DEVELOPMENTS IN
ENVIRONMENTAL MANAGEMENT 1

# ENVIRONMENTALLY BENIGN APPROACHES FOR PULP BLEACHING

BY
DR. PRATIMA BAJPAI

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Volume 1 Environmentally Benign Approaches for Pulp Bleaching
*P Bajpai*

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# Preface

Pulp and paper production has increased globally and will continue to increase in the near future. Approximately, 155 millions tonnes of wood pulp is produced worldwide and about 260 millions is projected for the year 2010. However, the industry is very capital-intensive, with small profit margins, which tends to limit experimentation, development and incorporation of new technologies into the mills. To be able to cope up with the increasing demand, an increase in production and improved environmental performance is needed as the industry is also under constant pressure to reduce environmental emissions to air and water. During the past decade, no segment of the pulping and papermaking process has received as much attention as the bleach plant. Literally slammed with the discovery in the mid-1980s that the U.S. chemical pulp mills using elemental chlorine and hypochlorite as their primary bleaching agent were discharging unusually high levels of carcinogenic dioxins and furans in their effluent streams, the industry undertook a very rapid process-about-face. The pace increased when further studies definitively tied the presence of these carcinogens to the use of elemental chlorine. Almost overnight most of the bleached chemical pulp mills around the world for that matter, instituted process changes away from elemental chlorine and towards combinations of chlorine dioxide, oxygen, hydrogen peroxide, ozone, peroxy acids and enzyme technologies. The focus of attention in bleaching research continues to be on development of alternatives to chlorine-containing compounds. Most efforts have centered on the oxygen families of chemicals. Metals management development is aimed at increasing the effectiveness or selectivity of expensive chemicals. The continuing pressure to further reduce air and water emissions is driving the development of technology to capture all mill effluents and return them to the process. Controlling the concentration and build-up of impurities in the liquor cycle is of paramount importance as more bleach plant effluents are collected for evaporation and burning. This book examines environmentally benign approaches for pulp bleaching and explores new and emerging bleaching technologies that are moving the industry towards effluent closure.

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# Chapter 1

## Introduction

New pulping and bleaching technology, more stringent effluent regulations, environmental pressure groups and new market demands have had a considerable influence on modern bleaching practices. New bleaching processes are being used and the consumption of different bleaching chemicals has changed. There has been a considerable decrease in the consumption of elemental chlorine in several countries and a steady increase in the consumption of oxygen and hydrogen peroxide. Chlorine dioxide is still an important bleaching agent and is still the only option for bleaching of kraft pulp to full brightness (90% ISO) without affecting the strength properties of the fibre. Paper manufacturers usually prefer elemental chlorine free (ECF) pulp, even if the gap between ECF and totally chlorine free (TCF) bleaching is narrowing. The reason is that ECF pulp is stronger. The move towards ECF bleaching consisted of several modifications of the conventional chlorine bleaching process, namely improved washing before the first bleaching stage, reduced kappa number before bleaching, reduced kappa factor and higher chlorine dioxide substitution in the first bleaching stage, complete elimination of hypochlorite, reinforcement of extraction stage with oxygen ($E_O$) and hydrogen peroxide ($E_{OP}$), higher temperature and pressure, medium consistency technology and efficient chemical mixers and improved process control (Rennel, 1995; Webb, 1994; McDonough, 1995; Albert, 1994, 1995a, 1995b; Axegard et al., 1996; Bajpai, 1996, 1997, 2001; Metcalfe, 1995; Rosa and Pires, 1995; Suntio, 1988; Malinen and Fuhramann, 1995; Folke et al., 1996; Kovacs, 1995; Gleadow et al., 1995; Lovblad and Malmstrom, 1994; Stauber et al., 1995; Eklund, 1995).

In the case of mills having oxygen delignification, the change from conventional bleaching to ECF bleaching was easy, provided they had sufficient chlorine dioxide generation capacity. In the Nordic countries, the conversion was fastest and complete (McDonough, 1995; Rennel, 1995). In other parts of the world, conventional bleaching is still quite extensively used in some mills in parallel with ECF bleaching. For mills still using elemental chlorine, the first step is to convert to ECF bleaching as it allows production of kraft pulps that meet the highest requirements with respect to brightness, brightness stability, cleanliness, strength properties, etc. ECF bleaching results in a higher production cost than conventional bleaching, since chlorine dioxide is more expensive than elemental chlorine (McDonough, 1995). Many mills, whether they use conventional or ECF bleaching, also produce TCF pulps in campaigns by final bleaching using only hydrogen peroxide. A low to moderately high brightness (about 85% ISO) can be achieved by final bleaching with only hydrogen peroxide, provided the pulp has a kappa number not higher than that corresponding to oxygen delignification. Under favourable conditions, an even higher brightness can be achieved. However, the cost is higher.

Peracids, e.g., peracetic acid and peroxymonosulphuric acid (Caro's acid), which belong to the group of chlorine-free bleaching chemicals, are alternatives to ozone in combination with alkaline peroxide. Certain type of hemicellulase enzymes can be used both in ECF and TCF bleaching. The enzymes can facilitate the change from coventional bleaching to ECF bleaching in mills operating with a high kappa number of unbleached pulp or which have a smaller chlorine dioxide generation capacity. In TCF bleaching with peroxide, enzymatic treatment is a cost-effective method for obtaining a higher final brightness. The process modification in delignification and bleaching reduce emissions of oxygen-consuming substances and chloro-organic substances. Future alternatives may include complementary treatments to extended cooking and oxygen delignification. These treatments are activation of lignin before the oxygen stage, treatments with enzymes, washing with hot alkali or other new developments. Bleached chemical pulp has generally been considered as a commodity product, with limited critical characteristics. Traditionally, fully bleached softwood kraft market pulp has been required to suit almost all paper and board grades. The present trend is towards a wider variety of pulp grades with specific properties.

Cost of bleaching chemicals is the most important factor affecting the cost of ECF and TCF bleaching (Rennel, 1996). The kappa number after cooking determines the chemical consumption, which together with unit prices gives the total bleaching cost. In TCF bleaching, the cost of hydrogen peroxide is of great importance, which comprises about 50% of the total bleaching cost. Prices of hydrogen peroxide vary considerably between countries, showing different regional prices of power, which together with oxygen determines the manufacturing cost of ozone. An alternative to ozone could be peracetic acid, the cost of which is also very much dependent on the cost of acetic acid. For ECF bleaching, the most critical item is the cost of chlorine dioxide. But not only the direct bleaching costs of chemicals are of interest. Cooking to low kappa number also reduces the yield.

Extended/modified cooking and oxygen delignification increase the load on recovery systems, and also generate more heat in boilers (Lindstrom, 2003; McDonough, 1995, 1996). In addition, oxygen delignification results in a lower kappa number before bleaching and thus gives cost savings in bleaching. It is interesting to note that the development in pulping towards lower kappa number ahead of the bleaching system has had a major impact on the capacity demand in the recovery area and, consequently, also the investment and the capital costs.

Effective reduction of dissolved organics in effluent is not obtained with the current TCF technology. Also, there are problems caused by the discharge of inorganic chemicals, such as nutrient compounds. It cannot be argued that TCF pulps or their end products are more environmentally friendly than those from the ECF process. Bleach plant emissions are strongly influenced by process conditions. A low kappa number after cooking and oxygen delignification and 100% chlorine dioxide substitution, i.e. ECF bleaching, results in a very low adsorbable organic halogen (AOX) level and many pollutants are below the detection limit. However, external treatment may be required to eliminate chlorate in ECF effluent. Higher removal of BOD, COD, AOX, EOX, and specific chlorinated compounds in ECF bleaching effluents is obtained in biological effluent treatment systems. The better removal of chlorinated compounds is due to the low degree of chlorination of the organic material (occurring mainly as mono and dichlorinated compounds). From biological testing and field studies, it seems safe to conclude that ECF bleaching followed by biological effluent treatment would result in a harmless environmental impact. Investigations reveal that ECF/TCF effluents even before treatment show very low acute and subacute toxicity, much lower than that of chlorine bleaching. TCF effluents show slightly lower toxicity than ECF effluents, and natural wood compounds (e.g., extractives) may be responsible for the remaining biological effects (Rennel, 1995).

In the bleach filtrate closure race, significant progress has been made by both ECF and TCF camps. Several TCF mills in Scandinavia have successfully closed the loop, while ECF mills have been equally successful, particularly *Champion International's Canton*, NC, mill (Johansson et al., 1995; Ahlenius et al., 1996; Maples et al., 1994; Manolescu, 1995; Annergren, 1996; Canovas and Maples, 1995). However, environmentalists feel uneasy about effluent closure of ECF mills. They fear the release of organochlorine compounds in various forms into the atmosphere via chemical recovery boiler stacks. ECF mills claim the same unknowns for the closed TCF processes. Either way, effluent closure will likely continue to fuel future bleaching developments, and more totally effluent free (TEF) pulps can be expected in the industry's marketplaces well into the next century.

Some industry observers see a possible melding of ECF and TCF approaches in the near future, combining into various D–Z or Z–D sequences. This will most likely occur, some predict, as mills face the expensive replacement or upgradation of aging chlorine dioxide generation systems as the costs of ozone generation come down. This book reviews environmentally benign approaches for pulp bleaching that can help solve some of the problems associated with the conventional bleaching technologies.

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# Chapter 2

## General backgrounds

### 2.1 Pulping and bleaching

The two major alkaline processes for producing chemical pulps are the alkaline sulphate or 'kraft' process and the soda process (Smook, 1992; Reeve, 1996a). In both these processes, wood chips are cooked with sodium hydroxide in order to dissolve the lignin that binds the fibres together. Sodium sulphide is an additional component of the pulping chemical mix in the kraft process. Both processes are named according to the regeneration chemicals used to compensate for sodium hydroxide: sodium sulphate and sodium carbonate. The kraft process is not only the dominant chemical pulping process but also the most important overall in terms of the various production methods. The soda process is important largely in the production of non-wood pulps. Various modifications to the kraft and soda processes have been devised in order to attempt to overcome low pulp yields and environmental problems. These generally involve the addition of chemicals to the digest liquor. The most important of these is anthraquinone (AQ). The benefits of AQ pulping include increased delignification rates together with reduced alkali charges and improved pulp properties.

An integral and economically vital part of alkaline pulping mill operations is the regeneration of the cooking liquors (Minor, 1982). The recovery cycle is well defined for the kraft process and is designed to recover pulping chemicals, reduce water pollution by combusting organic matter in the spent liquor, generate process heat and recover valuable by-products. The main steps in the process are the evaporation of the black liquor drained from the digester after wood chip digestion, combustion of the concentrated liquor to produce a mineral 'smelt', causticisation of the smelt and regeneration of the lime used in the process. The energy content of the black liquor is high. Gullichsen (1991) notes that half of the wood is dissolved during the manufacture of chemical pulp, and this, when combusted in the recovery boiler, provides heat for the plant systems. The heart of the process is the recovery furnace. The black liquor is evaporated to a solids content of between 60%

and 75% using a 5–6 stage system and is followed by direct contact evaporation in which flue gas from the recovery boiler is brought directly into contact with the liquor. Tall oil soaps are recovered during the evaporation stages. Oxidation of the liquor prior to evaporation can be carried out to reduce the emission of malodorous compounds. When the black liquor is concentrated, sodium sulphate and other chemicals are added to compensate for those lost in the pulping process. In the recovery boiler, the organic content is combusted to produce heat. Carbon dioxide reacts with sodium hydroxide to produce sodium carbonate. The added sodium sulphate is reduced to sodium sulphide and hence the solid smelt produced by the boiler contains largely sodium carbonate and sodium sulphide. This is dissolved in a tank to produce the green liquor, which is subsequently filtered and treated with calcium hydroxide (slaked lime) to convert the sodium carbonate into sodium hydroxide. The resulting white liquor is then returned to the digestion process. The lime is regenerated by heating and mixing with water removed from the green liquor. This process is, therefore, theoretically closed in relation to water use but not with respect to atmospheric emissions, spills and condensate generation.

Pulps produced by the kraft process are characterised by good strength properties. They are, therefore, the preferred grades in strong paper grades such as the liner in corrugating boards or bag and wrapping papers. Hardwood kraft pulps are used in many printing papers for bulking purposes, in mixture with softwood pulps. The residual lignin present in the pulp is expressed in terms of the ‘kappa number’, which is determined by the oxidation of lignin by potassium permanganate under acidic conditions. The lower the kappa number of a pulp, the lower the level of residual lignin. The kraft process is the principal chemical pulping technology used in industry today (around 70% of world production), accounting for the most recent growth in world wood pulp supply. In The United States, approximately 85% of the pulp is produced by using the kraft process. Like many mature industries, bleached kraft pulp production is capital-intensive and requires large economies of scale to remain competitive. A modern bleached kraft mill has a capacity of 500, 000 tonnes/year, more than two-fold that of 20 years ago. A greenfield mill can cost in excess of US$1 billion, which represents more than US$1 million per employee. As a result, kraft pulp is mainly purchased from the market by papermakers rather than being vertically integrated into production.

Pulps prepared by most pulping processes are too dark in colour to be used for many paper products without some form of bleaching. This is particularly true of pulps derived from alkaline processes, such as the kraft process, which are brown. Unbleached pulps from these processes are used mainly for packaging grades. Pulps from mechanical and sulphite processes are lighter in colour and can be used in products such as newsprint. The sulphite process produces chemical pulps with the lightest colour. The brightness of pulp is widely used as an indication of its whiteness and provides a convenient way of evaluating the results of bleaching processes. Brightness is calculated from the reflectance of sheets of paper made from the pulp, using a defined spectral band of light having an effective wavelength of 457 nm. A disadvantage of this measurement is that the wavelength lies in the violet-blue region of the spectrum and does not adequately measure the optical properties of unbleached and semibleached pulps. Two standard procedures have been developed for the measurement of pulp brightness, the main differences between them being related to the geometry and calibration of the measuring instruments. The results of optical measurements are dependent on the geometry of illumination and viewing. TAPPI (Technical Association of Pulp & Paper Industry) or GE brightness is measured with an instrument in which the illumination of the sample is directional, oriented at 45° to the surface. The most common standard, developed by the International Organization for Standardization (ISO), requires the use of a photometer with diffuse sample illumination. The GE standard uses magnesium oxide as the reference standard, to which a reflectance value of 100% is assigned. The ISO standard uses an absolute reflecting diffuser with a 100% reflectance value. Brightness values obtained from these two methods are expressed as % GE and % ISO, respectively. Because of the differences in geometries of the specified instruments, there is no method for interconverting the brightness values obtained by the two methods. However, there is usually no more than about 2 brightness units difference between the two systems (Bristow, 1994). Brightness levels of pulps can range from about 15% ISO for unbleached kraft to about 93% ISO for fully bleached sulphite pulps.

Bleaching of pulp is done to achieve a number of objectives. The most important of these is to increase the brightness of the pulp so that it can be used in paper products, such as printing grades and tissue papers. For chemical pulps an important benefit is the reduction of fibre bundles and shives as well as the removal of bark fragments. This improves the cleanliness of the pulp. Bleaching also eliminates the problem of yellowing of paper in light, as it removes the residual lignin in the unbleached pulp. Resin and other extractives present in unbleached chemical pulps are also removed during bleaching, and this improves the absorbency, which is an important property for tissue paper grades. In the manufacture of pulp for reconstituted cellulose, such as rayon and for cellulose derivatives, such as cellulose acetate, all wood components other than cellulose must be removed. In this situation, bleaching is an effective purification process for removing hemicelluloses and wood extractives as well as lignin. To achieve some of these product improvements, it is often necessary to bleach to high brightness. Thus, high brightness may in fact be a secondary characteristic of the final product and not the primary benefit. It is therefore simplistic to suggest that bleaching to lower brightness should be practised based on the reasoning that not all products require high brightness.

The papermaking properties of chemical pulps are changed after bleaching. These changes have been reviewed by Voelker (1979). Removal of the residual lignin in the pulp increases fibre flexibility and strength. On the other hand, a lowered hemicellulose content results in a lower swelling potential of the fibres and a reduced bonding ability of the fibre surfaces. If bleaching conditions are too severe there will be fibre damage, leading to a lower strength of the paper. The purpose of bleaching is to dissolve and remove the lignin from wood to bring the pulp to a desired brigthness level (Reeve, 1989, 1996a; Farr et al., 1992; Fredette, 1996; McDonough, 1992). Bleaching is carried out in a multi-stage process that alternate delignification and dissolved material extracting stages. Additional oxygen- or hydrogen peroxide-based delignification may be added to reinforce the extracting operation. Since its introduction at the turn of the century, chemical kraft bleaching has been refined into a stepwise progression of chemical reaction, evolving from a single-stage hypochlorite (H) treatment to a multi-stage process, involving chlorine ($Cl_2$), chlorine dioxide ($ClO_2$), hydrogen peroxide and ozone ($O_3$). Bleaching operations have continuously evolved since the conventional CEHDED sequence and now involve different combinations with or without chlorine containing chemicals (Rapson, 1979; Reeve 1996a). The common compounds used in kraft bleaching, together with their symbols, are listed in Table 2.1.1.

The introduction of $Cl_2$ and $ClO_2$ in the 1930s and early 1940s, respectively, increased markedly the efficiency of the bleaching process (Rapson, 1979; Reeve 1996a). Being much more reactive and selective than hypochlorite, $Cl_2$ had less tendency to attack the cellulose and other carbohydrate components of wood, producing much higher pulp strength. Although it did not brighten the pulp as hypochlorite, it extensively degraded lignin, allowing much of it to be washed out and removed with the spent liquor by

**Table 2.1.1 Chemicals used in bleaching processes**

| Symbol | Chemical | Symbol | Chemical |
|---|---|---|---|
| C | Chlorine | Z | Ozone |
| D | Chlorine dioxide | E | Sodium hydroxide |
| H | Hypochlorite | X | Enzymes |
| O | Oxygen | Q | Chelating agents |
| P | Hydrogen peroxide | A | Acid |

subsequent alkaline extraction. The resulting brownish kraft pulp eventually required additional bleaching stages to increase brightness, which led to the development of the multi-stage process. Chlorine dioxide, a more powerful brightening agent than hypochlorite, brought the kraft process efficiency one step further (Rapson, 1979; Reeve, 1996a). Between the 1970s and 1990s, a series of incremental and radical innovations further increased the efficiency of the process, while reducing its environmental impacts (Reeve, 1996b). Development of oxygen delignification, modified and extended cooking, improved operation controls, e.g., improved pulp and chemical mixing, multiple-splitted chlorine additions and pH adjustments increased the economics of the process and led to significant reduction of wastewater (McDonough, 1995; Malinen and Fuhramann, 1995). In addition, higher $ClO_2$ substitution, lowered significantly the generation and release of harmful chlorinated organic compounds. Table 2.1.2 details different considerations

**Table 2.1.2 Functions and economic and technological implications of bleaching agents**

| Oxidant symbol | Code/form | Function | Advantages | Disadvantages |
|---|---|---|---|---|
| C | $Cl_2$ gas | Oxidize and chlorinate lignin | Effective, economical | Can cause loss of pulp strength |
| O | $O_2$ gas used with NaOH solution | Oxidize and solubilize lignin | Low chemical cost, provide chloride-free effluent for recovery | Large amount required, expensive equipment, can cause loss of pulp strength |
| H | $Ca(OCl)_2$ or NaOCl | Oxidize, brighten and solubilize lignin | Easy to make and use | Can cause loss of pulp strength if used improperly, expensive |
| D | $ClO_2$ | Oxidize, brighten and solubilize lignin | Achieves high brightness without pulp degradation, good particle bleaching | Expensive, must be made on-site |
| P | $Na_2O_2$ (2–5%) solution | Oxidize and brighten lignin | Easy to use, high yield and low capital cost | Expensive, poor particle bleaching |
| Z | $O_3$ gas | Oxidize, brighten and solubilize lignin | Effective, provides chlorine-free effluent for recovery | Expensive, poor particle bleaching |
| E | NaOH (5–10% solution) | Hydrolyze and solubilize lignin | Effective and economical | Darkens pulp |

Based on Gulichsen (2000) and Reeve (1996a).

that have affected the development and use of the main bleaching chemicals over time. The information contained in the table provides an overview of economic and product quality considerations associated with pulp-bleaching techniques and chemicals. Until recently, it was believed that a 90° brightness could not be achieved without the use of chlorine and chlorine-containing chemicals as bleaching agents. The implementation of modified cooking and oxygen-based delignification impacted on the entire process by lowering the kappa number of the pulp prior to bleaching, thereby reducing further the amount of bleaching chemicals needed. Under tightening regulations and market demands for chlorine-free products, the industry eventually accelerated the implementation of elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching processes, by substituting oxygen-based chemicals to hypochlorite, $Cl_2$ and $ClO_2$, although the timing and scale of these trends have varied between regions (McDonough, 1995).

## 2.2 Bleaching sequences

Single application of chemicals have a limited effect in brightness improvement or in delignification. Multi-stage application of bleaching chemicals can provide much greater benefits. A bleaching sequence for a chemical pulp consists of a number of stages. Each stage has a specific function (Reeve 1996a). The early part of a sequence removes the major portion of the residual lignin in the pulp. Unless this is done, a high brightness cannot be reached. In the later stages in the sequence, the so-called brightening stages, the chromophores in the pulp are eliminated and the brightness increases to a high level. Most bleaching chemicals are oxidizing agents that generate acidic groups in the residual lignin. If a bleaching stage is performed under acid conditions, it is followed by an alkaline extraction to remove the water-insoluble acidic lignin products. Modern bleaching is done in a continuous sequence of process stages utilizing different chemicals and conditions in each stage, usually with washing between stages. The commonly applied chemical treatments and their symbols are as follows:

| | |
|---|---|
| O | oxygen ($O_2$) delignification (reaction with $O_2$ at high pressure in alkaline medium) |
| C | chlorine ($Cl_2$) (reaction with elemental chlorine in acidic medium) |
| D | chlorine dioxide ($ClO_2$) (reaction with $ClO_2$ in acidic medium) |
| (C + D) and (D + C) | mixtures of $Cl_2$ and $ClO_2$ (major component being first listed) |

| | |
|---|---|
| H | hypochlorite (reaction with hypochlorite in alkaline medium) |
| E | alkaline extraction (dissolution of reaction products with NaOH) |
| ($E_O$) | alkaline extraction reinforced with $O_2$ |
| ($E_P$) | alkaline extraction with addition of hydrogen peroxide ($H_2O_2$) |
| ($E_{OP}$) | alkaline extraction with addition of $H_2O_2$ and reinforced with $O_2$ |
| Q | treatment with a metal-chelating chemical |
| A | acid treatment |
| Z | ozone |
| P | alkaline hydrogen peroxide |
| (PO) | pressurized alkaline hydrogen peroxide treatment |
| Pa | peroxyacetic (peracetic) acid |
| Px | peroxymonosulphuric acid |

The practice of designating bleaching stages and sequences using this symbolic shorthand has evolved informally over many years. However, the complexity of modern bleaching practices coupled with variable symbolism has caused misunderstandings regarding bleaching practices. Adherence to standardized guidelines are now necessary to facilitate clarity in technical communication (Reeve, 1996a). The following has been extracted from a comprehensive protocol submitted by the TAPPI Pulp Bleach Committee (Tappi information sheet TIS 0606-21, 1988): (a) a conventional five-stage bleach sequence consisting of chlorination, alkaline extraction, chlorine dioxide, alkaline extraction and chlorine dioxide is designated as CEDED. (b) When two or more bleaching agents are added as a mixture or simultaneously, the symbol of the predominant chemical is shown first, and the symbols depicting all of the added chemicals is enclosed in parentheses and separated by a plus sign. For example, when a lesser percentage of chlorine dioxide is added with chlorine in the chlorination stage, the sequence is designated (C+D)EDED. If chlorine dioxide is the dominant chemical species in the chlorination stage, the designation is (D+C)EDED. (c) When two or more chemicals are added sequentially with mixing in between points of addition, the symbols depicting the added chemicals are shown in order of addition and shown in parentheses. For example, when chlorine dioxide is added before chlorine in the chlorination stage, the designation is (DC)EDED. (d) If the ratio of added chemicals is to be shown, the percentage number should immediately follow the symbol of the designated chemical and should be expressed in terms of oxidizing equivalence. For example, the term (D70C30) indicates sequential addition of 70% $ClO_2$ and 30% $Cl_2$, all expressed as active chlorine (Smook, 1992).

Cost and selectivity are two very important aspects of establishing the proper sequence of bleaching chemicals. Chlorine is less expensive than chlorine dioxide, so chlorine should be used earlier in the sequence where more lignin is present and more chemical is required (Reeve, 1996a). Thus, for greater economy, the preferred sequence is CED instead of DEC. Also, chlorine is less selective than chlorine dioxide, so the former should not be used at the end of the sequence where the lignin content is low and the possibility of degrading carbohydrates is greater (Reeve, 1996a). Thus, to achieve greater selectivity, the preferred sequence is CED instead of DEC. Sulphite pulps and hardwood kraft pulps are 'easier bleaching' than softwood kraft pulps. Both have lower lignin content, and in the case of sulphite pulps the lignin residues are partially sulphonated and more readily solubilized. Consequently, a somewhat simpler process can be used to achieve a comparable brightness level. For softwood kraft pulps, a number of bleach sequences utilizing between four and six stages are commonly used to achieve 'full-bleach' brightness levels of 89–91. Numerous CEHDED and CEDED full-bleach systems are in operation dating from the 1960s and 1970s; sequences more typical of modern mills are (D+C)(E+O)DED and O(D+C)(E+O)D. Lower brightness levels can be achieved with fewer stages. A level of 65 can be easily reached with a CEH or OH sequence. Intermediate levels of brightness can be achieved with CED, DED, OCED, CEHH, CEHD or CEHP. In most cases, each bleaching stage is followed by a washing stage to remove reaction products; and subsequent bleach stages serve the same purpose, while creating additional reaction products. For this reason, the industry has often employed sequences with alternating acid/alkaline stages. Some commonly used industrial bleaching sequences are given in Table 2.2.1. Table 2.2.2 shows non-traditional sequences which are designed to reduce or replace $Cl_2$. ECF bleaching involves replacement of all the molecular chlorine in a bleaching sequence with chlorine dioxide. The term ECF bleaching is usually interpreted to mean bleaching with chlorine dioxide as the only chlorine-containing bleaching chemical. TCF bleaching uses chemicals that do not contain chlorine, such as oxygen, ozone, hydrogen peroxide and peracids. The use of chlorine dioxide and the various chlorine-free chemicals are discussed in detail later.

Gierer (1990) and Lachenal and Nguyen-Thi (1993) have suggested that the main bleaching chemicals can be divided into three categories based on their reactivity. This concept is presented in Table 2.2.3. Each chlorine-containing chemical has an equivalent oxygen-based chemical. Ozone and chlorine are placed in the same category because they react with aromatic rings of both etherified and nonetherified phenolic structures in lignin and also

**Table 2.2.1 Established pulp bleaching sequences showing the predominant role of $Cl_2$ and $ClO_2$ in the industry**

| Pulp type | Sequence |
|---|---|
| Sulphite and Bisulphite Pulp | |
| Three-stages | C-E-H |
| Four-stages | C-E-H-H |
| | C-E-H-D |
| | C-E-D-H |
| | C-C-E-H |
| | C-H-E-H |
| | H-C-E-H |
| | C-E-D-D/H |
| | C+D-E-H-D |
| | E-C-H-D |
| Five stages | C-E-H-D-H |
| | C-C-E-H-H |
| Kraft Pulp | |
| Three-stage, semi-bleached | C-E-H |
| | D/C-O-D |
| Four-stage, partly semi-bleached | C-E-H-D |
| | C-E-H-P |
| | C-E-H-H |
| | C-H-E-H |
| | C-D-E-D |
| | O-C-E-H |
| | O-C-E-D |
| | O-D-E-D |
| | O-D-O-D |
| Five stages | C-E-H-P-D |
| | C-E-H-D-P |
| | C-E-H-E-H |
| | C-E-D-E-D |
| | C-E-D-P-D |
| | C-E-H-E-D |
| | C-H-D-E-D |
| | D-E-D-E-D |
| | C-C/H-E-H-H |
| Six stages | C-H-E-D-E-D |
| | C-E-H-D-E-D |
| | C-E-H-E-H-D |
| | C-E-H-D-P-D |
| | C-E-H-E-D-P |
| | C+D-E-H-D-E-D |
| | O-C-E-D-E-D |
| | O-C+D-E-D-E-D |
| | O-D-E-D-E-D |
| | O-C-D-E-H-D |
| Seven stages | C-H-H-D-D-D-P |

**Table 2.2.2 Bleaching sequences designed to reduce or eliminate the use of chlorine-based compounds and chlorine**

| Application | Bleach sequence |
|---|---|
| Reduced chlorine | (C)-P-H<br>(C)-P-D-H<br>(C)-P-H-D-H |
| Peroxide replacement | P-D-P<br>P-D-H<br>P-H-H<br>P-H-D<br>D-P-D<br>P-H-D-H<br>P-D-P-D |
| Oxygen bleaching | O-P<br>O-D<br>O-H<br>O-P-D<br>O-D-P<br>O-C-P<br>O-H-P<br>O-C-P-D<br>O-D-P-D |
| Ozone bleaching | Z-E-P<br>Z-E-Z<br>Z-E-Z-P |
| Peracaetic acid | P-A-P<br>A-E-A-E-A |
| Others | O-Q-P<br>O-Q-P-P<br>O-Q-P-Z-P |

**Table 2.2.3 Classification of bleaching chemicals**

| Category 1 | Category 2 | Category 3 |
|---|---|---|
| $Cl_2$ | $ClO_2$ | NaOCl |
| $O_3$ | $O_2$ | $H_2O_2$ |

1—reaction with any phenolic group and double bond; 2—reaction with free phenolic group and double bond; 3—reaction with carbonyl groups.
Based on data from Lachenal and Nguyen-Thi (1993).

with the double bonds. Ozone is found to be less selective than chlorine, as it attacks the carbohydrates in pulp. These chemicals are well suited for use in the first part of a sequence, as they are very efficient at degrading lignin.

Chlorine dioxide and oxygen are grouped together because they both react primarily with free phenolic groups. They are not as effective as chlorine and ozone in degrading lignin. Chlorine dioxide is used extensively in the early stages of bleaching sequences as a replacement for chlorine even though it is slightly less effective. The classification is somewhat simplistic in this respect and, moreover, does not take into account that chlorine dioxide is reduced to hypochlorous acid and that oxygen is reduced to hydrogen peroxide during the bleaching reactions. Chlorine dioxide is also used as a brightening agent in the latter part of a sequence. Sodium hypochlorite and hydrogen peroxide react almost exclusively with carbonyl groups under normal conditions. This results in the brightening of pulp without appreciable delignification. The selection of a suitable bleaching sequence based on this classification has been discussed by Lachenal and Nguyen-Thi (1993). An efficient bleaching sequence should contain at least one chemical from each category. A chlorine-based sequence such as CEHD is an example of this principle. An example of a TCF sequence is OZEP; which was proposed by Singh (1979).

## 2.3 Environmental issues in pulp bleaching

Environmental issues have emerged as crucial, strategic factors for western industrial enterprises. Environmental concern and awareness have grown considerably and have been globalized. There have been environmental campaigns on particular subjects, such as industrial use of chlorine, dioxins from pulp bleaching and old-growth forestry. The complexity and sophistication of environmental criteria have increased dramatically in the last two decades. Toxicity testing of bleach plant effluents previously was limited in Canada to the acute toxicity test for rainbow trout. Now, there is a very wide array of biological response tests. There has been a significant increase in the scope and restrictiveness of environmental regulations in the last two decades. Certainly in the next decade more testing will be required to meet even stringent regulations. In the 1970s, regulation of biochemical oxygen demand, suspended solids and the use of acute toxicity tests became common as the main concern of regulators was to avoid killing of fishes and prevent oxygen reduction of receiving waters (Rennel, 1995; Nelson, 1998). In the 1980s, the condition changed, especially after a Swedish study of the Norrsundet mill that discharged effluents into the Baltic sea. Sodergren (1989) and Sodergren et al. (1988) observed considerable effects on fish which were attributed to the presence of organochlorine compounds in the effluent. Later, it was found that the results of the study were misinterpreted because the effect of pulping liquor spills as a source of toxicity was ignored

(Owens, 1991). However, the release of the report resulted in regulatory authorities applying very stringent controls on the discharge of organochlorine compounds from bleached pulp mills thus compelling the industry to develop technology that reduces or eliminates their formation. This resulted in the wider use of processes, such as extended delignification, oxygen delignification, oxygen reinforcement in alkaline extraction stages and the substitution of elemental chlorine with chlorine dioxide (McDonough, 1995). Secondary treatment of effluent became more extensive, as this reduced the amount of organochlorine compounds. The organochlorines (measured as AOX—adsorbable organic halogen) in pulp mill effluents decreased when the above-mentioned technologies were introduced. Testing of effluents of Swedish mills in model ecosystems led to the conclusion that it was not possible to predict the environmental impact of an effluent exclusively on the basis of its AOX content at levels below ~ 2 kg/ton of pulp (Haglind et al., 1993). A laboratory study of effluents from Canadian mill showed that there was no correlation between acute or sublethal toxicity and AOX levels below ~ 2.5 kg/ton (O'Connor et al., 1994). A study by Folke et al. (1996) showed that reduction of the AOX level in various mill effluents below 1.2kg/ton did not result in a further reduction in toxicity (Table 2.3.1). These results showed that this residual toxicity was due to components other than organochlorines. The environmental organization Greenpeace started a campaign in Germany in the late 1980s, which convinced many consumers in the German-speaking region of Europe that use of paper bleached with chlorine chemicals was unwanted (Rennel, 1995). In Germany, the pulp is produced using the sulphite process. Sulphite pulps can be easily bleached without the use of chlorine chemicals. The high-quality pulp purchased from Scandinavia is made by the sulphate process, and at that time bleaching was done with chlorine chemicals. So, the pulp mills in that region were forced to adopt TCF bleaching to maintain their dominance of the bleached kraft pulp market in Germany. The North American industry was not affected by

**Table 2.3.1 Relationship between AOX and the toxicity of various pulp mill effluents**

| AOX (kg/t pulp) | Toxicity (log $TEF_{SA}$) |
|---|---|
| 0.35 | 8 |
| 1.4 | 9 |
| 2.0 | 35 |
| 2.9 | 68 |
| 3.5 | 72 |
| 3.9 | 100 |

Based on data from Folke et al. (1996).

the same need to change to TCF bleaching as it exports very little bleached pulp to Germany. However, in North America, the presence of dioxin (2,3,7,8-tetrachlorodibenzo-*p*-dioxin) in pulp mill effluents, in bleached pulp, and its accumulation in biota near pulp mills were main environmental issues. In Canada, because of the high dioxin content in crabs, fishing grounds were closed (Muller and Halliburton, 1990). The industry rapidly found solutions of reducing/eliminating the formation of dioxins (Berry et al., 1989). It is well documented that increasing chlorine dioxide substitution eliminates 2,3,7,8-TCDD and 2,3,7,8-TCDF to non-detectable levels (Bajpai, 1996, 1997, 2001). Increasing chlorine dioxide substitution also reduces the formation of polychlorinated phenolic compounds. At 100% substitution, tri-, tetra- and pentachlorinated phenolic compounds were not detected (O'Connor et al., 1994). These results for dioxin, furan and polychlorinated phenolic compounds were confirmed in a study of seven Canadian bleached kraft pulp mills using ECF bleaching (NCASI, 1995). An ecological risk assessment of the organochlorine compounds produced with ECF bleaching reached the following conclusions that the environmental risks from these compounds are insignificant at mills bleaching with chlorine dioxide, employing secondary treatment and with receiving water dilutions typically found in North America (Solomon et al., 1993).

To achieve compliance with the Cluster rule, most of the mills in The United States are using 100% chlorine dioxide substitution. The specific limit for AOX is 0.512 kg/t of pulp (annual average). Many studies have investigated the quality of bleaching effluents from ECF and TCF bleaching processes (Nelson et al., 1995; Grahn and Grotell, 1995). The general conclusion from each of these studies is that the differences in toxicity in a wide variety of test species are not significant, and the secondary biological treatment removes toxicity from the effluents. The effluent from a modern bleached kraft pulp mill is found to show a low level of toxicity when subjected to very sensitive tests, such as the induction of mixed function oxygenase (MFO) enzymes in the livers of fish (Hodgson, 1996). There is proof that chlorine compounds are not exclusively responsible for the induction, as it has been shown that an important source of MFO inducers in bleached kraft pulp mill effluents was spent pulping liquor (Martel et al., 1994; Schnell et al., 1993). The chemical compounds causing the induction have not been identified, but wood extractives are supposed to be involved (Martel et al., 1994; Hodson et al., 1994). Hewitt et al. (1996) have found that in Canada, MFO inducers were not removed by secondary treatment of effluents. The residual low toxicity of effluents is one reason for the view that in the long term the only environmentally acceptable pulp mills may be those that have completely closed-cycle pulping and bleaching (Albert, 1996). A number of companies are moving towards closed-cycle bleaching

(Johansson et al., 1995; Ahlenius et al., 1996; Maples et al., 1994; Manolescu, 1995; Annergren, 1996). However, this approach must be used with caution, as it can transfer pollutants from the liquid effluent to air and solid waste.

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# Chapter 3

## Options for environmentally benign bleaching

### 3.1 Oxygen delignification

#### 3.1.1 Introduction

One area that has exhibited dramatic growth over the past few years, has been oxygen delignification or oxygen bleaching (Lindstrom, 2003; McDonough, 1990, 1995, 1996). The terminology depends on where the line is drawn between pulping and bleaching. Oxygen delignification in the prebleaching stages decreases the kappa number prior to chlorination and therefore the effluent load (BOD, COD, colour, AOX, chlorinated phenolics and toxicity to fish) emanating from the bleach plants is reduced. Oxygen delignification involves an extension of the delignification started in the cooking process and provides the bleaching plant with a pulp that has a considerably reduced kappa number. The primary advantages of oxygen delignification coupled with modified bleaching over conventional bleaching include the partial replacement of chlorine-based chemicals (especially chlorine gas) for ECF pulp production; the elimination of all chlorine-based chemicals in TCF sequences; the retainment and the recycling of the extracted organics and chemicals applied in the oxygen stage; the incineration of the recycled organics to generate energy; and the energy savings. Oxygen production requires only 12.5% of the energy of chlorine dioxide expressed as equivalent chlorine (McDonough, 1990, 1995, 1996; Simons and AF-IPK, 1992; Nelson, 1998; Jones, 1983; Gullichsen, 2000; Pikka et al., 2000; Tench and Harper, 1987). The ‘oxygen stage’ was developed in the late 1960s when serious concerns about energy consumption, pollution control and bleach plant effluent discharges began to surface. These concerns were originally directed at reductions in BOD, COD and colour. The major areas of growth for oxygen delignification initially were Sweden in the 1970s and Japan in the 1980s, to save bleaching chemical costs. The late 1980s saw a widespread growth due to the chlorinated organics issue. For TCF production, oxygen is essential to obtain a major decrease in lignin prior to the bleach plant. The choice of oxygen delignification is based on economical, technical and environmental needs at a particular mill. In Scandinavia, the main purpose of oxygen delignification is the reduction in the formation of chlorinated organics, especially chlorinated phenolics, to minimize the biological impact of the bleaching effluent on the environment. Most American and Canadian mills apply oxygen delignification to assist in the economics of bleach plant modernization or expansion, although more and more interest is being placed on the reduction of environmental pollutants (Tatsuishi et al., 1987; Enz and Emmerling, 1987). In Japan, oxygen bleaching is used mainly to lower the bleaching costs.

Oxygen delignification involves reacting the pulp with oxygen under alkaline conditions and then washing to recover the dissolved lignin. This process is usually conducted under pressure, and delignification is normally in the range of 35–50%. This technology is more selective than most extended delignification processes, but may require significant capital investment to implement (Gullichsen, 2000; McDonough, 1990, 1995, 1996; Tench and Harper, 1987). The main benefits of oxygen bleaching are environmental. They derive from the fact that both the chemicals applied to the pulp and the materials removed from the pulp are compatible with the kraft chemical recovery system. This enables the recycling of oxygen-stage effluent to the recovery system by way of the brown stock washers, decreasing the potential environmental impact of the bleach plant. The decrease is roughly proportional to the amount of delignification achieved in the oxygen stage. This applies not only to chlorinated organic by-products, but also to other environmental parameters associated with bleach plant effluents, including BOD, COD, and colour. The decrease in colour, however, is larger than expected on the basis of the lignin removed in the oxygen stage.

The industrial application of oxygen bleaching has expanded very rapidly in recent years. On the basis of on a survey conducted by NCASI (2003), it is estimated that there are at least 252 oxygen delignification installations in operation worldwide with the capacity for producing an estimated 195,561 AD metric tons of pulp per day. The greatest increase in the capacity occurred during the decade 1985–1995, and this was due mainly to the stricter emission limits on liquid effluents imposed on mills by regulatory authorities. Nearly all the chemical pulp mills in Scandinavia use oxygen delignification, whereas in North America less than 50% of the mills have installed this technology (Harrison, 1994; Johnson,1993; Eklund, 1995; Pryke, 1995). Today, North American mills are showing greater interest for the technology, principally because of increased environmental concerns, and also because the application of medium-consistency equipment now provides more process options. As trends away from the use of chlorine and chlorine-containing compounds intensify, both technical and economic considerations will mandate the use of oxygen. Ozone, for example, although possesses certain advantages over oxygen, will probably see application only in conjunction with oxygen. Oxygen will be used to predelignify pulp to the point where the necessary ozone charge becomes small enough to be economical and selective. The technology is used commercially on both softwood and hardwood and is usually applied to kraft wood pulps but can also be used for sulfite, secondary fibre, nonwood, and other pulp types. Fig. 3.1.1 shows the growth trend in this technology since the first installation in 1970 (Lindstrom, 2003; Harrison, 1994; Johnson,1993). It was developed commercially during the late 1960s and early 1970s in Sweden and South Africa. The obstacle preventing earlier exploitation of oxygen as a bleaching agent had been its lack of selectivity. The potential for oxygen and alkali to delignify pulp became apparent from the research of Soviet scientists in the late 1950s (Nikitin and Akim, 1956, 1958, 1960a, b). The researchers obtained satisfactory results with dissolving pulps, but when papermaking pulps were used there were serious problems with degradation of the carbohydrates and a reduction in the tearing strengths of the pulps. A major breakthrough in oxygen delignification occurred in the 1960s when Robert et al. (1966) and Robert (1964) found that the strength properties of pulp could be maintained by the addition of magnesium salts. This made possible the use of oxygen delignification on a mill scale, and the first commercial installation was built in South Africa at SAPPI's Enstra mill in 1970 (Johnson, 1993).

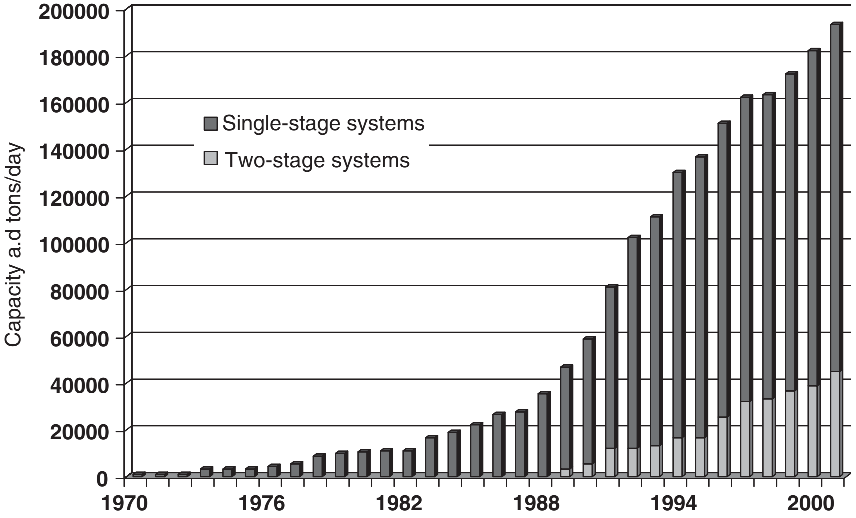

**Fig. 3.1.1. Worldwide production of oxygen-delignified pulp.**

Typically, it is possible to reduce the lignin content by up to 50% in the oxygen delignification stage; further delignification would cause excessive cellulose degradation. A commensurate reduction in the discharge of pollutants is achieved by washing the dissolved solids from the oxygen-delignified stock and recycling them to the pulp mill recovery system. As a result, the total solids load to the recovery boiler will increase significantly, by about 3% with softwood pulp and 2% with hardwood pulp. Since these solids are already partially oxidized, steam generation will increase by only 1–2%. Most kraft mills employing oxygen delignification systems use oxidized white liquor as the source of the alkali in order to maintain the sodium/sulphur balance in the chemical cycle (Leader et al., 1986; Colodette et al., 1990). In most instances, air systems are used for white liquor oxidation because they are more economical to operate, even though the initial capital cost is higher than for oxygen systems. The use of oxidized white liquor increases the load on the causticizing plant and lime kiln by 3–5%.

