Chapter 4

Pulp Bleaching Technology

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THE BLEACHING PROCESS

Bleaching is the treatment of cellulosic fiber with chemicals to increase brightness (see box 4-A). Brightness may be achieved by either lignin removal (delignification) or lignin decolonization. Lignin remains a major constituent of pulp even after digestion by chemical pulping. For example, kraft pulp may contain up to 6 percent lignin based on its dry weight.[1] Unbleached groundwood spruce pulp may contain 27 percent lignin.

If chemical pulping removes the lignin from wood fibers, why then does some lignin remain after the pulping process? The strength of paper is largely due to the chemical bonds (hydrogen bonds) formed between cellulose fibers. Although longer and more severe pulping might remove more of the lignin, thus reducing the amount of bleaching needed, the cellulose molecules might be degraded and their bonding power diminished. Should this happen, the strength of the pulp would be reduced. The removal of lignin by bleaching is regarded as a continuation of the pulping process, albeit somewhat gentler and less destructive, but bleaching too can degrade cellulose if done improperly.

Lignin imparts a color to the raw pulp (hence its name “brown stock”) and unless removed, will continue to darken with age (note the yellowing, darkening, and enbrittlement of newspaper exposed to sunlight). Bleaching by removing the lignin gives higher brightness to the paper than is possible by leaving the lignin in the pulp and brightening by decolonization, and also leads to a more durable and stable paper.

In addition to the removal and decolonization of lignin, bleaching serves to clean the pulp of dirt and foreign matter that escaped the digestion process. Bleaching also removes hemicellulose and extractives (hemicellulose is nearly completely removed for the production of dissolved pulps). Bleaching pulp adds significantly to its value as market pulp because the demand for bleached paper is increasing.

Historical Development of Bleaching Technology

Bleaching of fibers for decolonization has been practiced since early times. Sunlight was one of the earliest bleaching agents. Japanese paper makers were known to bleach fibers by soaking them in water from high mountain streams that contained ozone (the first use of oxygen for bleaching). In 1774, Karl Wilhelm Scheele discovered chlorine and its bleaching action on vegetable fibers. Several years later in 1799, Charles Tennant invented ‘ ‘bleaching powder’ (calcium hypochlorite), thereby converting chlorine to an easily transportable form. For the next 130 years it remained the only available bleaching agent. The first time a U.S. paper mill used chlorine for bleaching was in 1804.

Rapid developments in bleaching technology occurred between 1900 and 1930. Multistage bleaching using calcium hypochlorite followed by an alkaline extraction stage, then a repeat of the hypochlorite bleach stage was first adopted by the industry. Later, technologies that allowed the use of gaseous chlorine began to displace hypochlorite in the first bleach stage. The use of chlorine reduced bleaching costs. New equipment developments further improved bleaching efficiency.

Improvements in the manufacture of chlorine dioxide and dioxide bleaching technology were developed in the 1940s. By the 1950s, these developments led to the adoption of the five-stage bleaching sequence that is still used extensively in the industry: (1) chlorine+(2) alkaline extraction→(3) chlorine dioxide→(4) alkaline extraction→(5) chlorine dioxide. The five-stage bleaching sequence allowed very bright pulp to be produced with minor losses in fiber strength.

Oxygen bleaching was discovered in 1952 by V.M. Nikitin and G.L. Akim in the Soviet Union. In the late 1960s, oxygen bleaching was commercialized, followed by the installation of the first displacement bleach plant in the 1970s. This resulted in more rapid bleaching by displacing chemicals through a pulp mat rather than mixing the chemicals

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[1] Douglas W. Reeve, “The Principles of Bleaching, 19/37 *Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. 3.

Box 4-A—What Is Pulp "Brightness"? How Is It Measured?

"Brightness' is the reflecting properties of a sheet of pulp. It is *a physical* and measurable phenomenon. Some mistakenly equate "whiteness" with brightness, but whiteness is a *physiological* phenomenon, measured subjectively by the impression and perception of the human eye. For instance, if blue dye is added to a lightly yellow tinted paper, the sheet will *look* whiter but the sheet will *measure less* reflected light (less brightness).

Since reflectance is affected by the nature and the angle of incident light, the surface properties of the pulp sheet, and other factors, the measurement of brightness has been standardized: Brightness is the reflectance of blue light with a spectral peak at 457 millimicrons from an opaque sample of pulp sheets compared to a specified standard surface.

There are two recognized methods for measuring pulp brightness in North America: 1) the TAPPI method (Technical Association of the Pulp and Paper industry), Standard T-452; and 2) the CPPA method (Canadian Pulp and Paper Association).

TAPPI Method

Reported in units of *%GE Brightness.* Illuminating light is aimed at 45 degrees to the sample and the reflected light is measured perpendicular to the sample (90 degrees). Reflectance is compared to magnesium oxide powder (98 to 99 percent absolute reflectance). Calibrated opal glass standards are used for routine measurements.

CPPA Method

Reported in units of ISO *Brightness.* The sample is illuminated with diffused light using a highly reflecting integrating sphere. Reflected light measurement is taken at 90 degrees to the sample. Reflectance is compared to absolute reflectance from an imaginary perfectly deflecting, perfectly diffusing surface. Calibrated opal glass standards are used on a routine basis.

