF) sequences. Sequences that use no chlorine compounds or molecular chlorine are referred to as totally chlorine-free (TCF) sequences. The latter sequences generally have higher costs and are less able to achieve high brightness and high strength simultaneously. With reference to **Table 2**, examples of ECF sequences are D(EPO)DED, OD(EO)D, and OZED. Examples of TCF sequences are OXQPPP and OQPZQ(PO).

Process Conditions

The operating state of a bleaching stage is generally characterized in terms of chemical charge, consistency, time, temperature, and terminal pH. Some bleaching stages, such as a brightening D stage, are invariably operated within a narrow range of conditions that have been determined to give near-optimum results. Others, such as the oxygen stage, exist in a variety of different forms, each with its own range of operating conditions. Thus oxygen stages may be operated at medium consistency (10–14%, MC) or high consistency (20–27%, HC) and initial chlorine

 Table 2
 Examples of delignification and brightening partial bleach sequences

Delignification	Brightening
CE	Н
(C+D)E	HEH
(DC)(EO)	HED
D(EPO)	D
ODE	DD
OD(EO)	DED
OXD(EPO)	DEDP
OXQP	DPD
OZ	(EPO)P
OOQP	PP
OQPZ	Q(PO)

dioxide (D₀) stages may be operated at low consistency (3.5-4%, LC) or MC. Typical process conditions for some bleaching stages are given in Table 3.

Bleaching of Mechanical and Other High-Yield Pulps

Among the principal virtues of mechanical pulps are their very high yields. Unavoidably associated with such high yields are correspondingly high lignin contents. Since the lignin content of the wood raw material may be as high as 30%, mechanical pulps may have lignin contents approaching this figure. This precludes bleaching by lignin removal, which would negate the yield benefit and consume inordinately large amounts of bleaching chemicals. Consequently, high-yield pulps are bleached with chemicals that decolorize lignin instead of removing it, sometimes referred to as lignin-preserving bleaching agents.

The two main bleaching chemicals used for this purpose are sodium dithionite (commonly known as sodium hydrosulfite) and hydrogen peroxide. Bleaching with hydrosulfite, a powerful reducing agent, is used when the required brightness increase is relatively small. The maximum brightness increase achievable depends on the wood species, but is almost never greater than 10 points. To illustrate, a mill making thermomechanical pulp as the main component of a newsprint furnish may use hydrosulfite to increase the brightness of the pulp from 55 to 60, a value typically required for newsprint. Hydrosulfite bleaching is conducted at low or, less often, at medium consistency and at the highest feasible temperature, usually 60-70°C. It is necessary to exclude air, since oxygen rapidly destroys hydrosulfite.

The ability of hydrogen peroxide to serve as a lignin-preserving bleaching agent may seem counterintuitive, given the above reference to its use as a delignifying agent for chemical pulps. It is found, however, that if the conditions are appropriately

Stage	0	D	(EPO)	D	Е	Ζ	Q	Ρ	(PO)	Α
Variant	Medium consistency	Delignifying		Brightening	Second extraction	Medium consistency				
Chemical applied (kg t ⁻¹)	ŗ									
Oxygen	30		5			50			30	
Ozone					5	5				
Magnesium sulfate	1							1	1	
Chlorine dioxide		20		10						
Sodium hydroxide Hydrogen peroxide	30		25 5	5	5			10 15	30 30	
DTPA							1			
Consistency ^c (%)	12	3.5	12	12	12	12	12	12	12	12
Time (min)	60	30	60 ^a	180	60	3	60	240	120	240
Temperature (°C) Average pressure (kPa)	90 500	60	70 100 ^b	70	70	40 800	70	90	110 500	95
Terminal pH	10.5	2.5	10.5	4	10.5	3	6	10.5	10.5	3

Table 3 Typical process conditions for individual bleaching stages

^aOf which 10 min is under oxygen pressure.

^b Pressure supplied by hydrostatic head in upflow tube, decreasing from 200 to 0 kPa.

^cConsistency is the fiber concentration, defined as (weight of dry fiber)/[(weight of dry fiber) + (weight of water)], expressed as a percentage.

DTPA, diethylenetriaminepentaacetic acid.

chosen, the action of the peroxide will be limited to destruction of chromophoric structures within the lignin without degrading it to the extent that it would dissolve and be removed. The conditions are milder than those used to delignify chemical pulp and include the use of sodium silicate and magnesium sulfate to stabilize the peroxide toward metal-catalyzed decomposition. Bleaching is usually conducted at the highest possible consistency, a temperature in the range 40-60°C, and in the presence of sufficient alkali to result in a terminal pH of about 10.5. Under favorable conditions, peroxide bleaching may be capable of raising the brightness by 20 points or more, so it is used when the brightness gain needed is greater than can be achieved with hydrosulfite alone. Still higher brightness gains can be achieved by sequential bleaching with peroxide and hydrosulfite, usually in that order, though the brightness gains are far from additive. Hydrosulfite applied after a peroxide stage may result in only 1-3 points brightness increase.