### 3.1.2 Overview of the process

Fig. 3.1.2 shows the basic process (McDonough, 1996). Pulp discharged from the repulper of the last brown stock washer is passed to a steam mixer and then to a feed tank. Sodium hydroxide or oxidized white liquor is added to the pulp at the base of the feed tank and mixed with the pulp by the discharge pump. The pulp then goes to one or more medium consistency, high-shear mixers where oxygen gas is added together with additional steam. The mixers disperse the oxygen in the pulp, which then passes to an upflow pressurized reactor. After a retention time of about 1 h, the pulp is blown to a gas separator mounted on a blow tank. Unreacted oxygen and product gases are

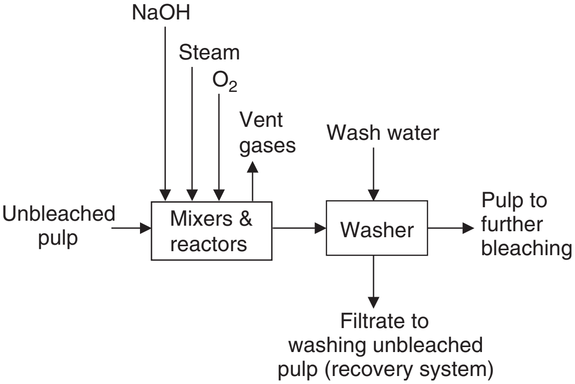

**Fig. 3.1.2. Flowsheet of oxygen-delignification stage. (From McDonough, 1996; reproduced with permission from Tappi Press.)**

vented, and the pulp enters the first of two washing stages, perhaps a wash press followed by a rotary drum washer. The use of two washing stages at this point reflects the importance of complete removal of material dissolved in the oxygen stage. This is necessary to take advantage of the environmental benefits of the oxygen stage by capturing the lignin and other material dissolved here and returning it to the mill recovery system. Any dissolved material that escapes to the following bleaching stages becomes part of the effluent of those stages and is a potential environmental liability.

Oxygen delignification can also be done at high consistency in the range of 22–30%. The idea is to get direct contact between fluffed high-consistency fibre flocs and the gas. This requires the use of thickening devices, fluffers and a downflow reactor with a free gas atmosphere.

### 3.1.3 The basic chemistry of oxygen delignification

McDonough (1990) reviewed the fundamental principles associated with oxygen delignification. The phenolic groups in the residual lignin in the pulp have been shown to play an important role. Phenolate ions are formed under the alkaline conditions, and these react with oxygen to give phenoxyl radicals, which undergo further reaction with superoxide radicals to form a hydroperoxide intermediate. Fig. 3.1.3 shows examples of the possible reactions

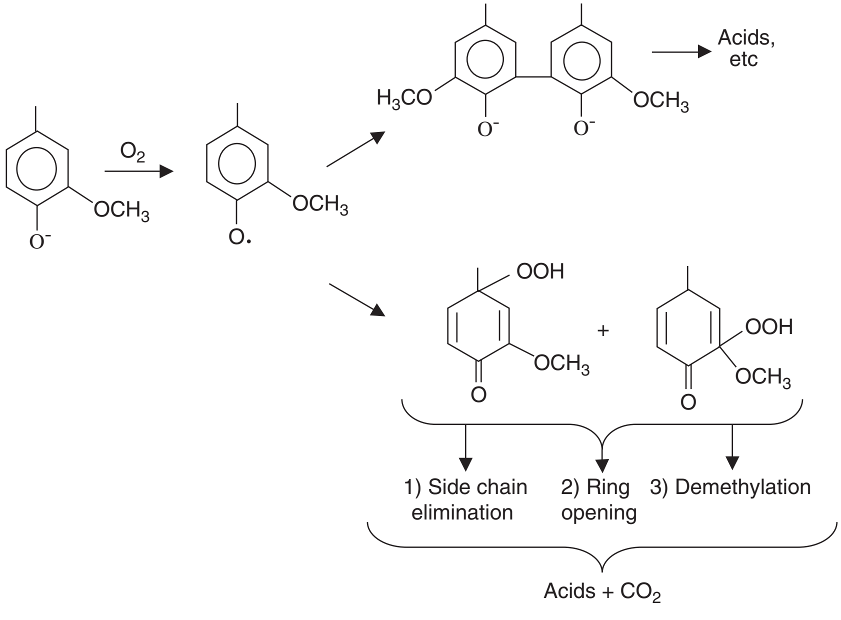

**Fig. 3.1.3. Reactions between oxygen and phenolic structures in lignin. (From Nelson, 1997; reproduced with permission from John Wiley & Sons, Inc.)**

involving oxygen and phenolic structures in lignin (Ljunggren, 1985). One possible pathway involves lignin condensation, and other pathways can lead to opening of the aromatic rings. Oxygen is reduced to hydrogen peroxide, which can further react with lignin and carbohydrates (Gierer and Imsgard, 1977). Several free radicals such as hydroxyl radicals and superoxide radicals are likely to be formed during the delignification (Gierer, 1995). Sjostrom (1981) has reviewed the reactions of carbohydrates under conditions of oxygen delignification. The presence of heavy metal ions, particularly iron, cobalt and copper, resulted in appreciable degradation. This was attributed to the effect of reactive radicals formed by the decomposition of peroxides catalysed by the metal ions. Addition of magnesium salts inhibited the degradation, provided a threshold ratio of magnesium/metal ion was exceeded. The inhibition by magnesium was attributed to the ability of the magnesium hydroxide, which is precipitated in alkaline solution after addition of a magnesium salt, to absorb heavy metal ions or their hydroxides. Studies on the kinetics of oxygen delignification revealed that the lignin in kraft pulp consists of two types that differ in their ease of removal. The first type is removed rapidly within about 10 min, whereas the second type is removed more slowly (Olm and Teder, 1979; Evans et al., 1979).

### 3.1.4 Selectivity in oxygen delignification

Selectivity may be defined as the amount of lignin removed from pulp (measured as the reduction in kappa number) for a given amount of carbohydrate degradation (measured as the decrease in viscosity). It is affected by the presence of pulp contaminants and process conditions. Oxygen is not a selective bleaching chemical as compared with chlorine or chlorine dioxide (or a combination of both) (McDonough, 1996). The latter chemicals can remove about 90% of the lignin in a kraft pulp, measured after alkaline extraction. Of the factors governing selectivity in oxygen delignification, one of the most important is the transition metal content of the pulp, because these metals catalyse the generation of harmful radical species. Most pulps contain appreciable quantities of iron, copper and manganese, all of which have this effect. One approach for dealing with transition metals is to remove them by washing with acid before the oxygen stage, and another is the addition of compounds to the pulp that inhibit carbohydrate degradation. These compounds are called carbohydrate protectors. Magnesium ion is found to be the best protector. Its effectiveness was reported by Robert et al. (1963), which provided a great motivation for the development of oxygen delignification. Since then a large number of compounds have been found to be effective, but none is as economical as magnesium sulphate or its heptahydrate (Epsom salt). It is normally used at levels as low as 0.05–0.1%

$Mg^{2+}$ on oven dry pulp. It functions by precipitating as magnesium hydroxide, which adsorbs the metal ions, making them unavailable for catalysis of peroxide decomposition or by forming complexes with them (Robert and Viallet, 1971; Gilbert et al., 1973). Fig. 3.1.4 illustrates the effectiveness of magnesium in preserving pulp viscosity and is typical of selectivities obtained in the bleaching of softwood kraft pulp (Berry, 1991). The nonlinear nature of the curves in Fig. 3.1.4 shows that selectivity does not remain constant as the kappa number of the pulp is decreased to progressively lower levels. However, selectivity usually remains nearly constant until about 50% of the lignin has been removed from the pulp after which it deteriorates. In virtually all of the existing pulping systems, the target degree of delignification is 60% or less. When delignification is no greater than 45–50%, the resulting pulp may be fully bleached to give a final product of strength equivalent to that of the corresponding conventionally bleached pulp, although its viscosity is usually slightly lower.

Selectivity is affected by process variables and may be different for different process types. The main reasons for these effects are probably related to the multiplicity of reactive oxygen-containing species present and their different reactivities with the variety of lignin and carbohydrate structures available to them. Hydroxyl radicals, which are among the least selective of the reactive species present, have been specifically studied from this viewpoint by measuring their reaction rates with compounds representative of lignin and carbohydrate structures (Ek et al., 1989). The ratio of the lignin rate constant to that for carbohydrate was observed to range between 5 and 6. Hydrogen peroxide addition can increase selectivity presumably because

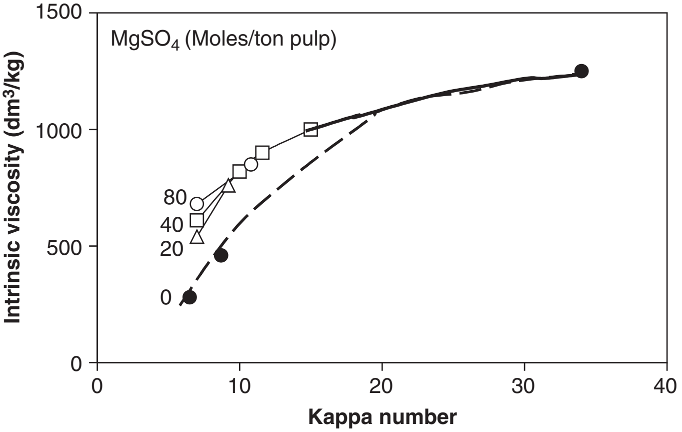

**Fig. 3.1.4. Effect of addition of magnesium ion on selectivity. (From McDonough, 1996; reproduced with permission from Tappi Press.)**

it favourably affects the composition of the reactive species mixture present (Parthasarthy et al., 1990). Colodette et al. (1990) have reported that carry-over of black liquor from the brown stock washers into the oxygen stage adversely affects selectivity.

A number of treatments of Kraft pulp before oxygen delignification have been investigated with the aim of increasing the extent of delignification without appreciably reducing the viscosity of pulp (Suchy and Argyropoulos, 2002). Pretreatments with compounds such as nitrogen dioxide, chlorine, hydrogen peroxide improves oxygen delignification by enhancing the selectivity of the delignification allowing for extending the delignification without significant losses in pulp quality (Abrahamsson et al., 1981; Lindqvist et al., 1986; Samuelson and Öjteg, 1987 and 1994; Fossum and Marklund, 1988; Lachenal et al., 1989; Lachenal and Muguet, 1991). Very low lignin content without any serious viscosity loss is obtained when the pulp is pretreated with nitrogen dioxide. Nitrogen dioxide pretreatment of kraft pulp causes partial demethylation of the lignin and also causes the fragmentation of ether bonds within residual lignin with the consequent formation of new free phenolic groups (Abrahamsson et al., 1981; Lindeberg and Walding, 1987). These reactions are expected to increase the reactivity of the lignin and decrease the possibility of cellulose attack by oxygen and radical species. These reactions are also thought to contribute to the alkali solubility of the lignin, in a sodium hydroxide impregnation stage, before oxygen delignification stage. A dramatic increase in the efficiency and the selectivity of oxygen delignification was observed when softwood kraft pulp of 3.5 kappa number was subjected to a two-stage $NO_2$ pretreatment process, followed by an oxygen delignification stage (Samuelson and Öjteg, 1987). Nitrogen dioxide pretreatment described above has been evaluated and implemented on a pilot scale in Sweden (Samuelson and Öjteg, 1987). Lindqvist et al. (1986) reported that the nitrogen dioxide pretreatment improved an oxygen delignification stage by reducing the kappa number while retaining pulp viscosity.

Pretreatment of kraft pulp with a low charge ($< 2\%$) of chlorine also showed very interesting results. Up to 75% of the residual kraft lignin was found to be removed in a subsequent oxygen stage, while the pulp properties were maintained. Lachenal and de Choudens (1986b), Soteland (1988) and Fossum and Marklund (1988) have independently confirmed the positive effects of such a chlorine pretreatment allowing for extensive delignification (kappa number $< 10$) in a subsequent oxygen delignification stage. The reason is attributed to the generation of new phenolic groups with chlorine, which allows for a more selective reaction of oxygen with lignin. Fossum and Marklund (1988) reported that chlorine dioxide showed similar effects at a given active chlorine charge. This is a better option from an environmental point of view, since chlorine dioxide produces less AOX. Also, chlorine dioxide is considerably less corrosive than chlorine.

The activating effect of ozone as a pretreatment to oxygen delignification was studied by Dr. Lachenal's group (Lachenal and de Choudens, 1986b). These researchers observed small improvements, whereas Fossum and Marklund (1988) found no synergistic effects operating on the selectivity between the ozone pretreatment and the oxygen stage. Pretreatment with acidic hydrogen peroxide is also beneficial in improving the selectivity of an oxygen delignification stage but the effect is lower than that of $NO_2$ or chlorine. Use of hydrogen peroxide under neutral conditions significantly reduced these effects (Fossum and Marklund, 1988). Pretreatments with sulphur dioxide, sodium sulphite, and sodium hypochlorite did not show any significant effect on the selectivity of subsequent oxygen delignification stages (Fossum and Marklund, 1988). When sulphide containing green liquor was used as a pretreatment of kraft pulp before oxygen delignification, improved selectivity was observed by Andrews et al. (1983). However, Fossum and Marklund (1988) found no selectivity improvements when sulphide was used as a pretreatment compared to conventional oxygen delignification.

Suss and Helmling (1987) invoked oxidation and hydroxylation reactions occurring between peroxymonosulphuric acid and the aromatic rings of lignin. These reactions increase the number of free phenolic groups in lignin thus increasing the number of and sites available for oxygen attack during the alkaline oxygen delignification stage. Springer and McSweeny (1993a) reported that peroxymonosulphuric acid pretreatment before oxygen delignification was comparable to that of chlorine provided that the transition metals were removed before the treatment. Poppius et al. (1989) found that the use of peroxyformic acid, generated insitu from a mixture of formic acid and hydrogen peroxide, before oxygen delignification allowed 83.4% delignification without any serious drop in viscosity. Kappa numbers as low as 4–6 were obtained for both pine and birch kraft pulps after the (PFA)O stage. Prior to the process, however, metals had to be removed in order to prevent the decomposition of the peroxyformic acid. The reason was attributed to the increased reactivity of the residual lignin towards oxygen delignification, allowing for a substantial reduction in the kappa number in the oxygen stage.

### 3.1.5 Oxygen delignification processes and equipment

The evolution of oxygen delignification technology is shown in Fig. 3.1.5 (Lindstrom, 2003). Two types of systems are used commercially for oxygen

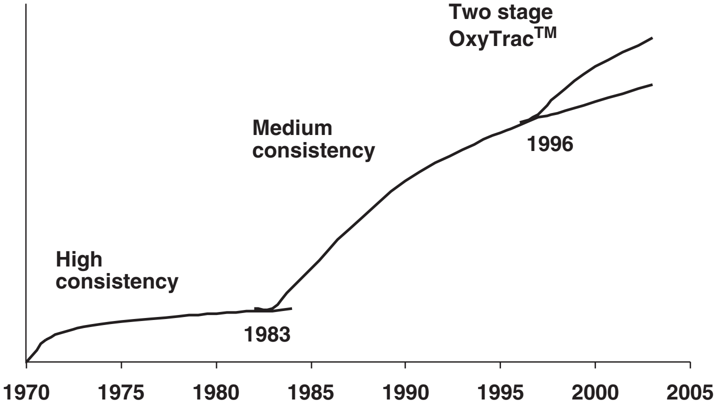

**Fig. 3.1.5. Evolution of oxygen-delignification technology.**

delignification; these are generally characterized as high- and medium-consistency systems (Tench and Harper, 1987; Reeve and Earl, 1986; Kleppe and Storebraten, 1985; Kawase, 1987; Enz. and Emmerling, 1987; Annergren and Nasman, 1979; Kalish, 1986; Tatsuishi et al., 1987; Greenwood, 1990; Arhippainen and Malinen, 1987; Rowlandson, 1971; Munro, 1987; Smith, 1982; Lindstrom, 1990; Svensson, 1978; Jamieson, 1971; David et al., 1976; Coetzee, 1974; McDonough, 1996; Smook, 1992). Low-consistency systems have been attempted, but have proven to be unsuccessful. Most systems being installed currently are of the medium-consistency type. High-consistency systems constituted the majority of those installed during the first 15 years of commercial oxygen bleaching, beginning in 1970. Both types have advantages and continue to be available, and a few high-consistency systems have been installed recently. Typical operating data range for the two types are given in Table 3.1.1 (Tench and Harper, 1987; Miller et al., 1993).

### *3.1.5.1 High-Consistency System*

Fig. 3.1.6 shows process flowsheet for high-consistency oxygen delignification system. Typically, a press is used to raise the feed consistency to about 25–30%. Fresh caustic or oxidized white liquor along with the magnesium protector is added to the pulp at the discharge of the press. A thick stock pump then transfers the pulp to a fluffer via a feed pipe in which a gas-tight plug is formed. The fluffed pulp flows down the pressurized reactor as a loose bed, while gaseous oxygen is continuously dissolved into the liquid phase and reacted with the pulp. In order for the oxygen to move freely from the gaseous to the liquid phase, a high specific surface is important. In some high-consistency reactors, a series of tray-like compartments are used to avoid excessive compaction of the pulp as it moves down the tower. Steam

**Table 3.1.1 Typical operating data for oxygen delignification of kraft softwood pulp**

| | Medium consistency | High consistency |
|---|---|---|
| Consistency (%) | 10–14 | 25–28 |
| Retention time (min) | 50–60 | 30 |
| Initial temperature (°C) | 85–105 | 100–115 |
| Inlet pressure (kPa) | 700–800 | 415–600 |
| Outlet pressure (kPa) | 450–550 | 415–600 |
| Delignification (%) | 40–45 | 45–55 |
| Low pressure steam (kg/t) | 40–110 | 30–50 |
| Medium pressure steam (kg/t) | 40–180 | 75–175 |
| Power consumption (kwh/t) | 35–45 | 40–50 |
| Alkali consumption (kg/t) | 18–28 | 18–23 |
| Oxygen consumption (kg/t) | 20–24 | 15–24 |

Based on the data from Tench and Harpner (1987).

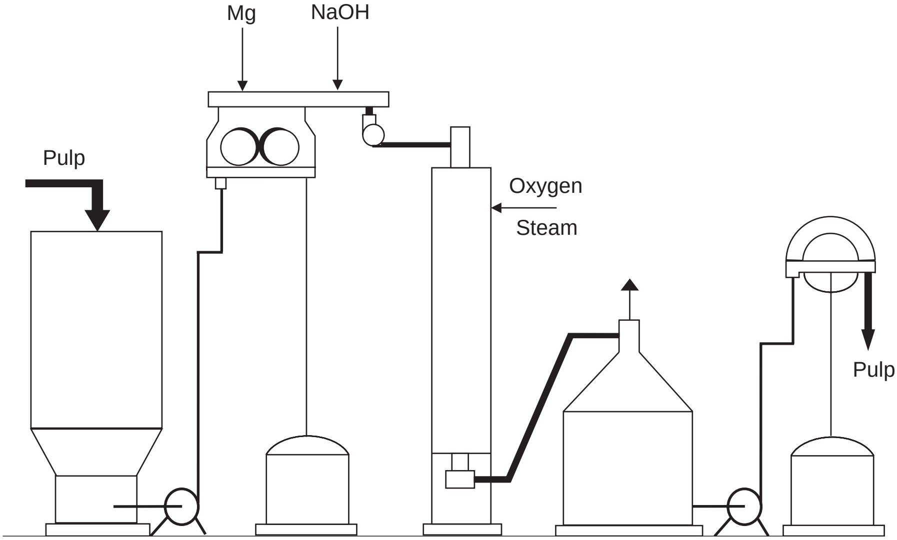

**Fig. 3.1.6. High-consistency oxygen delignification process flowsheet. (From Reeve, 1996b; reproduced with permission from Pulp & Paper Technical Association of Canada.)**

is injected into the top of the reactor to maintain temperature in the range 90–130°C. Oxygen is added to either the top or bottom to maintain a partial pressure within the 90–130 psi range. Relief is taken from the head space at the top of the tower to remove combustibles and other noncondensible gases, and control overall reactor pressure. At the bottom of the tower, the reacted pulp is diluted with post-oxygen filtrate and pumped at about 6% consistency to a blow tank. From the beginning, safety has been a major concern with the high-density systems. However, through the use of continuous-monitoring systems coupled with a properly designed safety system, these reactors have proven to be safe and reliable (Smook, 1992; McDonough, 1996).

### *3.1.5.2 Medium-consistency system*

Fig. 3.1.7 shows process flowsheet for medium-consistency oxygen delignification system. Pulp from decker or brown stock washer at about 10–14% consistency is charged with sodium hydroxide or oxidized white liquor. It is then preheated in a low-pressure steam mixer and pumped through one or more medium-consistency gas mixers to an upflow pressurized reaction tower. Steam and oxygen are added in the upstream of the medium-consistency mixer or directly into it. The reactor bottom may be hemispherical or conical, and the top is equipped with a discharger. Often, post-oxygen filtrate is added at the top of the reactor to facilitate discharging the pulp. The stock is depressurized through a separator where steam is flashed and small amounts of by-product gases, oxygen and other noncondensibles are released. In some medium-consistency systems, the top of the reactor is at atmospheric pressure. This type of system is sufficient for delignifying sulphite pulps and may be used for kraft pulps to obtain a 30–35% reduction in lignin content (Smook, 1992; McDonough, 1996).

Good results are obtained from both types of oxygen delignification systems. However, the trend is towards medium-consistency systems because of their lower capital cost and inherently safe operation (Tench and Harper, 1987; Miller et al., 1993; Greenwood, 1990; Idner et al., 1987; Lindstrom,

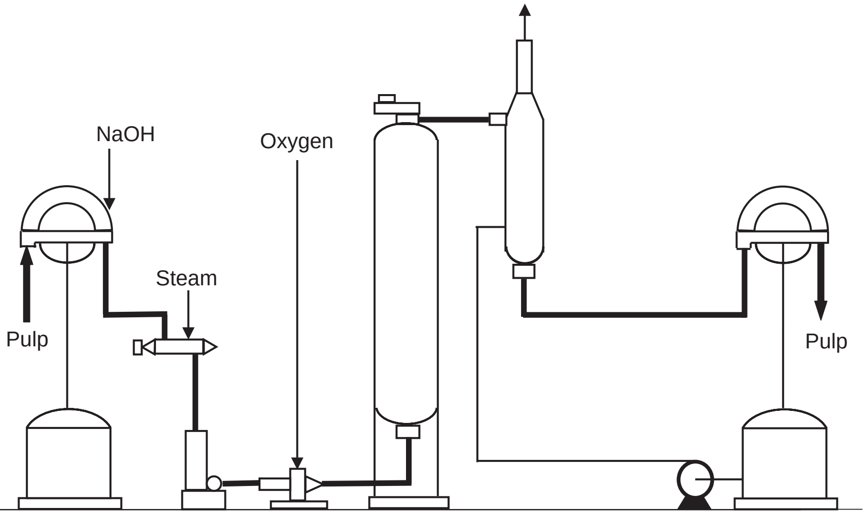

**Fig. 3.1.7. Medium-consistency oxygen delignification process flowsheet. (From Reeve, 1996b; reproduced with permission from Pulp & Paper Technical Association of Canada.)**

1990; Arhippainen and Malinen, 1987). Prior to 1983, virtually all installations were of the high-consistency type, but now most of the installations are of medium consistency. Medium-consistency systems accounted for 82% of installed capacity in 1993. The reasons are lower capital costs, greater ease of stock handling with medium-consistency mixing and pumping technology, and improved selectivity in the presence of appreciable amounts of black liquor solids. On the other hand, chemical consumption is in the medium-consistency systems higher than in the high-consistency systems and the extent of delignification tends to be lower. Those favouring the high-consistency process claim that the advantages of the medium-consistency approach are overstated. The investment difference is mainly the result of a simpler feeding system for medium consistency and elimination of a press upstream of the reactor. However, to maintain the same level of preoxygen washing, the medium-consistency system requires an extra washer to replace the press, lessening the advantage. Laboratory data indicate no difference in selectivity at the same level of magnesium addition (Liebergott et al., 1985). High-consistency systems often provide substantially more delignification and the chemical consumption difference may be significant. In summary, both process types should be considered for any new installation (McDonough, 1996).

Oxygen delignification process is available in both the single- and two-stage system. About 10% of the oxygen delignification throughout the world is done with two-stage systems. All of these operate at medium consistency. Multistage oxygen delignification can be beneficial when higher degrees of delignification are required. However, there is no improvement in the delignification selectivity as compared with that of conventional oxygen delignification (Johnson, 1993). A typical two-stage installation is shown in Fig. 3.1.8 (Kiviaho, 1995). It consists of two reactors in series and two medium-consistency mixers. The longer total retention time and extra mixing result in greater delignification than in a single-stage system. A survey of six mills using this system showed that softwood kraft pulp was delignified to between 53 and 58% and hardwood kraft to about 48%. The comparable values for commercial single-stage medium-consistency installations were 40–52% for softwood and 36–44% for hardwood pulps. One commercial installation includes an intermediate washing and chelating stage (Kiviaho, 1995). Kleppe and Peterson (1994) designed a two-stage oxygen delignification process to improve the delignification effectiveness of medium consistency oxygen stages, by dividing the oxygen and the alkali charge in two separate stages using two separate mixing systems. With this, it was possible to increase the delignification while preserving the viscosity. The delignification efficiency of the two-stage oxygen delignification could be increased by maintaining a high pH, by adding fresh alkali, and by remixing

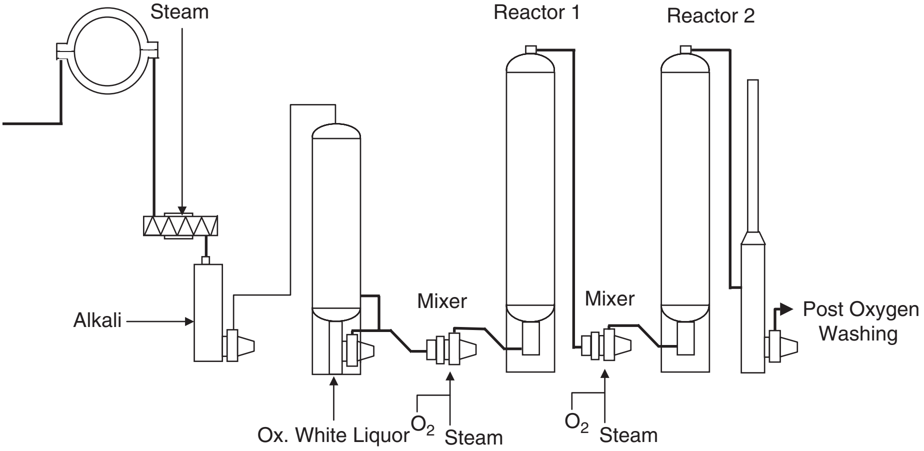

**Fig. 3.1.8. Flowsheet for a two-stage oxygen-delignification installation. (From Kiviaho, 1995; reproduced with permission from Miller Freeman Inc.)**

the pulp before the second oxygen stage (McDonough, 1995). About 70% delignification was obtained when two-stage oxygen was used in the absence of interstage washing, compared to 53% delignification usually obtained during a single oxygen stage.

The structure of the residual lignin is considerably changed after oxygen delignification making the residual lignin less reactive to another oxygen stage (Argyropoulos and Liu, 2000; Asgari and Argyropoulos, 1998; Akim et al., 2000). Attempts to increase the delignification during the second oxygen stage, have been focused around modifications of the residual lignin aimed at increasing its reactivity towards oxygen (Suchy and Argyropoulos, 2002). Various pretreatments to activate the lignin prior to oxygen delignification have also been reported with marked improvements in selectivity (Suchy and Argyropoulos, 2002). These pretreatments include nitrogen dioxide (Abrahamsson et al., 1981), ozone and peroxide (Fossum and Marklund, 1988), sulphur dioxide, sulphite, and sulphide (Fossum and Marklund, 1988), hypochlorite (Fossum and Marklund, 1988), chlorine and chlorine dioxide (Lachenal et al., 1989), peracids (Liebergott, 1994), and also enzymes (Nelson et al., 1995).

Lachenal et al. (1989) examined two-stage oxygen delignification with an interstage chlorine (X) treatment. The OXO process was more extensively studied and optimized by Lachenal and Muguet (1991). The use of chlorine between the two oxygen stages provided a well–delignified softwood kraft pulp with improved strength properties since the selectivity of the second oxygen stage was significantly improved. Chlorine was found to be more efficient than chlorine dioxide in inducing the activation. Finally, commercial implementation of the OxO process was reported in 1990 (Muguet et al., 1990).

The use of an ozone treatment as an activating stage between two oxygen bleaching stages was examined by Rost et al. (1993). This resulted in lower kappa numbers as a function of the ozone charge. A second oxygen stage, after an OZ sequence, reduced the kappa number by approximately 5 units, independent of the ozone charge. The selectivity of the OZO bleaching sequence was found to be better when compared to the OO bleaching sequence. The efficiency of ozone decreased with increasing pH and temperature. At low charges (0.2%) and at 50°C and pH of 4–5, ozone can be used as an activator between two oxygen stages without negatively affecting the selectivity of the process. The efficiency of peroxymonosulphuric acid (Px), peroxyacetic acid (Paa) and ozone (Z) as interstage activating agents for a two–stage oxygen delignification of softwood kraft pulp was compared by Li et al. (1995). The conditions of the Paa and Px stages were optimized. Under optimized conditions, the OPaaO sequence showed the best delignification efficiency and selectivity. The viscosities of the OPaaO and OPxO pulps were found to be superior to those obtained by OO and the OZO bleaching sequences. An examination of the molecular mass distributions of lignin dissolved in the acidic Paa, Px or Z stages, and of the lignin dissolved in the ensuing alkaline oxygen stages, showed the depolymerizing effects of peroxyacids and ozone, which were thought to be responsible for the lower kappa numbers obtained after the activated two-stage bleaching sequences.

Dimethyldioxirane (DMD) was studied as an interstage treatment preceding the second oxygen delignification stage in an OTO bleaching sequence by Hunt and Lee (1995). The efficiency of DMD with chlorine dioxide in the ODO bleaching sequence was compared. DMD was found to significantly increase the kappa number reduction in the second oxygen stage. It was also shown that DMD is of the same selectivity as chlorine dioxide. As an interstage treatment, it showed a greater brightness gain per kappa unit reduction than chlorine dioxide. The major drawback of this process remains the need of using acetone in a pulp mill.

The use of xylanase enzyme as an interstage treatment in a two-stage oxygen delignification process was studied by Nelson et al. (1995). It was found that in the presence of the enzyme, at least 15% more lignin was removed, and the resulting pulps were of higher viscosity. The precise mechanism of the action of xylanase on the pulp fibre has not yet been fully elucidated. A number of propositions do exist, however, including that these enzymes act mainly on the removal of some alkali-resistant reprecipitated or reabsorbed xylans, thus promoting the extractability of lignin (Kantelinen et al., 1991, 1993; Buchert et al., 1993).

Interstage treatment with peroxymonosulphuric acid (Px) was used by Allison and McGrouther (1995) to improve the two-stage oxygen delignification process. A dose of 2% of peroxymonosulphuric acid was found to improve the overall selectivity of an OPxO sequence. Using this combination of chemicals it became possible to delignify the pulp at a 70% level with better viscosity than a comparable pulp delignified at the same kappa number with a conventional OO sequence. The Px treatment was effective under both acidic and alkaline conditions at moderate temperatures (75ºC) and contact times of about 30 min. By adding hydrogen peroxide to the product solution of an on-site generated peroxymonosulphuric acid, it was found that it enhanced the overall selectivity of the process. The presence of hydrogen peroxide was found to be synergistic with peroxymonosulphuric acid. Interstage treatment with peroxide alone had no effect on selectivity, and treatment with peroxymonosulphuric acid alone (in the form of triple salt of potassium peroxymonosulphate) improved the selectivity but not to the same extent as the treatment with the combination of both oxidants. Detailed study on the effect of hydrogen peroxide on OpxO was reported by Allison et al. (1994). These researchers found no benefits to the overall process selectivity when hydrogen peroxide was present in the Px stage. However, the presence of peroxide in the final oxygen stage of the OPxO process was found to be beneficial. This contradiction with the conclusion of the earlier work of Allison and McGrouther (1995) has been caused by residual chemical carryover. Most of the original hydrogen peroxide in interstage treatment mixture survived the short Px interstage and was thus present during the final oxygen delignification stage. Subsequently, the presence of hydrogen peroxide in the second stage improved the overall delignification efficiency of the OPxO process, and not the presence of hydrogen peroxide in the Px interstage itself. These researchers also studied the effect of metal ions on the selectivity of the treatment. Metal ions were found to catalyse the reactions causing cellulose degradation when present in peroxymonosulphuric acid treatments. Direct addition of the chelating agent to the Px stage did not, however, minimize the harmful effects of the metal ions. So, it was concluded that metals must be removed by EDTA pretreatment followed by a wash prior to the Px treatment. The ideal operating conditions of the OPxO bleaching sequence were found to be metal removal prior to the peroxide free Px treatment, washing after the Px interstage, and peroxide reinforcement of the second oxygen delignification stage. Initial pilot plant trials confirmed that very low kappa numbers for hardwood and softwood kraft pulps could be obtained via an OQPx(OP) sequence. However, careful control of the peroxymonosulphuric acid reactions is required since extensive reaction during the Px stage could reduce the overall selectivity of the process. McGrouther and Allison (1995) also studied the addition of acetone to the peroxymonosulphuric interstage treatment with the objective to further increase the two-stage oxygen delignification selectivity. It was found that the addition of acetone was beneficial only at $HSO_5$ charges $> 2.5\%$. Below these levels the peroxymonosulphate reaction with acetone, known to form dimethyldioxirane (DMD) in situ, appeared to be unable to compete effectively with the peroxymonosulphate reactions with the pulp. These researchers also examined the effect that acetone addition has on the brightness development of the OPxO bleaching sequence, since earlier studies showed that peroxymonosulphate effectively delignified the pulp without, however, promoting subsequent brightening stages (McGrouther and Allison, 1995). An interstage treatment with Px (5%)/acetone (4%), followed by a second oxygen delignification stage with 3% NaOH, resulted in an increased final pulp brightness when compared to the control OPxO pulp. The effect of enzyme pretreatment prior to the Px stage on the overall OPxO effectiveness and selectivity was examined by Allison et al. (1996). In this study, oxygen delignified kraft pulp was pretreated with combinations of a commercial xylanase enzyme and a chelating agent prior to the peroxymonosulphate treatment and the oxygen stage. Use of enzyme increased the efficiency of the subsequent peroxymonosulphate delignification stage with little viscosity loss. The resulting increase in the overall OPxO selectivity allowed a decrease of up to 25% in the peroxymonosulphate charge required to obtain an OPxO pulp of a given kappa number and viscosity.

The Oji Kasugai Mill in Japan has two 20 min reactors with a high shear mixer between reactors designed to operate without an inlet distributor or outlet discharger. Delignification of 55% for softwoods and 45% for hardwoods have been reported (Meadows, 1993). The same basic system has been installed at the other five Oji mills in Japan.

The Sunds OXYTRAC system (Bokström and Nordén, 1998) is an example of a modern two-stage oxygen delignification process system. The first installation of this design was at SCA's Östrand mill in Sweden. Very high delignification degrees, approximately 70%, have been achieved through optimization of the system. It is claimed that chemical consumption has been reduced and pulp quality improved with better selectivity than with the single-stage oxygen delignification this system replaced. The OXYTRAC design utilizes two reactor stages (Fig. 3.1.9) (Lindstrom, 2003); the first operates at high chemical charge and pressure (8–10 bar) but at a relatively low temperature (85ºC) and with a short retention time (20–30 min). The high pressure is used to keep the concentration of dispersed oxygen high. The second reactor operates at a lower chemical concentration and pressure but with a higher temperature(100ºC) and a longer retention time (60 min). Only direct steam to heat the stock is added between the reactors. Other

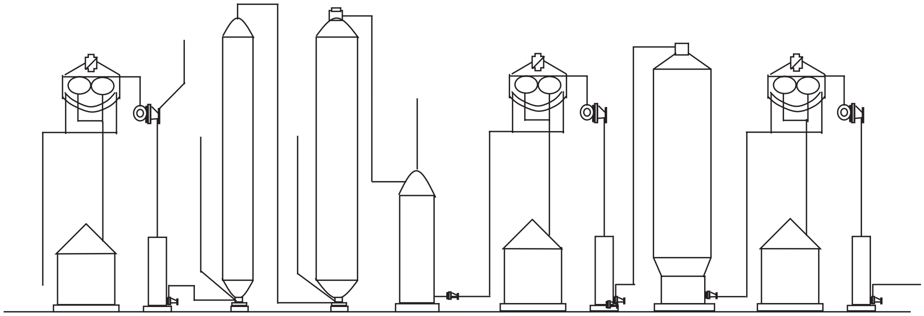

**Fig. 3.1.9. OxyTrac$^{TM}$ enhanced oxygen delignification.**

variations on the two-stage oxygen delignification include systems in which washing is carried out between the two oxygen reactors. Studies have shown that interstage washing improves the delignification power of the system (lower kappa out) and reduces the alkali charge required to maintain satisfactory pH levels due to the buffering characteristics of the lignin dissolved in the first stage (Allison and Wrathall, 1998). It does not appear that dissolved solids carried over from the first reactor have any adverse impact on the selectivity of the system.

Two-stage systems with interstage washing are fairly rare (Carter et al., 1997). Now, many newer two-stage systems have been designed and installed to allow for the possibility of adding an interstage washer at some time in the future. A "mini" oxygen delignification stage (also called brownstock EO stage) is an option that has been implemented by some mills as a means of decreasing the kappa number entering the bleach plant (Dyer and Ragauskas, 2002). A mini oxygen delignification stage can provide approximately 25% additional delignification capacity in the fibreline. A typical arrangement, such as that installed in the Pope and Talbot mill near Nanaimo, British Columbia, involves the installation of a pressurized reactor tube between the last brownstock washer and the unbleached high-density storage tower (NCASI, 2003). A single stage of washing follows the high-density tower, and this washer is "open" in that the washer filtrate is used for tower dilution but is otherwise directed to the waste treatment plant.

### 3.1.6 Process conditions

The process variables that can affect the results of oxygen delignification have been extensively studied by several researchers and comprehensively reviewed by Tench and Harper (1987), McDonough (1996) and Gullichsen (2000). The main process variables are pulp consistency, alkali charge, oxygen pressure, temperature and time.

### *3.1.6.1 Pulp consistency*

Two systems are used for oxygen delignification on a commercial scale—high consistency (about 30%) and medium consistency (about 10%). Low-consistency (3–5%) systems have been attempted but were not viable commercially (Tench and Harper, 1987). Oxygen has a low solubility in water (0.045 g/L at 25ºC), and so the equipment used for oxygen delignification must ensure that there is adequate oxygen transfer to the pulp. The early installations used high pulp consistency because this minimized the water layer around the pulp fibres and made it easy for the oxygen to react with the pulp. The development of efficient medium-consistency mixers in the early 1980s enabled medium-consistency oxygen delignification systems to be used. Medium-consistency mixers subject the pulp—gas mixture to high shear forces, and the oxygen is dispersed in the pulp suspension as fine bubbles, which subsequently dissolve and react as the oxygen in the liquid phase is removed by reaction with lignin (van Lierop, 1996). In recent years, the medium-consistency alternative has been the dominant technology, with about 80% of the oxygen delignification plants using this system (Lindstrom, 2003). Tench and Harper (1987) have reviewed the merits of the two systems, concluding that the final decision on which is the more suitable will be specific to each site.

### *3.1.6.2 Alkali charge*

Both delignification and carbohydrate degradation increase as the alkali charge is increased (Liebergott, 1985). The amount of alkali applied to the pulp is based on the viscosity level required for the pulp. The alkali charge is usually about 2–3% (pulp basis) and depends on the type of pulp. Most oxygen delignification installations use oxidized white liquor as the alkali. Pulping liquor is treated with air or oxygen to oxidize the sodium sulphide component to sodium thiosulphate, which does not interfere with the oxygen delignification process. The filtrate from the oxygen delignification stage is usually returned to the recovery boiler. The use of oxidized white liquor thus avoids problems with the sodium/sulphur balance that may occur if fresh sodium hydroxide is used.

### *3.1.6.3 Oxygen pressure*

The effect of oxygen pressure within a range 0.2–1.5 MPa is small in comparison with the effects of alkali charge and temperature (Hartler et al., 1970). Commercial oxygen delignification plants use pressures in the range 415–670 kPa with medium-consistency systems using higher pressures than high-consistency operations (Harrison, 1994). About 2% oxygen (pulp basis) is consumed.

#### *3.1.6.4 Temperature and time*

Delignification is considerably accelerated by increases in temperature; the point of alkali exhaustion is reached much more rapidly at 130 than 85°C. The parallel between delignification and carbohydrate degradation rates leads to a good correlation between viscosity and kappa number (Berry, 1991). This relationship tends to be moderately independent of process variables although selectivity does suffer if the temperature is increased beyond about 120ºC or if all of the alkali is consumed. Temperatures in the range of 85–110°C are used, with high-consistency systems employing a temperature at the upper end of this range (Johnson, 1995). The decrease in kappa number with time at fixed alkali concentration exhibits two distinct stages, both of which are first-order rate processes. There is an initial rapid kappa number drop followed by a slower one. This is interpreted to be caused by the presence of two types of lignin that differ in the ease of removal. The two delignification stages are directly paralleled by two corresponding cellulose depolymerization stages. A consequence of the first-order nature of the delignification process is that, given enough alkali, the kappa number continues to drop indefinitely. This is in contrast to the normal observation that the process appears to stop when a limiting kappa number is reached (Hartler, 1970). The latter behaviour is seen when the alkali charge is exhausted.

### 3.1.7 Reinforcement of oxygen delignification stage with hydrogen peroxide and peracids

Numerous papers have been published, which show that reinforcement of oxygen delignification stage with hydrogen peroxide and with peracids increase the delignification efficiency without appreciably reducing the viscosity of the pulp. Lachenal et al. (1986a) and Klein et al. (1990) observed synergy between oxygen and hydrogen peroxide when hydrogen peroxide was used for the reinforcement of alkaline extraction stages. Reduced kappa numbers and higher viscosities were obtained. Later on, in an attempt to improve the oxygen delignification stage itself, hydrogen peroxide-reinforced oxygen delignification was suggested to increase the delignification. Hydrogen peroxide was found to have an additive effect with oxygen on the delignification of pine kraft pulps, resulting in improved selectivity and delignification efficiency (Parthasarathy et al., 1990). Addition of 0.5% hydrogen peroxide into an oxygen delignification stage, resulted in 60% reduction in kappa number as compared to a 50% maximum reduction possible for single-stage oxygen delignification. Compared to conventional oxygen delignification, hydrogen peroxide reinforcement (at lower alkali charges) produced delignified pulps of the same kappa number with higher viscosity than those obtained without hydrogen peroxide. Hydrogen peroxide-reinforced oxygen delignification also allowed the use of lower temperatures with similar kappa number reductions. The effect of adding hydrogen peroxide and activated hydrogen peroxide on the selectivity and delignification efficiency of oxygen delignification was examined by Odermatt et al. (1994). By the use of diethylenetriamine pentaacetic acid (DTPA) and an acid pretreatment to control peroxide decomposition, oxygen delignification in the presence of cyanamide activated hydrogen peroxide resulted in pulps of low lignin content (>60% delignification was obtained), while maintaining good selectivity. About 82% delignification was achieved by using double oxygen treatments reinforced with cyanamide activated hydrogen peroxide.

The hydrogen peroxide reinforcement of a two-stage oxygen-delignification process was studied by Parthasarathy et al. (1990). Using a (PO)(PO) process, about 73% delignification was achieved with the kraft pulps as compared to 61% for a two-stage oxygen delignification process, in the absence of peroxide. At similar kappa numbers, hydrogen peroxide reinforced two-stage oxygen delignification produced pulps with higher viscosities and better strength properties. It was assumed that hydrogen peroxide has to be added during the first stage of a two-stage oxygen bleaching to realize potential benefits from the second oxygen stage that may or may not be reinforced with hydrogen peroxide.

Acidic peroxide was also studied to reinforce oxygen delignification (Suss and Helmling, 1987). This treatment improved the delignification rate of a subsequent alkaline stage. In another study, the addition of molybdate ions was explored in acidic peroxide-assisted oxygen delignification (Agnemo, 1997). Use of 1% peroxide together with molybdate (300 ppm as Mo) was found to reduce the kappa number to 10.3, as compared to a kappa number of 16.8 of the control experiment. However, serious drop in viscosity was observed. Acidic peroxide (AP), peracetic acid (Pa), peroxymonosulphuric acid (Px) and mixed peracids solution (Pxa) were studied under acidic conditions with oxygen on an oxygen delignified softwood pulp by Liebergott (1996). Higher delignification efficiencies of the order of 63% (kappa 7.5) and 67% (kappa 6.7) were obtained when Px/O and Pxa/O treated pulps were subjected to $E_{OP}$ extraction.

### 3.1.8 Effects of oxygen delignification on pollution loads

Oxygen delignification results in significant reduction in COD, BOD, colour and AOX in effluents (Lindstrom, 2003; Gullichsen, 2000; McDonough, 1990, 1996). Table 3.1.2 shows typical effluent properties for the conventional $C_DE_ODED$ bleach sequence and for the short sequence $OC_DE_OD$ (Tench and Harper, 1987). Carpenter et al. (1976) reported that compared to the conventional bleaching sequence, oxygen prebleaching resulted in 31% BOD, 61% COD and 85% colour-loading reductions for softwood pulps and 63% COD and 74% colour loading reductions for hardwood pulps.

**Table 3.1.2 Generation of pollutants in bleaching of oxygen-delignified softwood and hardwood kraft pulp**

| | $C_DE_ODED$ | | $OC_DE_OD$ | | Reduction (%) | |
|---|---|---|---|---|---|---|
| | Softwood | Hardwood | Softwood | Hardwood | Softwood | Hardwood |
| $BOD_5$ (kg/metric t) | 15–21 | 10–15 | 8–11 | 5–7 | 40–50 | 40–55 |
| COD (kg/metric t) | 65–75 | 40–45 | 30–40 | 20–25 | 45–55 | 40–55 |
| Color (kg Pt/metric t) | 200–300 | 90–125 | 80–120 | 15–25 | 60–75 | 75–85 |
| TOCL (kg/metric t) | 5–8 | — | 3–4 | — | 35–50 | — |
| Flow ($10^3$ L/metric t) | 20–25 | 20–25 | 15–20 | 15–22 | 25–30 | 25–30 |
| Reduction in oxygen-stage kappa number: 45–50% | | | | | | |

Based on the data from Tench and Harpner (1987).