A third brightness standard is used throughout the rest of the world: The Zeiss Elrepho standard. It is measured in units termed *Elrepho Brightness.* GE Brightness is measured with a reflectance meter manufactured by the General Electric Corp., while Elrepho Brightness is measured by an instrument manufactured by Zeiss, the German optical company. Since the two meters have different light geometries, there is no simple relationship between the two measurements. In general, Elrepho Brightness is, on average, 0.5 to 1.0 percent higher than GE Brightness.

with the pulp in the conventional way. Since the late 1970s development has taken place in the use of oxygen enrichment in alkaline extraction stages, to further delignify pulp after extended cooking (modifications of the cooking process to improve delignification), and in short bleaching sequences where oxygen is used to supplement chlorine.

Extent of Bleaching in the Industry

Nearly 55 percent of the chemical pulp currently produced in the United States is bleached (table 4-l). By far the greatest proportion of bleached chemical pulp is produced by the kraft process (about 88 percent of the pulp bleached in 1987 was kraft pulp). Very little mechanical pulp has been bleached in the past, however, this is currently changing. Mechanical pulp bleaching is growing at more than twice the rate of chemical pulp bleaching worldwide and it is likely that this trend will continue in the United States as well.[2] Overall, the tendency has been to bleach more pulp as the demand for products using bleached paper increases (nearly 39 percent of the domestic paper and paperboard currently produced is from bleached pulp).

Bleaching Methods

Bleaching Agents

Pulp cooking can safely dissolve up to about 90 percent of the lignin without degrading the cellulose fiber. Additional delignification is done by bleaching. Bleaching of high-yield chemical pulps is achieved by decolonizing with either an oxidizing agent (combines oxygen) or a reducing agent (combines hydrogen). Chlorine gas, sodium hypochlorite, chlorine dioxide, oxygen gas, and hydrogen peroxide are oxidants. Sodium hydrosulfite is a reductant. Alkali is used to remove the solubilized

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[2] Ibid., p. 2.

Table 4-l-Domestic Bleached Pulp Capacity
(thousand metric tons)

Grade	1971	1987[a]
Bleached sulfite ... , ...	1,774	1,256
Bleached kraft.	13,364	21,259
Dissolving (bleached) ., ...	1,604	1,455
Total chemical pulp produced	32,779	43,800
Percent of chemical pulp bleached . .	51.1%	54.7%

[a] Estimate

SOURCE: Douglas W. Rowe, "The Principles of Bleaching," *1987 Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA. TAPPI Press, 1987), p. 2.

lignin from the cellulose. Each has its advantages, disadvantages, and limitations (table 4-2).

Since the 1930s, chlorine gas has been the predominant chemical used for the delignification of pulp. Chlorine dioxide can brighten pulp without damaging the cellulose. Oxygen is comparatively inexpensive and is now coming into its own both for delignification (immediately after digestion and before the bleach cycle) and as a supplement in the first extraction (alkali) stage of the bleach sequence. Hydrogen peroxide is expensive, so it is used much less than other bleaching agents. The effectiveness of a bleaching agent, although a major factor in determining its use in a pulp bleaching sequence, may be offset by the cost of the chemical or the equipment needed to handle it.

A critical determinant in choosing a bleaching chemical is the ''selectivity" of the agent. Selectivity refers to the capacity of the chemical to attack lignin while doing minimal damage to the cellulose fibers. Unbleached pulp (brown stock) contains high levels of lignin, therefore less selective chemicals (e.g., oxygen and chlorine) can be used in the initial stages of the bleach cycle. With further delignification and lower residual lignin content of the pulp, more chemical is available to react with the cellulose and pulp strength may suffer.

Chlorine dioxide and hydrogen peroxide are highly selective, thus they react rapidly with lignin but affect cellulose very little. The highly selective chemicals are generally used in later bleach stages when the lignin content is low and the cellulose is susceptible to degradation. However, both chemicals are expensive and are therefore used sparingly. Sodium hydrosulfite, a reducing agent, and hydrogen peroxide are used for bleaching lignin-rich mechanical pulp.

Table 4-2-Bleaching Chemicals: Form, Function, Advantages, Disadvantages

Chemicals	Function	Advantages	Disadvantages
Oxidants			
Chlorine	Oxidize and chlorinate lignin	Effective, economical delignification	Can cause loss of pulp strength if used improperly
Hypochlorite	Oxidize, brighten and solubilize lignin	Easy to make and use	Can cause loss of pulp strength if used improperly
Chlorine dioxide	1) Oxidize, brighten and solubilize lignin 2) In small amounts with chlorine gas to protect against degradation of pulp	Achieves high brightness without pulp degradation	Must be made at the mill site
Oxygen	Oxidize and solubilize lignin	Low chemical cost	Used in large amounts. Requires expensive equipment. Can cause loss of pulp strength
Hydrogen peroxide . .	Oxidize and brighten lignin in chemical and high-yield pulps	Easy to use. Low capital cost	Expensive
Reductant			
Hydrosulfite	Reduce and decolonize lignin in high-yield pulps	Easy to use. Low capital cost	Decomposes readily. Limited brightness gain
Alkali			
Sodium hydroxide . . .	Hydrolize chlorolignin and solubilize ligin	Effective and economical	Darkens pulp

SOURCE: Douglas W. Reeve, 'The Principles of Bleaching," *1987 Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press), p. 6.

Bleaching Sequences

A combination of bleaching and extracting treatments is generally used for bleaching chemical pulps (box 4-B). The bleaching chemicals and the order in which they are used make up the “bleaching sequence. ” Bleaching sequences generally contain two phases within each sequence: 1) a delignification segment, whose function is to remove the lignin; and 2) a brightening segment, whose principle function is to increase the brightness of the pulp. Examples of delignifaction stages or segments include oxidation by chlorine (C) followed by extraction of the dissolved lignin with sodium hydroxide (E). Brightening segments use sodium hypochlorite (H) and/or chlorine dioxide (D). Oxygen can be used for delignification and for reinforcing extraction of the dissolved lignin in the alkali stage.