Bleaching of Recycled Fiber

Recycled fiber often contains chemical pulps mixed with mechanical pulps, chemimechanical pulps, or both. For this reason recycled pulps are usually bleached with lignin-preserving bleaching agents. Complicating factors not encountered in the bleaching of virgin pulps are incomplete ink removal, the presence of dyes, and the greater contribution of resistant chromophores to the color of the pulp, the less resistant ones having been removed during virgin fiber processing. All of these factors are obstacles to the attainment of high brightness. Hydrogen peroxide may be used during repulping or deinking, to prevent alkali-induced yellowing and perhaps achieve some degree of brightening, and may also be used in a subsequent bleaching stage. Dithionite may be used subsequently for 'color stripping' or decolorization of dyes. Another powerful reducing agent, formamidine sulfinic acid (FAS) may be used for the same purpose. FAS is more expensive than hydrosulfite, but may be cost-effective. Ozone can also be used for colorstripping. Because of the extreme variability in the characteristics of recycled fiber feedstocks, it is difficult to generalize further. Experimentation is necessary to identify appropriate bleaching processes and conditions for any given recycled fiber supply.

Bleaching Equipment

A pulp bleaching stage normally consists of a mixer, a pump, a retention tower, and a washer. Good mixing is a critical prerequisite for efficient bleaching and good bleached pulp quality. Mixing equipment found in bleach plants may be of several types: continuous stirred tanks, peg mixers, static mixers, and high-shear mixers. High-shear mixers, introduced in the early 1980s, have allowed efficient fiberscale mixing to be achieved at medium consistency and have enabled medium-consistency applications of gaseous bleaching chemicals that were previously impossible. These include medium-consistency delignification with oxygen or ozone and oxygenreinforced alkaline extraction. High shear is created by passing the pulp suspension through a narrow gap between two surfaces moving at a high velocity relative to one another.

Bleaching towers are vertical, cylindrical, plug-flow reactors that provide the necessary time for microscale chemical concentration gradients to be evened out by diffusion and for the bleaching reactions to be completed. There are three basic types: downflow, upflow, and upflow-downflow. Downflow towers are used for bleaching chemicals that are not gases under normal conditions. Upflow towers are used for stages employing gaseous bleaching chemicals. The hydrostatic head of the pulp column provides sufficient pressure to prevent loss of gas from the pulp suspension before it has had time to react. Upflowdownflow towers combine the advantages of both component types. The pulp and bleaching chemical enter at the base of the upflow tube, which provides the hydrostatic head necessary to keep gaseous bleaching chemicals in solution. It provides sufficient retention time for much of the bleaching chemical to be consumed by the pulp, thus reducing the likelihood of gas loss at the top of the tube. The pulp then falls into the downflow part of the tower, where the reaction is completed. The retention time can be controlled by controlling the depth of the pulp bed in the downflow part of the tower.

The pulp emerging from a bleaching stage is generally washed before entering the next stage. This removes organic material that would otherwise consume chemical in the next bleaching stage, as well as spent and residual bleaching chemical. The type of washer most often used is the rotary drum filter, though diffusion washers and wash presses may also be used.

Figure 1 is a schematic representation of a generic bleaching stage, showing the washer following the previous stage, a steam mixer discharging to a standpipe feeding a stock pump, a high-shear chemical mixer, an upflow-downflow tower, and the bleached pulp washer.

Novel Bleaching Systems

Most of the bleaching systems discussed above have found wide commercial application. Some newer technologies have been implemented only recently and can, at the time of writing, be found in only a few operating mills. Still others are at the research stage and may hold promise for the future.



Figure 1 Schematic representation of a generic upflow–downflow bleaching stage. Reproduced with permission from Dence CW and Reeve DW (eds) (1996) *Pulp Bleaching: Principles and Practice.* Atlanta, GA: TAPPI Press.

Peracids

Peracids, more correctly called peroxyacids, are analogs of hydrogen peroxide in which one of the hydrogens is replaced by an acyl group. They can be prepared by reacting an acid with hydrogen peroxide. Acetic acid gives peracetic acid and sulfuric acid gives peroxymonosulfuric acid, also known as Caro's acid. Both of these peracids are selective pulpdelignifying and brightening agents. They are more reactive than hydrogen peroxide and therefore can be used under milder reaction conditions. Peracetic acid is currently being used for pulp bleaching in a few mills in Europe.

Dimethyldioxirane

Dimethyldioxirane is derived from acetone by inserting a peroxidic oxygen into the carbonyl group, forming a molecule with a reactive, three-membered ring. It is both reactive and selective, but would have to be generated on site because of its relative instability. In principle, its generation is straightforward, involving preparation of Caro's acid from sulfuric acid and hydrogen peroxide, followed by reaction of the Caro's acid with acetone. However, the economics of the system depend on cheap and efficient recovery of both acetone and sulfuric acid, an engineering challenge that has not yet been met.