Approximately 40–50% chloride is reduced due to the reduction in chlorine dosage. Results from mill experiences (Jones, 1983) showed that oxygen bleaching reduced the effluent volume from 8900 to 4000 gallons per tonne of pulp. The BOD and colour loadings were reduced by 40% and 90%, respectively. Oxygen bleaching was reported as a method to reduce dioxin formation during the chlorine bleaching (Kringstad and McKague, 1988). Oxygen bleaching was the first step taken to close the bleach plant in Sweden (Eklund, 1995; Pryke, 1995). Today, all Swedish kraft mills have oxygen bleaching processes installed. Medium consistency oxygen bleaching produces less BOD, COD and TOCl loadings than high consistency oxygen bleaching at the same degree of delignification. Germgard et al. (1988) showed that although the installation of oxygen bleaching systems significantly reduced the TOCl by 70%, ether-soluble TOCl and the total chlorinated phenolic compounds, the chemical composition of the spent bleaching liquor was similar to conventional bleaching liquor. In other words, oxygen bleaching only decreased the amount of chlorinated organic material produced in the subsequent bleaching. Swedish researchers showed that although addition of oxygen bleaching led to a strong reduction in the release of pollutants (BOD, COD, TOCl and colour loading), it did not reduce the biological effects of bleaching effluent to any significant degree (SSVL Project, 1982). Overall, the following benefits of oxygen bleaching were claimed: a reduction in pollution loads (BOD, COD, colour loading, TOCl and dioxin) by 30–70% for both softwood and hardwood kraft pulps; the potential to shorten the bleaching sequence; a reduction in the effluent volume (closed system); a decrease in the chloride content (corrosion and deposit); and the elimination of the hypochlorite stage ($CHCl_3$ source).

### 3.1.9 Effects of oxygen delignification on pulp quality

Oxygen delignification allows the production of low kappa pulp for bleaching without serious pulp quality problems if lignin removal does not exceed beyond 50%. Oxygen delignification is neutral or slightly positive in terms of pulp cleanliness, pitch content, brightness stability, and bleachability. The strength properties of oxygen-delignified pulps are similar to those made without oxygen delignification. Refining energy requirements have been observed to decrease upon installation of an oxygen stage (Munro, 1985). Yield selectivity is better when the pulps are cooked to low kappa numbers (McDonough, 1990, 1996; Munro, 1985; Jamieson, 1979; Jamieson and Smedman, 1974).

### 3.1.10 Impact on recovery and energy consumption

The total solids load to the recovery boiler will increase as a result of recovering and recycling solids from the oxygen stage. It has been reported that with 80% recovery of the oxygen-stage solids, the increase in solids to the recovery boiler will be about 3% for softwoods and 2% for hardwoods (Tench and Harper, 1987; McDonough, 1996). Also, the recovery of digester black liquor solids will increase as a result of the extra post-oxygen washing stages. The extra digester solids recovered will typically be about 1% when the oxygen stage is installed as part of a new fibreline. However, this percentage can be higher if the oxygen stage is installed in an older fibreline that is less efficient in brownstock washing. Therefore, in a new fibreline with oxygen bleaching, the total additional solids load to the recovery boiler will be about 4% with softwoods and 3% with hardwoods. When oxygen bleaching has been incorporated into an older mill, increases up to 10% have been reported (Tench and Harper, 1987).

With oxygen bleaching, the heating value of black liquor is somewhat lower because part of the solids are partially oxidized. The additional steam generated in the recovery boiler will be about 1.5–2.5% less than the percentage increase in solids load.

The use of oxidized white liquor as an alkali source in the oxygen stage increases the load on the causticizing plant and lime kiln by about 3–5%. Additional steam may be required in the evaporation plant because of the recovery of the steam and white liquor or caustic added to the oxygen stage. On the other hand, it may be possible to reduce the wash water flow because there are more washing stages and the consistency of the pulp discharged from the post-oxygen washers is normally higher than that from brownstock washers.

The additional evaporator steam requirements can range from 4 to 10% for a medium-consistency system and 0 to 4% for a high-consistency system. The higher steam usage in medium-consistency reactors accounts for the greater evaporator steam requirements. Table 3.1.3 shows a comparison of the estimated net energy requirements for the CDEODED and high-consistency

**Table 3.1.3 Comparison of energy consumption for a high-consistency oxygen reactor using softwood kraft pulp at 50% oxygen delignification**

| | $C_DE_ODED$ | $OC_DE_OD$ |
|---|---|---|
| Power usage (KWh/metric t) | | |
| Bleach plant and chemical preparation | 160 | 170 |
| Turbine increase | 0 | −10 |
| | 160 | 160 |
| Steam usage (kg/metric t) | | |
| Bleach plant | 500 | 600 |
| Chemical preparation | 370 | 250 |
| Evaporator, increase | 0 | 40 |
| Recovery boiler, increase | 0 | −100 |
| | 870 | 790 |
| Kiln fuel, increase in L oil/metric t | — | 2 |

Based on the data from Tench and Harpner (1987).

OCDEOD bleaching of kraft softwood. As can be seen, the overall energy consumption is approximately equal for the two sequences.

### 3.1.11 Washing

An integral part of oxygen delignification is pre- and postwashing of pulps (Magnotta and Courchene, 1982). Washing is actually the major capital investment in oxygen delignification. Prewashing of brownstock is necessary to decrease COD carryover with the pulp and to improve oxygen stage efficiency (Miller et al., 1993; Greenwood, 1990; Magnotta and Courchene, 1982; Jamieson and Smedman, 1974). A desirable carryover level of approximately 10 kg $Na_2SO_4$/ADT typically requires three stages of washing ahead of the oxygen stage. A number of mills employ more than three stages. There are, however, some installations in which two stages have been installed, and no problems have occurred. In the high-consistency process, a design using two washers plus a press is most common for batch digesters, and a design using one washer plus a press is common for Kamyr digesters with high-temperature washing. In the medium-consistency process, an additional washer instead of the press would normally be used.

Postwashing of oxygen-delignified pulp well is also very important. It minimizes the carryover into the bleach plant, which increases the consumption of bleaching chemicals (Lindstrom,1990). In the absence of good washing, the resulting increase in bleaching chemical use would increase pulp bleaching costs, and also increase discharges of AOX and COD from the bleach plant. Normally two washing stages are employed. In few installations, three washing stages are employed.

Pulp washing between stages may not be necessary to achieve higher delignification. Not washing the pulp after the first oxygen treatment results in a decreased alkali demand and an increased kappa number reduction in subsequent stage(s) (Parsad et al., 1993). Higher delignification for unwashed pulps entering a second oxygen stage may be due to carryover alkali with the pulp. This provides an increased alkali concentration at the beginning of the second stage, which enhances delignification.

### 3.1.12 Screening

Screens can be located before or after the oxygen stage (Tench and Harper, 1987). The screen room decker is employed either as a washer upstream of the oxygen stage or as the final post-oxygen washer. Although most mills screen the pulp before oxygen delignification, there are some mills that screen after the oxygen stage. One kraft mill which practices both methods reports no difference in pulp cleanliness. The main criteria to consider while evaluating the two methods are the capital costs and the heat balance. Such factors as plant layout and the number, type, and efficiency of both existing washers and new washers will influence the overall economics and heat balance. Two-stage oxygen delignification has been found to be more efficient in resolving screen rejects leaving less dirt and shives than single-stage delignification (Parsad et al., 1993).

### 3.1.13 Benefits and drawbacks of oxygen delignification

The major benefits of oxygen delignification are related to its beneficial effects on environmental parameters, although there are also some operating cost advantages (McDonough, 1990, 1996; Tench and Harper, 1987). Its chief disadvantages are capital costs and increased demand on the mill recovery system. The most obvious beneficial effect of installing an oxygen predelignification stage in a chlorine compound-based bleach plant is decreased need for oxidizing chemical in the delignifying part of the bleaching sequence. If this is chlorine or chlorine dioxide, there is a corresponding decrease in chlorinated organic by-products in the bleach plant effluent (as measured by adsorbable organic halide, AOX). When the delignification stage oxidant is chlorine dioxide, the effect is smaller because chlorine dioxide generates much less AOX, but the chemical cost saving is greater. In either case, the oxygen stage leads to a major decrease in BOD, COD and colour. Lower chemical cost results from the decreased requirement for delignifying oxidizing chemical (e.g. chlorine, chlorine dioxide or ozone), because oxygen is less expensive, and oxidized white liquor usually provides the necessary alkali for the oxygen stage at a low cost. Further savings result from a decrease in the chlorine dioxide charge needed for final bleaching stages. Both decreases in chlorine dioxide requirement translate into the additional advantage of allowing a smaller chlorine dioxide generator to be used. Additional savings result from a decrease in the caustic (i.e. sodium hydroxide) required in the first extraction stage.

Of the disadvantages, capital cost is the most apparent. In the course of one economic comparison of bleaching alternatives (Arhippainen and Malnen, 1987), the cost of a medium-consistency oxygen delignification system was estimated to be $14.1 million. It has been estimated that the installed cost of such a system with two post-oxygen washing stages is in the range $13–26 million, depending on equipment selection and site. A further drawback is the possibility of overloading systems in the chemical recovery area of the mill. The use of oxidized white liquor as an alkali source requires additional causticizing. Recycling of oxygen-stage solids to the recovery system increases recovery boiler loading and water added as steam and with chemicals, increases evaporator loading (Tench and Harper, 1987). An additional drawback is the tendency of oxygen bleaching to be nonselective at higher degrees of delignification. This is not a problem if a suitable carbohydrate protector is used and the degree of delignification is not too high, i.e., not more than about 50%. Other drawbacks are increased steam costs, higher maintenance costs, and an increase in the overall process complexity.

### 3.1.14 Conclusions

The use of oxygen delignification systems is increasing throughout the world. These systems are expected to play a major role in the industry's efforts to develop an effluent-free bleached pulp mill. Oxygen delignification can be used successfully to delignify kraft softwood and hardwood pulps, sulphite softwood and hardwood pulps, and speciality pulps. These pulps are used in a wide variety of products, including printing and writing papers, copy paper, newsprint, grease proof paper, paper board, tissue, and diapers. The discharge of bleach plant pollutants and the operating cost of bleaching are reduced by the use of an oxygen delignification system. The technology is compatible with new developments aimed at reducing the discharge of bleach plant effluents, such as extended delignification, $NO_2$ pretreatment, and peroxide and ozone bleaching.

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## 3.2 Ozone bleaching

### 3.2.1 Introduction

Ozone ($O_3$), a very reactive, poisonous gas, is a powerful oxidizing agent for ligno-cellulosic material (Rice and Netzer, 1982). It was introduced as a bleaching chemical on an industrial scale in the beginning of 1990s. It is now used in about 25 mills in the world for the bleaching of chemical pulps (Lachenal, 2004). Ozone is found to efficiently delignify all types of chemical pulps. It is used either at medium or high pulp consistency in elemental chlorine- free and totally chlorine-free bleaching sequences (Liebergott and van Lierop, 1978; Gellman, 1991; Schwarzl, 1991; Sixta et al., 1991; Gotlieb, 1994; Nutt, 1993; Peter, 1993; Helander et al., 1994; Singh, 1982; Funk et al., 1992; van Lierop et al., 1996; Gullichsen, 2000; Nelson, 1998; Pikka et al., 2000; Lindstrom, 2003). The typically used charges of ozone are lower than 6–7 kg/t of pulp. As ozone is a very efficient delignifying agent, it can partially or totally replace chlorine dioxide in an economical way (1 kg of ozone replaces about 2 kg of pure chlorine dioxide). The effluent from ozone prebleaching can be used in brown stock counter-current washing and taken to the chemical recovery system, provided its acidic nature is taken into account.

When compared with the industrial development of oxygen delignification, which was initiated more than 30 years ago, the implementation of ozone for pulp bleaching has grown quite rapidly (Fig. 3.2.1) (Govers et al., 1995). The main reason underlying this evolution is the necessity to respond to growing environmental awareness, reflected both in regulatory constrains

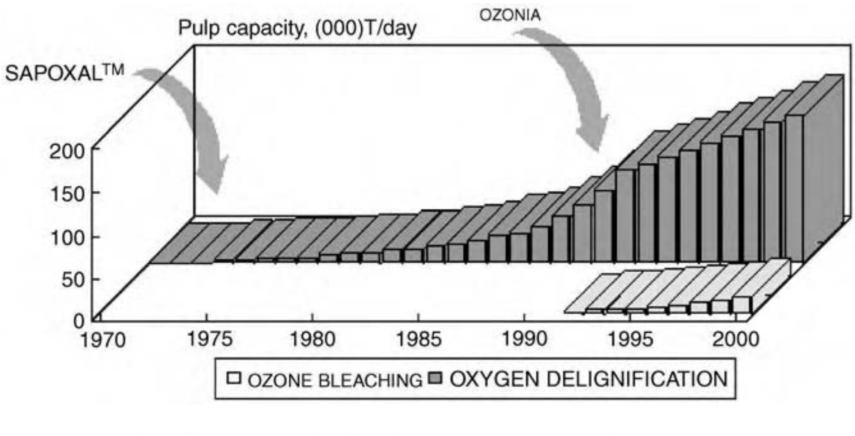


**Fig. 3.2.1. Evolution of oxygen delignification and ozone bleaching as measured by the daily pulp tonnage employing these processes worldwide. (From Govers et al., 1995; reproduced with permission from Air Liquide Inc.)**

and market demands. The fact that ozone is finding growing acceptance as a bleaching chemical compatible with these requirements results from a combination of advances with regard to the bleaching process and associated equipment on the one hand, and ozone production and handling on the other. Recent advances in ozone generation, and in particular the development of Ozonia's AT95 technology, as well as the lowering of oxygen cost by means of on-site production, have established ozone as a highly competitive bleaching chemical.

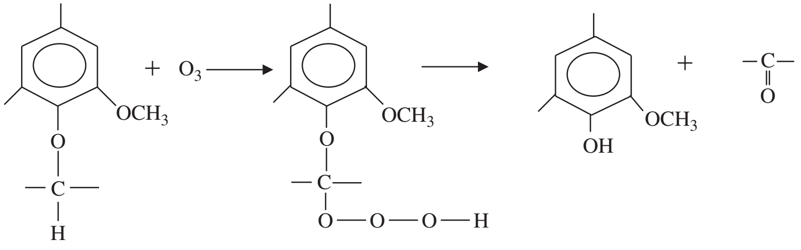
It is not surprising that TCF sequences combining ozone and hydrogen peroxide are significantly less costly than those employing hydrogen peroxide only, it should be stressed that ECF sequences that combine ozone with chlorine dioxide are more cost-effective than ECF sequences using only chlorine dioxide. Ozone is today about 1.5 times less expensive than chlorine dioxide, when compared on the basis of the same costing structure, i.e. allowing for operating expenses and investment costs in both cases, and at equal bleaching power.

Ozone is manufactured by passing air or oxygen through a corona discharge. The electrical potential used to maintain the discharge is usually in excess of 10000 V. When oxygen is used, it is possible to produce a mixture of ozone and oxygen containing up to about 14% of ozone by weight. The manufacture of ozone requires a relatively large amount of electricity. At the Lenzing mill in Austria, about half of the operating cost of ozone generation is for energy and the other half is for the oxygen.

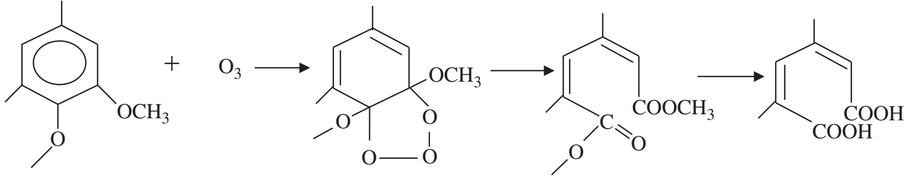
Ozone is less selective towards lignin than are chlorine and chlorine dioxide and low charges are required to prevent strength loss. Unwanted reactions with cellulose leading to a deterioration in pulp quality occur when large doses are applied (Procter, 1974; Soteland, 1974; Kamishima et al., 1976; Colodette et al., 1994; Lindholm, 1990; Allison, 1991; Gupta and Eckert, 1984; Lachenal, 2004). A highly selective ozone treatment remains elusive in spite of the substantial efforts directed towards elucidating the mechanisms of ozone and carbohydrate reactions and the conditions required to minimize these reactions.

### 3.2.2 Chemical reactions of ozone with lignin and carbohydrates

A number of references describe the mechanisms of the reactions of ozone with pulp and define the best conditions for bleaching with ozone (Gellman, 1991; Liebergott et al., 1992a, b; Allison, 1991; Byrd, 1992; Singh, 1982; van Lierop et al., 1996; Gullichsen, 2000; Nelson, 1998). Ozone is a strong electrophile that reacts with functional groups in residual lignin (Fig. 3.2.2). Conjugated aliphatic double bonds and enol ether structures react with ozone via intermediates to form carbonyl groups and peroxides. Ozone may



ß - Arylether cleavage by ozone



Ring attack by ozone

Attack on double bonds

**Fig. 3.2.2. Reactions between ozone and various lignin structural units. (From Nelson, 1997; reproduced with permission from John Wiley & Sons, Inc.)**

also react with aromatic lignin structures to form acids. Most phenolic groups are oxidized by ozone. Ozone is better than chlorine and chlorine dioxide in solubilizing lignin by these reactions, and is much more reactive towards lignin than carbohydrates. But intermediate inorganic by-products formed by direct decomposition, such as the hydroxyl and perhydroxyl radicals, can be very reactive with carbohydrates. Carbohydrate degradation results from the formation of functional groups such as carbonyl and carboxyl structures (Chandra and Gratzl, 1985). The reaction of carbohydrates with the hydroxyl radical involves the removal of carbon-bound hydrogen atoms, resulting in the formation of hydroxy alkyl radicals which are then converted into the corresponding carbonyl structures after reacting with oxygen (Ek et al., 1989). The carbonyl groups produced on the polysaccharide chain in a highly oxidizing environment under acidic conditions later induce chain cleavage when the polysaccharide is exposed to an alkaline environment such as that present in alkaline extraction and peroxide stages and in the cuene viscosity test (Chandra and Gratzl, 1985; Ek et al., 1989; Godsay and Pearce, 1984). Reduction of ozonated pulp with a strong reducing agent such as sodium borohydride converts the alkali-sensitive carbonyl groups into alkali-stable hydroxyl groups, thus preventing the alkali-induced chain cleavage (Kassebi et al., 1982; Laxen et al., 1990). Although sodium borohydride treatment of pulp prevents viscosity loss, the amount required (up to 2% on pulp) does not make it a cost-effective option in a commercial operation (Ek et al., 1989; Chirat et al., 1993; Kassebi et al., 1982). The use of ozone in delignification/bleaching will increase dramatically if a cost-effective reducing agent is found. Another approach to prevent the hydroxyl radical–carbohydrate reactions is to use radical scavengers such as methanol and acetic acid to destroy the hydroxyl radicals as they are formed (van Lierop et al., 1996). The response of pulp to an ozone treatment is usually characterized by the amount of lignin removal (as measured by kappa number) and the degree of carbohydrate degradation (as measured by pulp strength or viscosity). Pulp quality will be compromised if too much lignin is removed by ozonation.

### 3.2.3 Process variables

The process variables for treatment of pulp with ozone have been studied extensively by many researchers. The results of these studies have been comprehensively reviewed by Liebergott et al. (1992a, b), Byrd et al. (1992), van Lierop et al. (1996) and Gullichsen (2000). The main process variables in ozone delignification are consistency, ozone charge and form of charging, pH, time and temperature, chemical additives, carryover of dissolved organic matter from delignification or bleaching stages and treatment history prior to ozonation.

#### *3.2.3.1 Pulp consistency*

The effect of pulp consistency on ozone consumption and selectivity has been studied mainly with laboratory-scale equipment (Lindholm, 1987; Allison et al., 1993). Most of the early work on ozone bleaching focused on low and high consistencies. The optimum ozone consumption was obtained in a consistency range of 30–40% (Table 3.2.1) (Liebergott et al., 1992b). Low-consistency ozonation tend to maintain pulp yield, viscosity and strength better than high-consistency ozonation but required a higher dose of ozone (Byrd et al., 1992). Medium consistency ozonation in a high-shear mixer gave results comparable to low-consistency ozonation, if a high concentration of ozone in the gas phase was used (Laxen et al., 1990). The development of ozone generators capable of manufacturing high concentrations of ozone and the availability of high-shear pulp mixers has enabled medium-consistency ozonation to be studied.

The commercial ozone bleaching installations around the world are operated at medium (about 10%) and high (about 35%) pulp consistencies, with the majority using medium consistency. Each of these systems has advantages and disadvantages, and there is no general agreement as to which is superior. A higher degree of delignification is achieved under high-consistency

**Table 3.2.1 The effects of pulp consistency and ozone charge on pulp properties after ZE stage**

| $O_3$ added (%) | Ozone consumed (% on pulp) | | | Kappa number | | | Viscosity (mPa s) | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1.0 | 1.5 | 2.0 | 1.0 | 1.5 | 2.0 | 1.0 | 1.5 | 2.0 |
| *Softwood kraft*[a] | | | | | | | | | |
| 30 | 0.93 | 1.40 | 1.85 | 21.4 | 19.0 | 18.0 | 25.1 | 21.6 | 18.5 |
| 36 | 0.93 | 1.44 | 1.90 | 17.1 | 15.1 | 12.8 | 24.6 | 21.2 | 18.4 |
| 45 | 0.98 | 1.44 | 1.91 | 14.3 | 12.1 | 9.9 | 24.1 | 21.1 | 18.0 |
| 53 | 0.96 | 1.42 | 1.89 | 13.6 | 11.9 | 9.5 | 23.9 | 20.2 | 17.9 |
| 60 | 0.78 | 1.33 | 1.81 | 15.0 | 13.0 | 11.8 | 22.0 | 18.7 | 17.5 |
| *Hardwood kraft*[b] | | | | | | | | | |
| 30 | 0.91 | 1.32 | 1.71 | 9.0 | 7.4 | 6.6 | 11.5 | 9.6 | 8.3 |
| 35 | 0.93 | 1.35 | 1.82 | 5.7 | 4.8 | 3.6 | 11.4 | 9.6 | 8.5 |
| 45 | 0.93 | 1.38 | 1.81 | 4.5 | 3.5 | 2.6 | 11.3 | 9.4 | 8.4 |
| 53 | 0.94 | 1.38 | 1.89 | 4.3 | 3.4 | 2.2 | 11.2 | 9.3 | 8.3 |
| 60 | 0.82 | 1.22 | 1.76 | 4.7 | 3.7 | 2.5 | 10.5 | 9.0 | 8.1 |
| *Softwood kraft–oxygen*[c] | | | | | | | | | |
| 28 | 0.86 | 1.28 | 1.43 | 8.8 | 8.0 | 6.9 | 19.7 | 17.8 | 16.6 |
| 36 | 0.95 | 1.39 | 1.86 | 6.7 | 5.8 | 5.1 | 19.6 | 17.2 | 16.5 |
| 46 | 0.95 | 1.41 | 1.88 | 5.5 | 4.4 | 4.1 | 19.0 | 17.0 | 16.2 |
| 52 | 0.93 | 1.38 | 1.84 | 5.3 | 4.2 | 3.9 | 18.4 | 16.4 | 15.5 |
| 61 | 0.84 | 1.29 | 1.45 | 5.5 | 4.6 | 4.2 | 17.6 | 16.0 | 14.8 |
| *Hardwood kraft–oxygen*[d] | | | | | | | | | |
| 25 | 0.83 | 1.22 | 1.43 | 4.4 | 3.6 | 3.2 | 14.2 | 17.5 | 10.4 |
| 35 | 0.91 | 1.39 | 1.85 | 3.3 | 2.6 | 2.1 | 13.5 | 11.2 | 10.2 |
| 45 | 0.93 | 1.38 | 1.81 | 2.8 | 2.2 | 1.7 | 12.9 | 10.9 | 9.9 |
| 52 | 0.89 | 1.28 | 1.79 | 2.7 | 2.2 | 1.5 | 11.8 | 10.0 | 9.1 |
| 60 | 0.82 | 1.21 | 1.42 | 2.9 | 2.5 | 1.8 | 10.5 | 8.5 | 8.0 |

From Liebergott et al. (1992a); reproduced with permission from Tappi Press

[a] Kappa no. = 29.4, viscosity = 32.9 mPa s.

[b] Kappa no. = 14.5, viscosity = 17.6 mPa s.

[c] Kappa no. = 17.7, viscosity = 23.2 mPa s.

[d] Kappa no. = 11.1, viscosity = 18.6 mPa s.

conditions because a greater charge of ozone (about 0.8%, pulp basis) can be applied to the pulp. In case of medium consistency, it is difficult to apply more than about 0.5% ozone (pulp basis). Ozone is used under pressure (0.8–1 MPa) with medium-consistency technology to obtain adequate ozone consumption by the pulp, and mixing is critical. High-consistency ozone bleaching uses a gas pressure slightly above atmospheric pressure, and this low pressure minimizes the chance and severity of a gas leak. High pulp consistency involves prior removal of a larger proportion of the liquor in the pulp. The advantage is that there are lower amounts of dissolved organics and heavy metals remaining in the pulp. Medium-consistency technology is better suited for a retrofit of a fibreline, as existing equipment can be used in many cases. However, the costs for ozone generation and compression in this case are higher (Kappel et al., 1994).

### *3.2.3.2 Effect of pH*

Liebergott et al. (1992b) have reported that acidification of pulp to a pH of about 2 before the ozone stage gives the lowest kappa number and highest viscosity. An oxygen-delignified softwood kraft pulp was treated with ozone at 40°C with a pulp consistency of 45%. An alkaline extraction stage (1–1.5% NaOH at 60°C for 1 h) followed the ozone treatment. The results showed that pulps with lower kappa numbers and higher viscosities were obtained as the pH of the pulp was decreased from 6 to 2. Rounsaville and Rice (1995) have reported that ozone bleaching of pulps is performed at pH of 2–4 on a mill scale. Improved ozone bleaching at low pH has been attributed to low concentration of hydroxide ions, which catalyse the decomposition of ozone in water and lead to the formation of unselective hydroxyl and perhdroxyl radicals (Pan et al., 1984). Acidification of the pulp may play a key role in the removal of heavy metal ions (Chirat and Lachenal, 1995c). These ions cause decomposition of ozone and reduce the effectiveness of ozone treatment (Gierer and Zhang, 1993). The decomposition products may include hydroxyl radicals, which have been implicated in the reactions that cause damage to the carbohydrates in the pulp (Gierer and Zhang, 1993; Zhang et al., 1994).

### *3.2.3.3 Temperature*

Increase in the reaction temperature is found to be detrimental to the delignification and viscosity of the pulp (Byrd et al., 1992). This effect is attributed to the increase in decomposition of ozone with increase in temperature (Allison, 1985). Ozone reacts with water to form very reactive radicals either from direct decomposition of ozone or from decomposition of reaction products. Eriksson and Gierer (1985) have shown that hydrogen peroxide is formed during ozonation reactions:

$$\text{Ozone}\quad O_3 + H_2O \rightarrow 2HO\cdot + O_2$$
$$O_3 + HO\cdot \rightarrow HOO\cdot + O_2$$

$$\text{Peroxide}\quad 2H_2O_2 \rightarrow HO\cdot + HOO\cdot + H_2O$$
$$H_2O_2 + HO\cdot \rightarrow HOO\cdot + H_2O$$

The hydroxyl radicals (HO·) are very reactive and attack any available compounds including carbohydrates. Their reaction with the cellulose in pulp can contribute significantly to its depolymerization, and it has been a widely held view that this is the principal cause of loss in pulp strength. However, studies by Chirat and Lachenal (1995a) and Ni et al. (1996) have shown that the main degradation of carbohydrates is due to the action of ozone itself. Wang and Patt (1984) have recommended that ozonation temperature should exceed room temperature only if intense mixing and short reaction times are used. Ozonation of hardwood and softwood kraft pulps was studied at temperatures in the range 20–80°C by Liebergott et al. (1992a). They found that a temperature up to 60°C could be used without serious effects on the kappa number and viscosity (Fig. 3.2.3). In case of radiata pine kraft pulp, it was found that the treatment effectiveness was reduced by <10% as the temperature was increased from 25 to 70°C (Allison, 1985). Ozone bleaching on a mill scale is usually done at a temperature in the range 50–65°C (Rounsaville and Rice, 1995).

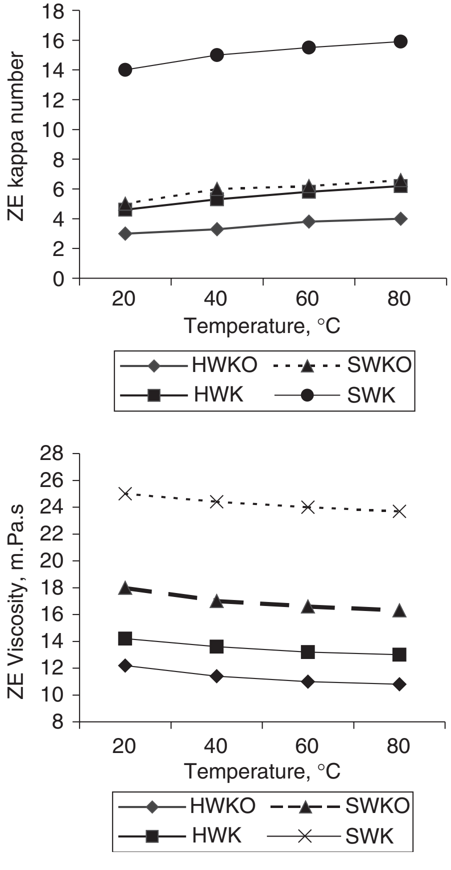


**Fig. 3.2.3. Effect of temperature on kappa number and viscosity after ZE applied to a softwood and hardwood pulp with and without oxygen delignification. (From Liebergott et al., 1992a; reproduced with permission from Tappi Press.)**

### *3.2.3.4 Effect of ozone charge*

The general agreement in the literature is that ~1% ozone charge is the maximum that can be applied before excessive fibre degradation occurs (Fig. 3.2.4) (Liebergott et al., 1992a).

### *3.2.3.5 Carbohydrate-protecting additives*

A wide variety of organic and inorganic additives have been examined for viscosity and strength preservation during ozone delignification/bleaching (Table 3.2.2) (Liebergott et al., 1992b). The improvement in ozone delignification supposed to result from the addition of acetic acid (Allison, 1985;

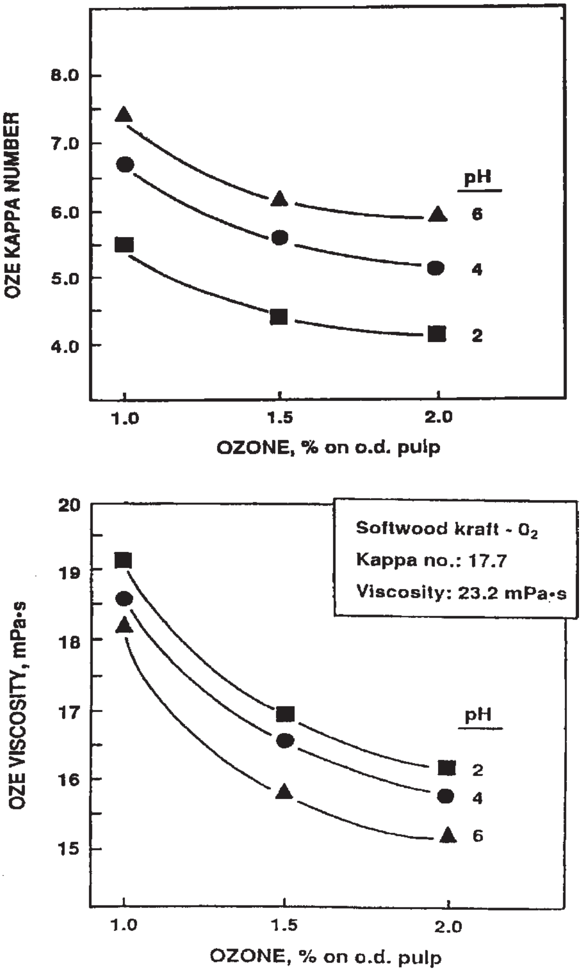


**Fig. 3.2.4. Effect of ozone charge in Z stage on kappa number and viscosity after OZE applied to a softwood kraft-oxygen pulp. (From Liebergott et al., 1992a; reproduced with permission from Tappi Press.)**

**Table 3.2.2 Chemicals examined for viscosity and strength preservation during ozone delignification/bleaching**

---

*Organic*
Acetone
Acetic acid
Formic acid
Galacturonic acid
Sulphamic acid
Peracetic acid
Oxalic acid
Methyl acetate
Ethylene acetate
Sodium acetate
Acetic anhydride
Nitromethane
Diazomethane
Methanol
Ethanol
Butadiene
*n*-Butanol
Methylethyl ketone
L-cystine
Thioglycolic acid
Acrylonitrile
Ethylene oxide
Pyridine
Methyl cellosolve
ρ-Phenylenediamine
Pyrogallol
Glucose
Dextrin
Starch
Lecithin
Urea
Lignin
CMC
EDTA/DTPA
DMSO
DMF
DABCO
Formamide
Hydroquinone
ρ-Benzoquinone
Triethanolamine
Monoethanolamine
Trioxane
Polyethylene glycol

*Inorganic*
Sodium carbonate
Sodium hydroxide
Sodium formate
Metal borohydrides
Hydrogen peroxide
Sulphur dioxide

**Table 3.2.2** (*Continued*)

Sulphuric acid
Chlorine
Hypochlorite
Hypochlorous acid
Hydrochloric acid
Chlorine dioxide
Oxygen
Magnesium compound
Iodine compounds
Hexadecyl, -nonyl-, or trimethyl $NH_4Br$
$NO_2$

From Liebergott et al. (1992a). Reproduced with permission from Tappi Press.

Brolin et al., 1993; Mbachu and Manley, 1981; Lachenal and Bokstrom, 1986; Xu et al., 1995), formic acid (Mbachu and Manley, 1981; Xu et al., 1995; Allison, 1982) and oxalic acid (Lindholm, 1989; Mbachu and Manley, 1981; Xu et al., 1995) remains contradictory, especially considering the excess of acid required to detect an advantage over sulphuric acid (Lindholm; 1989; Brolin et al., 1993). In general, the particular acid used to ensure efficient delignification is not as important as maintaining a pH of $<3$ during ozonation (Bouchard et al., 1995).

Jacobson et al. (1991), Kamishima et al. (1977) and Allison (1982) have reported that certain organic additives, specifically methanol, urea–methanol and dimethylformamide help to preserve viscosity to varying degrees during an ozone treatment, but the quantities required are very high. Study by Jacobsen et al. (1991) has shown that 50% replacement of water by methanol increased the viscosity of a softwood kraft pulp by only 100 viscosity units ($dm^3$ kg). Reitberger and Gierer (1988) have reported that methanol has the ability to act as a radical scavenger, thereby preventing free radical species from contacting the carbohydrate fraction. Ni et al. (1994), however, have observed a viscosity increase of only 2–3 mPa units when a kraft pulp acidified to pH 1.8 with sulphuric acid was impregnated with a 5% methanol solution before ozonation. The addition of small amounts of iron and copper salts (Ni et al., 1994; Chirat and Lachenal, 1995a; Kamishima et al., 1977) was found to increase cellulose degradation slightly. The presence of cobalt ($Co^{2+}$) and iron ($Fe^{2+}$ and $Fe^{3+}$) enhanced ozone decomposition in sulphuric acid at pH 3, but considerably less in acetic acid at pH 3 (Pan et al., 1984). Chirat and Lachenal (1995a) have reported that magnesium compounds did not protect cellulose during ozone delignification. Removal of transition metals before a peroxide stage is essential but whether this is necessary before an ozone stage is not quite clear. Colodette et al. (1994) and Ni et al. (1994) claim that ozonation at medium consistency is insensitive to metal ions. The improved effect of operating an ozone stage after an acid wash (Lachenal and Bokstrom, 1986; Bergnor et al., 1994) or after chelation with EDTA or DTPA (Chirat et al., 1992; Allison, 1985) has been attributed to the removal of metal ions. A detailed investigation aimed at isolating the effects of process variables and metal ions in pulp is necessary to clarify their effect on ozonolysis reactions.

Colodette (1994) and Brown et al. (1994) have reported that pretreatment with xylanase enzyme (X) provides a brightness increase of 2–4 points when it precedes an ozone stage in OXZP, XQP(ZE)P and OXZED sequence. A combination of the simultaneous use of ozone and chlorine dioxide seems to be an attractive proposition. For example, 6 kg/tp of ozone can save 10 kg $ClO_2$/tp in delignification of pulp to a given kappa number in (DZ) or (ZD) combinations. The formation of AOX is further reduced relative to 100% $ClO_2$ substitution in delignification. Mills that have ozone generation installed for occasional bleaching without chlorine compounds can utilize it continuously to save chlorine dioxide.

### *3.2.3.6 Extraction after ozonation*

Alkaline extraction reduces the kappa number of pulp after ozone treatment by 2–5 units and is beneficial to the bleaching process by reducing the need for the application of more costly bleaching chemicals in later oxidizing stages (Table 3.2.3) (Gullichsen, 2000). The effect of ozonation on carbohydrates becomes evident only in a subsequent alkaline treatment. The

**Table 3.2.3 Bleaching with and without alkaline extraction after ozone delignification of oxygen-delignified softwood kraft pulp**

| Pulp source | Western Canadian softwood | | Black Spruce | |
|---|---|---|---|---|
| Kappa number after cooking | 33.3 | | 30.6 | |
| Kappa number after ODL | 19 | | 15.1 | |
| Viscosity after cooking (mPa s) | 28.6 | | 42 | |
| Viscosity after ODL (mPa s) | 22.3 | | 29.7 | |
| Bleaching sequence | ZD | ZED | ZP | ZEP |
| Z, % $O_3$ | 0.5 | | 0.5 | |
| E, % NaOH | 1 | | 0.5 | |
| D, % $ClO_2$ | 1 | | — | |
| P, % $H_2O_2$ | — | | 2 | |
| Kappa number after Z or ZE | 6.8 | 5.7 | 6.8 | 5.8 |
| Brightness (% ISO) after D or P | 83.4 | 89.2 | 76.1 | 85.1 |
| Viscosity (mPa s) | | | | |
| After Z or ZE | 18.9 | 17.2 | 23.4 | 24.8 |
| After D or P | 16.7 | 15.4 | 21.6 | 22.8 |

*Notes*: Z stage: 40% consistency, ambient temperature; end pH = 2.5. E, D and P stages: 10% consistency; E: 70°C, 90 min; P: 80°C, 10 min, D: 70°C, 180 min. From Gullichsen (2000). Reproduced with permission from Fapet OY, Finland.

viscosity drop in the E stage is thus mainly related to reactions with ozone. This has been proven by reducing the pulp with borohydride after ozonation, which eliminates degradation (Gupta and Eckert, 1984; Hartler et al., 1987, 1991; Chirat and Lachenal, 1995c; Lindholm, 1993; Kordsachia et al., 1990). The alkaline extraction stage is clearly beneficial from a brightness point of view, and carbohydrate degradation is modest when using alkaline extraction after ozonation.

### *3.2.3.7 Carryover of dissolved organic matter from other delignifying or bleaching stages*

Adequate washing before ozone delignification is very important for efficient use of ozone as it reacts with dissolved organic material carried over from other delignifying or bleaching stages (Funk et al., 1993; van Lierop et al., 1996). Ozone delignification is very sensitive to carryover from earlier delignification stages (and also in some degree to other oxidation stages in bleaching) but not to direct carryback from itself and other Z stages. Munro (1993) has reported that carryback from the Z stage improves selectivity. Fig. 3.2.5 shows the effect of carryover from oxygen delignification on specific ozone consumption (van Lierop et al., 1996). It can be seen that half the ozone needed for delignification can be consumed by carryover if it is as high as 15 kg $O_2$/tbdp. In using COD as a measure of carryover, one needs to ascertain the origin of that COD. Nutt et al. (1993) have reported that the effect of the carrryover to the ozone stage is found to be less sensitive at high consistency than at medium consistency because more water is removed from the pulp ozonated at high consistency.

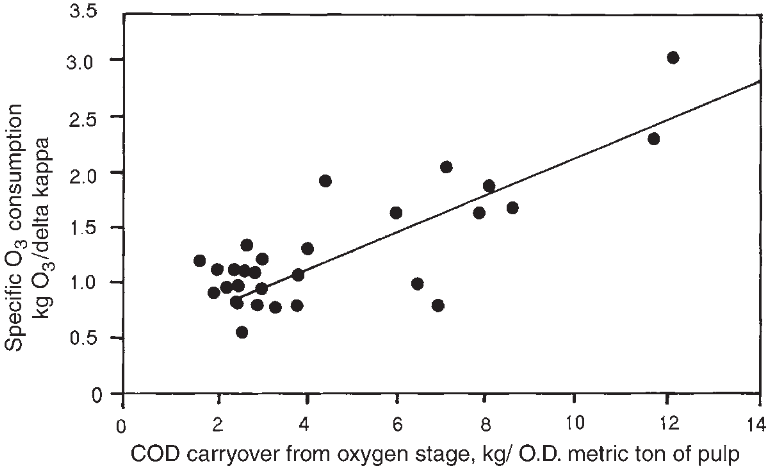


**Fig. 3.2.5. Effect of carryover from oxygen delignification on specific ozone consumption. (From van Lierop et al., 1996; reproduced with permission from Tappi Press.)**

### 3.2.4 Bleaching of different types of pulp with ozone

This subject has been comprehensively reviewed by Byrd et al. (1992). The results of laboratory studies on a range of kraft, kraft–anthraquinone, kraft–oxygen pulps from hardwoods and softwoods were reviewed. In general, better results were obtained with hardwood kraft pulps than with softwood pulps, particularly in relation to the strength properties of the bleached pulps. Although many of the researchers reported that results from ozone bleaching were not as good as those from chlorine bleaching, there were others who found that bleached pulps of comparable brightness and strength could be prepared using ozone. Byrd et al. (1992) concluded that, in general, sulphite and bisulphite pulps respond well to ozone delignification and bleaching. Many of the studies took advantage of the good response of these pulps to oxygen delignification and preceded the ozone stage with an oxygen stage. Response of soda–anthraquinone pulps bleached with ozone, were about the same as that of kraft pulp. Pulps prepared by oxygen pulping of hardwood were more responsive to ozone than kraft pulp, and the bleached pulp had strength properties superior to those of kraft pulp bleached conventionally.

Ozone has been recommended as a replacement for chlorine or chlorine dioxide in the first stage of bleaching. This is not practical if the entering kappa number is high. Kappa numbers decrease easily from >30 to <5 without any significant loss in pulp viscosity with standard chlorination stage followed by alkaline extraction . However, ozone cannot delignify as far, and causes serious viscosity reductions. So, the entering kappa number should be lower for ozone delignification, which can be achieved by using oxygen delignification, extended cooking, or both. Ozone is being used in both ECF and TCF bleaching sequences (Table 3.2.4). Ozone stage is commonly positioned after an oxygen delignification stage. Some sequences are arranged with an ozone stage even later in the sequence, following a peroxide stage. Final brightening is done with peroxide (TCF), chlorine dioxide (ECF) or both. Chelation stage is used in the sequence to improve the bleaching efficiency of the ozone or peroxide stage. Byrd (1992) has extensively studied the implications of where the ozone stage is placed within a bleaching sequence. The OZ sequence is preferred to ZO because a given kappa number can be achieved with less ozone consumption and viscosity loss (Lachenal and Nguyen-Thi, 1993). The work of Kobayashi et al. (1976), Mbachu and Manlay (1981), Rothenberg et al. (1975) has revealed that a multistage ozone treatment requires 20–50% less ozone than does a single stage, provided a washing step is placed between the ozone stages. The improved delignification of the multistage system was attributed to the intermediary removal of degraded lignin products which, when generated in a

**Table 3.2.4 Commercial ozone-bleaching sequences**

| |
|---|
| (EOP)ZP |
| OZ(EO)D |
| OQZP |
| O(DZ)(EOP)D(EP)D |
| OZ/Q(EOP)P |
| OQPZD |
| OQPZP |
| O(ZD)(EO)(ZD)(EP)D |
| OQZ/Q(EOP)ZP |
| ZEP |
| OPZEP |
| O(ZD)(EO)D |
| ZPZP |
| OZPZP |
| OZEDD |

single-stage treatment, consume part of the ozone. A sequence that includes ozone in several positions, for example OZEZP and OPZEZ, can provide an 88–89% brightness pulp (Phillips et al., 1983), but a final Z stage causes the bleached pulp to undergo considerable brightness reversion, unlike a pulp bleached in a sequence consisting of a peroxide stage at the end of the sequence (Lachenal and Nguyen-Thi, 1993).

Ozone is generally applied as part of an OZEP sequence (Libergott et al., 1992a, b; Sixta et al., 1991), but placing the Z stage towards the end of the sequence is found to increase the brightness and reduce the ozone requirement (Colodette et al., 1994; Kassebi et al., 1982; Lachenal and Nguyen-Thi, 1993; Earl and Nguyen, 1993; Dillner and Tibbling, 1993, 1994; Dahllof, 1994; Stromberg and Szopinski, 1994). A study by Earl and Nguyen (1993) has shown that placing an ozone stage between two peroxide stages "reactivates" the pulp so that it responds better to the second peroxide stage. This is shown by a comparison of OQPP, OZQPP and OQPZP sequences, which yielded kraft pulps having brightness values of 77.9%, 83.9%, and 89.9%, respectively (Table 3.2.5) (van Lierop et al., 1996). Peroxide stage delignifies and especially bleaches an oxygen-delignified kraft pulp more extensively than does an ozone stage (Table 3.2.6) (van Lierop et al., 1996). The extent of brightening and delignification depends on the placement of ozone and peroxide in a sequence. The OQPP, OZQP and OQPZ sequences produce pulps having similar brightness values (77.5–77.9%) but with markedly different kappa numbers: 5.9 after OQPP, 3.6 after OZQP and 2.7 after OQPZ (Table 3.2.6). Malinen et al. (1994) have compared OQZPZP and OQPZP sequences in which a 0.55% ozone charge was split between the two ozone stages in the first sequence; in this case, the OQPZP sequence produced a pulp having a slightly higher brightness and viscosity.