Box 4-B-Shorthand for Describing Bleaching Sequences

The pulp and paper industry has developed a series of shorthand descriptors for the multistage bleaching sequences. The following abbreviations are used to designate the bleaching agents:

C	Chlorination
E	Extraction with sodium hydroxide
H	Hypochlorite (sodium or calcium)
D	Chlorine dioxide
P	Hydrogen peroxide
O	Oxygen
N	Nitrogen dioxide
Z	Ozone

Bleaching sequences are designated by listing each treatment serially. For example, “CEDED” represents a commonly used five-stage bleaching sequence consisting of a first-stage chlorine treatment, followed by a second-stage alkali extraction stage, followed by a third-stage chlorine dioxide treatment, followed by a fourth-stage alkali extraction treatment, and a final fifth-stage chlorine dioxide treatment. Washing is conducted between each chemical application.

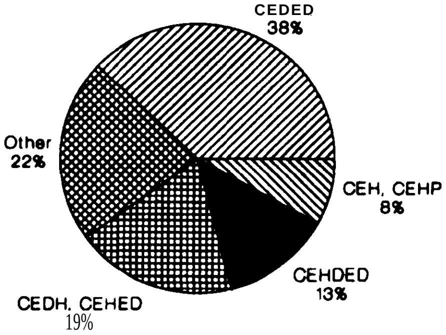
Two bleaching agents may be used in a single stage. For instance, chlorine gas and chlorine dioxide are sometimes combined in an early bleaching stage. If chlorine gas is the predominant agent in the mixture, the treatment would be designated as “C_D.” On the other hand, if the mixture contains more chlorine dioxide than chlorine gas, the treatment would be designated as D_c. Other commonly encountered oxidative extraction treatments include E_O (or E/P), E_P, E/H etc.

Several of the more commonly used bleach sequences in U.S. and Canadian mills are: 1) CEDED, 2) CEDH, 3) CEHDED, 4) CEH, and 5) CED (figure 4-l). Although these are the most prominent bleaching sequences currently in use, an increasing number of mills are now using oxygen in combination with alkali for extraction (E_o), and chlorine dioxide (C_D, D_c) in the chlorination stages. In addition, there area number of unique bleaching sequences used by some mills (e.g., CEHDH, CEHEDP, CEDPD, CEDE$_H$D and CEHCHDED).

Factors Affecting the Bleaching Process

Process engineers and paper chemists have a wide range of chemicals, processes, equipment, and operating conditions to choose from in optimizing a bleaching sequence. Cost of chemicals, capital cost of equipment, energy requirements, and other operating costs figure heavily in bleach plant decisions. While cost control is an important factor, the physical and chemical composition of the wood raw material (furnish) and the desired characteristics (brightness and strength) of the finished paper are often more important in selecting bleaching technologies. Bleaching sequences also depend on the pulping process used for initial delignification, some

Figure 4-l-Bleaching Sequences Used in U.S. and Canadian Pulp Mills



SOURCE: Data from David R. Forbes, “Upgrading Existing Bleach Plants,” 1987 *Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1967), p. 116.

of which leave higher residual lignin levels remaining in the brown stock than do others.

The efficiency of the bleach cycle (related to its cost effectiveness), also depends on controlling the operating environment within each bleaching stage. Bleaching is achieved through chemical reactions. Operating conditions are related to temperature, time, chemical concentrations, and degree of acidity or alkalinity (pH).[3] These factors must be kept in balance to achieve the desired degree of bleaching, while at the same time minimizing damage to the cellulose fiber. In addition, the "consistency" (amount of fiber being bleached in relation to the volume of liquid) of the fiber slurry being bleached affects chemical penetration and therefore must also be controlled. Computerization and improved sensors now allow nearly real-time control over the operating environment in all stages of the pulping and bleaching processes.[4]

Lignin Content— Lignin is a large, complex, organic molecule that still holds mysteries for wood chemists. Complete quantitative analysis of lignin from pulp samples would be expensive if performed with precision. This is not necessary from the standpoint of controlling the digestion and bleaching process, however, as simpler methods have been found. Index systems for ranking the lignin content of wood pulp have been devised by the industry (box 4-C).

The lignin content of unbleached pulp, expressed by its kappa number, determines the amount of bleaching required in the bleach sequence to obtain the brightness desired in the finished pulp. The key is to find the optimum point between cooking and bleaching (i.e., the best kappa number for unbleached pulp). For bleachable grades, kappa numbers of unbleached kraft softwood pulp may range between 20 and 40 and hardwood between 15 and 25 as it leaves the digesters in some mills (kappa number 35 represents approximately 5 percent lignin).

Using modem computer-controlled cooking, appropriate chip pretreatment, and chip equalizing systems, it is now possible for well-run kraft mills to produce unbleached softwood pulp consistently with kappa numbers between 28 and 32.[5] Unbleached hardwood pulps can be produced with kappa numbers between 20 and 25.[6] Pulp can be delignified to extremely low kappa numbers (2 to 4) by using chlorination followed by a alkali/oxygen (E_o) extraction stage.[7]

Lignin and Brightness— The lignin content, kappa number, and brightness of chemical pulps are somewhat interrelated. Since pulp brightness is the major objective of bleaching, measurements of brightness expressed as either GE Brightness or as ISO Brightness (see box 4-A) are often used to track progress through the bleaching sequence.