Lignin-Degrading Enzymes

The most important member of this class is laccase. Early attempts to bleach pulp with laccase failed because the laccase molecule is too large to diffuse into the pulp fiber, where the lignin is located. This problem was partially solved in the early 1990s, when it was discovered that certain compounds can serve as 'mediators.' Such a compound diffuses into the fiber and oxidizes lignin, thereby being reversibly converted to its reduced form. The reduced mediator diffuses out of the fiber into the bulk medium, where it is reoxidized by laccase, regenerating the oxidized form, which is capable of again diffusing into the fiber and further oxidizing lignin. Furnishing oxygen to reoxidize the laccase completes the cycle. The process is not yet commercial, since the known mediators are too expensive. It is possible that further research will solve this problem.

Polyoxometalates

Another process that has not yet reached the point of commercialization employs polyoxometalates (POMs), metal oxide anions (heteropolyanions) formed from simple oxides of vanadium, molybdenum, or tungsten. They have oxidized forms that are capable of oxidizing lignin and being regenerated by oxidation with oxygen or hydrogen peroxide. Current research envisages a zero effluent concept: an aqueous solution of POM is applied to the pulp under anaerobic conditions. It oxidizes and degrades the lignin and itself becomes reduced in the process. The spent liquor containing the reduced POM and the dissolved organic material (mostly oxidized lignin) is separated from the pulp and oxidized with oxygen at high temperature. The reduced POM catalyzes the destruction of the organic material, converting it to carbon dioxide and water. At the same time, the oxidized form of the POM is regenerated and can be used again for bleaching. From an environmental standpoint, this conceptual process is extremely attractive, since it emits only carbon dioxide and water and uses no chlorine compounds. However, considerable engineering development is still needed to realize the extremely high POM recoveries that would be needed to make it economically feasible.

See also: **Packaging, Recycling and Printing**: Paper Recycling Science and Technology. **Pulping**: Chemical Additives; Chemical Pulping; Environmental Control; Mechanical Pulping; New Technology in Pulping and Bleaching.

Further Reading

- Dence CW and Reeve DW (eds) (1996) Pulp Bleaching: Principles and Practice. Atlanta, GA: TAPPI Press.
- Hatch RS (ed.) (1953) *The Bleaching of Pulp*. TAPPI monograph series no. 10. Atlanta, GA: TAPPI Press.
- McDonough TJ (1986) Oxygen bleaching processes. *Tappi Journal* 69(6): 46.
- McDonough TJ (1992) Bleaching agents, pulp and paper. In: Howe-Grant M (ed.) *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edn, vol. 4, pp. 301–311. New York: John Wiley.

- McDonough TJ (1998) The revolution in bleached chemical pulp manufacturing technology. In: Turoski V (ed.) Chlorine and Chlorine Compounds in the Paper Industry, pp. 3–23. Chelsea, MI: Ann Arbor Press.
- McDonough TJ (2000) Pulping and bleaching technologies for improved environmental performance. In: Springer A (ed.) *Industrial Environmental Control, Pulp and Paper Industry*, Chapter 13. Atlanta, GA: TAPPI Press.
- Rapson WH (ed.) (1963) *The Bleaching of Pulp*. TAPPI monograph series no. 27. Atlanta, GA: TAPPI Press.
- Rydholm SA (1965) *Pulping Processes*. New York: Interscience.
- Singh RP (ed.) (1979) *The Bleaching of Pulp*. Atlanta, GA: TAPPI Press.
- Tench L and Harper S (1987) Oxygen bleaching practices and benefits: an overview. *International Oxygen Delignification Conference Proceedings*, pp. 1–11. Atlanta, GA: TAPPI Press.

New Technology in Pulping and Bleaching

R H Atalla, R S Reiner and C J Houtman, USDA, Madison, WI, USA

E L Springer, University of Wisconsin, Madison, WI, USA

Published by Elsevier Ltd., 2004

Introduction

Innovation in advancing technologies for production of pulp and paper has been driven, by and large, by the needs to reduce the environmental impact of pulp mills or to enhance the yield in processes of conversion of wood to fibers. 'Fiberization' of wood chips is carried out in two categories of processes. One, chemical pulping, relies on removing the lignin that binds the cellulose fibers together by chemical delignification processes. The other is based on mechanical fiberization of the wood while retaining much of the lignin. The resulting pulps have significantly different properties. The chemical pulps are used in the manufacture of paper or packaging materials that require the fibers to have excellent mechanical properties or to have high brightness for the manufacture of fine papers. The mechanical pulps are used as fillers or in the manufacture of papers that do not require fibers of high strength. Some chemical pulps are also used as a source of high-purity cellulose for the manufacture of cellulose derivatives or for the production of regenerated cellulose fibers. We will touch upon some advances in both arenas.