**Table 3.2.5 Brightness of a softwood kraft pulp bleached in TCF sequences**

| Bleaching sequence | Brightness (% ISO) |
|---|---|
| OQPP | 77.9 |
| OZQPP | 83.9 |
| OQPZP | 89.9 |

Based on data from van Lierop et al. (1996).

**Table 3.2.6 Kappa number and brightness of softwood kraft pulp bleached in TCF sequences**

| Bleaching sequence | Kappa Number | Brightness (% ISO) |
|---|---|---|
| OZ | 9.9 | 46.7 |
| OQP | 7.1 | 71.1 |
| OQPP | 5.9 | 77.9 |
| OZQP | 3.6 | 77.5 |
| OQPZ | 2.7 | 77.6 |
| OZQPP | 2.8 | 83.9 |
| OQPZP | Not determined | 89.9 |

*Notes*: Kappa number afer O, 15.0; Z: 0.5% $O_3$, 10% consistency; Q: EDTA chelation at pH 6; P: 2.5% $H_2O_2$ (0.9–1.9% consumed), final pH 11.
Based on data from van Lierop et al. (1996).

The combination of ozone and chlorine dioxide sequentially in a single stage as a (ZD) or (DZ) configuration early or later in a sequence is emerging in several mills (Finchem, 1998). In 1998, there were five or six DZ or ZD bleaching stages operating in the world. Investigating the combined stage, Chirat and Lachenal (1995b) have reported that replacing a portion of the $ClO_2$ charge in the first bleaching stage with $O_3$ has reduced the formation of AOX for both hardwood and softwood bleaching. In obtaining similar final brightnesses, replacement ratios (of $O_3$ for $ClO_2$) for hardwood pulps exceeded those for softwood pulps. For hardwood pulps, 0.6% $O_3$ replaced 1.31% $ClO_2$. For softwood pulps, 1.2% $O_3$ replaced 1.05% $ClO_2$ (Chirat and Lachenal, 1995b). Full replacement of the D1 stage by a Z stage required the use of significant amounts of $O_3$, which can explain the lower final pulp viscosities (Chirat and Lachenal, 1995b). It was found that when D and Z are combined into a single stage, synergies can be exploited. Chirat and Lachenal (1995b) identified several advantages of combining chlorine dioxide and ozone into a single bleaching stage, including the following:

(1) One washing stage can be eliminated, saving electrical energy and, depending on the filtrate recycling scheme, shower water.
(2) Chlorine dioxide stages are acidic, eliminating the need to acidify specifically for the ozone stage.

(3) Ozone is capable of reacting with (i.e. 'destroying') some AOX in bleaching effluents.
(4) The reaction chemistries of chlorine dioxide and ozone with residual lignin complement one another, making the combined stage particularly efficient as a delignifying stage.

According to the Chirat and Lachenal (1995b), the residual lignin in pulp is more depolymerized after a D stage than after a Z stage at the same lignin content. They point out there are more carboxyl groups formed on lignin during the ozonation reaction than during a typical first D-stage reaction. They proposed these phenomena as an explanation for the relative ease with which lignin can be solubilized during the Z stage. Ozone is also capable of reacting with almost all types of structures in the lignin, whereas $ClO_2$ reacts only with the free phenolic groups. Chirat and Lachenal (1995b) recommended adding $ClO_2$ first so it can react with the free phenolic groups before the highly reactive ozone is introduced, concluding that reaction kinetics clearly favoured the DZ approach relative to the ZD approach. They reported that 1 kg could replace from 2 to 4 kg of chlorine dioxide when added to the first stage of a DEDED bleaching sequence. Studies have continued to investigate the reaction kinetics and to compare the results of DZ and ZD bleaching (Chirat et al., 1996; Homer et al., 1996, 1997).

Norman Liebergott of Liebergott and Associates Consulting Inc. in Laval (Quebec, Canada) reports that while the DZ vs. ZD debate is continuing, the choice should hinge on the existence of an upstream oxygen delignification process (Finchem, 1998). For oxygen-treated pulps, the initial $ClO_2$ of a DZ stage does not seem to give the same result as the initial charge of $O_3$ in a ZD stage. The reason is that the $ClO_2$ competes to react with the same structural groups that the oxygen reacted with. On the other hand, $O_3$ reacts with different structural groups. One of the major drawbacks to the ZD approach is the pH shift, which is required. The pH is to be slightly increased between the addition of $O_3$ — and its reaction — and the addition of $ClO_2$. If the pH is not increased then the pH will be very low (about 2.0) before the $ClO_2$ is added. The low pH favours the formation of chlorate, and chemical efficiency is negatively affected. Typically, it is required to add a small amount of alkali to increase the pH from 2.0 for the Z stage to a pH of 3.5–4.0 for the D stage to achieve maximum efficiencies for both stages. On the other hand, in a DZ sequence, the pulp typically exits the D stage at a sufficiently low pH for an effective Z stage. And for both approaches — DZ and ZD — the pulp should be degassed between chemical additions. According to Liebergott, most D stages in the United States run at fairly low consistencies (3.5%), which provides a challenge when implementing ozone. This low-consistency approach is an artifact of the D-stage origin. Most of the existing D stages are running in place of their predecessor chlorination stages and use much of the same equipment. Ozone, of course, runs much better at consistencies of 10%. This means that early adopters of Z-stage bleaching have had to raise the consistency of the pulp. Thus, there is a lot of work directed at running a Z stage at consistencies closer to 4%. The primary issue is mixing because, at low consistencies, considerable mixing is necessary.

According to David Scheeff, group director of pulp and paper at ozone supplier Air Liquide, ‘‘The real benefit of adding $O_3$ to the first D stage is that a mill can ‘beef up’ its bleaching sequence without increasing its $ClO_2$ capacity.” And the addition of $O_3$ to a typical low-consistency D stage can be uncomplicated. Most mills $O_3$ needs will be satisfied by third-party chemical specialty firms that build and operate the $O_3$ generator system, allowing the mill to buy their ozone ‘over the fence’. The big attraction is that no capital is needed. Presumably, the specialty firms enjoy lower costs of capital, as well as greater operating focus and expertise. Also, by integrating the oxygen plant with the ozone plant, some operating efficiencies can be achieved (Finchem, 1998). Jorge Colodette, professor of wood and bleaching chemistry at the Federal University of Viscosa in Viscosa, Brazil, points out that in terms of investment, DZ is the cheapest way to get $O_3$ into the process. It is much cheaper than adding a full Z stage (Finchem, 1998). If the chloride concentration of the effluent is not an issue, the success of DZ (or ZD) bleaching will hinge on the replacement ratio. For mills that are concerned about the chloride concentration in their effluents, DZ (or ZD) bleaching has an added advantage. As mills replace $ClO_2$ with $O_3$, they also reduce the chloride concentrations in their bleach plant filtrates. This makes effluent closure a less complicated issue. The replacement ratios in a mill setting are typically in the range 2–2.5 kg of $ClO_2$ to 1 kg of $O_3$. In many cases, it has been possible to reduce a mill’s chemical cost compared with the fully absorbed operating cost of adding a new $ClO_2$ plant or expanding the capacity of the old one, either physically or with a more efficient chemistry. Plants in the 3–5 tpd (i.e. replacing 6–12 tpd of $ClO_2$) are very cost-effective. The cost of smaller ozone plants-less than 1 tpd rises, making them uneconomical (Finchem, 1998).

Brazilian pulp producers have been aggressive in implementing ozone-bleaching sequences (Finchem, 1998). Of the four ozone installations in Brazil, two are Z stages within TCF bleaching sequences, one is a Z stage, which is part of an ECF sequence, and one is a DZ stage at Votorantim. E.B. Eddy’s Espanola Mill in Ontario has announced plans to modify its bleach plant to add a ZD stage. The mill opted for the ZD order since its fibreline includes oxygen delignification. The mill’s D0 stage currently runs near 10% consistency. When they add the $O_3$, they will be able to run the combined stage at 10% consistency (Finchem, 1998).

### 3.2.5 Ozone-bleaching processes and equipment

Two types of systems are used commercially for ozone delignification/bleaching; these are generally characterized as high- and medium-consistency systems (Singh, 1982; Nutt et al., 1993; Gotleib et al., 1994; Berry et al., 1995; Schwarzl, 1991; Peter, 1993; Munro, 1993; Funk et al., 1992; Dahllof, 1994). They differ considerably in equipment requirements and are based on different approaches regarding how to contact ozone containing gas with liquid in or around pulp. Both processes have residual gas containing not only oxygen but also ozone, which must be destroyed due to its toxic nature to prevent its release to the atmosphere. Lenzing AG in Austria was the first mill in the world to install an ozone stage with a medium-consistency Z stage in an (EOP)ZP sequence (Peter, 1993). In North America, the high-consistency ozonation was used by Union Camp at Franklin, Virginia, as part of an OZ(EO)D sequence (Nutt et al., 1993). The ozone- bleaching process implemented at Franklin was the first commercial utilization of high- consistency ozone bleaching of pulp in the world and was the world's first commercial use of ozone bleaching of any type for softwood pulp.

In December 2000, there were 25 ozone installations in operation worldwide and one under construction. Of these, three mills in North America utilize ozone for bleaching of virgin pulps (Union Camp in Franklin, VA; Consolidated Papers in Wisconsin Rapids, WI; Domtar (formerly E.B. Eddy Forest Products) in Espanola, ON). Recently, there have been new start-ups at Votorantim in Brazil and Domtar (formerly E.B. Eddy Forest Products) in Canada.

#### *3.2.5.1 High-consistency ozonation*

High-consistency ozonation occurs in a gas-phase reactor in which a mixture of ozone and oxygen gas and high-consistency fluffed pulp are in contact. The reactor can operate at modest pressures (Sonnenberg, 1994; Kappel et al., 1994; White et al., 1993). An example of high-consistency ozone stage is shown in Fig. 3.2.6 (van Lierop et al., 1996). The pulp is washed thoroughly to reduce the carryover of organic material into the Z stage and acidified to pH 2–3 and then thickened in a press to 30–40% consistency and transported in a plug screw feeder to a fluffer to increase the gas/solid interface by breaking flocs. The pulp is then dropped into a series of horizontal conveyor reactors having axially rotating shafts on which pitched paddles are mounted. The gas mixture is introduced at the bottom of the horizontal reactor so as to provide counter-current gas flow to pulp travelling from the top to the bottom of the system. The pulp is dropped into a receiving tank where it is diluted by intensive agitation to a consistency suitable for feeding a drum washer. The pulp is washed with extraction stage filtrate, and

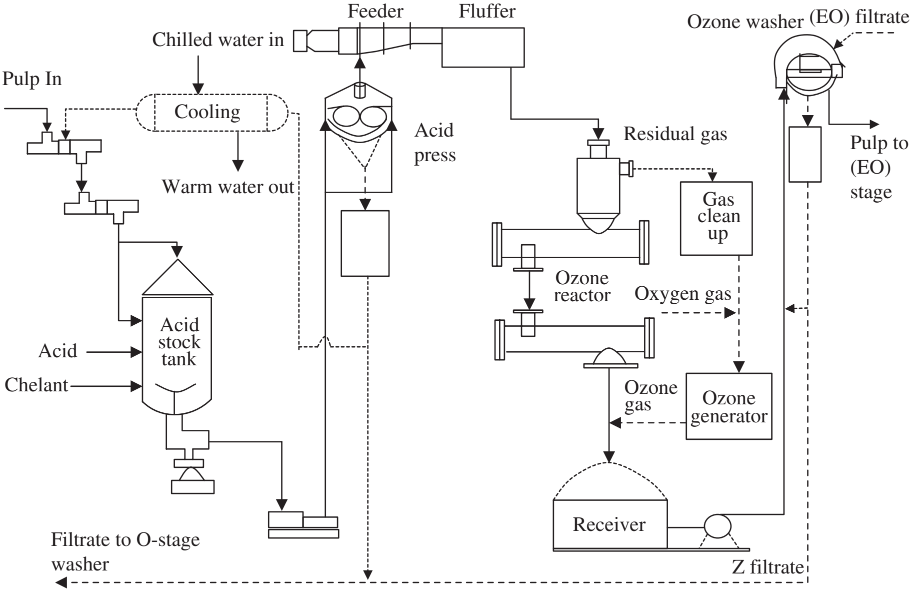


**Fig. 3.2.6. Flowsheet for high-consistency ozone bleaching system. (From van Lierop et al., 1996; reproduced with permission from Tappi Press.)**

then fed to the extraction stage. Off-gas still containing some residual ozone is led to a gas cleanup stage where ozone and other reaction product gases are destroyed; the pure oxygen is returned (after oxygen make-up) to the ozone generator. The pulp feeding system before the press includes a tank for acidification and a press filtrate circulation system for press feed consistency control and possible cooling (Gullichsen, 2000).

A typical high-consistency ozone stage preceded by chelation (Q) is shown in Fig. 3.2.7 (Pikka et al., 2000). Before entering the ozone reactor, the pulp is acidified to pH 2–3, and a chelating agent is added in the Q1 stage. The pulp is then pumped to a dewatering press, where the outlet consistency is adjusted to a value above 35%. The high-consistency pulp then passes through a plug screw feeder and into a fluffer before entering the ozone reactor. The reactor's internals are specially designed to provide mixing to ensure homogeneous delignification and ozone conversion. Indirect cooling controls the pulp temperature in the reactor. In order to minimize ozone decomposition and pulp strength losses, it is important to control the temperature of the pulp entering the reactor. From the ozone reactor, the pulp is deposited in a receiver tank for diluting and treatment with a chelant or in a short extraction stage before washing. The chelant treatment (ZQ) is used when the next bleaching stage is a peroxide stage, P or (Po). Alkaline extraction (ZE) is used when a chlorine dioxide stage follows the Z stage.

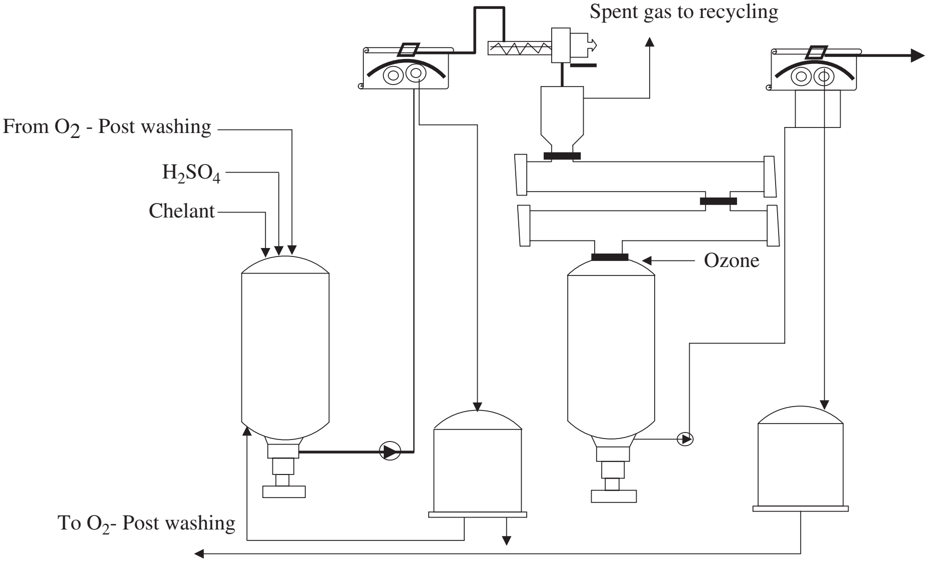


**Fig. 3.2.7. Z-stage with Q-stage tank, dewatering press, plug screw feeder, fluffer, ozone reactor, discharge tank (Q or E) and final washing on a displacement press. (From Pikka et al., 2000; reproduced with permission from Fapet OY, Finland.)**

**Table 3.2.7 Operating parameters for high-consistency ozonation**

| Parameters | High consistency |
|---|---|
| Temperature | <150°F |
| Pressure | Atmospheric |
| pH | 2.5 |
| Ozone (wt%) | 6–14% $O_3$ |

The washing is done on any efficient washer. Table 3.2.7 shows operating conditions for high-consistency ozonation.

Metso Paper has developed ZeTrac ozone-bleaching process, which marks a clear milestone in the development of environmentally sound bleaching methods (Lindstrom, 2003). This process operates at high consistency. It allows to combine high brightness and strength with cost efficiency. In fibre processing, ZeTrac represents a modern and intelligent way, in which caring for the environment is compatible with quality and production goals. Other ozone-bleaching processes in the market operate with medium-consistency pulp. In these systems, the high content of water prevents the effective use of ozone. ZeTrac works with a high consistency of up to 40 %. In the ozone reactor, the virtually dry fibres whirl around like flakes in a snowstorm allowing the ozone/oxygen mixture to effectively react with the fibres. Another advantage is that in high-consistency system the concentration of ozone used can be low, which means lower investment costs in ozone production. ZeTrac enables to build a more closed system with a lower effluent discharge. The system can be closed without mixing acid and alkaline washing filtrates that could lead to troublesome precipitation. Although ozone bleaching is an acidic process, there is no need for washing before alkali is added due to the high pulp consistency. When using ozone in mill operations, the safety aspect is of the utmost importance. The ZeTrac process has been designed in such a way that the reactor works at a slight under pressure and thus ensures that no gas can escape to the ambient air. In today's bleaching technology, ZeTrac represents by far the most intelligent way to combine high brightness with care for the environment. The first HC-ozone delignification process was brought into operation in 1992 at Union Camp's Franklin mill in the United States. Since then corresponding systems have been installed for many other customers worldwide. The ZeTrac process features the latest development in ozone-bleaching technology and the first system was taken into operation at the Burgo Ardennes mill in Belgium. The next ZeTrac projects are under construction for Oji Paper Nichinan mill in Japan and for VCP Jacarei in Brazil.

#### *3.2.5.2 Medium-consistency ozonation*

Medium-consistency processes for ozone bleaching have, so far, predominated in the industry because of lower capital cost, simplicity and ease of implementation compared with high-consistency processes (Sixta et al., 1991, 1994; Peter, 1993; Laxen, 1990; Berry et al., 1995; Homer et al., 1996; Helander et al., 1994; Oltmann et al., 1992; Greenwood and Szopinski, 1992; Funk et al., 1993). The main steps in medium-consistency ozonation are shown in Fig. 3.2.8 (van Lierop et. al., 1996). Pulp goes from a brown stock washer or decker after oxygen delignification at 12–16% consistency into a medium-consistency pump drop chute into which acid or acidic effluent is introduced for pH control at the suction side of the pump. The pulp suspension is then pumped to one or more medium-consistency high-shear mixers fed with the ozone–oxygen gas mixture, and then to a pressurized reactor. The gas is introduced under pressure (7–10 bar) via a compressor to reduce the absolute gas volume. The reacted pulp is blown out of the short retention time reactor tube to a degassing chute, where gas is separated and the pulp suspension is pumped to a washer, all at medium consistency without dilutions. Off-gas is scrubbed and excess ozone is destroyed; the remaining oxygen is piped either to reprocessing or to an oxygen-delignification stage. The mixing conditions concerning gas volume to fibre suspension volume are similar to those in medium-consistency chlorination. The system differs

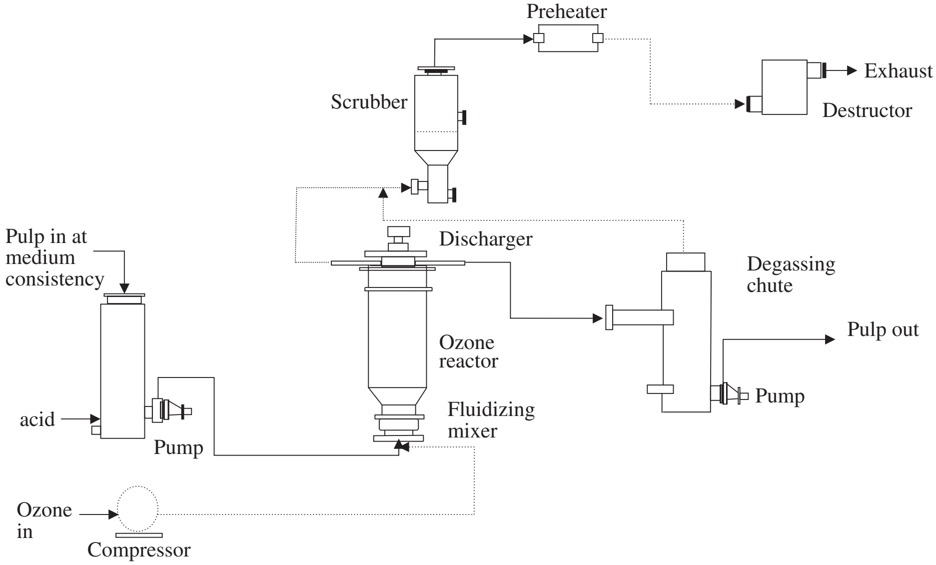


**Fig. 3.2.8. Flow sheet of a medium-consistency ozone delignification system. (From van Lierop et al., 1996; reproduced with permission from Tappi Press.**

from chlorination in that only a fraction of the gas is consumed (i.e. the ozone) and the rest passes unreacted. The gas–liquid–fibre dispersion is much more unstable than in chlorination, where all the gas is consumed within 20–40 s after addition. Ozone reaction tubes are therefore designed for high velocity to ensure stable flow in the reactor (Gullichsen, 2000).

Medium-consistency ozone bleaching was developed at the beginning of the 1990s. Ozone is an efficient delignifying agent, and its reaction with pulp is very fast. The essential components of the machinery in the bleaching stage are the mixers. Since the ozone concentration is only 10–14% (by wt) in the added gas, the total gas volume is high. The efficiency of the ozone stage depends on the gas volume. High pressure and high ozone concentration reduce the required mixing energy. The temperature in an ozone stage is normally about 50°C, and the pH is ~3. The kappa number reduction over an ozone stage is normally about 1 unit/kg ozone. At high kappa number levels, the kappa number reduction is higher than at lower levels.

MC ozone bleaching is not sensitive to transition metals, probably due to the very fast reaction rate. Theoretically, transition metals act as catalysts for ozone decomposition. Carryover from an oxygen stage consumes ozone. Good washing before the ozone stage is therefore beneficial. Ozone has a reputation for reducing the strength of pulp. This is primarily the result of laboratory studies in which the reaction time with ozone and pulp is long (~20 s). In mill scale, the viscosity loss is not as high as in laboratory scale, and no apparent strength losses over the ozone stage have occurred. The retention time in mill scale is normally less than 1 s in each mixer. Research on the kinetics in ozone bleaching shows that the reaction rate between ozone and lignin is much faster than the corresponding rate between ozone and carbohydrates (Pikka et al., 2000). This indicates that MC ozone bleaching in mill scale is more selective than in laboratory scale and explains why medium consistency is better than high consistency regarding selectivity.

The kappa number reduction achievable in mill applications is normally 0.7–0.9 kappa number/kg ozone for softwood and 0.9–1.1 for hardwood. In single-stage ozone bleaching, the charge is normally 3–5 kg/adt. If the sequence includes several ozone stages, the charge in the second stage is normally 2 kg/adt. Charges exceeding 6 kg/adt should be avoided, since they may affect the strength properties of the pulp. Table 3.2.9 shows mill results for an ozone stage.

Due to the high pressure of MC ozonation, the pressure of gas from the ozone generators is increased to approximately 1200 Mpa with water ring compressors. To prevent the decomposition of ozone, the water in the compressor must be acidic. Residual gas emissions from the ozone stage go to the ozone destructor through a gas washer. Normally, residual ozone decomposes into oxygen at high temperature. After this treatment, the gas containing primarily oxygen, can be used in other mill processes. It can also be cleaned and reused as gas feed to the ozone generators.

Table 3.2.8 shows operating conditions and Table 3.2.9 shows mill results from medium consistency ozonation (Pikka et al., 2000).

### 3.2.6 Advantages

For a while many mills looked at ozone bleaching to produce TCF pulps because of tightening environmental regulations. Today ozone is seen as a complement to produce ECF at a lower cost than standard ECF pulp without ozone. With replacement ratios of $ClO_2$ by $O_3$ in the range of 2.0–3.5, savings of US$6–8/mT of pulp net can be achieved.

**Table 3.2.8 Operating parameters for medium-consistency ozonation**

| Parameters | Medium consistency |
|---|---|
| Temperature | $<150°F$ |
| Pressure | 150 psig |
| pH | 2.5 |
| Ozone (wt%) | 10–14% $O_3$ |

**Table 3.2.9 Mill results from medium-consistency ozone bleaching**

| | Hardwood | Softwood |
|---|---|---|
| Capacity (ADT/day) | 1000 | 900 |
| Kappa number | 9–10 | 9.5–10.5 |
| Washing loss (kg COD/ADT) | 8–10 | 8–10 |
| Retention time (min) | 2.0 | 2.0 |
| Pressures (mixing point) (bar) | 9 | 9 |
| Temperature (°C) | 50–55 | 50–55 |
| pH | 3 | 3 |
| Consistency (%) | 12 | 12 |
| $O_3$ charge (kg/ADT) | 3.5–4.5 | 3.5–4.5 |
| $O_3$ concentration (%) | 9–9.5 | 9–9.5 |
| $O_3$ residual (%) | <5 | ~ 5 |
| $\Delta$kappa/kg/$O_3$ | 0.9–1.1 | 0.7–0.9 |

From Pikka et al. (2000); Reproduced from permission from Fapet OY, Finland.

### 3.2.7 Environmental benefits

Whenever chlorine bleaching chemicals are replaced by non-chlorine chemicals, a reduction in AOX is seen. When ozone completely substitutes the first chlorination stage (C/D), then the extract from the washers following the ozone stage can be recycled to the chemical recovery system leading them closer to closing the mill water loop. If an extraction stage follows the ozone stage, the extract from this washer can also be recycled. This is greatly desired since most of the COD and BOD are contained in this extract.

### 3.2.8 Conclusions

The development and utilization of ozone treatment technology in the bleaching process in the pulp and paper industry has allowed recycling of waste streams from the bleach plant, producing dramatic reductions in the volume of liquid effluent and with pollutants, such as BOD, COD, colour, and chlorinated organics. Ozone is being used by a growing number of mills to produce fully bleached hardwood and softwood pulps that have mechanical properties compatible with most paper-making applications. Significant progress has been made in the optimization of both ECF and TCF sequences.

From an economic point of view, ozone is a highly competitive bleaching chemical, which when compared at equal bleaching power, is typically 1.2–1.5 times less costly than chlorine dioxide. It can be purchased on an ‘over-the-fence’ basis, enabling the mill to benefit from the most appropriate oxygen + ozone supply solution without detracting capital and human resources from its core activities.

ECF sequences combining ozone and chlorine dioxide are economically competitive with sequences using chlorine dioxide only, even when capital expenses for modifying process equipment are taken into consideration. They have the advantage of improved performance and added flexibility with regard to effluent characteristics, and position the mill on the pathway to (nearly) effluent-free bleaching. In combination with (pressurized) hydrogen peroxide, ozone makes it possible to produce fully bleached TCF pulp while maintaining expenditures in bleaching chemicals at levels that are comparable, if not lower, than those pertaining to ECF bleaching. Bleaching lines equipped with oxygen delignification can be retrofitted to ozone-based TCF production with a full bleaching cost, including capital charges on process equipment, only about US$10 higher than that for ECF sequences. Mills that are considering modifying or expanding their effluent treatment facilities may well find that opting for TCF bleaching instead is economically more advantageous.

Bleaching plants that do not yet have oxygen delignification can achieve AOX levels of the order of 0.3 kg/tonne pulp after effluent treatment by combining ‘wise man’s’ delignification with D/Z-based ECF bleaching. The cost of such sequences, capital charges for process equipment included, is comparable or lower than that of standard ECF solutions, whose AOX levels are nearly twice as high. By adopting D/Z-based bleaching, the mill will be in a position to gradually upgrade its sequence to meet evolving effluent standards or market demands, while minimizing the risks of making soon-obsolete investments. Whether it concerns greenfield mills, new bleach lines or retrofit projects, whether the mill wishes to adopt ECF or TCF sequences, oxygen and ozone are today the most cost-effective bleaching chemicals available to the Pulp and Paper Industry.

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## 3.3 Hydrogen peroxide bleaching

### 3.3.1 Introduction

Hydrogen peroxide is a versatile and widely used oxidative bleaching agent in the pulp and paper industry (Anderson, 1992; Anderson and Amini, 1996; Gullichsen, 2000; Troughton and Sarot, 1992; Nelson, 1995, 1998; Lachenal et al., 1992, 1996; Reeve, 1996; Pikka et al., 2000; Beeman and Reichert, 1953; Holladay and Solari, 1963; Andrews and Singh, 1979). It decomposes to give water and oxygen only, so it is ideally suited to applications where the effect on the environment of effluents has to be minimal. Within the field of chemical pulp bleaching, hydrogen peroxide is used mostly as a reinforcement to existing bleaching stages (Anderson, 1992, 1996). Many mills use hydrogen peroxide as reinforcement in the first extraction stage after chlorination, with or without additional oxygen reinforcement and in the second extraction stage. Hydrogen peroxide in alkaline extractions reduces the generation of chlorinated compounds and gives a number of quality improvements to the pulp and the bleach plant effluents (Walsh et al., 1991).

Mills also use peroxide to reduce the total applied chlorine dioxide in the final D stage. As a final stage or in the bleached, high-density storage chest, peroxide is a good brightening agent and can provide increased brightness stability. When peroxide is used to reinforce an extraction stage, the process conditions are relatively mild, and decomposition is not a major factor. However, when peroxide is used as the primary bleaching and delignification reagent, it is usually necessary to operate the peroxide stage at higher temperatures (>100°C) and under pressure (Lachenal et al., 1992; Carlos et al., 1980). Under these conditions, the two competing reactions (pulp bleaching and peroxide decomposition) must be managed. Because transition metals catalyse the decomposition of hydrogen peroxide, this undesirable reaction must be minimized by reducing the metal content of the pulp. Specially designed pressurized hydrogen peroxide stages (PO) have been installed in commercial operations, and have resulted in improved bleaching response at lower hydrogen peroxide consumption (Tibbling and Dillner, 1993; Dillner and Tibbling, 1994; Germgard and Norden, 1994). Commercial sequences, combining an ozone stage and the (PO) stage, have taken the form OZQ(PO).

The conditions of these reinforced extraction stage have usually been those of the original extraction stages in the mill. Fortunately, hydrogen peroxide operates well under conventional extraction conditions in a conventional sequence and the usage of chlorine and chlorine-based bleaching chemicals can be reduced with the skillful application of modest quantities of hydrogen peroxide. The necessity for a reduction in the use of chlorine gas for the bleaching of pulps is no longer a question of debate. Increasingly, market pressure is driving pulp mills towards reduced emissions of all effluents with the eventual goal of a completely closed mill. Closure of a mill will be difficult to achieve if the recycling streams contain chloride ions because of their high corrosivity. As a consequence, one of the stages along the path towards mill closure is the development of a viable, TCF sequence. In the short term, a TCF sequence will allow mills to operate with the least pollution of the environment while the development of the necessary recycling processes is carried out. Additionally, a TCF bleaching process will not cause the formation of any organo-chlorine matter to the pulp.

Hydrogen peroxide is a strong candidate for use in TCF sequences (van Lierop et al., 1993; Troughton et al., 1994; Lapierre et al., 1995b). Hydrogen peroxide is best known for its bleaching reactions at alkaline pH in mechanical and chemical pulp bleaching as well as deinking. Hydrogen peroxide can also be used as a starting chemical for the production of peroxy acids. The peroxy acids, which have a higher oxidation potential than hydrogen peroxide, are capable of selectively oxidizing lignin (Basta et al., 1994a; Amini and Webster, 1994; Liebergott, 1994; Anderson et al., 1995; Seccombe, 1994; Geng et al., 1993; Devenyn et al., 1993, 1994; Poppius-Levlin et al., 1991; Lai and Sarkanen, 1968). Peroxy acids can increase the TCF pulp brightness threshold by 3–4 points when applied at the start of a kraft TCF bleaching sequence (Basta et al., 1994a). They are also being investigated as a means of activating oxygen stages and hydrogen peroxide bleaching stages (Amini and Webster, 1994; Liebergott, 1994).

With chlorine-free sequences, the conditions that hydrogen peroxide is being used in should be adjusted to those at which it operates the most effectively. These conditions can often be found readily in current pulp and paper mills. The recent advances in hydrogen peroxide bleaching have been possible because of a better understanding of the role of metal ions in the decomposition of peroxide (Lapierre et al., 1995b). Hydrogen peroxide is not a good delignifying agent, and under conventional conditions for kraft pulps, a residual amount remains in the liquor. If more severe conditions are used, the peroxide is decomposed by metal ions in the pulp. If the correct metal management procedure is used, the temperature and bleaching time can be increased to obtain more beneficial hydrogen peroxide consumption and a higher final brightness.

### 3.3.2 Fundamental aspects of peroxide bleaching

#### *3.3.2.1 Peroxide bleaching chemistry*

Chemistry of hydrogen peroxide bleaching has been reviewed by Anderson and Amini (1996) and Gullichsen (2000). Bleaching chemical pulps to high brightness with alkaline hydrogen peroxide requires: (1) the elimination of conjugated carbonyl groups in the lignin structures by the perhydroxyl anion $HOO^-$ and (2) an extensive removal of lignin through degradation/dissolution, by reaction with $HO^\bullet$ and $O_2^{-\bullet}$ radicals (Backman and Gellerstedt, 1993); the radicals react with the lignin aromatic rings in an oxidative decomposition, which increases the molecular hydrophilicity and solubility of the lignin.

The reactivity of $HO^\bullet$ and $O_2^{-\bullet}$ towards aromatic lignin (phenolic structures) is only slightly higher than towards cellulose (primary and secondary alcohols). Therefore, if $H_2O_2$ decomposes too fast and the concentrations of $HO^\bullet$ and $O_2^{-\bullet}$ become too high, selectivity towards lignin is lost and cellulose degradation as well as lignin degradation occurs. Lignin degradation increases hydrophilicity (water solubility), which assists pulp delignification while cellulose degradation decreases the degree of polymerization and eventually weakens the pulp. A slow $H_2O_2$ decomposition rate will also provide longer time for pulp exposure to $HOO^-$ anions giving better brightening. From this discussion, $H_2O_2$ decomposition is necessary to delignify/bleach pulp, but the rate of $H_2O_2$ decomposition into reactive intermediates must be controlled in order to achieve optimal bleaching (Backman and Gellerstedt, 1993). Untreated pulp contains high levels of metals, which catalyse $H_2O_2$ decomposition too rapidly for selective and efficient pulp bleaching. Controlled $H_2O_2$ decomposition through controlled metal content in pulp is thus necessary for pulp bleaching.

The objective of peroxide bleaching of mechanical pulp is different in that the objective is to brighten the pulp with almost no dissolution of wood constituents (Gellerstedt and Petterssen, 1982). In this case, the peroxide bleaching conditions are chosen to maximize reaction of lignin with perhydroxyl anion.

#### *3.3.2.2 $H_2O_2$ decomposition mechanisms*

Troughton and Sarot (1992) have reported that hydrogen peroxide is remarkably stable and can be stored for many months with negligible loss of available oxygen under acidic conditions and free from impurities. Under alkaline conditions or in the presence of heavy metal ions, $H_2O_2$ decomposes according to the following equations.

Equilibrium between $H_2O_2$ and $HOO^-$ in alkaline conditions:

$$H_2O_2 + OH^- \rightleftharpoons HOO^- + H_2O \tag{3.3.1}$$

Base-catalysed decomposition and radical formation:

$$H_2O_2 + HOO^- \rightarrow HO^\bullet + O_2^{-\bullet} + H_2O \tag{3.3.2}$$

$$H_2O_2 + HOO^- \rightarrow OH^- + O_2 + H_2O \tag{3.3.3}$$

Metal-catalysed decomposition and radical formation:

$$H_2O_2 + M \rightarrow HO^\bullet + HO^- + M^+ \tag{3.3.4}$$

$$H_2O_2 + HO^\bullet \rightarrow HOO^\bullet + H_2O \tag{3.3.5}$$

$$HOO^\bullet + M^+ \rightarrow O_2 + H^+ + M \tag{3.3.6}$$

$$HOO^\bullet + H_2O \rightarrow O_2^{-\bullet} + H_3O^+ \tag{3.3.7}$$

Francis (1989) has reported that catalysis by transition metals is much greater than by base; rate constants are of the order of 1000 times higher for transition metal catalysis. Even the presence of transition metals in trace amount affects the decomposition rate of $H_2O_2$ in alkaline solutions (Weaver et al., 1979) and hinders $H_2O_2$ brightening and bleaching. Reactions (3.3.4)–(3.3.6) show that the presence of metal ions, which can readily change oxidation states, will activate a catalytic cycle resulting in the rapid decomposition of hydrogen peroxide.

Metals differ in their ability to catalyse $H_2O_2$ decomposition. Since metal ions are alternately oxidized and reduced, those with higher electron transfer rates result in faster metal-catalysed $H_2O_2$ decomposition (Troughton and Sarot, 1992). For example, at pH 10.8, the decreasing order of metal activity for $H_2O_2$ decomposition is reported to be $Mn^{2+} \gg Cu^{2+} > Fe^{2+}$ (Colodette et al., 1989), with this activity being a function of pH. The $H_2O_2$ decomposition mechanism for $Mn^{2+}$ was reported as being different from that for $Fe^{2+}$ or $Cu^{2+}$; according to Chirat and Lachenal (1994), the addition of $Fe^{2+}$ or $Cu^{2+}$ to the hydrogen peroxide solution increased the formation of $HO^{\bullet}$ and $O_2^{-\bullet}$ radicals. No measurable amount of hydroxyl radicals was found when adding $Mn^{2+}$ cations. The reason as to why Fe and Cu cations give rise to hydroxyl radicals while the Mn cation does not, could be that Fe and Cu exist in valency states, which differ by one electron, whereas $Mn^{2+}$ is oxidized directly to $Mn^{4+}$, a two-electron change (Chirat and Lachenal, 1994). Some ions, e.g., magnesium, calcium and silicates are found to have a stabilizing effect on peroxide (Sinkey and Thompson, 1974; Basta et al., 1994b; Bambrick, 1985; Ali et al., 1986). These ions complex transition metal ions and lower their catalytic effect.

### 3.3.3 Factors affecting brightness development

Brightness development is affected by variety of factors like process conditions, type of wood, lignin content of feed pulp, liquor carryover and metal profile (Anderson, 1992; Anderson and Amini, 1996; Gullichsen, 2000; Troughton and Sarot, 1992; Nelson, 1995, 1998; Lachenal et al., 1992, 1996; Lapierre et al., 1995a, b; Reeve, 1996).

#### *3.3.3.1 Process conditions*

The main process variables are hydrogen peroxide dose, time, temperature, pH and pulp consistency.

*3.3.3.1.1 Hydrogen peroxide dose:* An increase in hydrogen peroxide dose leads to higher pulp brightness as long as the pretreatment and the stabilization have been optimized. Hydrogen peroxide is used in the extraction stage either to reduce the charge of chlorine in the first bleaching stage or to reduce the charge of chlorine dioxide in the later bleaching stage. It is also used to increase the final pulp brightness or to increase the brightness stability. In North America, the use of peroxide in the second extraction stage is most common. Less frequently, hydrogen peroxide is used in the first extraction stage. This practice is limited to a few installations (Reeve, 1996). A few mills use peroxide as the final bleaching stage or as a postbleaching treatment in pulp storage towers.

A peroxide bleach stage, P, is usually used to replace traditional bleaching stages in mills using TCF or ECF bleaching sequences. Typical hydrogen peroxide charges range from 1.5% to 4.5% in one or multiple application points. For a single application stage, the practical limit for the peroxide charge is approximately 2.5% on pulp. Desprez et al. (1994) have reported that in a well-run TCF sequence, approximately 80% hydrogen peroxide is consumed. The extremely high hydrogen peroxide charges required to produce high brightness TCF pulps provide an incentive for installing the more specialized hydrogen peroxide-bleaching stages. Mills are installing high-temperature, pressurized hydrogen peroxide stages for improving the efficiency of the hydrogen peroxide stage instead of capital investment for large towers to get increased retention time. The hydrogen peroxide dose is typically 1.5–2.5% on pulp, and these stages are capable of bleaching and delignifying the pulp.

For first extraction stage, the dose of hydrogen peroxide is 0.25–0.75% on oven-dry pulp, whereas for second extraction stage, the dose is 0.05–0.20% on oven-dry pulp. Anderson (1992) has reported that by limiting the peroxide charge in the second extraction stage, any harmful effect that peroxide may have on pulp viscosity is minimized. When the kappa factor of the first bleaching stage is less than 0.13, hydrogen peroxide charge of $> 1\%$ can be used in the first extraction stage. However, higher pH and temperature must be used to efficiently consume the higher dose of hydrogen peroxide and to increase the rate of reaction. Control of pH in the initial chlorine dioxide stage is an important feature of this application (Andrews and Singh, 1979). A two-stage hydrogen peroxide treatment with an intermediate washing stage can improve the brightness and delignification for a particular level of hydrogen peroxide (Troughton and Sarot, 1992).

Dissolved organics or transition metal ions present in the pulp or solution, may consume the bulk of the hydrogen peroxide. So, the pulp may not be bleached appreciably. Improved pulp preparation is therefore required to increase the efficiency of the hydrogen peroxide application and thus decrease the hydrogen peroxide charge.

*3.3.3.1.2 pH:* Peroxide bleaching is strongly affected by pH that must be adjusted and buffered at about 10.5 for best results. The concentration of active perhydroxyl ion increases with pH, according to the following reaction:

$$H_2O_2 + OH^- \rightarrow HOO^- + H_2O$$

At $\text{pH} > 10.5$, competition from undesirable side reactions detracts from the bleaching action. pH is usually controlled by sodium hydroxide and sodium silicate. The silicate usually with added magnesium sulphate acts as both a stabilizer and a buffering agent in the peroxide bleaching system. When short retention times are used in a peroxide stage, the alkali charge must be increased to achieve the same brightness. However, if the temperature is increased, the alkali charge must be decreased to obtain optimum bleaching results (Kappel et al., 1991). van Lierop (1993) has reported that softwood kraft pulps tolerate a wide range of alkalinity, when the P stage is preceded by a vigorous chelation stage (Table 3.3.1). Kappel et al. (1991) have reported that consistency also has a significant impact in determining the optimum alkalinity level. The optimum molar ratio of sodium hydroxide/hydrogen peroxide is approximately 1:1 in case of medium-consistency (9–12%) bleaching depending on other process parameters, whereas in case of high-consistency (20–30%) bleaching, the best results are obtained at a sodium hydroxide/hydrogen peroxide molar ratio of only 0.25 (Kappel et al., 1991).

*3.3.3.1.3 Consistency:* Bleaching performance is found to be better at higher pulp consistency (Kappel et al., 1991). This is presented in Tables 3.3.2 and 3.3.3 for a pressurized hydrogen peroxide-bleaching stage. The rate of peroxide bleaching strongly depends on the peroxide concentration in the solution. So, consistency increases at a given chemical's charge will improve the brightness development. The wash presses needed to operate a high-consistency bleach plant may provide a chance for interstage removal of metals. Alternatively, the press filtrate can be recycled to recover the value of the residual hydrogen peroxide.

*3.3.3.1.4 Temperature and duration:* The performance of a hydrogen peroxide-bleaching stage is poor when the temperature is below the optimum value of about 90°C (atmospheric towers). Process conditions in extraction stage in most pulp mills are generally sufficient to efficiently utilize the added hydrogen peroxide. The oxidative extraction stages are currently being designed to operate at temperatures of 90°C or higher and at pressures

**Table 3.3.1 Effect of addition of EDTA in a Q stage on the final brightness of a softwood kraft pulp[a] bleached in an OQP sequence**

| NaOH in P stage (kg/MT) | Brightness (% ISO) | | | |
|---|---|---|---|---|
| | OP | OQP | | |
| | | EDTA (0.2%) | EDTA (0.6%) | EDTA (1.2%) |
| 15 | 50 | — | — | — |
| 20 | 49.5 | 67.0 | 68.0 | 70.0 |
| 25 | 49.0 | 66.0 | 70.0 | 68.0 |
| 30 | 47.0 | 60.0 | 66.0 | 67.0 |

*Note*: Conditions: P stage—25 kg $H_2O_2$/MT, 90°C, 4 h.

[a] Kappa no. = 32.5

Based on data from van Lierop et al. (1993).

**Table 3.3.2 Effect of pulp consistency on the brightness of an oxygen-delignified softwood kraft pulp[a] bleached in a pressurized peroxide stage**

| Pulp consistency (%) | Brightness (% ISO) | |
|---|---|---|
| | 20 kg $H_2O_2$/MT | 40 kg $H_2O_2$/MT |
| 12 | 77.5 | 80.7 |
| 15 | 78.0 | 81.9 |
| 18 | 79.0 | 83.0 |
| 21 | 79.5 | 83.5 |
| 25 | 80.5 | 84.0 |
| 28 | 81.5 | 84.5 |
| 30 | 82.5 | 84.2 |

*Note*: Conditions: (PO) stage—100°C, 2 h.
[a] Kappa no. of $O_2$ delignified pulp = 9.
Based on data from Germgard and Norden (1994).

**Table 3.3.3 Effect of oxygen stage kappa number on final brightness of an oxygen-delignified softwood kraft pulp[a] bleached in an OQP sequence**

| $H_2O_2$ charge (kg/MT) | Brightness (% ISO) | | | |
|---|---|---|---|---|
| | 15.0[b] | 12.5[b] | 5.7[b] | 5.7[c] |
| 1.0 | 65.0 | — | 74.5 | 77.0 |
| 1.5 | 68.0 | — | 77.0 | 80.0 |
| 2.0 | 70.0 | 74.0 | 79.0 | 82.0 |
| 2.5 | 72.0 | 74.5 | 80.0 | 83.0 |
| 3.0 | 74.0 | 76.0 | 81.0 | 85.0 |
| 3.5 | 74.5 | 77.0 | 81.5 | 86.0 |
| 4.0 | 75.0 | 78.0 | — | 86.5 |

*Notes*: Conditions: P stage: 90°C, 4 h.
[a] Kappa no. 6.0
[b] Post-oxygen kappa no. at 12% consistency.
[c] Post-oxygen kappa no. at 25% consistency.
Based on data from Germgard and Norden (1994).