Unbleached kraft pulp has a very low GE Brightness (10 to 20 percent) because of the high absorption of reflected light by the residual lignin.[8] Kraft pulp can be bleached to a very high brightness of 90 percent GE by decreasing its lgnin content to near zero without affecting the strength of the pulp. It is possible to bleach kraft pulp to a brightness of 91 to 92 percent GE for special papers.[9] Unbleached acid sulfite pulp with GE brightness of about 60 to 66 percent can also be bleached to 90 percent by removing nearly all of the lgnin. Groundwood pulp may have brightness values of about 62 percent GE.

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[3] Rudra P. Singh, ''Principles of Pulp Bleaching," *The Bleaching of Pulp-Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 17.

[4] Thomas J. Boyle and Carr Smith, ''Bleach Plant Instrumentation and Computer Control, " *The Bleaching of Pulp—Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 487 et seq.

[5] Ingemar Croon, Alf de Ruvo, and Gunnar Tarnvik, ''Bleaching of Kraft Pulps: Oxygen Techniques Today and in the Future, ' *Svensk Papperstidning No 4, reprinted* by Sunds Defibrator in English (Stockholm, Sweden: Sunds Defibrator, 1985), p. 2.

[6] Kristina Idner, "Oxygen Bleaching of Kraft Pulp-High Consistency vs. Medium Consistency," *1987 International Oxygen Delinification Conference, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. 197.

[7] N. Liebergott and B. *van* Lierop, "Extraction, Part I: Oxidative Extraction, '' *1987 Bleach Plant Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press), p. 46,

[8] Reeve, op. cit., footnote 1, p. 4.

[9] W. Howard Rapson and Gene B. Stumila, ''Chlorine Dioxide Bleaching,'' *The Bleaching of Pulp, Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. *142.*

Box 4-C—Assessing Lignin Content and Pulp Bleachability

The Technical Association of the Pulp and Paper Industry (TAPPI) has devised two standardized procedures for determining and reporting the lignin content of pulp: 1) Permanganate (K) number (TAPPI Test Method T214), and 2) Kappa number (TAPPI Test Method T236). These indices are used by the industry to control cooking within the digester during pulping and for determining the bleachability of the pulp.

Both methods are chlorine demand tests and are based on the amount of permanganate needed to oxidize the contained lignin, The Permanganate, or K number, is used for determining the bleachability of chemical pulps having lignin contents below 6 percent (based on weight of oven-dry pulp). The kappa number is applicable to all grades of chemical and semi-chemical wood pulps, including higher lignin content pulps with yields as high as 70 percent.

Standard procedures have been established for both bleaching indices. Both are based on the amount of potassium permanganate that can react with dry pulp samples. Most modem pulp mills now use automated, continuous oxidation-reduction measurements or optical devices such as brightness meters for on-line measurements to gauge the progress of delignification and the need for additional bleaching. However, permanganate tests are still used in mill laboratories for verification of the instrument reading.

Bleaching Systems

Bleaching sequences apply various bleaching agents in different orders and combinations. Between each bleaching stage the pulp is generally (but not always) flushed with an alkali extraction solution to remove the dissolved lignin before it is sent to the next bleaching stage (figure 4-2). The first step of a bleaching sequence is designed to remove the bulk of the residual lignin (delignification) and involves little or no improvement in the brightness of the pulp (figure 4-3). This step, along with the following extraction stage, is called “prebleaching.” The purpose of prebleaching is to remove as much lignin from the pulp as possible to minimize the volume of more expensive bleaching chemicals (e.g., chlorine dioxide, hypochlorite, and hydrogen peroxide) needed in subsequent bleaching stages.

Chlorine gas and sodium hydroxide (CE) have been the preferred chemicals for the prebleach stage of the bleaching process. More recently, mixtures of chlorine and chlorine dioxide have been used in place of (or in addition to) pure chlorine treatment (table 4-3).[10] Other prebleaching processes are slowly displacing CE as the first stages of the bleach sequence at some mills. Prebleach oxygen delignification and extended cooking may shorten the bleaching sequence by reducing the amount of lignin carried forward to the bleaching process.[11]

Impetus for considering alternatives to the conventional CE stage are based partially on reducing the cost of bleach plant operations and partially on concerns about environmental impacts from discharged bleaching effluents. These concerns result from detection of chlorinated organic material containing chloroform and dioxins in bleached pulp mill sludge. Most of the chlorinated organics contained in bleach plant effluent originate from the first chlorine, alkaline extraction, and hypochlorite stages.

Brightening stages that follow prebleaching remove less lignin but bring out the brilliance of the pulp through bleaching action. The brighter the pulp desired, the more bleaching stages that must be used (table 4-2). Mill operators have a number of mix-and-match brightening processes to chose from for final bleaching. Choices are largely determined by the relative costs and efficiencies of the bleach options and the required brightness of the pulp being produced. The entire bleaching sequence is then a combination of the prebleaching stages and the brightening stages.