> 75 psig in order to obtain the maximum effect from oxygen and added peroxide (Young, 1993).

Igerud (1993) has suggested the combination of several bleaching towers in a single stage to increase the retention time and attain a higher brightness. Tables 3.3.4 and 3.3.5 show, however, that the brightness increase is modest even after an extended (> 10 h) retention time (Germgrad and Norden, 1994; Igerud, 1993). Table 3.3.4 also shows the effect of temperature on brightness development. The maximum operating temperature for an peroxide stage at atmospheric pressure is normally 90°C (van Lierop, 1993; Lachenal et al., 1994; Lachenal and Nguyen, 1993). Even at 90°C, however, the time required to attain the desired brightness may be longer than most

**Table 3.3.4 Effect of temperature on bleaching of an oxygen-delignified softwood kraft pulp[a] bleached with hydrogen peroxide**

| Time (h) | Brightness (% ISO) | | |
|---|---|---|---|
| | Temperature, 70°C | Temperature, 90°C | Temperature, 110°C |
| 2.0 | — | 76.9 | 81.6 |
| 3.0 | — | 78.8 | 82.1 |
| 4.0 | 72.5 | 80.2 | 83.5 |
| 4.5 | 73.0 | — | — |
| 5.0 | 73.5 | 81.2 | — |
| 5.5 | 74.0 | — | — |
| 6.0 | 74.5 | 82.5 | — |
| 7.0 | — | 83.0 | — |
| 8.0 | — | 83.5 | — |

*Notes*: Conditions: $H_2O_2$ charge—35 kg/MT; consistency—10–12%.

[a] Kappa no. = 6.0.

Based on data from Germgard and Norden (1994).

mills can achieve in their existing towers and it may be economically difficult to justify building additional towers. The retention time to reach a target brightness can be substantially decreased, however, by increasing the temperature of the peroxide stage. Germgrad and Norden (1994) have reported that for an oxygen-delignified softwood pulp, an equivalent brightness is achieved in only 2 h at 110°C compared with 6 h at 90°C (Table 3.3.5). Similar results have been reported by other researchers (Troughton et al., 1994; Dillner and Tibbling, 1994; Desprez et al., 1994; Stromberg and Szopinski, 1994). The application of pressure is an engineering device to maintain control of a high-temperature stage and avoid boiling. The advantages are higher brightness and reduced hydrogen peroxide charge (Germgrad and Norden, 1994) (Table 3.3.6). Some researchers have reported higher brightness when oxygen, instead of nitrogen, is used to provide the increased pressure; others have found little difference in results based on the method of pressurization (Germgrad and Norden, 1994; Desprez et al., 1994). To avoid the homolytic cleavage of the oxygen–oxygen bond in hydrogen peroxide, the maximum temperature of a hydrogen peroxide stage should be below 130°C (Desprez et al., 1994, Gratzl, 1990). It is possible to bleach kraft pulp to high brightness (88% ISO) in as little as 2 h when this temperature limit is approached (Ek et al., 1989).

### *3.3.3.2 Wood type*

There is not much difference in the hydrogen peroxide charge required for bleaching hardwoods or softwoods. Hardwood pulps have lower lignin content which allows operation of the chlorination stage at a lower kappa factor than would normally be used for softwood pulps. van Lierop (1993) has

**Table 3.3.5 Effect of hydrogen peroxide charge on bleaching of an oxygen-delignified softwood kraft pulp[a] bleached with hydrogen peroxide**

| Time (h) | Brightness (% ISO) | | |
|---|---|---|---|
| | 20 kg $H_2O_2$/MT | 30 kg $H_2O_2$/MT | 40 kg $H_2O_2$/MT |
| 1.0 | 75.0 | 75.0 | — |
| 2.0 | 81.2 | 82.0 | 83.5 |
| 4.0 | 82.0 | 84.0 | 85.8 |
| 6.0 | 82.5 | 85.0 | 86.0 |
| 10.0 | 83.5 | 86.1 | 87.2 |
| 15.0 | 84.5 | 87.0 | 88.0 |

[a]Kappa no. = 11.0.
Based on data from Igerud (1993).

**Table 3.3.6 Effect of a pressurized hydrogen peroxide on bleaching of an oxygen-delignified softwood kraft pulp[a]**

| $H_2O_2$ (kg/MT) | Brightness (% ISO) | | |
|---|---|---|---|
| | Temperature, 90°C | Temperature, 100°C | Temperature, 110°C |
| 10 | 66.5 | — | — |
| 20 | 73.0 | 77.0 | 81.0 |
| 30 | 76.0 | 79.0 | 83.0 |
| 40 | 78.0 | 91.5 | 84.5 |

*Notes*: Conditions: 90°C, 4 h; 100°C, 2 h, 5 bar; 110°C, 2 h, 5 bar.
[a]Kappa no. = 12.5
Based on data from Germgard and Norden (1994).

reported that the brightness of a peroxide-bleached pulp depends primarily on the structure of the residual lignin and the lignin content of the pulp entering the peroxide stage. Brightness is typically highest for sulphite pulps followed in order by hardwood and softwood kraft pulps in the TCF bleaching of kraft and sulphite pulps, at an equivalent hydrogen peroxide charge.

### *3.3.3.3 Lignin content of feed pulp*

van Lierop (1993) and Troughton et al. (1994) have reported that the brightness obtained in a hydrogen peroxide stage is inversely proportional to the kappa number of the incoming pulp and is independent of the delignification process used to produce the pulp entering the bleaching stage (Table 3.3.7). Germgrad and Norden (1994) have also found the beneficial effect of a low initial kappa number, on the final brightness of a peroxide-bleached pulp (Table 3.3.3).

### *3.3.3.4 Liquor carryover*

The performance of a peroxide stage can be improved by minimizing the carryover (from the pulping process) of alkali and materials that contribute

**Table 3.3.7 Effect of initial kappa number on the brightness of an oxygen-delignified softwood kraft pulp[a] bleached with peroxide in multistage sequences**

| Pre-QP kappa no. | Brightness (% ISO) | | | | | |
|---|---|---|---|---|---|---|
| | OQP | (EOP)QP | D(EOP)QP | A[b](EOP)QP | A(EOP)QP | O(ZE)QP |
| 2.5 | — | — | — | — | — | 86.5 |
| 4.5 | — | — | — | — | 86.0 | — |
| 5.5 | — | — | — | — | — | 82.0 |
| 10.0 | 80.0 | — | — | — | — | — |
| 13.0 | 73.5 | 74.0 | — | 72.5 | — | — |
| 15.0 | — | — | 71.5 | — | 70.5 | — |
| 16.5 | 70.5 | — | — | — | — | — |
| 17.0 | — | 68.5 | — | — | — | — |
| 17.5 | — | — | — | 67.5 | — | — |
| 18.0 | 70.0 | — | — | — | — | — |
| 18.5 | 69.0 | 67.0 | — | — | — | — |
| 19.0 | 65.5 | — | — | — | — | — |
| 21.5 | — | 65.0 | — | — | — | — |
| 22.0 | — | 64.0 | — | — | — | — |
| 22.5 | — | 64.0 | — | — | — | — |

*Notes*: Conditions: $H_2O_2$ charge—25 kg/MT; 90°C, 4 h, 10% cy.

[a] Kappa no. = 14.8.

[b] A = dioxirane.

Based on data from van Lierop et al. (1993).

to the chemical oxygen demand (COD). Carryover of liquor containing dissolved organic material generally increases the consumption of hydrogen peroxide. The peroxide has a free access to the dissolved organic fragments in the bleaching liquor, but its access to the lignin residue of the pulp (which is bound to the carbohydrate) is somewhat restricted. Peroxide is partly consumed in oxidation reactions with the organic compounds of the liquor. These reactions reduce the colour of the bleach plant effluent but do not lead to an increase in pulp brightness. This is needed but it is usually not the reason for using the hydrogen peroxide. The residual chlorine from the chlorination stage in the conventional bleaching stage enters the following alkaline extraction stage and reacts with the sodium hydroxide to form sodium hypochlorite. When hydrogen peroxide is added to the extraction stage, it reacts with both the chlorine and hypochlorite. These reactions consume part of the peroxide that would otherwise be available for pulp bleaching. Carryover of chlorine dioxide from a previous bleaching stage can also consume hydrogen peroxide and increase the peroxide demand. Therefore, an efficient washing stage between the two stages is required to minimize chlorine dioxide carryover (Anderson and Amini, 1996). On the other hand, because the carryover of residual peroxy acids or hydrogen peroxide from a peroxy acid stage appears to activate hydrogen peroxide (Liebergott, 1994), an interstage wash is neither needed nor recommended.

### *3.3.3.5 Optimal metal profile*

The objectives of a hydrogen peroxide bleaching are to obtain the highest brightness and lowest kappa number using the smallest amount of hydrogen peroxide and to achieve the kappa reduction with minimum loss in viscosity. To achieve these objectives, optimal metal profile is required (Troughton et al., 1994; Desprez et al., 1994; Stromberg and Szopinski, 1994; Igerud, 1993; Basta et al., 1991a, 1994b; Lapierre et al., 1995a, b; Devenyns et al., 1994a; Ek et al., 1994; Jayawant and Degraw, 1994). Certain transition metals (e.g. manganese, copper and iron) catalyse hydrogen peroxide decomposition and contribute to the formation of hydroxyl radicals and superoxide anion radicals. The presence of low concentrations of these radical species is actually necessary for hydrogen peroxide bleaching to proceed (Gellerstedt and Petterson, 1982). However, a high concentration of such radicals leads to poor selectivity and decreased bleaching. Chirat and Lachenal (1994) have reported that among the metal catalysts, $Mn^{2+}$ does not decompose hydrogen peroxide by a radical mechanism. Therefore, it is suggested that it cannot contribute to the formation of hydroxyl radicals. However, Ek (1994) has reported that bleaching is improved as the manganese level in the pulp is decreased. Colodette et al. (1989) have found that certain alkaline earth metals, e.g. magnesium, calcium and sodium silicate hinder hydrogen peroxide decomposition. These compounds may form a complex with the transition metals that catalyse the decomposition of peroxide and lower their catalytic activity. To obtain an appropriate metal profile, Basta et al. (1994a) and Ek (1994) have found that metal chelation at pH 4–7 followed by a washing or liquor removal stage and an acid treatment at $pH < 3$ followed by washing and treatment with magnesium salts to replenish the magnesium ions lost in the washing stage, gives good results. Table 3.3.8 lists the concentration range of some of the most significant metals for Canadian kraft pulps. Efficient peroxide bleaching requires an optimal level of alkaline earth metals (e.g. Mg and Ca) and the lowest obtainable level of transition metals (e.g. Mn, Fe and Cu) (Basta et al., 1994c): there is no report yet on loss in bleaching efficiency due to effective removal of these transition metals. It appears that even the best achievable transition metal removal leaves a high enough concentration of transition metals to catalyse $H_2O_2$ decomposition into the radicals needed for delignification.

**Table 3.3.8 Metal concentration range found in Canadian kraft pulps**

| Ca (ppm) | Cu (ppm) | Fe (ppm) | Mg (ppm) | Mn (ppm) |
|---|---|---|---|---|
| 1000–2500 | 0–10 | 20–100 | 200–400 | 50–250 |

Based on data from Lapiere et al. (1995).

*3.3.3.5.1 Chelation* The metals in the pulp are reduced and converted into their sulphides and hydroxides during kraft pulping and they become insoluble and remain strongly attached to the pulp fibres (Suss et al., 1989). The presence of a strong chelating agent, such as EDTA or DTPA, can displace the metals, making them soluble and easily removed by washing. Manganese is found to be removed at >90% efficiency with chelation or acid wash. The optimal metal profile can be established with a chelation treatment under appropriate conditions of pH, temperature, time and charge. Under such conditions, chelation removes the transition metal ions and leaves most of the Ca and Mg already present in the pulp. This is a result of the different affinities of the alkaline earth and transition metal ions for the chelating agent.

To create the optimal metal profile, chelation is generally performed using EDTA/ DTPA at a pH between 4 and 7, for 30–60 min, at 60–90°C (van Lierop, 1993; Basta et al., 1991a). This is followed by a standard wash prior to an alkaline peroxide stage. An example of the metal profile changes resulting from this procedure is presented in Table 3.3.9 (Basta et al., 1994c). Pulps with this profile undergoing peroxide bleaching show the highest kappa reduction, brightness and viscosity with the lowest peroxide consumption. Chelation treatments at $\text{pH} < 3$ (which are similar to acid washes) result in poorer bleaching because of lower amounts of Mg in the pulp. Chelation treatments at $\text{pH} > 8$ also does not result in good bleaching because of larger amounts of Mn in the pulp (Basta et al., 1994c).

The washing step is critical. The performance of seven chelating agents was evaluated first in a chelation stage followed by a wash (neutral pH) before $H_2O_2$ bleaching, and second directly in the peroxide stage itself. The second method gave lower brightness with all the chelating agents (Xu et al., 1994). Chelation alone does not necessarily remove the $H_2O_2$ catalytic properties of a metal; the rate of electron transfer can be either increased or decreased by complexation with the metal ion (Troughton and Sarot, 1992). The catalytic activity of the Fe-DTPA chelate was found to be higher than that of Fe while the activity of the Mn-DTPA chelate was lower than that of $Mn^{2+}$ (Agnemo and Gellerstedt, 1979; Walling et al., 1970). As the transition metal content depends on the pulp origin and species, it is not possible to prepare a standard formula for a chelation stage applicable to all pulps.

**Table 3.3.9 Metal profile in pulp before and after chelation (Q)**

| | Ca (ppm) | Mg (ppm) | Fe (ppm) | Mn (ppm) | Cu (ppm) |
|---|---|---|---|---|---|
| Before Q | 1400 | 380 | 11 | 47 | 0.6 |
| After Q | 500–1000 | 120–280 | 6–8 | <5 | 0.1–0.2 |

Based on data from Lapiere et al. (1995).

Differences in the ease of extraction are also exhibited from sample to sample. These differences can be accounted for only by differences in the strength of the chemical binding of the metals to the pulp. The chelation stage must therefore be optimized for each specific pulp (Troughton and Sarot, 1992). EDTA has been recommended as a sequestrant for all pulps on the grounds that the slight improvement in performance provided by DTPA does not justify the additional cost (Troughton and Sarot, 1992).

*3.3.3.5.2 Acid treatment* Acid treatment at pH 1.5–3.0 reduces the concentration of all transition and alkaline earth metals present in the pulp. Removal efficiency of transition metals is as good as with chelation but, contrary to chelation, alkaline earth metals are removed far too efficiently. Therefore, restoration of the appropriate alkaline earth metal profile is necessary for the subsequent peroxide bleaching stage to prevent unwanted viscosity (strength) loss and to maximize brightness gain. Basta et al. (1994c) found that peroxide bleaching of an acid-washed pulp with readdition of alkaline earth metal ions gave the same brightness but lower viscosity than the equivalent bleaching of a chelated pulp, despite the overall metal profiles of the two pulps being similar. Addition of both chelant and alkaline earth metal ions to the acid-washed pulp eliminated the loss in viscosity. Similarly, higher brightness was found for pulps bleached after chelation than after acid treatment with readdition of magnesium ions (Ek et al., 1994). It was concluded that acid treatment is not as effective as chelation in eliminating the influence of transition metal ions before a hydrogen peroxide stage. However, according to Bouchard et al. (1995), an optimized acid treatment (pH, time and temperature) to remove most metal ions, followed by an optimal addition of $MgSO_4$ to replace the native magnesium, can replace chelation without causing deterioration of pulp brightness and viscosity during hydrogen peroxide bleaching. Suss et al. (1989) and Kappel (1992) have also successfully used acid wash plus magnesium or silicate addition as a pretreatment, without adding a chelating agent, and also report no problems with pulp properties . Differences in pulp source, process conditions and/or optimization might account for these different conclusions.

*3.3.3.5.3 Contribution of magnesium and silicate to pulp stability* The addition of $Mg^{2+}$ and/ or $SiO_3^{2-}$ to hydrogen peroxide improves bleaching efficiency (Troughton and Sarot, 1992). $Mg^{2+}$ and $SiO_3^{2-}$ complex with harmful transition metals through oxy or hydroxy bridges (Abbot, 1991) that change the catalytic activity of the transition metals with regard to $H_2O_2$ decomposition (Abbot, 1991; Abbot and Brown, 1990), again not always in the way required.

Abbot (1991) has reported that the $H_2O_2$ decomposition rate in the presence of $Mn^{2+}$ is decreased when $SiO_3^{2-}$ is added, but increased when $Mg^{2+}$ is added. On the other hand, $H_2O_2$ decomposition in the presence of $Fe^{2+}$ is decreased by the addition of $Mg^{2+}$ (Abbot, 1991; Samuelson and Ojteg, 1994). Polarography studies have also shown that the catalytic decomposition of $H_2O_2$ in water containing trace metal contaminants was reduced when $Mg^{2+}$ was added (Sinkey and Thompson, 1974). One way to explain how $Mg^{2+}$ and $SiO_3^{2-}$ contribute to pulp stability during hydrogen peroxide bleaching is as follows. A chelation or acid wash will not remove all the transition metals that decompose hydrogen peroxide, and in particular will not remove all the iron. During peroxide delignification, these metals can be released and inhibit the action of peroxide. With $Mg^{2+}$ or $SiO_3^{2-}$ present, however, these released metals are complexed so their overall effect is limited. $Mg^{2+}$ provides a net benefit due to the larger amount of Fe compared to Mn left in the pulp. However, one has to be careful as negative effects like lower pulp brightness, and viscosity are encountered when high amounts of Mg is added (Xu, 1994; Bouchard et al., 1995). Critical Mg/Mn ratio to obtain optimal brightening is around 30 for chemical pulps and considerably lower for mechanical pulps (Devenyns and Plumet, 1994b). This seems contradictory to the increased $H_2O_2$ decomposition reported when Mg is added to a $H_2O_2$ solution in the presence of Mn . More work is needed to advance the understanding of this multicomponent system.

### 3.3.4 Peroxide bleaching processes

Eka Nobel company in Sweden has developed a two-stage (QP) procedure known as the Lignox® process (Basta et al., 1991a–c, 1992). The main step in the process is the removal of metals from the pulp prior to the alkaline peroxide stage. The profile of metals in the pulp after the first stage is a deciding factor in the performance of the subsequent peroxide treatment. Pulp is pretreated with EDTA at a pH range of 4–7, temperature of 90°C for 1 h. These conditions give the highest kappa number reduction, brightness and viscosity with the lowest hydrogen peroxide consumption. Table 3.3.10 shows that maximum brightness is obtained at a pH range of 4–7 (Basta et al., 1994b). Under these conditions, about 50% of the lignin in an oxygen-delignified softwood kraft pulp was found to be removed. The pretreatment establishes a metal profile such that the manganese content is reduced while the magnesium level is kept as high as possible. The magnesium protects the carbohydrates from oxidative damage during the peroxide treatment. The optimum metal profile prior to peroxide bleaching of Scandinavian softwood pulp was Mn $<5$ ppm, Mg$=$120–180 ppm and Ca$=$500–1000 ppm (Basta et al., 1994b). Treatment of the pulp with acid removes a large proportion of the alkaline earth metals as well as heavy metals, and the alkaline earth metal profile must be restored and EDTA added if this treatment is to be as effective as the Lignox process. To obtain fully bleached pulps, the Lignox treatment is followed by further bleaching with chlorine dioxide. The use of additional hydrogen peroxide stages or ozone or peracid treatment yields

**Table 3.3.10 Pulp brightness after P stage versus pH of pretreatment stage**

| Pretreatment pH | Brightness (% ISO) |
|---|---|
| 2.0 | 64.0 |
| 2.3 | 64.5 |
| 2.9 | 72.5 |
| 3.8 | 81.5 |
| 4.0 | 82.0 |
| 5.5 | 82.0 |
| 5.8 | 81.0 |
| 7.0 | 80.5 |
| 8.0 | 78.0 |
| 9.5 | 72.5 |
| 10.8 | 61.5 |
| 11.0 | 62.0 |

Based on data from Basta et al. (1994b).

TCF pulps with high brightness levels (Basta et al., 1991c). The Lignox process can be easily used in existing bleach plants without the requirement for large capital investment. Aspa Bruk mill in Sweden has been using this process for several years (Nelson,1995,1998). Another development in hydrogen peroxide bleaching has been a process designated P*. In this process, single alkaline peroxide stage at 80–90°C is used for bleaching softwood and hardwood kraft pulps to 90° ISO brightness (Desprez et al., 1993). The process was improved when the temperature was increased to 120°C (Desprez et al., 1994). The P* technology was first developed using softwood kraft pulp that had been delignified with chlorine and chlorine dioxide. The P* stage was used to brighten the delignified pulp. The optimum conditions for this stage involved control of metal ions, high consistency and long residence time. To obtain fully bleached pulp it was essential to keep the manganese content of the pulp below 3 ppm and the kappa number below 5 for a softwood kraft pulp. The P* stage has been also used in TCF bleaching sequences in which delignification of the pulp was done with various combinations of oxygen delignification, alkaline hydrogen peroxide and peracids. Desprez et al. (1993) have reported that the kappa number of the pulp prior to the P* stage has a large effect on the final pulp brightness, as shown in Table 3.3.11. The conditions in the P* stage were kept constant (30% consistency, 80°C, 4 h, 2% hydrogen peroxide, stabilization and optimal alkali application). When the kappa number of the softwood kraft pulp was higher than ~5 the final brightness decreased sharply.

An important development in hydrogen peroxide bleaching technology has been the development of pressurized hydrogen peroxide bleaching (PO). This technology was developed by Kvaerner Pulping Technologies in 1993 and is being used by number of mills (Tibbling and Dillner, 1993; Dillner

**Table 3.3.11 Effect of kappa number of pulp on the brightness after P stage**

| Kappa no. | Brightness (% ISO) | | |
|---|---|---|---|
| | $Cl_2$ or $ClO_2$ | Peracetic acid | Hydrogen peroxide |
| 2.0 | 89.2 | — | — |
| 2.2 | 88.0 | — | — |
| 2.5 | 89.5 | — | — |
| 2.8 | — | 89.0 | — |
| 3.8 | — | 90.5 | — |
| 4.5 | 90.5 | — | — |
| 5.0 | — | 88.8 | — |
| 5.3 | — | 89.0 | — |
| 5.7 | — | 87.5 | — |
| 7.5 | — | 82.5 | — |
| 9.5 | — | — | 77.5 |

Based on data from Desprez et al. (1993).

and Tibbling, 1994). In this process, the pulp and bleaching liquor are heated at a temperature of 100–120°C in a vessel pressurized with oxygen. In this process a high pulp consistency, a pulp with a low lignin content, a high temperature, and an oxygen pressure of at least 0.5 MPa is used. Use of high temperature results in a high consumption of the applied peroxide charge and rapid bleaching. With pressurized peroxide bleaching, a brightness of 83% ISO was obtained with a softwood kraft pulp in only 2 h as compared with 15 h with conventional bleaching at atmospheric pressure (Dillner and Tibbling, 1994). The main advantage of the (PO) process is that a single stage can replace several atmospheric pressure stages in a bleach line. Data obtained by Germgard and Norden (1994) clearly illustrate this point (Table 3.3.12). Increasing the temperature not only increases the reaction rate, but also increases the brightness level that is attainable with a particular peroxide charge. A 6–8% ISO higher brightness can be obtained with a (PO) stage at 110°C and 2 h. The beneficial effects of the process is contributed to the use of oxygen to pressurize the reaction vessel. The bleaching conditions in a PO stage are similar to those used for oxygen delignification. So, it is possible that the oxygen is involved in reactions that also occur during oxygen delignification. This is expected to reduce the lignin content of the bleached pulp, which, in turn, would increase the brightness level. Germgard and Norden (1994) have reported that increasing the pressure from 0 MPa (nitrogen atmosphere) to 0.5 MPa with oxygen increased the final brightness of a softwood kraft pulp (oxygen-delignified, kappa number = 6.7) by about 2 units (Table 3.3.13) The use of nitrogen instead of oxygen does not result in an increase in final brightness. In these experiments the bleaching conditions were 4% hydrogen peroxide (pulp basis), 12% pulp consistency, 110°C and 1 h. Similar results were obtained

**Table 3.3.12 Pulp brightness after pressurized (PO) stages at 100 and 110°C and a conventional P stage at 90°C**

| Peroxide charge (kg/ODT) | Brightness (% ISO) | | |
|---|---|---|---|
| | P (90°C, 4 h) | PO (100°C, 2 h) | PO (110°C, 2 h) |
| 10 | 67.0 | — | — |
| 20 | 72.5 | 76.5 | 80.5 |
| 30 | — | — | — |
| 40 | 78.0 | 81.5 | 84.0 |

Based on data from Germgard and Norden (1994).

**Table 3.3.13 Effect on pulp brightness of pressurization with oxygen as compared with use of nitrogen**

| Peroxide charge (kg/ODT) | Brightness (% ISO) | |
|---|---|---|
| | $N_2$ | $O_2$ |
| 0.0 | 83.0 | — |
| 0.2 | — | 84.3 |
| 0.3 | 82.9 | — |
| 0.4 | — | 84.8 |
| 0.5 | — | 85.1 |
| 0.6 | 82.8 | 85.2 |
| 0.8 | — | 85.1 |

Based on data from Germgard and Norden (1994).

in bleaching of oxygen-delignified eucalyptus kraft pulp, and in that case the use of oxygen increased the brightness by about 1% ISO. The kappa number of the bleached pulp was marginally lower (5.0 vs. 5.2) when oxygen was used (Nelson et al. 1995). Germgard and Norden (1994) have reported that the use of the O(QZ)Q(PO) sequence with pulps prepared by extended delignification will produce 90% ISO brightness pulps economically. In this sequence, there is no pulp washing between chelation and ozone treatment.

### 3.3.5 Characteristics of peroxide-bleached pulps

The strength properties of pulps from chlorine chemical bleaching sequences, where peroxide is used to reinforce extraction, are found to be comparable with those bleached without peroxide (Reid et al., 1991). Softwood TCF pulps, bleached to high brightness using hydrogen peroxide, can approach the brightness levels obtained in ECF bleaching. For such pulps, however, Dillner and Tibbling (1994), Desprez et al. (1994) and Ek et al. (1994) report a 5–10% lower tear index at the same tensile index compared to oxygen-delignified ECF pulps. With ozone or peroxy acids, the TCF and ECF pulps that are obtained are roughly equivalent in strength (Basta et al., 1994a, b; Germgrad and Norden, 1994; Eket al., 1994; Anderson et al;, 1995; Devenyns et al., 1993; Seccombe et al., 1994).

Hydrogen peroxide is effective in eliminating carbonyl groups (Lachenal and Nguyen-Thi, 1993) which are known to be responsible for photosensitizing heat-induced (Edwards, 1962) and photochemically induced (Argyropoulos, 1995) brightness reversion of bleached pulps. Final P stage leads to excellent brightness stability in TCF sequences even when the bleached pulp has a relatively high residual lignin content. Suss and Nimmerfruh (1993) have reported that the brightness reversion was only 2–3 points for samples of softwood and hardwood sulphite pulps (kappa numbers, 2–4) that were bleached in TCF sequences. The initial brightness range for the pulps was 81–88% ISO and the reversion was measured at 100°C for 2 h using the standard TAPPI heat-aging test. The reversion was 3.5–4 points after a 3-day light-induced yellowing test. Results for softwood kraft pulps were similar. Brightness stability is the main benefit of a peroxide stage in the last final stage of a conventional bleaching sequence such as (C/D)(E+O)DP. Carmichael and Althouse (1986) have found that reversion for a fully bleached (90% ISO) pulp, prepared using a sequence with a final P stage, can be limited to 1–2 points compared with 3–4 points in a sequence without a final P stage. When hydrogen peroxide is applied to reinforce the oxidative extraction stage of an ECF sequence, the brightness reversion can also be slightly improved (Young et al., 1992).

For bleaching shives and dirt, hydrogen peroxide is not found to be as effective as chlorine dioxide. Mills producing TCF pulp with high dose of hydrogen peroxide, but without having made the investment in adequate pulp preparation, do not achieve the expected pulp brightness and cleanliness. When hydrogen peroxide is used in an $E_{OP}$ stage in an ECF sequence for the purpose of reducing the kappa factor, it is essential to adjust the conditions of the chlorine dioxide stages to maintain pulp cleanliness (Anderson, 1992; Anderson and Amini, 1996). Although some of shive removal may take place in the ($E_{OP}$) stage, it is important to reduce the pH in the Dl stage for shive control. The chlorine dioxide charge in the first stage may also have to be increased to completely remove shives.

### 3.3.6 Process flowsheets

Figs. 3.3.1–3.3.4 shows process flowsheets for TCF sequences suitable for refitting into existing bleach plants, typical hydrogen peroxide-reinforcement application in an oxidative extraction stage, TCF sequence using advanced nonchlorine delignification technology and washing/pressing and

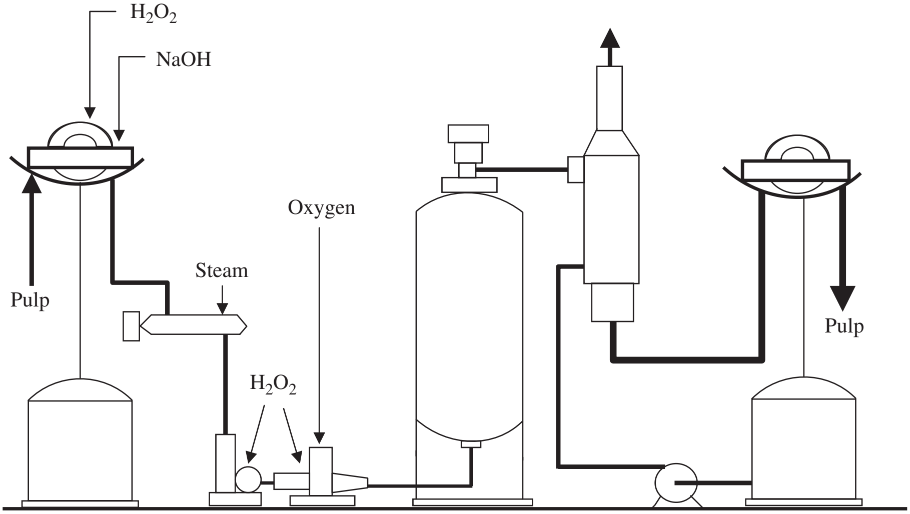

**Fig. 3.3.1. Process flowsheet of a typical hydrogen peroxide-reinforcement application in an oxidative extraction stage. (Lachenal, 1996; reproduced with permission from Tappi Press.)**

a pressurized hydrogen peroxide (PO) stage in greater detail (Igerud, 1993; Gratzl, 1990; Anderson and Amini, 1996; Pikka et al., 2000). Pressurized peroxide bleaching reduces the reactor volume and allows high-temperature operation. Higher brightness occurs with the same peroxide charge and consumption. The stage itself is invariably preceded by a chelation stage with about 1 h of retention time, pH ~5 and a temperature of 80–90°C. Washing after chelation must be very good to ensure that transition metals in the carryover is low enough for safe peroxide bleaching. Certain precautions should be taken to remove from circulation at least a fraction of the chelation stage effluent in a way which keeps dissolved transition metal accumulation at a low level. Medium-consistency pressurized peroxide stage requires two reactors, one atmospheric for chelation and one pressurized for bleaching, and two washers, one before and one after bleaching (Fig. 3.3.4). The chelation reactor can be combined as a post-ozone reactor without intermediate wash as indicated in Fig. 3.3.5. Peroxide bleaching generates oxygen that can influence operation of the reactors. Gas removal between the reactors is very important especially with large peroxide charges. In the peroxide stage, only a few kilograms of oxygen are charged per ton of pulp to balance the decomposition of peroxide. In some retrofitting applications, the pressurized stage is combined with an existing atmospheric reactor. This is necessary in existing systems in which a pressurized stage precedes an extraction stage alkali or a chlorine dioxide reactor. The temperature

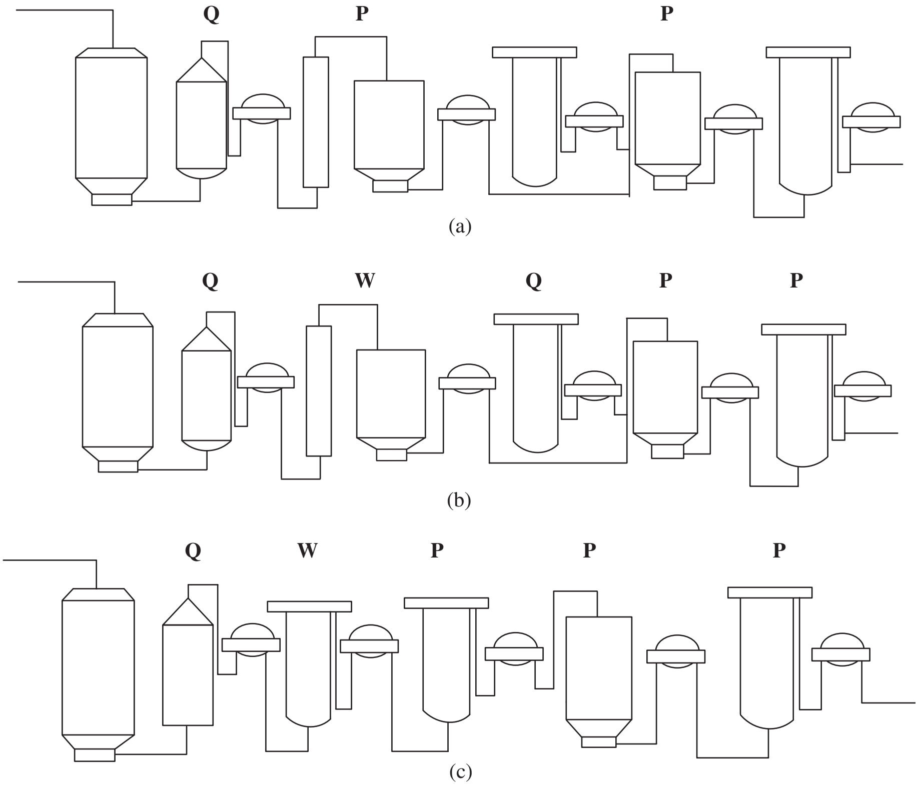

**Fig. 3.3.2. Process flowsheets for refitting TCF-bleaching sequences into existing bleach plants. (From Anderson and Amini, 1996; reproduced with permission from Tappi Press.)**

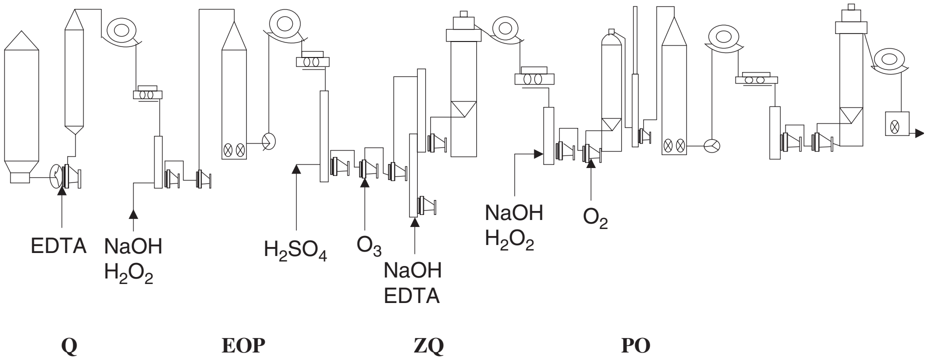

**Fig. 3.3.3. Process flowsheet of a TCF sequence using advanced nonchlorine delignification technology and washing and pressing. (From Anderson and Amini, 1996; reproduced with permission from Tappi Press.)**

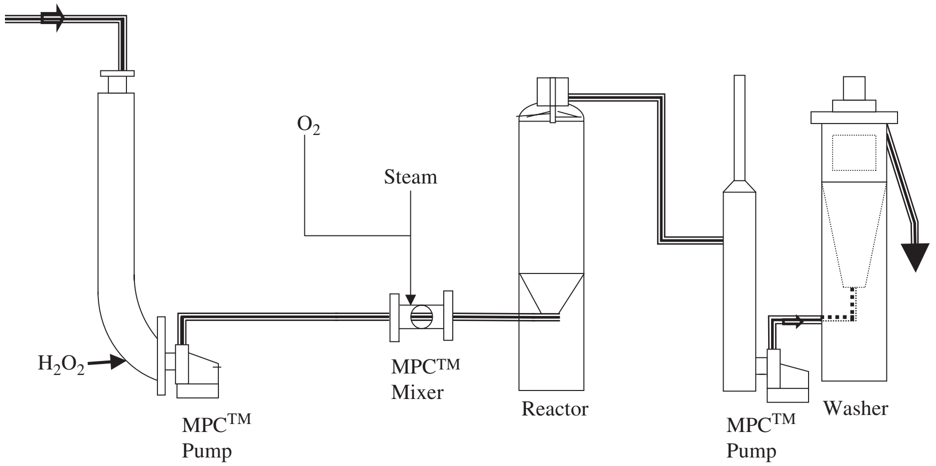

**Fig. 3.3.4. Process flowsheet for a pressurized peroxide stage. (From Anderson and Amini, 1996; reproduced with permission from Tappi Press.)**

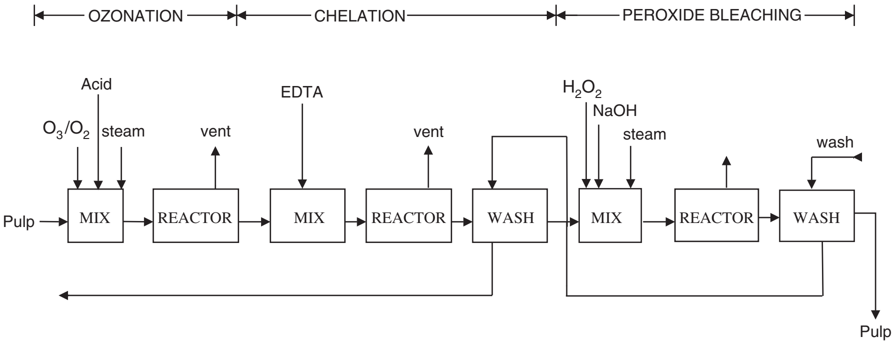

**Fig. 3.3.5. Block Diagram for a (ZQ)P sequence. (From Gullichsen, 2000; reproduced with permission from Fapet OY, Finland.)**

must then be about 80°C. Gas removal located after the pressurized stage improves operation of the atmospheric reactor. Table 3.3.14 summarizes the conditions normally used in a pressurized peroxide stage.

The use of hydrogen peroxide bleaching stages into existing bleach plants and the use of multiple towers for prolonged P stage retention time, generally requires the use of a stage designed primarily for chlorine dioxide application (Anderson and Amini, 1996). Some mills have found grout damage or disappearance, and deterioration of tile lining, especially at the tile edges (Igerud, 1993). At high temperature, pH and peroxide charge, possibility exists for titanium corrosion. Calcium, magnesium and silicates are found to effectively inhibit titanium corrosion (Reichert, 1994; Schutz and Xiao, 1994).

**Table 3.3.14 Typical operating conditions in pressurized hydrogen peroxide bleaching**

| | |
|---|---|
| Time | 30–180 min |
| Temperature | 80–110°C |
| Final pH | 10.5–11 |
| Pulp consistency | 10–15% |
| Pressure | 0.3–0.8 mPa |
| Oxygen charge | 2–10 kg/MT |
| Hydrogen peroxide charge | 2–40 kg/MT |

Based on the data from Pikka et al (2000).

The P stage can be carried out in any alkaline peroxide-compatible vessel available. As the main parameters for ensuring maximum effect from the hydrogen peroxide dosed are the temperature and the retention time, the vessels should be chosen to ensure that these are as high as possible. The addition point for hydrogen peroxide should be isolated from the injection points of other chemicals such as sodium hydroxide or live steam. This is particularly important for high-temperature P stages.

### 3.3.7 Activation of hydrogen peroxide

This subject has been comprehensively reviewed by Suchy and Argyropoulos (2002). Considerable research has been carried out on the stabilization of hydrogen peroxide under conditions conventionally applied during the bleaching of chemical pulps (Geng et al. 1993; Devenyns et al. 1993, 1994a; Lachenal and Papadopoulos,1988; Poppius-Levlin et al., 1989, 1991; Lachenal et al., 1980; Basta et al., 1991a, 1994c; Troughton et al., 1994; Lapierre et al., 1995a, b; Bouchard et al., 1995; Roy et al., 1995; Breed et al., 1995; Jameel et al., 1996). Several investigators have reported the effect of transition metals on peroxide decomposition, and the need of their efficient removal before peroxide treatment (Basta et al., 1991a, 1994c; Troughton et al.,1994; Devenyns et al., 1994a; Lapierre et al., 1995a, b; Bouchard et al., 1995). Stabilized peroxide actually acts as a lignin-preserving bleaching agent, preferably removing chromophoric structures in residual lignin, but not capable of degrading the lignin network (Suchy and Argyropoulos, 2002). Severe reaction conditions were used by Roy et al. (1995), Breed et al. (1995) and Jameel et al. (1996) to increase the reactivity of peroxide. Delignification increased but viscosity loss was also observed, especially in the presence of transition metals. Efforts were made by Lachenal et al. (1980) to pretreat the pulp prior to an alkaline peroxide stage for improving the overall selectivity of peroxide delignification. Treatment of softwood kraft pulp with 3% nitrogen dioxide (on o.d. pulp) at 70°C and 40% consistency for 15 min, followed by washing and alkaline peroxide stage (1% $H_2O_2$ on the o.d pulp) at the same temperature, removed about 60% of the residual lignin. Lindeberg and Walding (1986) reported that nitrogen dioxide pretreatment resulted in fragmentation of ether bonds of lignin, and the formation of new phenolic groups which make the lignin more reactive towards the alkaline peroxide. Pretreatment of kraft pulps with peracids followed by a washing stage also increases the delignification and brightness of subsequent peroxide stage (Geng et al., 1993; Devenyns et al., 1993). Poppius-Levlin et al., (1989) have reported that prebleaching pine kraft pulp with peroxyformic acid reduced the kappa number by 25–80%, depending on the charge of hydrogen peroxide, the concentration of formic acid and the temperature of the treatment. These pulps reached a brightness of 80–85% in the subsequent alkaline peroxide bleaching stage. Increase in brightness was attributed to the increased reactivity of the kraft residual lignin towards alkaline hydrogen peroxide (Poppius-Levlin et al., 1991). A process for kraft pulps has been reported which consists of an activation stage (pulp pretreatment by $Cl_2$, $NO_2$ or $O_3$) and a peroxide delignification stage at high temperature (90°C) (Lachenal and Papadopoulos,1988). Delignification efficiency was in the range of 50–80% with unbleached softwood and hardwood kraft pulps with only a 1% peroxide charge. After the peroxide stage, the degree of polymerization of the cellulose of the pretreated pulps was found to be higher when compared to the peroxide-bleached pulp without the pretreatment. Increased delignification efficiency of peroxide was attributed to the formation of new phenolic hydroxyl groups possibly occurring via lignin demethylation reactions.

Numerous peroxide activators containing nitrogen and transition metals have been investigated (Evtuguin et al., 1998; Eckert, 1982; Kubelka et al., 1992; Suchy and Argyropoulos, 2000; Bortolini et al., 1986; Agnemo, 1997; Jakara et al., 1995a, b; Chen et al., 1999; Patt and Mielisch, 1997; Patt et al., 1998; Cui et al., 1998,1999; Collins et al., 1998; Bianchi et al., 1998; Evtuguin et al., 1998; Hammer et al.,1991; Sturm, 1991; Sturm and Kuchler 1993; Kadla et al., 1998a, b; Kang et al., 1998; Croud and Mathews, 1996; Turner and Mathews, 1998; Jaschinski and Patt, 1998). The addition of an activator to the hydrogen peroxide stage, generates a more powerful oxidant insitu, allowing higher delignification with little or no viscosity loss (Suchy and Argyropoulos, 2002). Among the nitrogen centred peroxide activators, cyanimide and its dimer occupy a important position. Hammer et al. (1991) and Sturm (1991) patented the cyanamide-activated peroxide bleaching process of chemical pulps. Alkaline hydrogen peroxide reacts with cyanamide to form a peroxyimidic acid intermediate that has a higher oxidation potential than peroxide, so it is more effective (Sturm and Kuchler 1993). The pulp brightness increased by about 10 ISO units and the viscosities were comparable (Hammer et al., 1991; Sturm, 1991). Chen (1997) reported that dimer of cyanamide is more effective peroxide activator. Kang et al. (1998) studied the effect of adding cyanamide and molybdate ions in a neutral peroxide delignification of oxygen delignified softwood kraft pulp. A neutral peroxide stage in the absence of an activator produced only 4.1% delignification, whereas the addition of 2% of cyanamide increased the delignification to 23.5% and addition of 500 ppm of $Mo^{6+}$ ions increased the delignification to 27.9%. Delignification further increased to 36.9% with no decrease in the viscosity of the resulting pulp when cyanamide and $Mo^{6+}$ were added simultaneously. The effect of $W^{6+}$, $V^{5+}$ in the cyanamide/metal-activated peroxide system were also studied. $V^{5+}$ was totally ineffective whereas $W^{6+}$ showed similar results to those of $Mo^{6+}$. Croud and Mathews (1996) reported that tetra acetyl ethylene diamine (TAED) increased the brightening with peroxide by generating peracetic acid insitu as a result of the interaction of TAED with peroxide. TAED is thought to react with peroxide to produce peracetic acid or peracetate anion which are stronger oxidants than hydrogen peroxide. The optimum pH of TAED-assisted alkaline peroxide delignification is lower than that used in conventional alkaline peroxide stages. TAED also reacts with peroxide under neutral and even acidic conditions while under such conditions peroxide alone is ineffective as a delignifying agent. Use of TAED can be safely incorporated into ECF and TCF bleaching sequences for different types of pulp (Turner and Mathews, 1998). Polypyridines are also found to significantly improve the delignification and brightness of chelated oxygen-delignified softwood kraft pulps when added into an alkaline peroxide stage (Jaschinski and Patt 1998). Use of 0.025% of 4-Methyl-1,10-phenenanthroline showed significant brightness gains (11% ISO) when compared to control experiments with minimum viscosity losses. The brightness gains were found to be dependent on the dose of polypyridine. 4-methyl-1,10- phenanthroline and 2,2′-bipyridine were found to be the most effective in enhancing the delignification.