Prebleach Delignification

Chlorination-Chlorine selectively reacts with lignin and under normal bleaching conditions does little harm to cellulose fibers. Because of its relative

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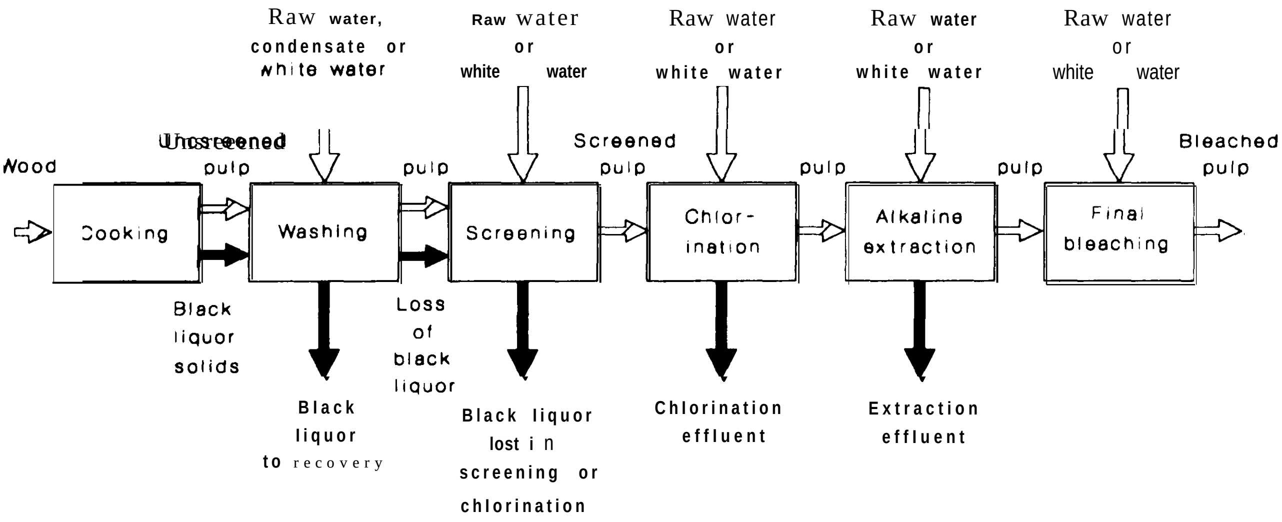
[10] Rudra P. Singh and Edward S. Atkinson, “The Alkaline Extraction,” *The Bleaching of Pulp, Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 89.

[11] Johan Gullichsen, “The Past and Future of Pulp Bleaching,” 1987 *Bleach Plant Operations Seminar, TAAPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. 19.

Figure 4-2-Sequence for the Production of Fully Bleached Chemical Pulp



SOURCE: Carlton W. Dence and Goran E. Annergren, “Chlorination,” *The Bleaching of Pulp, Third Edition* (Atlanta, GA: TAPPI Press, 1978), p. 51.

cheapness in comparison with other bleach chemicals it became widely used for delignification after the pulping process. Chlorination in the prebleach cycle begins with washed brown stock pulp slurry at low consistency (3 to 5 percent weight of pulp to water) being pumped into a chlorination mixer. Chlorine gas, which is often dispersed in water, is added to the pulp slurry in the mixer and is vigorously mixed (figure 4-4).

The reaction between chlorine and lignin begins immediately in the mixer, and the reaction is completed in a chlorination tower designed to give the proper retention time. If chlorination is conducted at low temperatures (5 to 45 “C) retention time may range between 15 and 60 minutes. Higher temperatures reduce the time necessary to complete the chemical reaction. The chlorinated pulp is washed before being sent to the alkali extraction stage.

Chlorination is sometimes repeated after extraction if additional delignification is needed, but because of possible cellulose damage a chlorine dioxide stage is often used. Throughout the process brightness, kappa number, and other indicators of pulp quality are monitored.[12]

There is a trend toward modification of the first chlorination stage by including other bleaching agents (e.g., chlorine dioxide, with the chlorine charge). Inclusion of these chemicals can reduce cellulose degradation, improve pulp strength, and reduce environmental releases. Chlorine dioxide is sometimes used sequentially preceding the chlorine treatment and has been shown to be more effective than when the two chemicals are mixed. ’s Chlorine dioxide can be used to completely replace chlorine in the first delignification stage, but its gains in pulp quality do not offset the additional expense, and pulp brightness equivalent to t-hat produced by chlorine can not be achieved.[14] Pretreatment with sodium hypochlorite prior to chlorination has improved the delignification of resinous woods.

Alkaline Extraction-Hot alkaline extraction is the second stage in the pulp bleaching process and completes the prebleaching delignification process.

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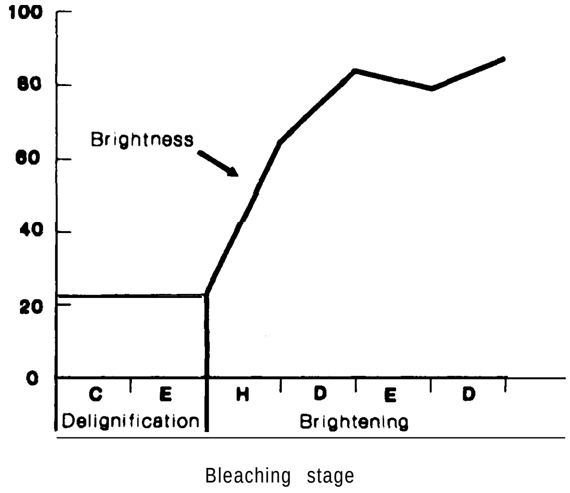
[12] Douglas W. Reeve, ‘‘Pulp Chlorination,’ *1987 Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. 37.

[13] Carlton W, Dence and Goran E. Annergren, “Chlorination,” *The Bleaching of Pulp, Third Edition* (Atlanta, GA: TAPPI press, 1979), p. 65.

[14] Douglas C. Pryke, ‘‘Chlorine Dioxide in the Chlorination Stage,’’ *1987 Bleach Plant Operation Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. 55.

Figure 4-3-Pulp Brightness at Stages of the Bleaching Sequence CEHDED



SOURCE: N. Liergott and B. Van Lierop, "Oxidative Bleaching A Review: Part 1: Delignification," *Pulp & Paper Canada*, vol. *87, No. 8,* 1986, p. 58.

Moderate temperature or cold temperature alkaline extraction is also used after later bleach stages in the brightening process of multistage bleaching sequences. Cold alkaline extraction is particularly important in the production of dissolving pulps for the manufacture of rayon and acetate. Alkaline extraction removes the soluble colored components and lignin released in the preceding delignification stage (chlorination or oxygen), therefore reducing the amount of bleaching chemicals needed in subsequent stages and improving the durability of the pulp.

Sodium hydroxide has been shown to be the most efficient alkali for decreasing the kappa number of pulp. Efficient extraction is nearly as important as prebleach delignification in the first bleaching stage. For instance, after chlorination and washing, but before alkaline extraction, about 30 to 50 percent of the chlorinated lignin in removed. After alkaline extraction, 80 to 90 percent of the lignin is removed.[15] A second hot alkaline extraction is sometimes used later in the bleach sequence after bleaching with chlorine dioxide or sodium hypochorite (e.g., CEHED, CEHDED, or CEDED sequences) to improve pulp brightness stability and conserve bleach chemicals. ’b

Table 4-3-Examples of Prebleaching Sequences for Pulp Delignification

CE	Chlorine - Alkali extraction
CDE . . .	(Chlorine+ Chlorine dioxide) - Alkali extraction
CE_O . . .	Chlorine - (Alkali + Oxygen extraction)
OC_DE . .	Oxygen - (Chlorine + Chlorine dioxide) - Alkali extraction
DCE . . .	Chlorine dioxide - Chlorine - Alkali extraction

SOURCE: Douglas W. Reeve, "The principles of Bleaching," *1987 Bleach Plant Operations* Seminar, *TAPPI Notes* (Atlanta, *GA:* TAPPI Press, 1987), p. 10.

The pulp is subjected to the alkaline extraction treatment for 60 to 90 minutes at most mills in the first post-chlorination extraction stage, although some operate on a shorter schedule. The second alkaline extraction usually lasts from 30 to 60 minutes.

The first alkaline extraction stage contributes the largest potential pollutant load released from the pulp bleach plant. It may be possible to reduce the pollutant loss from the extraction stage considerably by substituting oxidative extraction, particularly sodium hypochlorite, for the first alkaline extraction stage (e.g., CHED, bleaching sequences) .17 Sodium hypochlorite added to the sodium hydroxide extraction solution (E_H) may reduce the color (a rough indicator of pollution load) in waste water by about one-half.[18] Even larger reductions in waste water color (about three-quarters) have resulted when hydrogen peroxide is added at the alkaline extraction stage.

Oxidative Extraction-Oxygen gas added to sodium hydroxide in the extraction stage (E_o) decreases the kappa number, conserves chemicals in subsequent bleaching stages (in some cases it can reduce the number of bleaching stages), and reduces pulp strength loss and coloration in the waste Water.[19] Studies have shown that the addition of

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[15] B. van Lierop et al., "Caustic Extraction, Part I: Reaction Variables," 1987 *Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. 44.

[16] Singh and Atkinson, op. cit., footnote 10, p. 91.

[17] Ibid., p. 99

[illegible] and van [illegible] op. cit., [illegible] 7, p. 46.

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other oxidizers, such as hydrogen peroxide or sodium hypochorite, to an E_o extraction stage might allow for a shortened, three-stage bleaching sequence capable of bleaching pulp to high brightness (88 to 90 percent ISO). The E_o extraction stage has gained rapid acceptance since only modest additional investment in new equipment is needed.

Oxygen has been substituted for alkaline extraction immediately after the chlorination stage.[20] If coupled with a following chlorine dioxide bleach stage, the COD sequence can produce fully bleached pulp with major savings in chemicals. A three-stage sequence using oxygen in the second stage following a chlorine dioxide-chlorine delignification stage ((DC)OD) has been used by the Chesapeake Corp. at West Point, Virginia since 1972. The Chesapeake mill was the first commercial application of oxygen in the extraction stage.

Table 4-4-Common Sequences Used To Bleach Kraft Pulp to Various Degrees of Brightness

Range of GE% brightness	Sequence
70-80	CEH
	CEHH
	CHEH
80-85	CEHEH
	CC_HEHH
	CED
	CEHD
85-92	CHED
	CEHDD
	$C\ C_HE\ D_H$
	CEDED
	CEDHED
	$C_DE_OD\ E\ D$
	$O\ C_DE\ H\ D$

SOURCE. Adapted from Allan M. springer, *Industrial Environmental Control: Pulp and Paper Industry (Naw York, NY:* John Wiley & Sons, 19S6), p. 161.

Brightening Stages

Chlorine Dioxide—Chlorine dioxide is very selective in attacking lignin without significantly degrading cellulose, while producing high brightness pulp. In the dioxide bleach stage, chlorine dioxide is generated as a gas at the mill and dissolved in cold water. The aqueous chlorine dioxide solution is mixed with the prebleached pulp, heated to about 70 “C, and is normally held in a reaction vessel for approximately 3 hours.[21]

Because of chlorine dioxide’s high cost, it is most commonly used at or near the end of bleaching sequences (e.g., CEHD, CEHED, CEDED, and CEHDED). Sequences using chlorine dioxide in only one bleach stage generally produce lower brightness pulps.[22] For instance, the CEHD sequence on softwood kraft pulp would probably be limited to 85 percent G.E. brightness. In order to achieve the highest brightness (90+ percent G.E.), two chlorine dioxide stages are generally required (e.g., CEDED and CEHDED sequences). Chlorine dioxide can also be used in conjunction with a hydrogen peroxide bleach stage (CEHDP or CEDPD) to produce 90+ percent G.E. brightness pulp.[23]