Peroxide stage is improved by the addition of transition metals—tungsten, molybdenum, chromium, osmium and selenium (Eckert, 1982). The tungsten ion-catalysed acidic peroxide delignification of hardwood kraft pulp was compared with alkaline peroxide bleaching (Eckert, 1982). The brightness and pulp viscosities were found to be similar, but the degree of delignification for the tungsten-assisted acidic peroxide delignification stage was higher. Transition metal oxides, under acidic conditions, reacted with peroxide to form transition metal peroxocomplexes, which are stronger oxidants than peroxide. Kubelka et al. (1992) studied the use of molybdate metal oxides to catalyse the acidic peroxide delignification of kraft pulps. Bortolini et al. (1986) attributed the catalytic effect of molybdate to its ability to form reactive diperoxo complexes with peroxide. Addition of 500 ppm of sodium molybdate under acidic conditions (pH 5) and a 2% peroxide charge reduced the kappa number by approximately 10 units. Acidic peroxide alone, in the absence of molybdate, reduced the kappa number of the same pulp by only 3 units. However, drastic reduction in viscosity was observed (Kubelka et al., 1992). Jakara et al. (1995a) reported 40–60% delignification with silicomolybdate-activated peroxide in process-scale trials without any adverse impact on the viscosity. Under acidic conditions, silicomolybdate ions react with peroxide to form silicoperoxomolybdates, which are anticipated to be selective delignifying agents. It was possible to obtain a fully bleached (89% ISO) softwood kraft pulp, both in the laboratory and mill-scale studies, by using only oxygen and activated peroxide as the bleaching agent. These researchers (Jakara et al.,1995b) compared the delignification efficiency of silicomolybdate, activated hydrogen peroxide with distilled and equilibrium peracetic acid. Both, peracetic acid (2.5% charge) and molybdate (450 ppm, calculated as Mo) were found to activate hydrogen peroxide (1.5% charge) and reduce the kappa number of softwood kraft pulp by about 44%. Agnemo (1997) reported significant delignification with ammonium molybdate, but using only peroxide at pH~5, no delignification was observed. Suchy and Argyropoulos (2000) studied the effect of a transition metal peroxo complex on an alkaline peroxide delignification. Ammonium triperoxo-phenanthroline vanadate was initially synthesized and then added to the alkaline peroxide stage. At 0.5% activator charge, 61% delignification was obtained using a single alkaline peroxide stage. The brightness of the pulp was increased by 5.7% ISO when compared to an alkaline peroxide-bleaching stage under the same conditions in the absence of the activator. Evtuguin et al. (1998) have examined heptamolybdopentavanadophosphate heteropolyanion–(HPA-5) towards activating an acidic peroxide delignification stage. Delignification was found to be quite high but pulp viscosity reduced significantly. This was due to the extensive decomposition of hydrogen peroxide and hydroxyl radical attack of the cellulose. Tungstate- and molybdate-based polyoxometalates and metal oxides such as tungstate, molybdate and methyltrioxorhenium were evaluated as potential catalysts of acidic peroxide delignification by Chen et al. (1999). The catalysed acidic peroxide stage increased the delignification of oxygen-delignified softwood kraft pulp with increased selectivity compared to control bleaching. Simple metal oxides (tungstate, molybdate) were found to be equally as effective as their polyoxometalate counterparts in catalysing acidic peroxide bleaching. Methyltrioxorhenium was found to be inactive in acidic peroxide bleaching of kraft pulps. Patt and Mielisch (1997) reported higher delignification efficiency when peroxide stage was catalysed by metal complexes. In peroxide-reinforced oxygen delignification also, higher delignification was obtained. A bi-nuclear manganese complex in which the manganese ions are present in the +IV and +III oxidation states, linked via an acetate and two oxygen bridges was shown to selectively improve peroxide delignification. The effectiveness of the proposed system for the production of a fully bleached TCF softwood kraft pulp using an OQ(OP)P bleaching sequence was reported by Patt and Mielisch (1997) and Patt et al. (1998). This system was found to activate peroxide at the relatively low temperature of 50ºC, while higher temperatures offered significantly reduced retention times. The proposed catalyst could be applied either in one or two P stages. A brightness of 88% ISO was obtained when the catalyst was applied at a level of 20 ppm, during the OP stage and when the catalyst was also applied in the subsequent P stage, a brightness of 90% ISO was obtained at higher temperatures. Collins et al. (1998) have reported a new class of iron (III) complexes involving macrocyclic tetraamides. These complexes were shown to activate aqueous hydrogen peroxide offering a variety of oxidation reactions. Using softwood kraft pulp, the above-mentioned systems could catalytically activate peroxide rapidly bleaching kraft pulp under mild conditions in basic aqueous media (Collins et al.,1998). A 1 h peroxide bleaching stage at 90ºC with a charge of 4% peroxide (on o.d. pulp) and 80 ppm of activator showed about 64% delignification of a softwood kraft pulp while the viscosity was acceptable. Bianchi et al. (1998) and Evtuguin et al. (1998) have identified tungstate, molybdate- and vanadate-based polyoxometalates as activators of acidic peroxide delignification. Various types of heteropolyacids (HPA) of Keggin type as potential catalyst of acidic peroxide delignification were investigated (Bianchi et al., 1998). Using 0.5 mmol/L $H_3PMo_{12}O_{40}$ and 0.1% $H_2O_2$ at a temperature of 70°C for 4 h, a hardwood kraft pulp with a kappa number of 2.1 and viscosity higher than control experiments under the same conditions without employing a HPA as a catalyst, can be achieved. However, the use of HPAs as catalysts was not found effective for delignification of softwood pulps.

The reactivity of lignin towards hydrogen peroxide catalysed by binuclear manganese complex, $[LMn(IV)(\ m\text{-}O)_3Mn(IV)]^{2+}$ (abbreviated as Mn(IV)-$Me_4$DTNE), where L stands for 1,2-bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane was reported by Cui et al. (1998). It was suggested based on the model compounds reaction studies, that hydrogen peroxide catalysed by Mn(IV)-$Me_4$DTNE would be capable of oxidizing the $\alpha$-hydroxyl groups and conjugated C–C double bonds in the residual lignin of chemical pulps. The resulting carbonyls and epoxides would be then susceptible to nucleophilic attack leading to further degradation and fragmentation of the residual lignin (Cui et al., 1998). The efficiency of Mn(IV)- $Me_4$DTNE catalysed hydrogen peroxide in the delignification of a pine kraft pulp was examined (Cui et al., 1999). The addition of Mn(IV)-$Me_4$DTNE (60 ppm on o.d. pulp) to the peroxide bleaching stage at 80°C with a charge of 4% peroxide at 10%

consistency for 120 min significantly improved the degree of delignification from 25 to 46%, compared to the noncatalysed delignification under the same reaction conditions.

### 3.3.8 Environmental aspects

Hydrogen peroxide bleaching facilitates the recycle of bleach plant effluents to the recovery cycle. This would help to reduce water use in a mill and will eventually lead to elimination of effluent discharge. Hydrogen peroxide reinforcement of the oxidative extraction stage can be used to decrease the colour of mill effluent (Anderson, 1992).

Several unsolved problems related to the accumulation of both organic and inorganic substances in pulp mill effluent recovery systems have impeded full system closure. The need to eliminate the detrimental effects of transition metals on peroxide decomposition (by acid washing, chelation and use of inorganic inhibitors) has limited system closure applications to a level comparable to those achievable with more conventional bleaching methods. Peroxide bleaching effluents, treated mechanically and biologically, offer no ecological benefits over those from chlorine chemical bleaching. Peroxide bleaching will, however, reduce the concentration of AOX in effluents in proportion to how much it can substitute for the use of chlorine chemicals. It has similar effects on the reduction of AOX discharges as oxygen and ozone. Peroxide residues in effluents to biological treatment are detrimental to microbial activity there, and must be avoided. This can be done by destroying peroxide residues by treating with $SO_2$ or sodium bisulphite.

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## 3.4 Bleaching with chlorine dioxide

### 3.4.1 Introduction

Chlorine dioxide is a very strong oxidizing agent and reacts with the lignin in a pulp without significantly degrading the cellulose or hemicellulose; it thus preserves pulp strength while giving high and stable brightness. Aldehyde groups in carbohydrates may be oxidized to carboxylic acid groups (Reeve, 1996a–c; Gullichsen, 2000; Rapson and Strumila, 1979; Rydholm, 1965; Harrison, 1953; Rapson, 1958, 1963; Casciani, 1953; Smook, 1992; Pikka et al., 2000). It was first used commercially for pulp bleaching in 1946, and by the late 1950s was an integral part of virtually all bleaching sequences for high-brightness kraft pulp. It can be used to achieve high brightness and has been essential in the manufacture of strong, stable, clean, high-brightness kraft pulp. It is a multi-purpose bleaching agent and is efficient in both delignification and brightening of pulp by reducing or eliminating residual lignin content without significant carbohydrate losses and by reducing chromophores in pulp. The capability to decolorize dirt specks makes chlorine dioxide the most efficient bleaching agent in use. Kraft pulp could not be bleached to high brightness (90% ISO) before chlorine dioxide came into use in mid-1940s. Chlorine dioxide is an unusual chemical compound because it has a single unpaired electron and thus is a free radical. At ambient temperature it is an unstable gas that explodes if compressed. It cannot be transported safely and therefore must be manufactured at the site where it is used. As soon as it is formed, it is dissolved in chilled water to form a dilute solution, generally 8–12 g/L at 5–10°C. Depending on the generator process, some chlorine may be present in the solution. When cold chlorine dioxide solution is added to hot pulp, chlorine dioxide vapour can be released. To prevent such release, chlorine dioxide bleaching towers are designed to provide a significant hydrostatic head at the point of chemical addition which maintains sufficient pressure to keep the chlorine dioxide in solution until it reacts with pulp. Chlorine dioxide bleaching towers are therefore upflow towers or upflow–downflow tower.

Commercial bleaching of pulp with chlorine dioxide started in Canada and Sweden in 1946. Before the availability of chlorine dioxide it was not feasible to bleach kraft pulp to a brightness beyond 85% ISO. The use of two chlorine dioxide stages in the later part of a bleaching sequence increased the attainable brightness from 88 to 90% ISO. The sequence for fully bleached kraft pulp evolved from CEHDED to CEDED during the 1960s and to (D+C)EDED in the 1970s. By the early 1990s there were many mills using 100% chlorine dioxide for bleaching.

### 3.4.2 Manufacture of Chlorine Dioxide

Detailed descriptions of the various manufacturing processes of chlorine dioxide is given by Reeve (1996b) and Partridge (1979). It is manufactured at the mill site as a dilute aqueous solution by reduction of sodium chlorate. Most of the mills purchase sodium chlorate as a crystalline solid and store it until required. Sodium chlorate is prepared by the electrolysis of a sodium chloride solution in a cell; this allows the chlorine gas and sodium hydroxide to react as they are formed. The sodium hypochlorite that is produced decomposes to form a mixture of sodium chlorate and sodium chloride. From the concentrated solution, the sodium chlorate is isolated by selective crystallization. The reduction of sodium chlorate is done under highly acidic conditions, with the various processes using different reducing agents. The basic reaction in all the processes is the reaction of chlorate and chloride to form a mixture of chlorine dioxide and chlorine gas.

$$2HClO_3 + 2HCl \rightarrow 2ClO_2 + Cl_2 + 2H_2O$$

When sodium or hydrogen chloride is the only reducing agent, the aqueous chlorine dioxide solution from these processes contains chlorine, because it is difficult to selectively absorb chlorine dioxide in water from the mixture of the two gases. Processes that incorporate additional reducing agents such as methanol or sulphur dioxide reduce the chlorine to chloride and produce relatively pure chlorine dioxide. The chloride is returned to the system for reuse.

### 3.4.3 Chemistry

Chlorine dioxide is a more environmentally acceptable bleaching agent. Chemical properties of chlorine dioxide are very much different from those of molecular chlorine and yield very different end results. If the oxidizing ability of the two chemicals is fully utilized, the reactions may be written as follows:

$$Cl_2 + 2e \rightarrow 2Cl^-$$
$$ClO_2 + 2H_2O + 5e \rightarrow Cl^- + 4OH^-$$

Chlorine dioxide accepts five electrons while elemental chlorine accepts two electrons from the material undergoing oxidation. Chlorine dioxide has 2.5 times more potential oxidizing power than chlorine on a molar basis (2.63 times on a pound per pound basis). On a weight basis, the different molecular weights must be taken into account (71 vs. 67.5), and 1 kg of chlorine dioxide is equivalent to 2.63 kg of chlorine. The quantity of chlorine dioxide used to bleach a pulp is often expressed in chlorine equivalents.

Compared to chlorine, chlorine dioxide produces a much lower quantity of organochlorines during bleaching (Bajpai and Bajpai, 1996, 1997). It introduces about one fifth of the chlorine into a bleaching reaction at the same oxidant equivalence. This is the basis for the formula devised by Germgard and Larsson (1983) to predict the quantity of chlorinated organics (measured as AOX) in the effluent from bleaching with chlorine and chlorine dioxide:

$$\mathrm{AOX} = 0.1(C + D/5)$$

where AOX is the organically bound chlorine (kg/t pulp) in the effluent, $C$ the amount of chlorine gas used (kg/t pulp), and $D$ the amount of chlorine dioxide used (kg of active chlorine/t pulp).

The factor 0.1 comes from experimental observation that about 10% of the chlorine in the bleaching chemical becomes organically bound during bleaching.

This formula shows that when chlorine is replaced by chlorine dioxide, the AOX level in a bleaching-stage effluent will be reduced by a factor of ~5. This is the case in practice. Liebergott et al. (1991) found that AOX level in the effluent reduced when elemental chlorine in the first bleaching stage in a C(EO)DED sequence was replaced with increasing amounts of chlorine

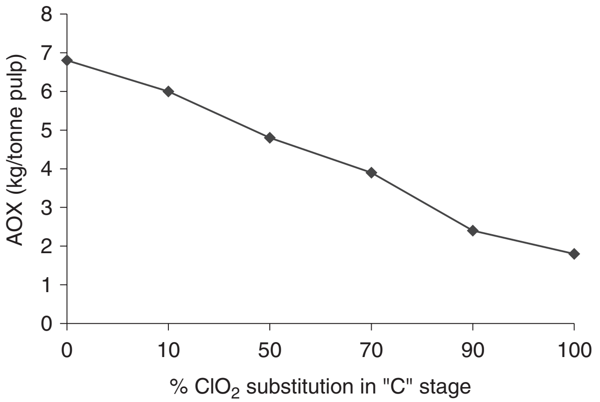

**Fig. 3.4.1. AOX levels in the bleaching filtrates versus percentage of chlorine dioxide substitution in the sequence C(EO)DED. (From Liebergott et al, 1991; reproduced with permission from Pulp & Paper Technical Association of Canada.)**

dioxide. The results are presented in Fig. 3.4.1. The AOX level reduced from 6.7 to 1.7 kg/t of pulp when elemental chlorine was completely replaced with chlorine dioxide. The colour and BOD of the effluent were reduced whereas the COD was only marginally reduced. The chlorinated phenols in the combined C(EO) effluents reduced from about 120 to 5 g/t of pulp (Fig. 3.4.2).

The chemical reactions of lignin with chlorine dioxide have been reviewed by many researchers (Brage et al., 1991a, b; Rydholm, 1965; D'Aveni and Robert, 1982, 1985; Wartiovaara, 1982, 1986; Soila et al., 1962; Gullichsen, 2000). Studies on the reactions of chlorine dioxide with lignin model compounds showed that it reacts with phenolic and olefinic structures in lignin. The liking for phenolic structures is obvious from the observation that the reaction of the phenolic compound creosol was seven times faster than its methylated analogue, 4-methylveratrole. Chlorine dioxide is reduced by lignin to chlorite and hypochlorous acid. Chlorinated organics are formed by the reaction of hypochlorous acid (in equilibrium with molecular $Cl_2$) with lignin. A suggested pathway for reactions between phenolic lignin groups and chlorine dioxide is presented in Fig. 3.4.3 (Brage et al., 1991a). Chlorine dioxide is reduced to chlorite and phenol is oxidized to the phenoxyl radical. The radical can react with chlorine dioxide to form a chlorite ester, which subsequently undergoes hydrolyses, heterolytic fragmentations and eliminations to give products such as those shown in Fig.3.4.3. Brage et al. (1991a, b) have reported that nonphenolic groups react slowly with chlorine dioxide to form radical cations, which undergo subsequent reactions leading to cleavage of carbon $\alpha$–$\beta$ bonds, formation of ketone quinones and ring opening. Examples of some of these reactions are

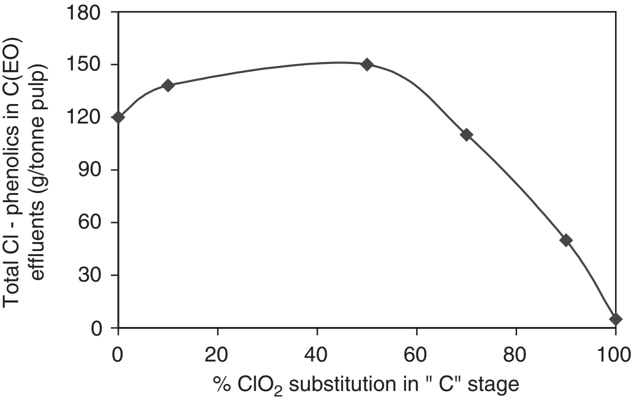

**Fig. 3.4.2. Amounts of chlorinated phenols in combined C(EO) filtrates at various levels of chlorine dioxide substitution. (From Liebergott et al, 1991; reproduced with permission from Pulp & Paper Technical Association of Canada.)**

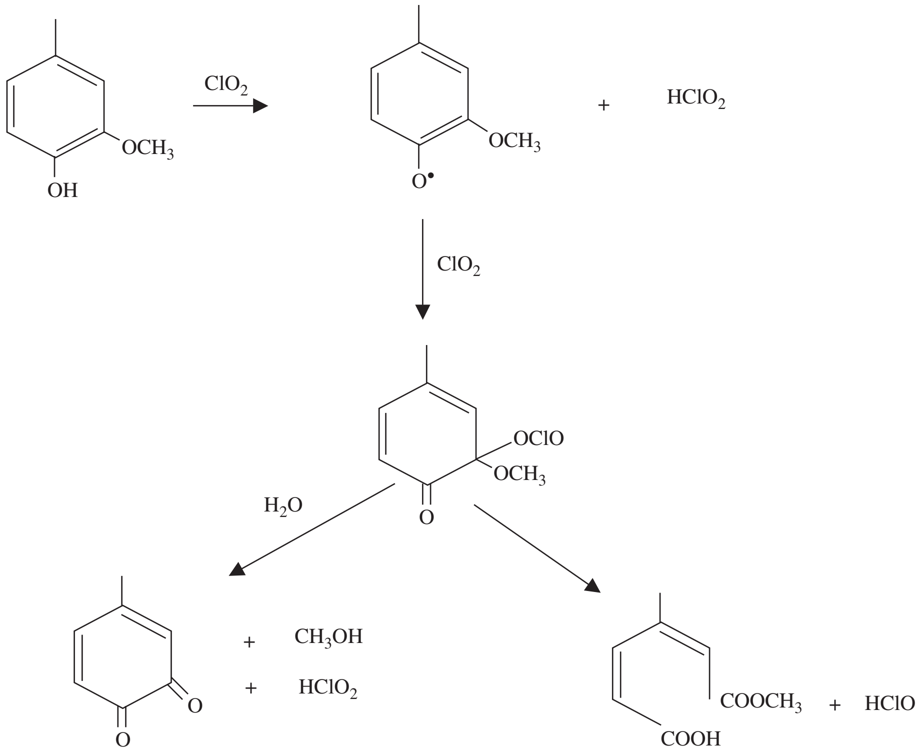

**Fig. 3.4.3. Reactions between phenolic lignin units and chlorine dioxide. (From Nelson, 1998; reproduced with permission from John Wiley & Sons Inc.)**

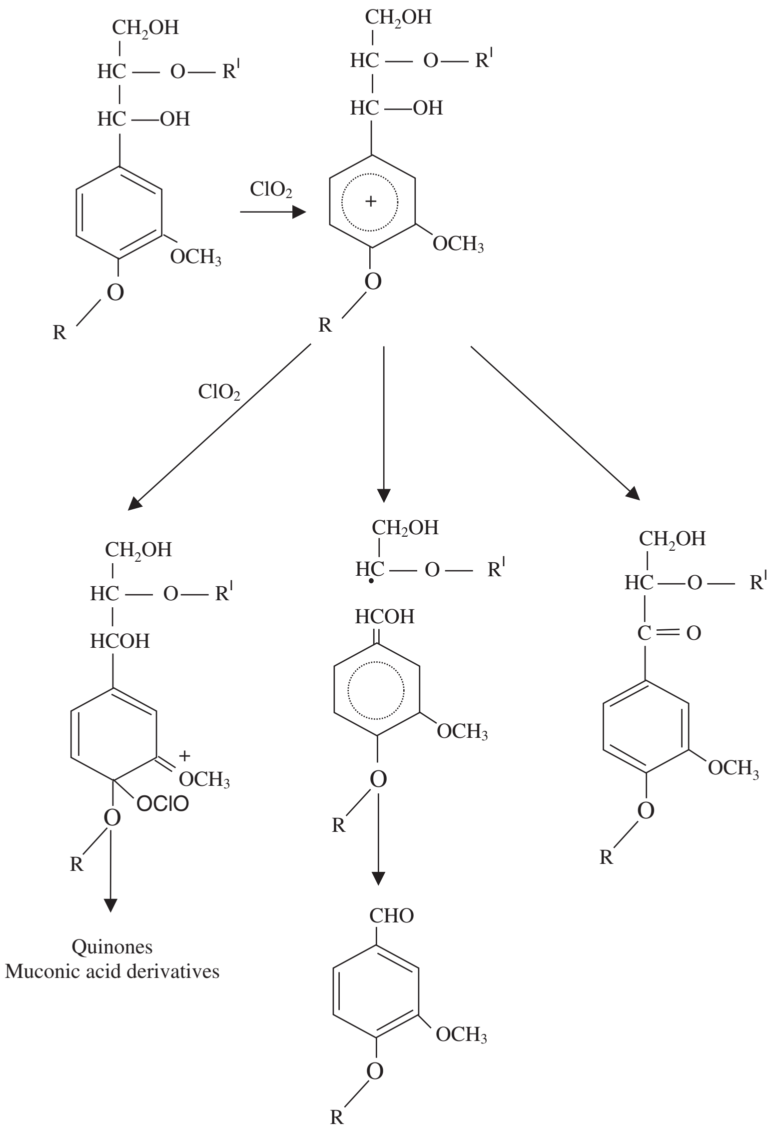

**Fig. 3.4.4. Reactions between nonphenolic lignin units and chlorine dioxide. (From Nelson, 1997; reproduced with permission from John Wiley & Sons Inc.)**

shown in Fig. 3.4.4. Chlorine dioxide and one of its reduction products, the chlorite anion, may complement each other in the degradation reactions of lignin (Brage et al., 1991b). Chlorine dioxide is an electrophile and attacks aromatic rings, whereas chlorite is a nucleophile and adds to carbonyl and conjugated carbonyl (e.g., quinone) structures. The relationship is similar to that of oxygen and the hydroperoxyl anion, which is one of the reduction products of oxygen.

Compared to chlorine, chlorine dioxide has lower reactivity towards lignin. The kappa number of the pulp in a DE sequence is higher as compared to CE sequence with equivalent amounts of chemicals. This is presented in Table 3.4.1, which shows the results of treating a birch kraft pulp and an oxygen-delignified softwood kraft pulp with an initial CE sequence and then progressively substituting chlorine with chlorine dioxide (Pryke, 1989). In both cases a higher kappa number was obtained with 100% chlorine dioxide.

### 3.4.4 Generation of organochlorine compounds

Several studies have been conducted on the generation of organochlorine compounds during reaction of chlorine dioxide with unbleached pulp (Ni et al., 1992, 1994a; Axegard, 1987; Solomon et al., 1994; Morgan et al., 1991; Smith et al., 1995; Kolar et al.,1983; Dahlmann et al., 1995; Wallis and Wearne, 1994). About 50% of the applied chlorine dioxide is converted into hypochlorous acid (Kolar et al., 1983). The organochlorine compounds are formed by the reaction of lignin and hypochlorous acid (Ni et al., 1994a). All the organically bound chlorine (in the pulp and in the liquor) is produced in the first 10 min of the reaction (Ni et al., 1992). Substitution of chlorine dioxide for chlorine in a bleaching sequence reduces the AOX level in the bleaching filtrates, and also changes the nature of the organochlorines formed during bleaching (Axegard, 1987). When 100% chlorine dioxide is used for

**Table 3.4.1 Kappa numbers of birch and oxygen-delignified softwood kraft pulps after “C” E treatment versus percentage of chlorine dioxide in mixtures of chlorine and chlorine dioxide**

| % $ClO_2$ | Postextraction kappa no. | |
|---|---|---|
| | Birch | Softwood |
| 0 | 4.7 | 4.2 |
| 10 | 4.6 | 3.8 |
| 25 | 4.5 | — |
| 30 | — | 4.0 |
| 50 | 4.8 | 4.3 |
| 51 | 4.7 | — |
| 70 | — | 4.6 |
| 75 | 5.2 | — |
| 77 | 5.2 | — |
| 90 | — | 5.4 |
| 99 | — | 6.3 |
| 100 | 6.8 | 6.1 |

Based on data from Pryke (1989).

bleaching, the level of 2,3,7,8-TCDD and 2,3,7,8-TCDF in pulp mill effluents is reduced to nondetectable levels (Solomon et al., 1994). The amounts of polychlorinated phenols were also reduced as chlorine dioxide substitution was increased to 100% in bleaching of softwood kraft pulp (Solomon et al., 1994). At the Crofton pulp mill, a study revealed that complete replacement of chlorine with chlorine dioxide reduced most of the chlorinated phenols below the detection limit (Morgan et al., 1991). A laboratory study conducted by Smith et al. (1995) on the bleaching of oxygen-delignified eucalyptus kraft pulp with a D(EO)D sequence showed that 2-chlorosyringaldehyde was the only significant chlorinated phenol in the effluents. It was also found that use of 100% chlorine in the first stage gave a 2,6-dichlorosyringaldehyde as the major component (Smith et al., 1995). A large proportion of the material in the filtrate from bleaching of kraft pulps is of high molecular weight (molecular weight $>1000$). Solomon et al. (1994) reported that when 100% chlorine dioxide was used for bleaching, about 50% of the organic material in the effluent was of high-molecular-weight, as compared with 70 to 80% when 100% chlorine was used. The high-molecular-weight material in untreated bleach plant effluents from mills using 100% chlorine dioxide was analysed by Dahlmann et al. (1995). It was found that the chlorine content was comparable to that of naturally occurring humic materials. The carbon chlorine ratio was about 100:1, which is much higher than that of the high–molecular–weight material resulting from bleaching with chlorine (ratios in the range 10 – 20:1) (Solomon et al., 1994). The material resulting from the bleaching of hardwoods was mainly nonaromatic, and the softwood-derived high –molecular–weight material contained a significant amount of aromatic structure. Solomon et al., (1994) also observed that high–molecular–weight material in effluents derived from hydrogen peroxide-based TCF bleaching contained small amounts of chlorine (carbon chlorine ratios in the range 500–501, 400:1). Wallis and Wearne (1994) reported that in bleaching of eucalyptus kraft pulp, the carbon chlorine ratio in high-molecular-weight material from bleaching with chlorine dioxide was about seven times higher than that in material derived from bleaching with chlorine. Spectral data revealed that the material derived from bleaching this pulp with chlorine dioxide contained mainly aliphatic structural elements. The exact structure of high-molecular-weight material resulting from chlorine dioxide bleaching is not known, but there is enough evidence to indicate that it will not degrade in the environment to form highly chlorinated compounds.

### 3.4.5 Formation of chlorate

Chlorate is produced during bleaching with chlorine dioxide and has environmental implications. It is formed from the reaction of hypochlorous acid with chlorite ions (Ni et al., 1993; Germgard et al., 1981; Asplund and Germgard, 1991; Lindgren and Nilsson, 1975; Bergnor et al., 1987). Chlorate does not react with the pulp and also represents a loss of bleaching potential (Nilsson, 1974; Rapson and Anderson, 1977; Reeve and Rapson, 1981; Germgrad et al., 1981; Bergnor et al., 1987). Chlorate formation is proportional to chlorine dioxide consumption and is strongly dependent on the bleaching pH. The yield of chlorate can be as much as 50 mol% of the chlorine dioxide used (Germgard et al., 1981):

$$HClO + ClO_2^- \rightarrow Cl^- + ClO_3^- + H^+$$

Germgard et al. (1981), and Asplund and Germgard (1991) have reported that larger amounts of chlorate are produced in the brightening stage of a bleaching sequence than in the initial delignification stage. The extent of the conversion of chlorine dioxide into chlorate is dependent on the substrate (Lindgren and Nilsson, 1975; Bergnor et al., 1987). A study of its reaction with lignin model compounds revealed that with phenolic compounds the yield of chlorate was about the same as that in the first stage of bleaching kraft pulp. With nonphenolic compounds the higher yield of chlorate was comparable with that in the last stage of a sequence. These results are consistent with the view that there are phenolic groups in the lignin in the delignifying stage of a sequence, but in the final stage there is a predominance of nonphenolic structures remaining in the lignin.

Chlorate is toxic to brown algae in marine waters (Rosemarin et al., 1990). It was responsible for the destruction of a large area of bladder wrack in the Baltic Sea (Lehtinen et al., 1988). Malmquist et al. (1991) have reported that it is easily removed during biological treatment of mill effluent if an anaerobic stage is included in the treatment.

### 3.4.6 Process flowsheet and equipment

Fig. 3.4.5 shows the process flowsheet (Reeve, 1996a). Pulp exiting the washer of the preceding bleaching stage contains sodium hydroxide, often added in the repulper of the washer, and then typically falls into a steam mixer to increase and control the temperature. Pulp from the steam mixer is pumped through a chemical mixer, where chlorine dioxide solution is added, and then into the tower. Pulp leaving the tower proceeds to a washer. Chlorine dioxide solution is added after the pulp suspension has been pressurized and that pressure is maintained on this mixture by the hydrostatic head of the upflow tower. Traditional thick-stock, positive-displacement pumps have been substituted by fluidizing, medium-consistency pumps in newer systems or retrofitted systems. Chlorine dioxide solution is added in the turbulent zone on the discharge side of this type of pump and effective mixing is achieved without a separate mixer. The steam mixer may not be required in installations, where the temperature of the pulp entering the stage is sufficiently high. Upflow towers may be used in place of the upflow–downflow tower (Fig.3.4.5) (Reeve, 1996a). A stage with a downflow tower can tolerate variations in production rate better as compared to a stage with only an upward flow. Because chlorine dioxide is volatile, at least one initial upward flow tower is necessary to pressurize the pulp suspension and avoid chlorine dioxide degassing and gas accumulation. Otherwise uneven bleaching and explosion can occur, since chlorine dioxide gas decomposes if its concentration is too high. Another reason to use an upflow–downflow tower is when the required pulp capacity is too large that a single upflow tower would be too high. A split into two towers then becomes necessary.

### 3.4.7 Process conditions

The process variables for treatment of pulp with chlorine dioxide have been studied by many researchers. The results of these studies have been reviewed by Reeve (1996a, b) and Gullichsen (2000). Important process variables are chemical (chlorine dioxide and sodium hydroxide) charge, end pH, temperature, time, pulp consistency, residual oxidant concentration, and carryover of dissolved organic matter. One of the most important variables is the amount of chlorine dioxide applied. In the $D_1$ stage, this will range from 5 to 15 kg/t and in the $D_2$ stage from 2 to 8 kg/t. Sodium hydroxide is

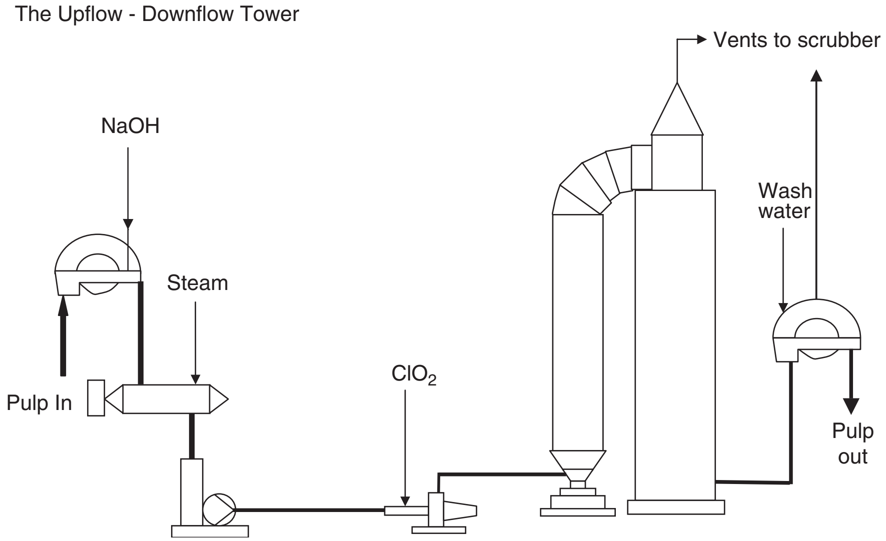

**Fig. 3.4.5. Process and equipment flowsheet for a chlorine dioxide bleaching stage. (From Reeve, 1996; reproduced with permission from Tappi Press.)**

added, particularly to the $D_1$ stage, to control the end pH. In the $D_1$ stage, the typical end pH is 3–4. The end pH in the $D_2$ stage is less critical and is generally somewhat higher. The temperature in chlorine dioxide stages is one of the principal control variables and will range between 50 and 90°C. Long retention times are desirable to achieve maximum brightness. In some instances, increased production capacity has resulted in decreased time available in chlorine dioxide stages, with some stages having as little as 120 min or less. The consistency is controlled by washer performance on the previous stage. Higher consistency is found to be better. Oxidant concentration at the end of the stage is usually at least a trace in order to make full use of the retention time for bleaching.

### *3.4.7.1 Chemical charge*

The brightness increases rapidly with increasing chlorine dioxide charge initially, then the rate of brightness gain decreases to approach an asymptotic limit (Tables 3.4.2 and 3.4.3) (Rapson, 1963; Rapson and Strumila, 1979). In spite of the use of higher dose in the $D_1$ stage, it is not possible to increase brightness further. However, use of alkaline extraction stage and a second chlorine dioxide stage after the first dioxide stage, leads to an increase in brightness (Table 3.4.3). Best use of chlorine dioxide is usually obtained when 20–30% of the total amount is applied in a second ($D_2$) stage. The requirement of chemical is much more when only one stage is used. Chlorine dioxide residual at the end of the chlorine dioxide stage is maintained to prevent brightness reversion. However, minimizing the residual is very important to reduce the excess chemical use, to avoid washer corrosion, emission of chlorine dioxide into the air, and complications in systems closure. Low residual chlorine dioxide bleaching is more economical and

**Table 3.4.2 Effect of the second chlorine dioxide stage ($D_2$) on the brightness of a softwood kraft pulp bleached in a CEDED sequence**

| % $ClO_2$ (final stage) | CEDED (brightness, % GE) |
|---|---|
| 0 | 80.0 |
| 0.18 | 90.0 |
| 0.23 | 91.5 |
| 0.35 | 91.9 |
| 0.42 | 92.0 |
| 0.52 | 92.0 |
| 0.60 | 92.0 |
| 0.78 | 92.1 |
| 0.95 | 92.2 |
| 1.32 | 92.5 |

Based on data from Reeve (1996a).

**Table 3.4.3 Effect of chlorine dioxide charge in the third ($D_1$) stage of a CEDED sequence on the final brightness of a softwood kraft pulp**

| % $ClO_2$ (third stage) | Brightness (% GE) | |
|---|---|---|
| | CED | CEDED |
| 0 | 37.0 | 72.0 |
| 0.18 | 51.0 | 74.0 |
| 0.28 | 56.5 | 76.0 |
| 0.38 | 61.0 | — |
| 0.40 | — | 76.5 |
| 0.48 | 64.0 | — |
| 0.53 | — | 77.0 |
| 0.60 | 66.5 | — |
| 0.66 | — | 77.5 |
| 0.74 | 69.0 | — |
| 0.77 | — | 77.5 |
| 0.86 | 69.5 | — |
| 0.90 | — | 78.0 |
| 0.98 | 70.0 | — |
| 1.00 | — | 77.5 |
| 1.08 | 70.5 | — |
| 1.13 | — | 77.5 |
| 1.18 | 71.0 | — |
| 1.25 | — | 77.0 |
| 1.35 | 71.0 | — |
| 1.38 | — | 77.0 |
| 1.48 | 71.0 | 77.5 |

Based on data from Reeve (1996a).

produces higher-quality pulp (Annergren et al., 1987). Normal chlorine dioxide stage residuals are in the range of 10–50 mg/L expressed as active chlorine. A 10 mg $ClO_2$/L residual in the vat corresponds to 1 kg of chlorine dioxide per metric ton of pulp. Some mills use antichlor at the end of a chlorine dioxide tower to minimize the negative effects of residual chlorine dioxide. The antichlor reacts with the chlorine dioxide and removes it. Sulphur dioxide dissolved in water and sodium hydroxide are used. Sodium hydroxide is added at the end of the tower to increase the pH to 6–7, converting residual chlorine dioxide into sodium chlorite which is nonvolatile and much less corrosive than chlorine dioxide. Sulphur dioxide acts as a reducing agent. Maintaining a certain concentration of chlorine dioxide throughout the bleaching stage provides a sufficient chemical driving force for the bleaching rate and for particle bleaching. Increasing the temperature of $E_2$ stage from 40 to 80°C provides a small increase in $D_2$ brightness; increasing the alkalinity of $E_2$ stage from pH 7 to 12 linearly increases brightness after $D_2$ stage. Relatively little time (5–10 min) is required for the $E_2$ stage to be effective (Axegard et al., 1984). Normally the pulp is washed after the $D_1$

and $E_2$ stages. However, Histed and Vega Canovas (1989) have shown that even without interstage washing, a (DED) sequence produces higher brightness pulp with significant chemical savings compared with a single D stage. Carre et al. (1982) have reported that oxygen enrichment of the first alkaline extraction stage produces brighter pulp in that stage and in the following $D_1$ and $D_2$ stages. A lot of work has been done on the use of the extraction stage kappa number to predict pulp bleachability in the following chlorine dioxide stages. As chlorine dioxide substitution increases, the lignin residual in the pulp is more oxidized and therefore is not accurately characterized by kappa number measurement. However, no impact on bleachability is found when chlorine dioxide substitution in the first stage varies from 10 to 90% (Axegard, 1984, 1987; Germgard and Karlsson, 1984, 1985a, b, 1988; Germgard and Lundqvist, 1990; Germgard and Vannfalt, 1990; Asplund and Germgard, 1991). The total amount of chlorine dioxide required to bleach to 90% brightness is linearly related to the $E_1$ kappa number (Germgard and Lundqvist, 1990).

### *3.4.7.2 pH*

The importance of pH in chlorine dioxide bleaching has been studied by Wartiovaara (1986). When the pulp is treated with chlorine dioxide, organic and hydrochloric acids are formed and the pH decreases rapidly. Wartiovaara (1982) has reported that the initial pH after chemical addition is quite high and then decreases within first 10 min of reaction to target brightness (Table 3.4.4). Sodium hydroxide is added to the pulp before addition of chlorine dioxide to increase the starting and the end pH. Rapson (1956) obtained maximum brightness over a broad pH range centred at pH 6.0. In this study, buffer solutions were used to keep the pH constant. Rapson and Anderson (1957) and Rapson and Strumila (1979) observed the optimal end pH to be in the range of 3.5–4. Maximum brightness was obtained in this range as a result of a minimum loss of active bleaching chemical. A terminal pH of 3.5–4.0 has been recommended for optimum chemical usage in the first

**Table 3.4.4 Decrease in pH during chlorine dioxide bleaching**

| Reaction time (min) | pH | |
|---|---|---|
| | NaOH (0.0%) | NaOH (0.4%) |
| 0 | 8.5 | 11.0 |
| 10 | 3.0 | 5.0 |
| 60 | 2.2 | 3.8 |
| 120 | 2.5 | 3.5 |
| 180 | 2.8 | 3.1 |

Based on data from Reeve (1996a).

dioxide stage. However, a somewhat higher pH (5.5–6.0) has been found to provide the highest brightness from the second dioxide stage (Smook, 1992). Rapson (1956) has reported that chlorate formation decreases whereas chlorite formation increases with increasing pH. Although chlorite reacts with pulp when the pH is low ($< 4$) but as the pH increases beyond 4, its reactivity with pulp drops drastically. At a pH $> 5$, chlorite is stable in pulp suspensions, and therefore its potential for bleaching is not realized.

Solutions consisting only of chlorine dioxide, require ~0.6% sodium hydroxide on pulp for each 1% chlorine dioxide applied to the pulp. Chlorine dioxide solutions containing chlorine require more sodium hydroxide. Only a small amount of sodium hydroxide is required to increase the end pH from 4 to 7. So, there is significant danger in exceeding the target pH when it is set at 4. Pattyson et al. (1981) have reported that the shive removal capacity decreases significantly when the pH increases $> 4$. Seger et al. (1992) has proposed a two-step process for increasing the efficiency of chlorine dioxide bleaching. In the first step, the pulp is held for 5–15 min at an end pH of 6–7.5 and then the mixture is acidified to pH 3.5–4 for the time remaining in the stage. In this method, less chlorate is formed, and the savings in chlorine dioxide can be as high as 24%.

### *3.4.7.3 Time and temperature*

Consumption of chlorine dioxide is higher and the pulp brightness increases when the reaction time of a chlorine dioxide bleaching stage is increased. The pH drops very rapidly at the beginning of the stage (Table 3.4.5) (Teder and Tormind, 1977, 1980). So, chlorine dioxide stages are designed for long retention times, often as upflow–downflow tower combinations where the upflow tube has a retention time of 30 min which consumes most of the chlorine dioxide, a down flow tower with up to 2.5 h retention time for brightness development and shive removal. Direct upflow towers for 3 h or more retention time are also used but at high mill production rates they have

**Table 3.4.5 Effect of time of a chlorine dioxide bleaching stage on pH, chlorine dioxide consumption and brightness**

| Bleaching time (min) | $ClO_2$ (mmol/L) | Brightness (% ISO) | pH |
|---|---|---|---|
| 0 | 5.8 | — | 6.0 |
| 5 | 2.90 | 75.0 | — |
| 10 | — | 77.0 | 3.7 |
| 30 | 2.10 | 79.0 | 3.4 |
| 60 | 1.40 | 81.5 | 3.2 |
| 120 | 0.60 | 83.5 | 3.1 |
| 180 | 0.30 | 85.0 | 3.0 |

Based on data from Reeve (1996a).

to be tall, an inconvenience overcome by the upflow–downflow combination. Under normal circumstances it is desirable to operate chlorine dioxide towers with the maximum practical retention time to ease elimination of bleachable particles.

The temperature in a chlorine dioxide stage is generally in the range of 70–75°C. Brightness development and chlorine dioxide consumption are higher and residual is lower at higher temperature. The upper temperature limit in chlorine dioxide stages is generally fixed by the practical limitations of feeding steam into a steam mixer. When the mixer is operated beyond its capacity, steam blows back into the washer repulper. In some systems, 90°C can be achieved. Retaining a certain chlorine dioxide residual is desirable throughout the stage to facilitate brightness increase and also shive removal. The temperature of the stage is adjusted by adjusting the flow rate of steam to the steam mixer to achieve a desired residual. The temperature of chlorine dioxide solution is usually in the range of 5–10°C. Addition of chlorine dioxide solution decreases the temperature of the pulp in the tower. The temperature drops from 70 to 67°C, when a 10 g/L chlorine dioxide solution at 5°C is added to pulp of 12% consistency at 70°C at the rate of 10 kg chlorine dioxide per metric ton of pulp.

#### *3.4.7.4 Consistency*

Chlorine dioxide bleaching is usually carried out at medium consistency (9–15%), the exact level depend on washer discharge consistency. Overloaded washers may deliver as low as 9% consistency, but some washers deliver 16% or more. Consistency over this range has a negligible effect on reaction chemistry or bleaching efficiency. Chlorine dioxide has been shown to be very efficient at consistencies in the range of 30–40%. However, operation in this range requires a very high capital investment and is not practised. At higher pulp consistency, channelling tendency is reduced. At lower pulp consistency, steam requirement for heating is higher and the retention time in a tower is shorter at a given production rate. The upper consistency limit is usually dictated by pumping constraints. Pulp consistency decreases from 12 to 10.7% with addition of 10 kg chlorine dioxide per metric ton of pulp at 10 g/L.

#### *3.4.7.5 Effect of chlorine on chlorine dioxide bleaching*

Several researchers have studied the effect of chlorine on chlorine dioxide bleaching (Reeve and Rapson, 1981; Rapson and Anderson, 1957; Macas and Evans, 1987). Chlorine is usually present in chlorine dioxide solutions from certain types of generators which may produce up to 9% chlorine (calculated on total active chlorine produced). No significant effect of such concentrations of chlorine on bleaching efficiency is found with the exception of cases where there is high carryover of extraction-stage filtrate into the chlorine dioxide bleaching stage. No effect on pulp viscosity has been observed. Reeve and Rapson (1981) have reported that the oxidizing power of chlorine is utilized as effectively as if it were chlorine dioxide. When chlorine is present in the chlorine dioxide solution, more alkali may be required to control the pH. The addition of chloride ion is found to influence chlorine dioxide reactions. Rapson and Anderson (1957) found that addition of 2 g/L sodium chloride led to a brightness increase by about 2 points and lower chlorate formation. Chlorine in chlorine dioxide bleaching will produce organochlorine compounds. These quantities are small however, compared with what is produced in chlorination.