Peroxide-Hydrogen peroxide is a very effective cellulose-preserving bleach agent and is well suited for improving the brightness of highly lignified pulps, such as mechanical groundwood or chemimechanical pulps, without significantly reducing its yield. Hydrogen peroxide is an extremely versatile delignifying chemical and has been proposed for use as a chip pretreatment before kraft pulping and as a delignifier in the prebleach stage prior to, or as a substitute for, the C, C_D, or D_c prebleaching stages.[24] It is also used in association with sodium hydroxide in alkaline extraction (E_p) Because of its high cost, hydrogen peroxide is used most often in the later stages of pulp bleaching.

Peroxide is used in the intermediate stages of the bleaching sequence as a replacement for hypochlorite or chlorine dioxide. It is frequently used as the last stage in the bleach sequence where it can add a few points of brightness to the pulp and improve its brightness stability. Peroxide alone is a relatively

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[20] Rudra P. Singh and Bjom C. Dillner, “Oxygen Bleaching, ” *The Bleaching of Pulp, Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 181.

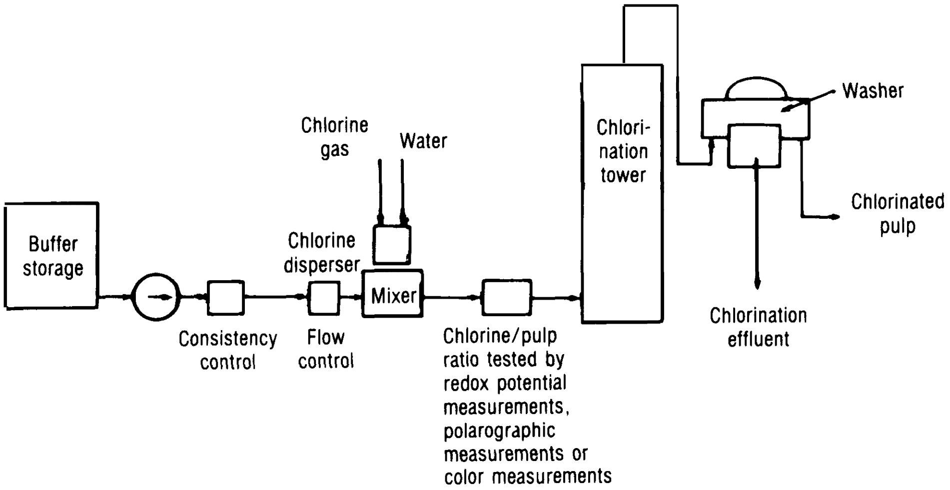
[21] Rapson and Strumila, op. cit., footnote 8, p. 114.

[22] Douglas W. Reeve, “Chlorine Dioxide Bleaching,” 1987 *Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. 67.

[23] Rapson and Strumila, op. cit., p. 1a”

[24] J.R. Presley and R.R. Kindron, ‘Hydrogen Peroxide Bleaching,’ *1987 Bleach Plant Operations* Seminar, *TAPPI Notes* (Atlanta, GA: TAPPI Press, 1987), p, 75.

Figure 4-4-Schematic Diagram of the Chlorination Process



SOURCE, Carlton W. Dence and Goran E. Annergren, "Chlorination," *The Bleaching of Pulp, Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 52,

ineffective means for bleaching krafl pulp.[25] However, when used in sequences with chlorine-based bleaching agents, peroxide is an efficient delignifier and brightner. Peroxide is also used for intermediate bleaching stages of the kraft bleaching sequence or as a final treatment to increase and stabilize the brightness of chemical pulps.[26]

The peroxide bleach liquor is usually in the range of 1 to 3 percent hydrogen peroxide. An appropriate volume of peroxide liquor, sodium hydroxide, and other chemicals to stabilize the peroxide are mixed with pulp and heated with steam to the reaction temperature (35 to 70 ‘C). The peroxide-pulp mixture is allowed to react under controlled temperature for an optimum time (1 to 5 hours). When the reaction is complete, the pulp is washed and sent to the next bleaching stage or washed and neutralized with sulfur dioxide if it is the final bleach stage.

Peroxide, coupled with oxygen and/or ozone, shows some promise in research laboratory evaluations for formulating chlorine-free bleach sequences to reduce release of chlorinated organics in the waste stream. A three-stage sequence OZP (oxygen, ozone, peroxide) has yielded brightness values of 85 percent GE in eucalyptus kraft pulp.[27] However, the pulp suffered a substantial loss in tear strength, The ZP bleaching sequence produced southern pine oxygen pulps of 80 percent GE brightness with good brightness stability. In contrast to peroxide and oxygen bleaching, ozone bleaching has not been developed to the point of commercialization.

Hypchlorite—The use of hypochlorites for bleaching wood pulp began in the early 1880s. Although the development of chlorine bleaching technology in the 1900s led to a decrease in the use of sodium and calcium hypochlorite, still about 40 percent of the kraft pulp mills in the United States and Canada use at least one hypochlorite stage in their bleach sequence. Hypochlorites have been used effectively on sulfite pulps where an alkaline extraction stage is interposed with two hypochlorite stages (HEH),[28]

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[25] D.H. Andrews and R.P. Singh, “Peroxide Bleaching, ” *The Bleaching of Pulp, Third Edition* (Atlanta, GA: TAPPI Press, 1987), p, 237.