#### *3.4.7.6 Carryover of dissolved organic material*

The effluent that is not removed from the pulp contains dissolved organic fragments, which cause increased chemical consumption and also affects the brightness. Carryover is measured by kappa number or by light absorbance at 278 nm (Reeve and Rapson, 1981; Parming et al., 1988). Prediction of the effect of carryover on chlorine dioxide bleaching is possible with kinetic studies and mathematical model (Parming et al., 1988). Addition of oxygen or peroxide to extraction stages reduces the absorbance of the effluent by decolourizing the dissolved lignin but does not significantly change the concentration of dissolved lignin in the effluent as measured by absorbance (Parming et al., 1988).

### 3.4.8 Bleaching sequences

Chlorine dioxide is used today in two types of ECF (elemental chlorine-free) sequence. Firstly, in conventional sequences such as $D_0$ E $D_1$ E $D_2$ or O $D_0$ E $D_1$ $D_2$, using 15–50 kg/ODT (oven-dried ton) of pure chlorine dioxide (40–130 kg/ODT of active chlorine). And secondly, in 'ECF-light' type sequences such as OQ (PO) DQ (PO), or OO Q (PO) $D_0$ E $D_1$, using generally less than 10 kg/ODT of chlorine dioxide (or 26 kg/ODT of active chlorine).

Given the relatively high cost of chlorine dioxide and the large quantities which are required, there is a strong motivation to find ways of improving chlorine dioxide bleaching. Added to that, regulations on mill effluents may change and become more stringent in certain countries. The main routes that are open to mills are:

- increasing the delignification efficiency when chlorine dioxide is used at the beginning of the bleaching sequence ($D_0$ stage).
- increasing the bleaching efficency when chlorine dioxide is used towards the end of the sequence ($D_1$ or $D_2$).
- further reduction in the mill's effluent load, particularly the AOX (adsorbable organic halogens) content.

Several research teams all over the world are currently working to improve these techniques. French researchers believe that there is a lot of scope for improvement in chlorine dioxide bleaching and have come up with several ways to help mills get the best out of their bleaching (Chirat and Lachenal, 1999). One of the main areas of improvement can be found in the efficient use of chlorine dioxide in delignification (in the $D_0$ stage). With a typical $D_0$ E delignification process applied on a 30 kappa softwood kraft pulp, the kappa number decreases from 30 to between 4 and 5. The chlorine dioxide charge required is 0.2 × kappa number = 6% active chlorine, or 2.3% for pure chlorine dioxide ($ClO_2$). If the calculation is made on 100 g of pulp, the quantity of $ClO_2$ is 2.3 g, which represents 0.034 mol. The redox reaction that takes place during delignification in a D stage shows that five electrons are exchanged:

$$ClO_2 + 5e^- + 4H+ \text{Ë } Cl^- + 2H_2O$$

This means that the DE process requires the exchange of 5 × 0.034 = 0.17 electron for a 25–26 kappa drop, ie., 0.007 electron per kappa unit.

Going back to chlorine dioxide chemistry, the theoretical number of electrons exchanged to fully oxidize (and remove) lignin during DE (from kappa number 30 to 4–5) is 0.075 (ie., 0.003 electron per kappa unit drop). This figure is about half of the total that is actually exchanged. The difference is very important and means that at least half of the chemical is wasted in other reactions. The same is true for other delignifying agents such as chlorine or ozone. One reason for the difference must be that the chemicals react with dissolved lignin moieties.

Table 3.4.6 presents the DE delignification data for a 30 kappa softwood kraft pulp (Chirat and Lachenal, 1999). It can be seen that the kappa drop is not strictly propor-tional to the quantity of chlorine dioxide consumed. Delignification is more efficient at low chlorine dioxide charges and gradually slows down when the chlorine dioxide consumption increases. The fact

**Table 3.4.6 Kappa no. after DE for a 30 kappa softwood kraft pulp**

| $ClO_2$ consumed ( kg/ODT) | Kappa no. after DE |
|---|---|
| 0.0 | 30.0 |
| 5.0 | 17.0 |
| 8.0 | 12.5 |
| 10.0 | 10.0 |
| 15.0 | 7.0 |
| 23.5 | 4.5 |

Based on data from Chirat and Lachenal (1999).

that the delignification slows down means that after a certain point, $ClO_2$ starts to be significantly consumed by solubilized moieties or side reactions.

Further improvements can be achieved by reducing the amount of AOX formed during chlorine dioxide bleaching. It is well known that the reaction of residual lignin in pulp with chlorine dioxide produces chlorite and hypochlorous acid simultaneously. When the pH is low enough, hypochlorous acid can be converted into chlorine. In most cases, a mixture of hypochlorous acid and chlorine is present during D stages and is responsible for chlorination reactions and consequently AOX formation.

A previous study by Joncourt et al. (1995) showed that by adding dimethylsulphone (DMSO) during a chlorine dioxide stage, the AOX formed could be significantly reduced. The main reason was that the DMSO selectively reacted with chlorine and hypochlorous acid. As a result, the delignification efficiency of the DE stage was also affected. This was probably caused by hypochlorous acid and/or chlorine directly participating in delignification during a D stage. The study showed that the AOX can potentially be reduced if appropriate ways can be found to capture some chlorine or hypochlorous acid.

It is well known that the chlorine dioxide used in a last bleaching stage is not very reactive and must be applied in rather large quantities relative to the modest chemical work performed. Added to that, it has to be used in tougher conditions than in $D_0$, typically at a temperature of 70–80°C for 2–4 h. In this case, there is also scope for improvement which could lead to reductions in the operating cost of a bleaching line. However, a better understanding of the chemistry involved in chromophore elimination is essential in this process.

According to research carried out at France, there are three main ways in which chlorine dioxide bleaching can be improved (Chirat and Lachenal, 1999):

(1) ($D_0$A) stages at high temperatures to improve delignification efficiency.
(2) Combinations of chlorine dioxide with ozone ($D_0$Z) or (Z$D_0$) to decrease bleaching chemical costs and AOX levels.
(3) Splitting chlorine dioxide and controlling pH to reduce the formation of AOX.

In the first area, one way to improve chlorine dioxide delignification (in $D_0$ stages) is to increase the temperature to 95°C and extend the retention time from 2 to 3 h. These conditions far exceed conventional operating conditions which take place at 40–60°C with 30–60 min retention time. The rationale behind the traditional operating conditions is that chlorine dioxide's reaction rate with lignin is already very fast at room temperature and does not need to be increased. However, efforts have been made in the past to work at higher temperatures with the aim of reducing retention time

(Norden and Mellander, 1996). Marechal (1993) and Vuorinen (1996) have reported that a treatment with sulphuric acid at high temperatures could reduce the kappa number of a hardwood kraft pulp by several units and improve the following oxygen or hydrogen peroxide stages, provided that the time in the acid stage was sufficiently long (Marechal, 1993; Lachenal and Papadopoulos, 1988).

Working at high temperatures with long retention times in a $D_0$ stage, the mill can take advantage of the low pH in $D_0$ to perform a combined (DA) stage (Lachenal and Chirat, 1998). At high temperatures (95°C), the chlorine dioxide is totally consumed in less than a few minutes. In spite of this, the kappa number continues to decrease slowly during the retention time which is extended from 1 to 3 h. The effect is much more pronounced with hardwood pulp than softwood. The results in Table 3.4.7 shows that with hardwood kraft pulps, full ECF bleaching is easily performed while saving up to 20% chlorine dioxide (Chirat and Lachenal, 1999). Hydrolysis of hexenuronic acids (Lachenal and Papadopoulos, 1988) and, to a minor extent, acidolysis of residual lignin by the acidic medium are assumed to be responsible for this effect. Pulp quality is not affected provided that the pH of the D stage is kept above 2.0 (Joncourt et al., 1995). The second measure that can be taken is to combine chlorine dioxide with ozone ($D_0Z$) or ($ZD_0$) to decrease the bleaching chemical costs. Dr Lachenal's group have carried out extensive research into the combination of chlorine dioxide (D) with ozone (Z) (Lachenal et al., 1992; Chirat and Lachenal, 1997; Chirat et al., 1997). In theory, 0.6 g of ozone is needed to exchange the same number of electrons as 1 g of chlorine dioxide in ZE and DE processes, respectively. This is the

**Table 3.4.7 Bleaching of an oxygen-delignified mixed hardwood kraft pulp[a] by $D_0$ $ED_1$ effect of temperature in $D_0$**

| Temperature (°C) | 45 | 95 | 95 |
|---|---|---|---|
| $ClO_2$ in $D_0$, (kg/ODT) | 13 | 10 | 10 |
| Time (min) | 90 | 15 | 90 |
| Initial pH | 3.0 | 3.0 | 3.0 |
| $ClO_2$ consumed in $D_0$ (kg/ODT) | 13 | 10 | 10 |
| Brightness, $D_0E$, (% ISO) | 75.9 | 72.1 | 73.3 |
| Kappa number, $D_0E$ | 2.1 | 3.4 | 2.2 |
| Final pH | 2.5 | 2.3 | 2.3 |
| $ClO_2$ in $D_1$ (kg/t) | 7.0 | 7.0 | 7.0 |
| $ClO_2$ consumed in $D_1$ (kg/t) | 6.7 | 7.0 | 6.8 |
| Final brightness (% ISO) | 89.3 | 87.1 | 89.2 |
| Total $ClO_2$ consumed (kg/ODT) | 19.7 | 17.0 | 16.8 |
| Viscosity (mPa s) | 20.0 | 20.0 | 19.0 |

[a] Kappa no. 8.9.

Based on data from Chirat and Lachenal (1999).

displacement ratio which should be observed when all the chlorine dioxide is replaced by ozone. Table 3.4.6 shows that in a $D_0$ stage the delignification rate slows down with a chlorine dioxide charge of ~10 kg/ODT. As a result, when chlorine dioxide is partially replaced by ozone, the replacement ratio is expected to be even higher, since the ozone replaces chlorine dioxide when this chemical begins to be less efficient. Trials at laboratory and pilot plants (Chirat and Lachenal, 1997; Chirat et al., 1997) have shown that in most cases the replacement ratio is $>2$ (2 g chlorine dioxide replaced by 1 g ozone). Mills are also catching onto the idea and have already started to use the process (Finchem, 1998). It is easy to calculate that in many cases, significant cost savings will be achieved by modifying a DEDED sequence into a (DZ)EDED sequence, or ODED into O(ZD)ED. Added to that, as less chlorine dioxide is used, the AOX level is also reduced. Another application of this (DZ) or (ZD) concept is to use it at the end of the bleaching sequence where the last points of brightness are difficult to obtain and significant chlorine dioxide charges are necessary. Chirat and Lachenal (1997) have reported that ozone used in final bleaching stages can be more efficient. Another measure which can be taken to improve chlorine dioxide bleaching is to split the chlorine dioxide and control the pH level which leads to reduced AOX formation. Attempts to reduce the amount of AOX formed during $D_0$ stage generally result in a parallel decrease in delignification efficiency, for example when additives are used (Joncourt et al., 1995; Ni et al., 1994b). One way to reduce the AOX while maintaining the same delignification efficiency is to apply chlorine dioxide under neutral conditions (pH 6–8), which generates chlorite. If the pH is allowed to decrease naturally, chlorine dioxide is regenerated from chlorite. The high concentration of chlorite favours a rapid reaction of chlorite with the hypochlorous acid which is efficiently captured and less susceptible to react with lignin (Joncourt et al., 1995). Chlorine dioxide splitting coupled with this procedure is particularly interesting and the effect can be clearly seen in Table 3.4.8 (Chirat and Lachenal, 1999). The idea is similar to that described for chlorination (Hise, 1989). Lower AOX is formed by $ClO_2$ splitting and adapted pH profile. At the same time, only a small loss in delignification efficiency is observed. It must be noticed that $ClO_2$ splitting alone does not bring any modification in either delignification or AOX formation and that the decrease in AOX appears only when neutralization is performed at the beginning of each $ClO_2$ phase (DnDnD).

### 3.4.9 Effect of chlorine dioxide bleaching on pulp quality

Chlorine dioxide preserves pulp strength while giving high and stable brightness. It is also very effective in particle elimination. Chlorine dioxide does not react extensively with carbohydrates although some oxidation of

**Table 3.4.8 Reduction of AOX in $ClO_2$ bleaching by splitting of chlorine dioxide and control of pH**

| $ClO_2$ charge (%) | 2.4 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 |
|---|---|---|---|---|---|---|---|
| $ClO_2$ consumed (%) | 2.4 | | | | | | |
| Kappa number in DE stage | 4.0 | | 3.9 | | | 4.3 | |
| Viscosity (mPa s) | 28.5 | | 27.8 | | | 26.7 | |
| Initial pH | 7.0 | 7.0 | 3.2 | 3.1 | 7.0 | 7.1[a] | 6.8[a] |
| Final pH | 3.0 | 3.6 | 3.2 | 3.1 | 3.5 | 3.5 | 3.5 |
| AOX (kg/t) | 1.21 | | 1.26 | | | 0.70 | |

*Notes*: Softwood kraft pulp, kappa number=30, initial viscosity 29 mPa s. $ClO_2$ bleaching: total time 90 min, 3.5% consistency, 70°C. With $ClO_2$ splitting, the phases lasted 15, 15 and 30 min. E stage: 3% NaOH, 5% consistency, 70°C, 60 min. AOX was measured after mixing D and E effluents. In the experiments with pH adjustment before D, NaOH in E was decreased so as to keep a 3% NaOH total charge. Based on data from Chirat and Lachenal (1999).

[a] The pH was readjusted to 7 with NaOH before the addition of $ClO_2$.

cellulose does take place. So there is very little pulp strength deterioration in chlorine dioxide bleaching (Teder and Tormind, 1979; Reeve, 1996a–c). Some acidic hydrolysis of cellulose can take place if the chlorine dioxide stage is very acidic. The viscosity loss in chlorine dioxide bleaching stages is found to be very low, but under aggressive conditions, such as pH 2 and at temperatures $> 80°C$, or when the chlorine concentration equals that of chlorine dioxide, some carbohydrate degradation may take place.

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## 3.5 Bleaching with peroxyacids

### 3.5.1 Introduction

The use of peroxyacids in delignification and brightening stages have been studied for about 50 years (Rapson, 1956; Basta et al.,1994; Amini and Webster, 1994; Liebergott, 1994; Johansson et al., 1994; Anderson et al., 1993, 1995; Seccombe et al., 1994; Geng et al., 1993; Allison and McGrouther, 1994; Devenyns et al., 1993, 1994; Poppius-Levlin et al., 1991a–c; Desprez et al., 1993, 1994; Suchy and Argyropoulos, 2002; Ricketts, 1997; Anderson and Amini, 1996). These acids, once thought impractical because of their high cost and poor selectivity, are being considered again as a potential complement to nonchlorine bleaching agents.

The collective group of chemicals commonly referred to as peroxy acids or peracids (designated by the symbol "A") is made up of inorganic and relatively weak organic acids that share a common "peroxy" (O–O) bond. This oxygen linkage is the basis for the peroxyacids' oxidizing power that makes them right candidates for delignification and brightening of pulps. The oxidizing power of peroxyacids is comparable to that of chlorine dioxide and chlorine. So, their delignifying and brightening potential should be similar to chlorine dioxide and chlorine with the obvious advantage of being chlorine free. The oxidation potential of peracetic acid and peroxymonosulphuric acid together with that of other oxidants is listed in Table 3.5.1. The ability of peroxyacids to delignify under acidic or neutral conditions, coupled with environmental pressures for replacing chlorine and chlorine containing chemicals, makes these compounds promising alternative oxidizing agents for chemical pulp bleaching. Peoxyacids have been examined as potential agents for replacing the chlorination stage (first bleaching stage) or immediately following an oxygen-delignification stage. They have been also used in the final brightening stages of a bleaching sequence and as activators before or between two oxygen or peroxide stages (Thomasfolk et al., 1996). Most commonly considered peroxyacids for use in kraft fibre lines are listed in Table 3.5.2.

Lai and Sarkanen (1968) have reported that peracetic acid is capable of hydroxylating the aromatic ring of a phenolic compound to form hydroquinone. Hydroquinones are readily oxidized to quinones, which then undergo ring opening to yield muconic, maleic and fumaric acid derivatives of the starting phenolic compound. Hydroxylation of phenolic compounds, epoxidation of olefinic bonds and the Baeyer–Villiger oxidation of ketones all involve oxidation of functional groups that are normally present in lignin.

**Table 3.5.1 Oxidation potentials of various oxidants**

| | Oxidation potential (e°, V) |
|---|---|
| $O_2 + 2H_2O + 4e^- \rightarrow +4OH^-$ | 0.40 |
| $ClO_2^- + 2H_2O + 4e^- \rightarrow Cl^- + 4OH^-$ | 0.78 |
| $HOO^- + H_2O + 2\,e^- \rightarrow 3OH^-$ | 0.87 |
| $ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$ | 0.90 |
| $CH_3CO_2H + 2H^+ + 2\,e^- \rightarrow CH_3CO_2H + H_2O$ | 1.06 |
| $ClO_2 + H^+ + e^- \rightarrow HClO_2$ | 1.15 |
| $Cl_2 + 2\,e^- \rightarrow 2Cl^-$ | 1.36 |
| $HSO_5^- + 2H^+ + 2e^- \rightarrow HSO_4^- + H_2O$ | 1.44 |
| $HOCl + H^+ + 2\,e^- \rightarrow Cl^- + H_2O$ | 1.49 |
| $HClO_2 + 3\,H^+ + 4\,e^- \rightarrow Cl^- + H_2O$ | 1.56 |
| $H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow 2\,H_2O$ | 1.78 |
| $O_3 + 2\,H^+ + 2\,e^- \rightarrow O_2 + H_2O$ | 2.07 |

Based on data from Anderson et al. (1995).

**Table 3.5.2 Peracids for kraft pulp delignification/bleaching**

| Compound | Chemical formula | Symbol |
|---|---|---|
| Peroxymonosulphuric (Caro's) acid | $H_2SO_5$ | Px, Ca |
| Peracetic acid | $CH_3CO_3H$ | Pa, Paa, PAA |
| Mixed peracids (mixture of peracetic acid and peroxymonosulphuric acid) | $CH_3CO_3H + H_2SO_5$ | Pxa |

Lignin-containing pulps are therefore susceptible to oxidation with peroxyacids and consequently there has been interest in using the compounds for delignification and bleaching of chemical pulps (Amini and Webester, 1994).

Peroxy acids are used for chemical syntheses and in laundry bleaching. In chemical synthesis, these acids are used especially for the epoxidation of olefins and the oxidation of cyclohexanone (Amini, 1994). Poljak in 1948 investigated the use of peracetic acid as a delignifying agent for preparing holocellulose from wood (Poljak, 1948). Study by Leopold (1961) confirmed that peracetic acid is highly selective in the removal of lignin from wood.

### 3.5.2 Production of peroxyacids

Peroxyacids of interest to the pulp industry are peracetic acid (peroxyacetic acid), peroxymonosulphuric acid and peroxyformic acid. Peroxymono-sulphuric acid is also known as Caro's acid. These chemicals are formed when hydrogen peroxide is reacted with the appropriate acid, as shown in the following equation:

$$HA + H_2O_2 \rightleftharpoons HOA + H_2O$$

The equilibrium mixture contains the peroxyacid and water as well as the acid and hydrogen peroxide.

Peracetic acid ($CH_3CO_3H$) is usually produced as a 35% solution by mixing hydrogen peroxide and acetic acid. An equilibrium mixture prepared from a 50% hydrogen peroxide solution contains about 35% peracetic acid and about 6% hydrogen peroxide. The free hydrogen peroxide is not easily utilized during the delignification process and contributes to fibre damage if it is decomposed by metal ions (Hill et al., 1992). If the peracetic acid is distilled from the reaction mixture, the distillate contains about 44% peracetic acid and less than 1% hydrogen peroxide. Distilled peracetic acid is an economical alternative to equilibrium peracetic acid, and it can remove up to 60% of the lignin in a kraft pulp in a PaE sequence. It is claimed that the cost is similar to that of chlorine dioxide (Hill et al., 1992). Another advantage is the very low content of hydrogen peroxide, which minimizes damage to the cellulose in the pulp (Nimmerfroh and Suss, 1996).

Peroxymonosulphuric acid is produced by mixing hydrogen peroxide and concentrated sulphuric acid. An equilibrium mixture is obtained and is used without purification. The reaction is strongly exothermic, and precaution must be taken to prevent overheating, which leads to decomposition of the product.

Peroxyformic acid ($HCO_3H$) is produced by mixing formic acid and hydrogen peroxide. It is the main pulping chemical in the Milox pulping process (Poppius et al., 1989a, b; Poppius-Levlin et al., 1991a–c).

The production costs for each of the various peroxyacid solutions are primarily determined by the unit costs of the raw materials and the peroxyacid yields or conversion ratios for each solution. Other factors affecting peroxyacid production costs are utility requirements (steam, electrical power and cooling water) and attendant costs for chelant addition, acid neutralization and possibly BOD control. For some of the more capital-intensive processes (e.g. a distilled peracid production system), maintenance and labour costs will need to be considered as well. Table 3.5.3 presents the raw material costs for a number of peroxyacid production scenarios. In general, the numbers indicate that the cost of equilibrium peracetic acid is significantly higher than the other peroxyacid chemicals. Distilled peracetic has the lowest raw material cost, but this must be weighed against other operating costs and the high capital cost for a system to produce it. The most cost-effective peracids appear to be peroxymonosulphuric acid and mixed peracids, provided neutralization costs are not excessive.

### 3.5.3 Application of peroxyacids in bleaching

#### *3.5.3.1 Peracetic acid*

The use of peracetic acid for chemical pulp delignification started in 1950s. However, its large industrial utilization was prevented due to its high cost and transportation complexities. In 1966, Bailey and Dence reported the use of peracetic acid for brightening and delignification of chemical pulp. These authors compared the kappa number and the optical and strength properties of the emerging pulps with those obtained from conventional bleaching and

**Table 3.5.3 Raw material cost ($ per lb of equivalent $H_2SO_5$)**

| | 50% peroxide | 70% Peroxide |
|---|---|---|
| Peracetic (PAAd) | 0.36 | — |
| Peracetic (PAAe) | 0.78 | 0.58 |
| | 0.61 | 0.41 |
| Mixed | 0.51 | 0.43 |

Based on data from Amini and Webster (1994).

delignification chemicals (Bailey and Dence, 1966). Peracetic acid showed great promise as a delignification agent. However, its cost and poor selectivity prohibited its industrial application. The peracetic acid used in these early studies was an equilibrium product prepared by mixing appropriate amounts of acetic acid and peroxide in the presence of sulphuric acid as a catalyst:

$$\mathrm{CH_3COOH + H_2O_2 \overset{H_2SO_4}{\equiv} CH_3COOOH + H_2O_2}$$

As implied by the above equilibrium and under conditions that promote it, peracetic acid typically contains high concentrations of acetic acid and hydrogen peroxide. The low amounts of peroxyacid present in the equilibrium mixtures severely affected the economics of the process. Sinkey and Thompson (1974) reported that the peroxide present in the mixture together with transition metal ion impurities of the pulp also may result in serious viscosity losses. In an effort to reduce the chemical costs associated with the process, Christiansen et al. (1966) explored the possibility of generating peracetic acid in situ during a bleaching stage. In their efforts, peracetic acid was formed in situ by reacting hydrogen peroxide and acetic anhydride. Brightness levels comparable to those obtained by chlorine dioxide at the same oxidation equivalent was obtained when kraft pulp was bleached with peracetic acid formed in situ, under optimum conditions. However, the strength of the pulp was significantly lower and its production costs significantly higher when compared to the chlorine dioxide bleached pulp.

Bailey and Dence (1966) investigated the effect of pH (in the range 3–9), temperature (in the range 50–85°C), and consistency on delignification and properties of kraft pulps treated with peracetic acid. At pH 7–9, the reduction in the kappa number of pulps oxidized with peracetic acid was essentially equivalent to the kappa number of similar pulp samples oxidized with an equimolar quantity of chlorine. Within a pH range of 5–9, reaction temperature and pulp consistency had a minimal impact on pulp strength. Pulp viscosity and strength, however, did decrease with increasing temperature when peracetic acid treatment was carried out at pH 3.

To improve the selectivity of peracetic acid, Hill et al. (1992) worked on transition metal control that was aimed at reducing the radical decomposition of the unreacted peroxide and of peracetic acid (Yuan et al.,1997). Other efforts involved the removal of peroxide from the peracetic acid equilibrium mixture by distillation (Hill et al., 1992). Distilled peracetic acid is prepared by vacuum distillation of a mixture of acetic acid, hydrogen peroxide and sulphuric acid (Devenyns et al., 1993; Basta et al., 1994). Delignification efficiencies of equilibrium (e) Paa with distilled (d) Paa in TCF-bleaching sequences of softwood kraft pulp have been compared by Jakara et al. (1995).

It was thus confirmed that different optimal initial pH values for ePaa (pH 4.5) and dPaa (pH 5–7) were required. The delignification efficiency of the ePaa and the dPaa stages showed little difference. However, as expected, considerable differences were observed in the total amount of chemical required. Vuorenvirta et al. (1998) compared the efficiency of using equilibrium and distilled peracetic acids in TCF softwood pulp bleaching. It was found that equilibrium and distilled peracetic acids have different optimum pH operating ranges. The optimum initial pH for ePaa was found to be 4–5, and for dPaa 5–8. However, the delignification achieved with distilled and equilibrium peracetic acids were the same when the bleaching was carried out under optimized pH conditions. These researchers also explored the possibility of reducing the consumption of Paa by applying an acid stage before bleaching. It was found that the final kappa numbers of the acid-washed and chelated pulp were about the same. However, there was a significant drop in chemical consumption if the reaction time of the acid stage was long enough (120 min). Factors affecting the kinetics of oxygen-treated pine kraft pulp delignification with peroxyacetic acid was studied by Jaaskelainen and Poppius-Levlin (1999). They found that equilibrium and distilled Paa gave equally high delignification rates and pulp viscosity, while ePaa led to slightly better pulp brightness, most likely due to the presence of peroxide in the ePaa mixture. The most important factors affecting the kinetics of delignification in the Paa stage were Paa concentration, temperature and pH (Jaaskelainen and Poppius-Levlin, 1999). A plant-scale trial using peracetic acid was carried out in Sweden in 1994 and in 1995, the first mill in the world started to use peracetic acid for TCF pulp production (Thomasfolk et al., 1996). Selective delignification, good pulp strengths and low investment costs were among the advantages claimed for this process when compared to other TCF sequences. However, production costs were higher. The possibility of using distilled peracetic acid was examined in various plant-scale trials in Finland (Ruohoniemi et al.,1998). This effort led to the conclusion that peracetic acid could be used for both brightening and delignifying purposes. In ECF bleaching, the advantage of Paa is a high brightness level and the reduced need for active chlorine in bleaching. The use of Paa in TCF bleaching resulted in a pulp with low kappa number and high brightness with good stability.

Optimum treatment conditions must be maintained for maximum pulp selectivity and for maximum peracid efficiency (1b of chemical applied per unit kappa drop), when peracids are evaluated for delignification (Ricketts, 1997). For peracetic acid, typical treatment conditions are: 120–160°F, a pH of 4–6 and a retention time of approximately 4 h. With the addition of a chelating agent, treatment temperatures of up to 195°F can be tolerated without an increase in strength loss. At these higher peracid delignification temperatures, less retention time is required. Similar results have been reported with distilled peracetic acid (without the addition of a chelating agent). Some investigators have reported kappa reductions of 2–3 units for each percentage point of peracid applied. Liebergott (1994) showed that peracids can be suitable substitutes for a chlorination stage for oxygen-delignified pulp. After extraction, the peracid-treated pulps had higher viscosities than ozone-treated pulps. Under the conditions studied, mixed peracids were found to achieve comparable delignification levels and brightnesses to ozone with about 10% higher viscosities. Perhaps the greatest opportunities for the use of peracids lie in the bleach plant for lignin activation ahead of a peroxide stage or for possibly final brightening. With the high peroxide charges commonly used in full-brightness TCF sequences, a point is reached where additional peroxide no longer reacts with the pulp and no further brightness gains can be realized. This brightness ceiling occurs when the residual lignin has no remaining phenolic hydroxyl groups to react with the alkaline peroxide. Peroxyacid treatment attacks the residual lignin, generating new phenolic hydroxyl groups that can respond to peroxide added in a subsequent stage (Desprez, 1994). Comparisons of sequences such as QPPP vs. QPAP demonstrate that with the peracid treatment it is possible to produce a pulp with a higher final brightness, lower final kappa number and similar physical properties (Ricketts, 1997). Other peracid sequences that have been proposed are OAQP vs. OPZP, OQEopAP vs. OQEopPP and DEopA vs. DcEopD. Most investigators agree that under optimum treatment conditions peracetic acid, peroxymonosulphuric acid, and mixed peracids produce comparable bleaching results. Amini et al. (1994) have reported that with mixed peracids—at the same active oxygen charge—solutions with higher conversion ratios have generally been shown to result in greater kappa reductions and higher final brightnesses. The same results should hold true for equilibrium peracetic and peroxymonosulphuric acid solutions. When peracids are used in the bleach plant, pH must be carefully controlled. A very low pH value can cause acid hydrolysis of the cellulose. In practice, the final pH of a peracid treatment stage should be kept above 2.5. Solutions with high residuals of acetic acid (e.g. equilibrium

**Table 3.5.4 Typical conditions for peracetic acid**

| | Peracetic acid |
|---|---|
| Peracetic charge (% as chemical) | 2–3 |
| Chelant charge (DTMPA) (%) | 0–0.5 |
| $MgSO_4$ (%) | 0 |
| Temperature (°F) | 120–195 |
| Retention time (h) | 2–4 |

Based on data from Devenyns et al. (1993).

peracetic) do not normally require end pH control since acetic acid is a buffer at a pH of 4.7. Typical conditions for peracetic acid usage for lignin activation ahead of a final peroxide stage are presented in Table 3.5.4.

#### *3.5.3.2 Peroxymonosulphuric acid and other peracids*

Poppius et al. (1989a, b), Song et al. (1993), Geng et al. (1993), Springer and McSweeny (1993a, b), Ricketts (1997) and Suchy and Argyropoulos (2002) have reported peroxymonosulphuric acid, its salts and performic acid as effective oxidizing agents for delignification and bleaching of chemical pulps. Peroxymonosulphuric acid belongs to the group of peracids (prepared from the interaction of hydrogen peroxide with sulphuric acid). This is also an equilibrium reaction similar to the one that describes the formation of peracetic acid.

$$H_2SO_4 + H_2O_2 \equiv H_2SO_5 + H_2O$$

The conversion of peroxide into peroxymonosulphuric acid is affected by the amount of water present in the reaction mixture. Its concentration reaches a maximum at about 45% conversion, when an excess of 99% sulphuric acid and 50% hydrogen peroxide (1.5:1.0 mole ratio) is used. The conversion of the process can be increased by minimizing the amount of water or by using more concentrated peroxide (70%) and sulphuric acid (oleum) (Szegda, 1994). Both of these routes, however, have aroused serious safety concerns (Amini and Webster, 1994). Despite these, mill trials using peroxymonosulphuric acid have been conducted yielding high brightness softwood and hardwood kraft pulps (Seccombe et al., 1994). Geng et al. (1993) have described another means of increasing the peroxide conversion to the peracid. By adding acetic acid to the equilibrium mixture of peroxymonosulphuric acid, a mixture of peracetic and peroxymonosulphuric acids is formed. This permits the high conversion of peroxide into the peracids without using excessively high peroxide and sulphuric acid concentrations:

$$H_2SO_4 + H_2O_2 \equiv H_2SO_5 + H_2O_2 +$$
$$CH_3COOH + H_2O_2 \equiv CH_3COOOH + H_2O$$

Song et al. (1993) reported that by adding 1 mol of acetic acid to the peroxymonosulphuric acid mixture increased the conversion of peroxide into peracids to a 94% level. The application of peroxymonosulphuric acid (Px) and mixed peracids (Pxa) in ECF and TCF bleaching sequences were investigated by several researchers (Geng et al. 1993; Song et al., 1993; Brasileiro et al., 1997; Devenyns et al., 1993). It was possible to obtain fully bleached softwood kraft pulp by using a peroxygen-based bleaching sequence (Devenyns et al., 1993). Oxygen-delignified and chelated pulp was prebleached with peroxide followed by a peracid stage (peracetic, Paa and peroxymonosulphuric Px acids). The final brightening was obtained by applying a P* stage (alkaline hydrogen peroxide at high consistency with particular attention being paid to transition metal removal and stabilization). Using the QPPaaP* and OQPPxP* sequences, fully bleached TCF kraft pulp was produced with adequate mechanical properties. The delignification efficiency of mixed peracids (Pxa) with oxygen was compared by Amini and Webster (1994). A comparison of oxygen delignification and mixed peracids stages followed by EOP, showed that both reduced the kappa number of pine kraft pulp (kappa 34) by half. The Pxa EOP stage, however, provided higher brightness. Experiments with eucalyptus kraft pulp (kappa number 20) showed an even better performance for peracids. A single Pxa stage was shown to have a higher delignification efficiency than a single oxygen-delignification stage. The combination of Pxa and EOP stages resulted in 60% delignification. This is substantially more than the delignification obtained after the single oxygen-delignification stage. When a Pxa EOP sequence was applied after an oxygen stage, the kappa number was reduced from 12 (after the oxygen stage) to 5.1, and the brightness reached 69% ISO. By comparing the delignifying and brightening efficiencies of peracetic acid, peroxymonosulphuric acid and mixed peracids, the researchers concluded that for a variety of conditions, equal amounts of peracid (equal active oxygen in its peracid form, or equal molar amounts of peracid) gives similar delignifying and brightening performance.

A TCF bleaching sequence using an acid pretreatment, acidic peroxymonosulphate, oxygen delignification and alkaline peroxymonosulphate brightening has been reported by Springer and McSweeny (1993a, b). Final brightness of 82 and 86% ISO was obtained with pine and aspen kraft pulp, respectively. Basta et al. (1994) compared bleaching with peracetic acid and peroxymonosulphuric acid. Oxygen-delignified softwood kraft pulp bleached with a sequence composed of a peracid treatment, followed by a chelating stage and a final alkaline peroxide stage, showed superior selectivity when peracids (for peracetic acid both dPaa and ePaa were used) were compared to peroxymonosulphuric acid. A similar comparison with ozone in a QPZP bleaching sequence again proved the higher selectivity of dPaa. Troughton et al. (1995) studied the effect of inserting a peracid stage into a TCF bleach sequence, consisting of a metal-controlling Q stage, followed by several alkaline peroxide stages. By inserting a peracid stage into the QPPP sequence, it was found that the pulp brightness increased by 5–10 ISO points without pulp strength losses. When the delignification efficiencies for the various sequences were compared, the effect of the peracid stage was found to be due to a more extended delignification. For example, when a softwood oxygen-delignified kraft pulp was bleached by aQPPxP sequence, its kappa number was reduced to 2.4. However, a better delignification was obtained when peroxymonosulphuric acid was replaced by peracetic acid. The final kappa number, after the QPPaaP sequence, was 2.1. Equivalent bleaching, using only peroxide (QPP) was found to reduce the kappa number to only 5.7. Delignification from 35 (QEOP) to 48.9% (PaEop) was obtained when unbleached softwood kraft pulp was pretreated with peracetic acid and subjected to EOP stage (Liebergott, 1996). Similar results were obtained when an oxygen-delignified softwood kraft pulp was used. The Pa treatment increased delignification after an EOP stage from 20 (for an OQEOP sequence) to 40% (for an OPaEOP sequence). The kappa number was reduced from 16.4 (after oxygen delignification) to 9.8. The use of peroxyformic acid in TCF bleaching has been reported by Poppius et al. (1989a, b). Depending on the concentration of formic acid, amount of peroxide and the temperature of the treatment, delignification with peroxyformic acid and hydrogen peroxide was 25–80% in case of a pine kraft pulp. Subsequent alkaline peroxide-bleaching stages raised the brightness to 80–85% ISO. In addition, the same team showed that peroxyformic acid may also increase the efficiency of an oxygen-delignification stage by ensuring a substantial decrease in the incoming kappa number prior to the oxygen stage (Poppius-Levlin et al., 1991a–c). Kappa numbers as low as 4–6 were obtained for pine and birch kraft pulps after the (PFA)O sequence. Consequently, brightness values of 90% ISO were reached for both the pine and birch kraft pulps predelignified with peroxyformic acid and bleached in a sequence using oxygen, ozone and alkaline peroxide. Peroxymonophosphoric acid was also studied as a possible delignification agent for wood and kraft pulp (Springer, 1997). Pine kraft pulp was delignified with a dilute aqueous solution of peroxymonophosphoric acid and its delignification selectivity was compared with peroxymonosulphuric acid. This study showed that, under identical reaction conditions, peroxymonophosphoric acid delignified more rapidly and more selectively than peroxymonosulphuric acid. However, the incompatibility of the phosphates with current mill recovery systems is a major drawback. Typical peroxymonosulphuric acid conditions are presented in Table 3.5.5.

**Table 3.5.5 Typical conditions for peroxymonosulphuric acid**

| | Peroxymonosulphuric acid |
|---|---|
| Peracid charge (% as chemical) | 3–4.5 |
| Chelant charge (DTMPA) (%) | 0.1–0.5 |
| $MgSO_4$ (%) | 0.1– 0.5 |
| Temperature (°F) | 120–195 |
| Retention time (h) | 2–4 |

Based on data from Devenyns et al. (1993).

Several issues must be considered by mills that are evaluating potential peracid applications (Rickets, 1997). The drawback in the use of peroxy acids, particularly in the pulp and paper industry, is their high manufacturing cost and the fact that they are generally not stable to be shipped or stored for long periods of time. Peroxyacids can be prepared on site by chemicals—this is in practice in most mills—with the exception of acetic acid, which is required for the production of peracetic acid or mixed peroxyacids. Glacial acetic acid introduces no serious health or safety risks as it is a weak acid. Because it freezes at 62°F, the acetic acid storage and distribution system should be designed with adequate freeze protection. Even with the higher peracid conversions resulting from the use of 70% peroxide, most mills will probably use 50% peroxide because of its reduced process safety risks. For most applications, stainless-steel construction is adequate for all process equipment and piping in contact with concentrated peracid solutions. Production of distilled peracetic acid at mill site introduces a number of new process safety issues, all of which can be managed through proper system design and operation. The distillation product, primarily a mixture of peracetic acid and water, will undergo explosive autodecompostion at approximately 175°F. This temperature may be lower when metal ions are present in the solution. If the peroxide concentration to the reactor is greater than 50%, or if the peroxide concentration in the reactor is not property controlled, a detonable mixture of acetic acid and concentrated peroxide could potentially be formed. Although distilled peracetic acid has been safely produced for years in the chemical industry, and similar risks are associated with chlorine dioxide production and handling, these concerns, nonetheless, may push some mills towards the use of other peracids. The greatest BOD contribution when peroxyacids are used for pulp bleaching is produced by equilibrium peracetic acid. The BOD results from residual acetates. The BOD contribution of acetates is reported to be approximately 0.7 lb BOD/lb acetate (Amini and Webster, 1994). With higher yield equilibrium peracetic, the BOD is less. In case of distilled peracetic, BOD is even lesser because it has relatively lower acetic acid residual. Of the organic peroxyacids, mixed peracid solution has the lowest overall BOD load. Peroxymonosulphuric

**Table 3.5.6 Effluent BOD (lb per lb of equivalent $H_2SO_5$)**

| | 50% peroxide | 70% peroxide |
|---|---|---|
| Peracetic (PAAd) | 0.36 | — |
| Peracetic (PAAe) | 0.78 | 0.58 |
| Caro's | 0.61 | 0.41 |
| Mixed | 0.51 | 0.43 |

Based on data from Amini and Webster (1994).

acid has no effluent BOD impact although its use results in the highest discharge of sulphates and requires the most caustic for neutralization due to the relatively low-end pH of a typical peroxymonosulphuric acid stage. Table 3.5.6 shows the effluent BOD data for peroxyacids.

### 3.5.4 Conclusions

The use of peroxyacids in bleaching should pose no particular problems as mills move towards more tightly closed bleach plants, provided the recovery furnace can handle higher solids and heat load. If effluent from peroxy stage is to be recycled to the chemical recovery loop, its impact on the sodium and sulphur balance must first be determined, particularly in the case of peroxymonosulphuric acid, which contributes the most significant amount of sodium and sulphur. For some mills, peroxyacids do offer distinct advantages in the bleach plant. Peroxyacids bleaching is an option for mills, considering TCF or ECF pulp production. It would be particularly useful for a mill that produces high-brightness TCF pulps only on a campaign basis. Peroxyacids can be used to provide a mill with TCF capability while using limited capital resources (vs. ozone), allowing the mill to postpone more significant capital investment until after TCF bleaching technology has matured. The long-term future for peroxyacids will depend on their ability to produce high brightness pulps with superior physical properties in a cost-effective way.

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## 3.6 Enzymatic prebleaching*

Enzymatic prebleaching is one of the promising alternatives for eliminating/reducing chlorine-based chemicals in pulp-bleaching process. Enormous efforts have been made to develop hemicellulase-aided bleaching (Turner et al., 1992; Lavielle, 1992; Jean et al., 1994; Scott et al., 1993; Yee and Tolan, 1997; Bajpai, 1997, 2004; Bajpai and Bajpai, 1992, 1996a, b, 1999; Bajpai et al., 1993, 1994; Farrell et al., 1996; Viikari et al., 1986, 1987, 1990, 1993, 1994, 1996; Suurnakki et al., 1997; Tolan and Guenette, 1997; Tolan, 1992, 2001; Tolan and Canovas, 1992; Tolan et al., 1996; Senior et al., 1999, 2000; Senior and Hamilton, 1991–1993). Also, considerable efforts have been made to study the potential of ligninolytic enzymes for bleaching of pulps (Call, 1993, 1994a, b, 1999, 2002; Call and Mucke, 1994a, b, 1995a, b, 1997; Bourbonnais et al., 1995; Paice et al., 1995a, b; Kondo et al., 1994–1996).

### 3.6.1 Bleaching with hemicellulase enzymes

*3.6.1.1 Introduction*

Bleaching with hemicellulase enzymes is the first full-scale biotechnical application in the pulp and paper industry. Hemicellulases are used to modify the structure of xylan and glucomannan in pulp fibres in order to enhance the chemical delignification. This technology can be combined with various types of kraft pulping processes and bleaching sequences. The aims of the enzymatic prebleaching depend on the actual mill conditions, and may be

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*Excerpted from Bajpai, P., 2004. With permission from Taylor and Francis related to environmental demands, reduction of bleach chemical costs and/ or improvement of product quality (Viikari et al., 1994).

The main enzyme needed to enhance the delignification of kraft pulp is reported to be endo-*β*-xylanase but enrichment of xylanases with other hemicellulases has been shown to enhance the effects of enzymatic treatment (Viikari et al., 1994). The use of xylanases to enhance the bleaching of the pulp was first reported in 1986 (Viikari et al., 1986). The Finnish companies were the first in the world to start mill scale trials in 1988. Presently, a significant number of mills in many parts of the world are bleaching full time with enzymes, and various paper products including magazine paper and tissue paper manufactured from xylanase-treated pulps have been successfully introduced to the market (Viikari et al., 1994; Suurnakki et al., 1997). Much of the motivation to use xylanases has been from the pressure on the mills to decrease the use of chlorine chemicals for environmental, regulatory and market reasons. In North America there are at least 16 pulp mills using xylanases (Hoddenbagh, 2004). Use of xylanases is more common in Canada than in the United States because of more stringent AOX levels (Senior et al., 1999). In 2001, nearly 20% of the bleached pulp in Canada was xylanase-treated (Hoddenbagh, 2004).

#### *3.6.1.2 Production and properties of hemicellulases*

Several articles have been published on the production and properties of hemicellulases especially on xylanases (Biely, 1985; Viikari et al., 1993; Wong et al., 1988). The strains used for commercial production of xylanases include *Trichoderma reesei*, *Thermomyces lanuginosus, Aureobasidium pullulans* and *Streptomyces lividans*. The productivity has been increased both by development of more efficient production strains and by optimizing the production methods (Bailey et al., 1993; Nevalainen et al., 1990; Suominen et al., 1992). Xylanases with high pH and temperature optima have been used for improving the bleachability of pulps (Pederson et al. 1992; Singh et al., 1995). Several alkali-tolerant strains of *Bacillus* have been used for production of xylanases with pH optima of around 9.0.

Several criteria are essential for choosing a microorganism to produce enzyme for bleaching. In addition to giving the desired biobleaching effect, the enzyme preparation must be produced in sufficiently high quantity and the technology must be compatible with the technology of a pulp mill. Also, it is essential that the enzyme should be completely free of cellulase side activity as it will have serious economic implications in terms of cellulose loss, degraded pulp quality and increased effluent-treatment cost. To produce xylanases, the selected organism is grown for several days in sealed fermentation vessels containing nutrients and oxygen under specific conditions of pH, temperature and agitation. During this time, it secretes enzymes into the growth medium. The living cell mass is then removed, leaving a xylanase-rich liquid. This is then concentrated, assayed to determine its activity and packaged for shipment to pulp mills. With the addition of bacteriostatic preservatives, the xylanase preparation remains stable for months. Excessive temperature and freezing can cause loss of activity and hence should be avoided. The xylanase preparation is not corrosive and does not need resistant materials for handling.

Table 3.6.1 shows the list of some of the commercial xylanases used for prebleaching.