[26] Ibid., p. 212.

[27] Ibid., p. 243,

[28] Lee E, Larsen and H, deV. Partridge, “Bleaching With Hypochlorites,'' *The Bleaching of Pulp, Third Editions* (Altanta, GA: TAPPI Press, 1979), p. 101.

Kraft pulps, being more difficult to bleach than sulfite pulps, require that a chlorine and alkaline extraction stage be added in the prebleach segment of the bleach sequence. Until chlorine dioxide and peroxides became available in the 1940s, kraft pulps of 85 percent GE brightness were the brightest that could be produced with hypochlorite bleaching and still maintain acceptable pulp strength, but these pulps had poor brightness stability.

Hypochlorite is nonspecific, that is, it attacks cellulose as well as lignin, therefore it requires careful control if a reduction in pulp strength is to be avoided.[29] Bleaching sequences such as CEHD, CEHED, and CEHHD are used widely for producing pulps of 86 to 88 percent GE brightness, CEHDED is used for pulps of 88 to 90+ percent GE brightness, and CEHDP and CEHEDP for pulps of 90 percent GE brightness using peroxides. Hypochlorite is also used in small amounts for oxidative extraction (see above). Some mills use hypochlorite as a replacement for the first alkaline extraction stage to reduce the color in bleach plant effluent.[30]

Retention times and chemical concentrations vary for hypochlorite bleaching depending on which stage it is being used in the bleaching sequence. Retention times range from a low of 30 minutes at some mills to 3.5 hours for those using hypochlorite in the brightening stage. Reaction temperatures for hypochlorite stages are generally kept low (85 to 110 ‘F) to minimize cellulose degradation.

A “simplified bleaching” process for hypochlorite has recently been developed.[31] Simplified bleaching uses a short (l O-minute) bleach cycle at higher temperatures than normally used (180 ‘F). The hypochlorite treated pulp is sent without washing to a chlorine dioxide stage. This ostensibly produces pulps of higher brightness at lower cost.

Studies have shown that one of the largest contributors to the environmental release of chloroforms from a bleach plant is the effluent from the hypochlorite stage.[32] It is hypothesized that chloroform is produced under specific conditions existing in the hypochlorite stage rather than simply as the result of chlorine-based chemicals. The specific conditions and reactions contributing to the production of chloroform are not well known, however, and more research is needed to establish causation. These early findings of the linkage between hypochlorite reactions and chloroform production has led some to propose that the release of chloroform compounds from pulp mills could be reduced by eliminating the large-scale use of hypochlorite in the bleach sequence.

Ozone-Ozone is one of the most powerful bleaching and oxidizing agents. It is a special form of oxygen produced by the discharge of an electrical current in oxygen gas. While oxygen atoms normally occur in pairs, the electrical discharge makes three atoms associate with one another, thus giving extraordinary oxidative properties to ozone. Its decomposition to oxygen after bleaching produces neither a residue, nor undesirable inorganic byproducts. Ozone, in a bleaching sequence with hydrogen peroxide, can produce high-brightness pulps. Ozone is not used commercially for pulp bleaching. Some pilot plant studies have been conducted, but additional development work would be needed to permit its widespread commercial use.

Ozone, in conjunction with preliminary oxygen delignification, holds promise for reducing the amount of chlorine and hypochlorite used in the prebleach and brightening stages of the bleaching sequence. Ozone bleaching is particularly well suited to bleaching sulfite pulps because of their low residual lignin content.[33] High-brightness, high-quality, hardwood kraft pulps can be produced by using ozone in the first stage of the bleaching

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[29] E.B. Althouse, J.H. Bostwick, and D.K. Jain, “Using Hydrogen Peroxide and Oxygen to Replace Sodium Hypochlorite in Chemical Pulp Bleaching, ’ *TAPPI J*, *vol. 70,* No. 6, June, 1987, p. 113.

[30] Larsen and partridge, op. cit., p. 102.

[31] R.G. Hise and H.L. Hintz, ‘‘Hypochlorite Bleaching, ” 1987 *Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. *65.*

[32] Ibid.

[33] R. Patt et al., “Laboratory and Pilot Plant Bleaching of Various Pulps With Ozone, ‘‘1984 *Oxygen Delignification Symposium, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1984), p. 33.

sequence (e.g., ZEP, ZEZP, and ZED).[34] Because it is a very powerful and nonselective chemical, its use is usually limited to the early bleaching stages.

Kraft softwood pulps must be delignified, preferably with oxygen or through extended cooking to reduce the need for chlorination in the prebleach segment, before bleaching with ozone. Low kappa number kraft softwood pulps bleached with the OZEP sequence produced pulp comparable in brightness and strength to those produced from the CEHED five-stage sequence.[35] Brighter kraft softwood pulp can be produced with oxygen-ozone-peroxide and/or chlorine dioxide bleaching sequences (e.g., OZEP, OZE$_P$P, OZEPD, OZED, and OZE$_P$D). For the highest brightness, chlorine dioxide was needed in the final bleaching stage,

Ozone is not currently used commercially by the industry. Experimental results and pilot plant operations indicate that ozone might have future promise as an alternative bleaching agent. Further discussion of oxygen-based, nonchlorine bleaching technology, including ozone bleaching, is found in chapter 5.

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[34] Steven S.K. Ow and Rudra P. Singh, "Advances in Ozone Bleaching, Part II: Bleaching of Softwood Kraft Pulps With Oxygen & Ozone Combination," *Oxygen Delignification Syposium, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1984), p. 43,

[35] Ibid., p. 49.