### *3.6.1.3 Performance of xylanases in bleaching*

The use of xylanases in different bleaching sequences leads to a reduction in chemical consumption. The benefits obtained by enzymes are dependent on the type of pulp and bleaching sequence used, and the final brightness and

**Table 3.6.1 Commercial xylanase suppliers**

| Product | Supplier |
|---|---|
| Cartazyme HS 10 | Clariant, U.K. |
| Cartazyme HT | Clariant, U.K. |
| Cartazyme SR 10 | Clariant, U.K. |
| Cartazyme PS 10 | Clariant, U.K. |
| Cartazyme MP | Clariant, U.K. |
| Cartazyme NS 10 | Clariant, U.K. |
| Cartazyme 9407 E | Clariant, U.K. |
| Irgazyme 40-4X/<br>Albazyme 40-4X | Genencor, Finland/<br>Ciba Geigy, Switzerland |
| Irgazyme-10A/<br>Albazyme 10A | Genencor, Finland/<br>Ciba Geigy, Switzerland |
| VAI Xylanase | Voest Alpine, Austria |
| Pulpzyme HA | Novo Nordisk, Denmark |
| Pulpzyme HB | Novo Nordisk, Denmark |
| Pulpzyme HC | Novo Nordisk, Denmark |
| Bleachzyme F | Biocon India, Bangalore |
| Ecopulp X-100 | Rohm Enzyme OY, Finland |
| Ecopulp X-200 | Rohm Enzyme OY, Finland |
| Ecopulp X-200/4 | Rohm Enzyme OY, Finland |
| Ecopulp TX-100 | Rohm Enzyme OY, Finland |
| Ecopulp TX-200 | Rohm Enzyme OY, Finland |
| Optipulp L-8000 | Solvay Interox, U.S.A. |
| Ecozyme | Thomas Swan Co., U.K. |
| GS-35 | Iogen Corporation, Canada |
| HS-70 | Iogen Corporation, Canada |
| Fiberzyme LBL | Dyadic International, U.S.A. |

Based on the data from Bajpai (2004).

environmental objectives of the mill. Xylanases are used in conventional, ECF and TCF bleaching. In conventional bleaching, xylanases are used to reduce the consumption of chlorine chemicals. In ECF and TCF bleaching, xylanases are used to improve the otherwise lower final brightness of pulp or to reduce the cost of bleaching chemicals. Results from laboratory studies and process-scale trials show about 35%–41% reduction in active chlorine (aCl) at the chlorination stage for hardwoods and 10%–20% for softwoods, whereas savings in total aCl were found to be 20%–25% for hardwoods and 10%–15% for softwoods (Tolan and Canovas, 1992; Skerker et al., 1992; Yang et al., 1992; Bajpai et al., 1993, 1994; Valchev et al., 1998, 1999; Zhan et al., 2000; Senior and Hamilton, 1991; Thibault et al., 1999). The effect of xylanase on conventional and ECF bleaching is shown in Tables 3.6.2 to 3.6.3. The ability of the xylanases to reduce bleaching chemicals makes it possible to consider significant modifications in the bleaching sequence. It is possible to completely exclude the first stage in a C/DE$_{OP}$DE$_P$D and replace it with an enzyme stage (X) to become XE$_{OP}$DE$_P$D. This has been verified in a mill trial in Spain (Turner et al., 1992). The advantage of this sequence is that filtrates from the E$_{OP}$ stage can be recirculated to the recovery system without risk of chloride-initiated corrosion. This approach helps in closing

**Table 3.6.2 Effect of xylanase treatment on chlorine requirement in conventional bleaching[1]**

| Total aCl | Final brightness (%) | |
|---|---|---|
| (%) | Control | Treated |
| 7.0 | — | 84.5 |
| 7.5 | — | 90.7 |
| 7.8 | — | 91.6 |
| 8.0 | 84.0 | 92.0 |
| 8.6 | 89.0 | — |
| 9.2 | 91.5 | — |

[1] Bleaching sequence-D/CE$_O$DED (50% ClO$_2$ substitution was used in chlorination stage)
Based on data from Tolan and Canovas (1992).

**Table 3.6.3 Plant-scale trial results with xylanases**

| | No enzyme | Enzyme |
|---|---|---|
| Pulp production (ADT/day) | 380 | 380 |
| Chemical addition (kg/ADT) | | |
| $ClO_2$ | 12.7 | 13.8 |
| $H_2O_2$ | 12.7 | 12.5 |
| Final brightness (% ISO) | 81.5 | 88.2 |
| Unbleached kappa number | 13.8 | 14.0 |
| E$_{OP}$ viscosity (dm$^3$/kg) | 799 | 809 |

Based on data from Skerker et al. (1992).

the water circulation system of the pulp mill and minimize effluent discharge. The following sequence options were tested on hardwood pulp with an incoming kappa number of approximately 14 and viscosity of 850–950 $dm^3/kg$ (Dunlop and Gronberg, 1994):

1. $XE_{OP}DE_PD$ (enzyme/ no chlorine)
2. $E_{OP}DE_PD$ (no enzyme/ no chlorine)

The advantage of options 1 and 2 is that filtrate from prebleaching can be kept separate from the filtrates of final bleaching and will therefore not contain components that could not be evaporated and burnt in the recovery boiler. The effluent load will, in these cases, be lower than that for the conventional sequence, even if the final bleaching in options 1 and 2 will require slightly higher chlorine dioxide ($ClO_2$) charges. The mill had previously tested the $E_{OP}DE_PD$ sequence without enzyme and could not achieve brightness values higher than 83% ISO. With Cartazyme HS-10, a brightness level of 88% was achieved (Skerker et al., 1992) (Table 3).

The potential for cost savings in TCF bleaching is particularly high. It has been shown in both laboratory-scale experiments and mill trials that hydrogen peroxide ($H_2O_2$) can be saved (Dunlop and Gronberg, 1994). Compared to a QPP sequence, the XQPP sequence can save 5–10 kg $H_2O_2$/t of pulp. In 1992, in a joint venture between Korsnas AB and Dutch company Gist Brocades, Korsnas started a full-scale study on TCF bleaching with enzyme Korsnas T6 xylanase. With this enzyme, it was possible to produce TCF pulp of high brightness (Sandstrom, 1993). Aanekoski mill in Finland used an enzyme with $O_2$ delignification and peroxide bleaching to produce over 50 000 t of TCF pulp (Anonymous, 1992). Dr Eriksson's Group in University of Georgia has developed an Enzone process for bleaching kraft pulps of different raw materials. This process features an oxygen–xylanase–ozone–peroxide sequence for hardwood pulp and an additional alkaline extraction (E) stage between ozone and peroxide stages for softwood pulps. The main advantage of this process is the xylanase step, which increases brightness by 3 – 8 points when compared with the control pulp (Young, 1994). Dr Eriksson's group has reported the use of an extremely high specific activity xylanase from *Orpinomyces* sp. strain PC-2 in ECF and TCF bleaching (Shah et al., 2000a). An overall brightness gain of 4.3% ISO was achieved in ECF(OXDP) or TCF(OXZP) sequence. The same group also carried out xylanase treatment from *Thermotga maritima* of oxygen-bleached hardwood pulp at a temperature of 90°C and pH of 10. About 25% saving in bleaching chemicals with 90.5% brightness was obtained. The brightness of untreated pulp was only 86% (Shah et al., 2000b).

A novel enzyme system for bleaching has been described by Lantto et al. (2000). Spruce pulp and oxygen-delignified spruce pulp were pretreated with commercial xylanase and proteinase. Lignin removal was increased and the bleachability of the pulp improved. The effects of xylanase and mannanase treatment on the bleachability of oxygen-delignified superbatch pulps have been studied by Suurnakki et al. (1998) using TCF bleaching. Xylanase pretreatment increased the final brightness of the pulps more than the mannanase treatment. The combination of the more neutral *T. reesei* xylanase treatment and chelation was more suitable than the acidic *Aspergillus kawachii* xylanase treatment at pH 2.5 for superbatch pulp TCF bleaching.

Crestbrook Forest Industries, Canada, used the enzyme Albazyme 10 to remove the bottleneck in $ClO_2$ generation and to increase the pulp production. Munksjo AB, Sweden, combines the xylanase with the Lignox process to produce TCF pulps, while Metsa-Sellu OY, Finland, uses it to reduce AOX from its kraft pulp mill. Metsa–Botnia's plant in Kasko produces ECF pulp by using oxygen delignification and xylanase bleaching. The pulp is used in the production of supercalendered, light-weight coated paper and tissue paper (Anonymous, 1991). The Weyerhaeuser mill in Prince Albert, Canada, has been using xylanases successfully since 1992 to enhance the bleaching (Yee and Tolan, 1997). On average, the enzyme-treated pulp uses 12% less chemicals than untreated pulp. The mill has been able to maintain dioxin-free effluent and is well within the AOX guidelines. The savings in $ClO_2$ has helped to maintain the desired pulp output. Yango mill in Japan has introduced enzyme bleaching into the hardwood pulp-bleaching process (Fukunaga et al., 2000). On-site production of xylanase from *Bacillus* sp. was carried out. The plant has been operating successfully with no adverse effect on pulp quality.

As the TCF market grows, Canadian mills, which are the world's largest exporters of market pulp, have started to investigate ECF bleaching with xylanases. European paper makers are requesting TCF pulps or bleaching pulps with extremely low AOX level in their effluents (Worster, 1993). Many Finnish companies are conducting research to develop ECF bleaching that involves the use of xylanases, oxygen, peroxide and ozone (Anonymous, 1992)

Most of the research on bleaching with hemicellulases has mainly focused on softwoods and hardwoods. Research efforts in this area on nonwoody plants is scanty, even though pulp production from nonwoody plants and agricultural residues is significant. Nevertheless, application of xylanases in prebleaching of bamboo kraft pulp, jute, maize, cotton stalks and sarkanda straws have been reported (Bajpai and Bajpai, 1996b; Martinez et al., 2000; Shobit et al., 2002; Zhao et al., 2002; Sarwarjahan and Talukdar, 2002; Feng et al., 2002; Bissoon et al., 2001; Spiridon et al., 1998; Weidong et al., 1999, Wang and Shih, 1996). Enzyme-treated pulps use 20%–25% less chemicals than untreated pulps.

Xylanases have also been studied in the bleaching of sulphite pulps (Viikari et al., 1994; Suurnakki et al., 1997). Due to the different location and limited accessibility of hemicellulose in sulphite pulps, as compared to kraft pulp, lower hydrolysis were obtained with xylanase. No effect on the brightness or the kappa number after one stage peroxide bleaching was observed.

Xylanase pretreatment has led to reductions in effluent AOX and dioxin concentrations due to reduced chlorine requirement (Jean et al., 1994; Werthemann, 1993; Bajpai et al., 1993; Senior and Hamilton, 1991, 1992a, b). It decreases the AOX in proportion to the decrease in chlorine compound usage. The level of AOX in effluents was found to be significantly lower for xylanase-pretreated pulps when compared with conventionally bleached control pulps. Because the bleach plant effluent colour is dependent on the chlorine usage, a decrease in chlorine compounds also decreases the effluent colour (Tolan and Guenette, 1997). There is an increase in the bleach plant effluent BOD of 2 – 5 kg/t resulting from the release of low-molecular-weight xylan from the pulp. This BOD is of an easily degradable nature in secondary treatment systems and no change in the treated effluent BOD has been observed.

The enzyme-treated pulp shows unchanged or improved strength properties (Yang et al., 1992; Bajpai et al., 1994; Bajpai and Bajpai, 1996b; Viikari et al., 1990, 1991, 1993; Tolan et al., 1996). Also, these pulps are easier to refine than the reference pulps (Dunlop and Gronberg, 1994). Improved viscosity of the pulp has been noted as a result of xylanase pretreatment (Yang et al., 1992; Paice et al., 1988). The effect of xylanase treatment on fibre morphology has been studied by Roncero et al. (1999, 2000), Viikari et al. (1996) and Ander and Nyholm (2001). Rancero et al. (1999, 2000) have studied the effects of xylanase treatment on fibre morphology with SEM in TCF and ECF bleaching of eucalyptus pulp. Xylanase treatment caused the appearance of cracks, flakes, filaments and peeling of cell walls, which in turn enabled increased contact between the bleaching agent and the substrate.

#### *3.6.1.4 Proposed mechanisms of xylanase action in kraft pulp bleaching*

Xylanases catalyse the hydrolysis of xylose–xylose bonds within the xylan chain and solubilize only a fraction of the total xylan present. However, the actual enzymatic mechanism in bleaching is not well understood. One hypothesis suggests that precipitated xylan blocks extraction and that xylanase increases the accessibility (Kantelinen et al., 1993a). Suurnakki et al. (1997) have reported that no extensive relocation of xylan to the outer surface occurs during pulping, so the occlusion model might not be a sound premise. Another possible explanation for xylanase action is that the disruption of xylan chain by xylanase interrupts lignin–carbohydrate bonds, improves the accessibility of the bleaching chemicals to the pulps and facilitates easier removal of lignin in bleaching (Paice et al., 1992). Skjold-Jorgensen et al. (1992) found that xylanase treatment decreased the demand for aCl for a batch kraft pulp by 15% but decreased aCl of pulp from a continuous process by only 6–7%. They also showed that DMSO extraction of residual xylan does not lead to an increase in bleachability but that xylanase treatment does. This shows that DMSO-extractable xylan is not involved in bleach boosting. Paice et al. (1992) have shown that the prebleaching effect on black spruce pulp is associated with a drop in the degree of polymerization, even though the xylan content decreases slightly. Senior and Hamilton (1993) have shown that xylanase treatment and extraction change the reactivity of the pulp by enabling a higher $ClO_2$ substitution to achieve a target brightness, and that they raise the brightness ceiling of pulps.

### *3.6.1.5 Location of xylanase treatment*

The conventional method is to add xylanase to the brownstock pulp prior to the high-density (HD) tower. The enzyme reaction takes place in the tower and the treated pulp then passes into the bleach plant. Various ways to add enzymes have been used including (1) spraying on the decker pulp mat, (2) adding to either the decker repulper or discharge chute, (3) adding into the stock of medium consistency pulp leading to the HD tower, and (4) adding directly into the HD tower. Xylanase has also been added later in the bleaching sequence rather than to the brownstock pulp (Popovici and Hoddenbagh, 2004). The application of xylanase to Do pulp in E stage has been demonstrated to result in $ClO_2$ and NaOH savings while providing pulps with improved D brightness compared to conventional DoEDED. The xylanase treatment in an E stage resulted in a bleach-boosting effect similar to conventional brownstock treatment with xylanase in XDoEDED bleaching sequence and can also potentially decrease caustic usage (Popovici and Hoddenbagh, 2004). This technology may be useful for mills currently using xylanase in a Hi-D application to further reduce chemical charges or by mills unable to use conventional xylanase technology.

The latest generation of alkali-tolerant enzymes require little, if any, addition of acid to adjust the pH. Earlier generation of enzymes had pH optima ranging from 5 to 6.5 and required acid addition. Instances of corrosion problems were seen when acid was incorrectly applied. New xylanases have higher pH optima and function optimally without pH adjustment (Bajpai, 2005).

The acid of preference by far has been sulphuric acid. However, with the development of alkaline xylanases, noncorrosive carbon dioxide is an excellent choice and also improves washer performance. Typical sites of acidification are indicated in Fig. 3.6.1. Acid can be added on the washer shower, bars shower or in the repulper discharge section. Experience has shown that prevention of corrosion must be a priority.

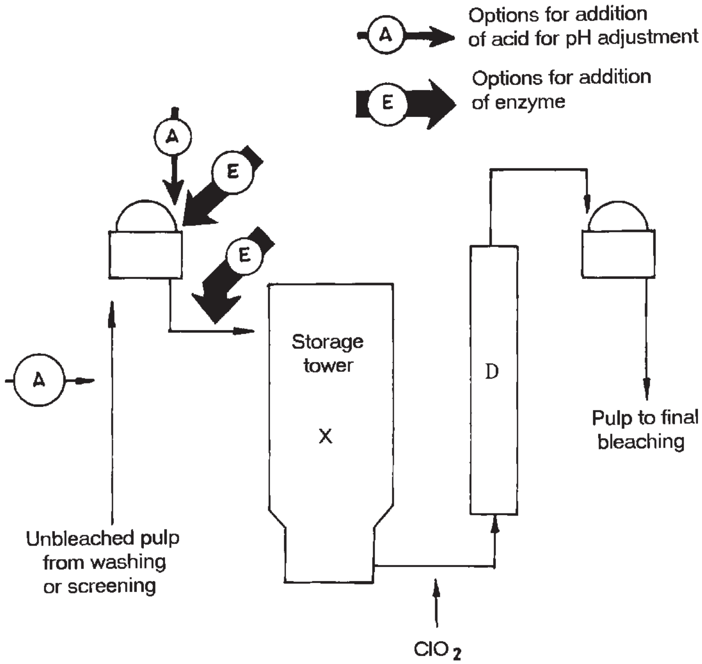

**Fig. 3.6.1. Typical xylanase and acidification sites. Based on the data from Bajpai (2004).**

Detailed laboratory work is needed to optimize and adapt the enzymatic treatment to individual existing mill conditions (Tolan and Guenette, 1997). Interestingly, however, xylanase bleaching has been scaled up directly from laboratory scale to the large industrial scale without intermediate pilot stages. No expensive capital investments have been necessary for full-scale runs. The most significant requirement is the addition of pH adjustment facilities. Xylanase pretreatment has been shown to be easily applicable with existing industrial equipment.

Bleaching with xylanase requires proper control of pH, temperature and retention time (Viikari et al., 1994; Tolan and Guenette, 1997; Suurnakki et al., 1997). The optimum pH and temperature for enzyme treatment varies among enzymes. Generally, xylanases derived from bacteria are most effective between pH 6 and 9 while those derived from fungi should be used within the pH range of 4–6. The optimum temperature ranges from 35 to 60°C with different enzymes. To obtain the best results from enzyme use, enzyme dosage must be optimized in each single case. In addition, the pulp consistency must be optimized to obtain effective dispersion of enzyme and improve the efficiency of enzyme treatment. Screw conveyers and static mixers are examples of efficient mixing systems. Most of the bleaching effect is obtained after only 1 h of treatment. Usually, the reaction time is set to 2–3 h. Xylanases are sold as concentrated liquids and the amount required per metric tonne of pulp is very low, less than a litre. The approximate cost of enzyme treatment is around $2/TP. Due to the low enzyme price and low capital costs of enzyme stage, the potential economic benefits of enzyme bleaching are significant.

### *3.6.1.6 Advantages of xylanase treatment*

Xylanase pretreatment of pulps reduces bleach chemical requirements and permits higher brightness to be reached. The reduction in chemical charges can translate into significant cost savings when high levels of $ClO_2$ and $H_2O_2$ are being used. A reduction in the use of chlorine chemicals reduces the formation and release of chlorinated organic compounds in the effluents and the pulps themselves. The ability of xylanases to activate pulps and increase the effectiveness of the bleaching chemicals may allow new bleaching technologies to become more effective. This means that for expensive chlorine-free alternatives, xylanase pretreatment may eventually permit them to become cost-effective. Traditional bleaching technologies also benefit from xylanase treatments. Xylanases are easily applied and essentially require no capital expenditure. Because $ClO_2$ charges can be reduced, xylanase may help eliminate the need for increased $ClO_2$ generation capacity. The benefit of a xylanase bleach boosting stage can also be taken to shift the degree of substitution towards higher $ClO_2$ levels while maintaining the total dosage of aCl. Use of high $ClO_2$ substitution dramatically reduces the formation of AOX. In TCF bleaching, the addition of enzymes increases the final brightness value, which is a key parameter in marketing ECF pulp. In addition, savings chemicals in TCF bleaching are important with respect to both costs and the strength properties of the pulp. Tolan et al. (1996) carried a survey of mill usage of xylanase. The survey revealed that the mills have spent most of their effort in decreasing AOX, followed closely by meeting customer demands (which in many cases was to decrease chlorine usage), and eliminating chlorine gas. These objectives were followed by efforts to decrease off-grade pulp, decrease BOD and cut costs. The least effort was devoted to increasing throughput, eliminating dioxin and converting into TCF. The most widely reported benefit of enzyme treatment is savings in bleaching chemicals.

### *3.6.1.7 Problems with xylanase treatment*

The most common problems with xylanase treatment cited in a mill survey has been corrosion of equipment and maintaining the brownstock residence time (Tolan et al., 1996). Sulphuric acid corrosion of mild steel has been encountered in several mills. The residence time must be maintained at least 1 – 2 hours to obtain the maximum benefits of enzyme treatment. This sometimes means that the mills must maintain the storage tower nearly full, which curtails its ability to act as a buffer between the pulping mill and the bleach plant. Other problems reported with enzyme treatment included difficulties in application and in bleach plant control. A decreased tear strength and pitch formation were also reported in some mills (Tolan et al., 1996).

### 3.6.2 Bleaching with ligninolytic enzymes

#### *3.6.2.1 Introduction*

Unlike xylanases, ligninolytic enzymes attack lignin directly, and hence are more effective. White-rot fungi are the main producers of ligninolytic enzymes. These fungi secrete a number of oxidative enzymes and some hitherto unknown substances (mediators) into their environment together effecting a slow but continuous degradation. The most important ligninolytic enzymes are lignin peroxidases (LiPs), manganese peroxidases (MnPs) and laccases. Several reports in the literature suggest that these enzymes could prove useful in bleaching kraft pulps (Call, 1993, 1994a, b, 1999; Call and Mucke, 1994a, b; 1995a, b; 1997; Bourbonnais et al., 1995; Paice et al., 1995a, b; Kondo et al., 1994-1996). Several patents have also been filed dealing with bleaching with these enzymes (Call, 1994a, b; Farrell, 1987; Farrell et al., 1987a, b; Olsen et al., 1989, 1991; Vaheri and Mikki, 1991; Vaheri and Pirainen, 1992; Gysin and Griessmann, 1991).

#### *3.6.2.2 Performance of ligninolytic enzymes in bleaching*

Unfortunately, for a long time, any attempt to use the ligninolytic enzymes of white-rot fungi as isolated enzymatic catalysts completely failed. An extensive delignification and brightening observed with the fungus were not achieved with the isolated MnP or LiP or laccase (Kantelinen et al., 1993b; Arbeloa et al., 1992). In the absence of the living organism, the various peroxidases and laccases perform very little reduction in kappa number (Egan, 1985; Kantelinen et al.,1993b; Arbeloa et al.,1992).

Although much of the research has focused on LiPs, these enzymes are not necessarily involved in lignin degradation and may not be secreted by all ligninolytic fungi. *C. versicolor* produces laccases as well as LiP and MnP. However, Archibald (1992) reported that LiPs secreted by *C. versicolor* did not appear to play an important role in lignin degradation. The enzyme is neither detected during bleaching nor is fungal bleaching enhanced by addition of exogenous enzyme. Furthermore, fungal bleaching is not inhibited by metavanadate ion, whereas LiP activity is. However, Iimori et al. (1996) have reported that bleaching by isolate SKB-1152 was better under conditions where LiP was detected than in its absence; thus it might contribute to bleaching by this strain. MnP is found to be a key enzyme in fungal bleaching. Cellobiose quinone oxidoreductase (CBQase), a quinone-reducing enzyme also plays a number of roles in delignification of pulp. Studies with CBQase have shown that the enzyme can reduce reaction products of laccase or peroxidase such as quinones, radicals and $Mn^{2+}$. Concurrently, cellobionate, a potential chelator of $Mn^{3+}$ is formed (Bao et al., 1993). However, cellobionate is less efficient than malonate or oxalate as a chelator in the MnP catalytic cycle, probably because it has a higher binding constant for $Mn^{2+}$ (Wariishi et al., 1992). Ander (1994) has suggested that enzyme mixtures for lignin degradation should probably contain this enzyme. It was shown to decrease the polymerization of kraft lignin by LiP. It is now known that LiPs and laccases play an important role in degrading the lignin *in vivo*; *in vitro* the oxidation reactions catalysed by the enzyme result in further polymerization of the lignin (Haemmerli et al., 1986). Hammel and Moen (1991) reported depolymerization of a synthetic lignin by a LiP in the presence of $H_2O_2$ and veratryl alcohol but this effect has not been demonstrated with lignin in wood or pulp. It is likely that fungi possess enzyme systems that prevent polymerization.

These results imply that single enzymes are not able to mimic the complete biological system. Small improvements can be achieved by the addition of low-molecular-weight aromatic compounds like veratryl alcohol or other substances such as ABTS and Remazol blue (Bourbonnais and Paice, 1990; Olsen et al., 1989). Inspite of this experience with isolated ligninolytic enzymes, Lignozym Gmbh, Germany, continued work with enzymes and chemical mediators that create a redox system throughout the pulp treatment period (Call, 1994a, b; Call and Mucke, 1994a, b; 1995a, b). Their idea was to find a system that is a good mimic of the natural situation. Starting in 1987 with the enzyme-mediator concept, Lignozym has now improved the performance of the mediator system for the laccase of *Trametes versicolor* by changing and further fine-tuning the chemical nature of the component. The mediator is hydroxybenzotriazole (HBT) (Call and Mucke, 1995a, b). The treatment of pulp with laccase alone does not result in any degradation of lignin but just in a structural change or repolymerization. The laccase-mediator system (LMS) causes a significant kappa number reduction at reasonable treatment times, even if the enzyme-mediator system is applied in several consecutive treatment steps to the same pulp. In contrast to commonly used pulp-bleaching chemicals, no passivation can be observed in enzymatic delignification. Laccase enzyme contains four copper atoms per molecule and requires oxygen as a cosubstrate for the oxidation reaction. Oxygen delignification is an existing technology in many mills and, therefore, most of the technical problems related with the introduction of gas into a three-phase system at high consistency are solved today. According to the present understanding, the laccase, while oxidizing the mediator generates a strongly oxidized comediator, which is the real bleaching agent (Fig. 3.6.2).

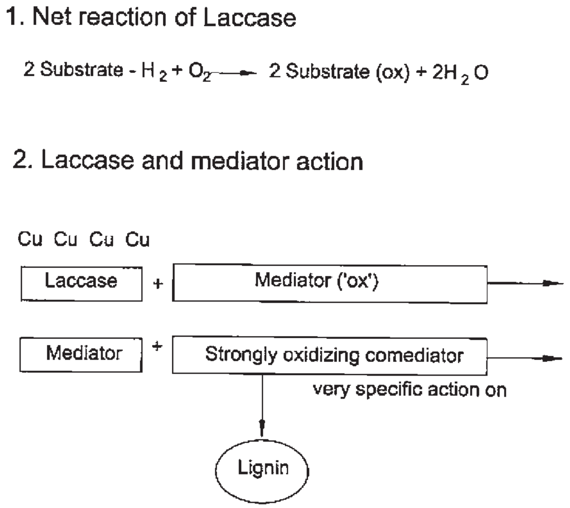

**Fig. 3.6.2. Possible mechanism of laccase and mediator action on lignin. Based on the data from Call and Mucke (1995a).**

The general technical conditions for enzymatic bleaching with the LMS are temperature 40–65°C, pH 4–7, consistency 1%–20%, pressure 1–14 bar and duration 1–4 h. The LMS provides a broad flexibility with respect to the pulp substrate, the technical requirements for application and the final quality of the pulp. The principal applicability has been demonstrated for different types of wood. A repeated enzyme treatment is possible and results in a 50%–70% kappa number reduction per treatment step. LMS is compatible with all other bleaching sequences. Depending on mediator dosage, consumption and price, recharging of mediator, *in situ* regeneration and recycling of the mediator is possible. The typical consumption of mediator during the enzymatically catalysed bleaching process is about 40%–50%. The waste after the treatment containing the unreacted mediator can be recharged upto the original mediator level before the next treatment step starts. Under continuous operation, this recharge can be repeated several times. Using an additional reactor in a bypass, the reaction product can be converted into the active form (regeneration step). The performance of the LMS system has been proven in pilot plant trials. The summary of the results are presented in Table 3.6.4 (Call and Mucke, 1997). A degree of delignification of >50% could be obtained in a single step, even if the mediator dosage is reduced by factor 0.6. Lignozyme has introduced a new mediator, *N*-hydroxyacetinalide (NHAA), which is biodegradable, and has been claimed to be cost-effective (Amann, 1997). Biobleaching with NHAA also allows the enzyme to maintain about 80% of its original activity after an hour treatment, whereas

**Table 3.6.4 Summary of results from the pilot plant trial with LMS**

| Sequence | Pulp | Dosage of enzyme/ mediator (kg/TP) | Degree of delignification (%) | Maximum brightness (% ISO) |
|---|---|---|---|---|
| L–E–Q–P | A | 2/13 | 56.6 | 76.5 |
| L–E–L–E–Q–P | A | 2×2/2×8 | 50.6/67.7 | 82.7 |
| L–E–Q–(P) | B | 2/8 | 44.2 | — |

*Conditions*

| Parameter | L stage | E stage | Q stage | P stage |
|---|---|---|---|---|
| Consistency (%) | 10 | 10 | 5 | 10 |
| Temperature (°C) | 45 | 60 | 60 | 75 |
| pH | 4.5 | 11.5 | 5 | 11.2 |
| Residence time (min) | 120 | 60 | 30 | 210 |
| Pressure (bar) | 2 | — | — | — |
| Dosage | Enzyme: 2 kg/t<br>Mediator: variable | NaOH | 0.2% DTPA | 3% peroxide |

Based on data from Call and Mucke (1997).

biobleaching with HBT causes a severe loss of enzyme activity. Attempts are being made to commercialize this technology (Call, 2005).

Sealey et al. (1997) reported that laccase-HBT biobleaching could obtain over 70% delignification when subjected to $E_{OP}$ stage. Further treatment of pulp with another laccase HBT stage increased the delignification to about 80%. The effect of ABTS on laccase-catalysed oxidation of pulp, was reported by Bourbonnais and Paice (1992). It was found that kappa number was decreased with ABTS. However, the brightness of the pulp decreased because the dye stuck to the pulp. Bourbonnais et al. (1995) compared the activities of induced laccases I and II (from *T. versicolor*) with and without ABTS on hardwood and softwood pulps. It was noted that in the absence of ABTS, the two purified laccases were not able to reduce the kappa number of either pulp. When ABTS was present, the two enzymes were equally effective in delignifying either pulp. The decrease in kappa number was found to be less with hardwood pulp.

To make the laccase–ABTS system compatible with industrial bleaching processes, Bourbonnais and Paice (1996) surveyed several process variables. A typical reaction was performed for 2 h at 60°C, pH 5.0 with 300 kPa of $O_2$, 1% ABTS and 5 units/g of laccase on 10% (w/v) pulp. After one stage of treatment followed by alkaline extraction, the delignification varied from 25 to 40% in various kraft pulps and was over 50% in a sulphite pulp. By repeating the treatment and alkaline extraction, the kappa number of a softwood pulp was decreased by 55%. Significant differences in reactivity between various fungal laccases for pulp delignification in the presence of

ABTS and HBT were found (Bourbonnais et al., 1997). A comparison of *T. versicolor* laccase with various mediators, including ABTS, HBT, remazol blue, nitroso-napthols and phenothiazines has shown that HBT gave the most extensive delignification, but deactivated the enzyme and, therefore, required a higher enzyme dosage. Both the initial lignin content and chemical structure of the pulp significantly influence mediator-aided laccase delignification and subsequent final bleaching with alkaline peroxide with or without a xylanase stage in the bleaching sequence (Poppius-Levlin et al., 1997). Three different pulps, i.e., a pine kraft pulp, a two-stage oxygen-delignified pine kraft pulp and birch formic acid/peroxyformic acid (MILOX) pulps were subjected to HBT- and ABTS-mediated laccase treatments. HBT was more effective than ABTS in the presence of laccase in delignification and gave higher pulp brightness. All the pulps showed an increased response to alkaline peroxide bleaching, and as a consequence oxygen-delignified pulp and MILOX pulp reached full brightness in one and two stages of treatment, respectively. Even the pine kraft pulp reached a final brightness of 83%. Moreover, a xylanase stage before or together with laccase/HBT slightly improved the effect of laccase/HBT and gave a higher final brightness after peroxide bleaching than without the xylanase treatment.

The effectiveness of HBT and NHAA in laccase-mediator systems has been confirmed (Chakar and Ragauskas, 2000). Higher levels of delignification were achieved for HBT compared to NHAA. Fu et al. (2000) bleached eucalyptus pulp with laccase in the presence of NHAA and obtained 43% reduction in kappa number after alkali extraction. Poppius-Levlin et al. (1999) have reported 60% reduction in kappa number after LMS treatment and alkaline extraction. Pulp yield and viscosity were found to be high. Li et al. (1997) have described a new technique for screening of new mediators. Chandra et al. (2001) have reported that the bleaching of high kappa pulps with an LMS provided 42.6– 61.1% delignification following an E+P stage when violuric acid was used as the mediator. The pulp yield after the treatment was +99.9%. Violuric acid was a superior reagent for LMS delignification of high-lignin pulps in comparison with HBT or *N*-acetyl-*N*-phenyl hydroxylamine.

In Paprican, the use of transition metal complexes as mediators in the enzymatic delignification of kraft pulps has been investigated (Bourbonnais et al., 2000; Paice et al., 2001). An oxygen-delignified softwood pulp was treated with laccase in the presence of potassium octacynomolybdate. At all charges of mediator, pulp delignification exceeded that of the control pulps. Pulp viscosity suffered a slight loss at the highest dosage of mediator. Treatment of hardwood pulp at the same reaction conditions produced similar results. The molybdenium mediator can be recycled after delignification and reused with the same efficiency as a fresh solution of mediator. LMS is also found to be effective in removing hexenuronic acid from kraft pulp (Fagerstrom et al., 2001; Call, 2002).

Most of the work on *in vitro* bleaching of pulp with MnP has been done in Japan and Canada. Kondo et al. (1994) examined *in vitro* bleaching of kraft pulp with MnP from *Phanerochaete sordida*. When the pulp was treated with MnP in the presence of $MnSO_4$, Tween 80 and sodium malonate with continuous addition of $H_2O_2$ at 37°C for 24 h, the pulp brightness increased by about 10 points and the kappa number decreased by about 6 points compared with control pulp. The pulp brightness also increased by 43 points to 75.5% by six treatments with MnP combined with alkaline extraction. The brightness was found to be comparable to that caused by whole fungal systems. Although this would be impractical for industrial application, the results demonstrate that under appropriate conditions, MnP can achieve most of the delignifying effect of the fungus. In another study, Kondo et al. (1995) reported that brightness increased by about 15 points and kappa number decreased by about 8 points, when pulp was treated with MnP from *P. sordida* in the presence of $MnSO_4$, Tween 80 and sodium malonate with the addition of $H_2O_2$ at a rate of 3 mL/h at 45°C for 12 h. To establish an absolutely chlorine-free bleaching process, oxygen-bleached pulp was treated with four-stage process consisting of sequential MnP treatment, alkaline extraction, MnP treatment and $H_2O_2$ treatment. Fully bleached pulp (brightness 91%, yield 97%) was obtained by combination of enzyme treatment and $H_2O_2$ bleaching. Harazono et al. (1996) studied *in vitro* bleaching of hardwood pulp with MnP without the addition of $MnSO_4$ in the presence of oxalate, malonate or gluconate as manganese chelator. When the pulp was treated without the addition of $MnSO_4$, the pulp brightness increased by about 10 points in the presence of 2 mM oxalate but the brightness did not significantly increase in the presence of 50 mM malonate, a good manganese chelator. Residual MnP activity decreased faster during the bleaching with MnP without $MnSO_4$ in the presence of malonate than in the presence of oxalate. Oxalate reduced $MnO_2$, which already existed in the pulp or was produced from $Mn^{2+}$ by oxidation with MnP and thus supplied $Mn^{2+}$ to the MnP system. The presence of gluconate also improved the pulp brightness, without the addition of $MnSO_4$, although treatment with gluconate was inferior to that with oxalate with regard to increase in brightness. To improve *in vitro* bleaching of the pulp with MnP, Kondo et al. (1996) characterized various MnPs from white-rot fungi. MnP from *Ganoderma* sp. was superior to MnPs from *P. sordida* and *Phanerochaete chrysosporium* in stabilities against high temperature and high concentration of $H_2O_2$.

At Paprican, MnP from *T. versicolor* was examined for bleaching of kraft pulp (Paice et al., 1995a, b). Studies on the effect of enzyme treatment on delignification of hardwood pulp showed about 14% reduction in kappa number. With softwood pulp, delignification was observed over a wide range of initial lignin contents (Paice et al., 1995a). Only the pulp of lowest initial kappa number gave a higher brightness after enzyme treatment. Subsequent treatment with alkaline peroxide resulted in pulps upto 7–8 points brighter than those obtained without enzyme (Paice et al., 1995b). Bermek et al. (2000) have reported that combination of MnP and xylanase has pulp-bleaching effects that are far superior to those of the individual enzymes used sequentially.

Not much information is available on the use of ligninolytic enzymes in bleaching of nonwoody raw materials. Vares et al. (1997) studied delignification of semichemical wheat straw pulp with LMS and MnP in combination with Tween 80. Differences between the enzymatically treated pulp and untreated control were rather small. However, some favourable effects were caused by Tween 80 alone or in combination with MnP and by laccase–HBT treatment followed by a chelating step. Martinez et al. (2000) found no adverse effect on strength properties of the pulp when wheat straw was delignified with enzyme from *Pleurotus* sp. Hatakka et al. (1997) reported degradation of wheat straw with enzymes from *P. chrysosporium* and *Ceriporiopsis subvermispora.* Enzymes from both the fungi decreased lignin and hemicellulose and increased the relative amount of cellulose. Herpoel et al. (2002) reported enzymatic delignifica-tion of wheat straw pulp by a sequential xylanase – LMS treatment. It was found that sequential treatment of wheat straw chemical pulp with xylanase and laccase followed by alkaline extraction lowered the kappa number by about 60% and increased the final brightness.

### *3.6.2.3 Effects on pulp properties, yield and effluent quality*

Limited information is available on the effect of ligninolytic enzymes on pulp properties, yield and effluent quality. Due to the specific action on lignin, these enzymes do not affect the viscosity, strength properties and pulp yield. Effluent properties are also expected to improve due to reduced chlorine consumption. In a pilot plant trial with LMS, the strength properties and viscosity of the pulp with L–E–Q–P sequence were not found to be affected (Call and Mucke, 1995a, b). Bourbonnais and Paice (1992) have reported that treatment of pulp with laccase–ABTS did not affect the pulp viscosity and zero–span breaking length. Arbeloa et al. (1992) reported that when softwood TMP was treated with LiP, some of the strength properties slightly increased. Kondo et al. (2001) found that MnP treatment is quite effective for improving the strength properties of kraft pulps and deinked pulp.

### *3.6.2.4 Advantages*

Treatment with ligninolytic enzymes requires milder conditions and results in the removal of more lignin as compared with oxygen delignification, which translates into substantial savings of energy and bleaching chemicals leading to lower pollution load. Moreover, as these enzymes are highly specific towards lignin, there is no damage or loss of cellulose resulting in better strength and bleached pulp yield.

#### *3.6.2.5 Limitations and future prospects*

Commercialization of bleaching process with ligninolytic enzymes faces a number of challenges: availability of enzymes, cost of mediators and enzyme stability. Currently, neither enzyme is available in sufficient quantity for mill trials, and scale-up of enzyme production from fungal cultures may be costly. Cloning of genes for both enzymes has been reported and may provide an alternative production route. The laccase-mediators are expensive and alternatives are less effective. There are two ways of improving LMS for pulp bleaching: one is to discover new laccases that have extraordinarily high redox potential and the other is to find a very effective laccase mediator. Since the laccase mediators reported so far have very wide structural variations, it should be possible to discover cheaper and more effective laccase mediators than what has been done to date. Chelating agents for $Mn^{3+}$ in the MnP reaction may also be a signficant cost item. MnP requires $H_2O_2$ but is inactivated by concentrations above ~0.1 mmol/L. Even when $H_2O_2$ is kept below 0.1 mmol/L, MnP becomes inactive relatively rapidly. Experience with xylanase and with other enzymes such as lipase and amylase has shown that enzymes can be applied successfully in a mill situation. Thus, oxidative enzymes, which can be regarded as catalysts for oxygen- and $H_2O_2$-driven delignification, may also find a place in the bleach plant in the coming years.

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## 3.7 Fungal prebleaching*

### 3.7.1 Introduction

Several fungi, which attack wood in nature, are capable of degrading lignin. So, there appears to be an opportunity to exploit them for direct attack on lignin in pulps, an attack that can be specific and effective even if the amount of residual lignin is low. The fungi that most effectively biodegrade lignin are basidiomycete fungi. Lignin-oxidizing species are called white-rot fungi, because they typically turn wood white as they decay. This effect is another indication that these fungi may be useful in pulp bleaching.

### 3.7.2 Performance of fungi in bleaching

The bleaching of pulp with microorganisms was first attempted by Kirk and Yang in 1979. They found that *P. chrysosporium* and some other white-rot fungi could reduce the kappa number of unbleached softwood kraft pulp by upto 75%, leading to reduced requirement for chlorine during subsequent chemical bleaching. The pulp was incubated with the fungi in shallow stationary layers for several days, and then extracted with alkali. Kappa number reduction was inhibited by nutrient nitrogen and enhanced by the oxygen enrichment of the atmosphere, as is lignin degradation by *P. chrysosporium*. Attack on the cellulose of the pulp was severe unless alternative carbohydrate sources were added to the cultures; even in the presence of glucose, the pulp showed a 60% drop in viscosity. Other fungi tested, including *T. versicolor*, had lesser effects. In contrast to the results of Kirk and Yang (1979), Pellinen

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*Excerpted from Bajpai, P., 2004. With permission from Taylor and Francis et al. (1989) reported that *P. chrysosporium* failed to delignify unbleached softwood pulp in stationary culture, but did so in agitated cultures. Tran and Chambers (1987) found that the effects of culture conditions on delignification of unbleached hardwood pulp by *P. chrysosporium* were similar to those observed by others with synthetic lignin or lignin in wood. Screening of several white-rot fungi at Paprican revealed that *T. (Coriolus) versicolor* could markedly increase the brightness of hardwood kraft pulp in 5 days in agitated, aerated cultures (Paice et al., 1989). Under these conditions, *T. versicolor* performed better than *P. chrysosporium*. The kappa number was decreased from 12 to 8, and the brightness increased from 34 to 48%; however, brightness can be further increased to 82% with DED bleaching. In initial experiments, Paice et al. (1989) did not observe similar brightening of softwood pulp. Subsequently, *T. versicolor* was found to delignify and brighten softwood pulps (Reid et al., 1990). After 14 days of treatment with the fungus followed by alkaline extraction, the pulp had kappa number 8.5 and could be bleached to 61% ISO brightness with a DED sequence; without fungal treatment, the pulp had kappa number 24 and was bleached to only 33% brightness. Mycelium of *T. versicolor* immobilized in polyurethane foam was also capable of delignifying the pulp. *T. versicolor* caused a much smaller direct increase in the brightness of softwood pulp than hardwood pulp. To determine the contributions of higher residual lignin contents and structural differences in lignins to recalcitrance of softwood pulps to biobleaching, Reid and Paice (1994a, b) tested softwood and hardwood pulps cooked to the same kappa numbers 26 and 12. A low-lignin-content softwood pulp resisted delignification by *T. versicolor*, but a high-lignin-content hardwood pulp was delignified at the same rate as a normal softwood pulp. The longer time taken to brighten softwood pulp was found to result from the higher residual lignin content of the softwood pulp. Softwood pulps, whose lignin contents were decreased by extended modified continuous cooking or oxygen delignification to kappa numbers as low as 15 were delignified by *T. versicolor* at the same rate as normal softwood pulp (Reid and Paice, 1994a, b). More intensive $O_2$ delignification, decreased the susceptibility of the residual lignin in the pulps to degradation by *T. versicolor.* This fungus was found to delignify and brighten pulp at low pulp consistency (1–2%). Delignification of both hardwood and softwood pulps with *T. versicolor* was found to be accompanied by a moderate decrease in viscosity (Reid et al., 1990; Ho et al., 1990). Addition of excess glucose to repress cellulose biosynthesis did not prevent the loss in viscosity (Kirkpatric et al., 1990a, b). Paper sheets made from pulp delignified with *T. versicolor* were slightly stronger than those made from unbleached pulp (Paice et al., 1989; Reid et al., 1990). Delignification by *T. versicolor* was not restricted to conditions of secondary metabolism (Roy and Archibald, 1993). Ho et al. (1990)

reported that when kraft pulp was added to inoculum of *T. versicolor*, the lag before the onset of brightening in subsequent pulp treatment was reduced.

Addleman and Archibald (1993) investigated the ability of several dikaryotic and monokaryotic strains of *T. versicolor* to bleach and delignify hardwood and softwood pulps. Dikaryotic strains produced brightness changes ranging from −2 to +22 points in hardwood pulp; monokaryons tended to give a higher brightness increase, with a maximum of 26 points. A monokaryon, 52 J, isolated by protoplasting the dikaryon originally used at Paprican, gave slightly higher brightening than its parents and was adopted for further work. In addition to better bleaching, the monokaryon had the advantage of less biomass production, no dark pigment formation and a simpler genome (Addleman and Archibald, 1993). In Japan, a 5-day fungal (F) treatment of hardwood pulp with IZU-154 replaced a $CE_1DE_2D$ sequence with an FCED sequence yielding a target brightness of 88% ISO with 72% less chlorine, 79% less NaOH and 63% less $ClO_2$ (Table 3.7.1) (Fujita et al., 1991). With softwood pulp, similar chemical savings were achieved (Fujita et al., 1993). The yield and burst strength of the pulp bleached with a CED sequence after delignification with IZU-154 were equivalent to those of a control bleached with CEDED sequence. However, the tensile and tear index of the fungus-treated pulp were decreased by 9% and 2.6%, respectively. To establish an absolutely chlorine-free bleaching process, Murata et al. (1992) applied the fungus IZU-154 to the delignification and brightening of oxygen-bleached hardwood pulp. The fungus brightened the pulp and simultaneously decreased its kappa number. Brightness was increased by 17 and 22 points by 3- and 5-day treatments, respectively, and kappa number was decreased from 10.1 to 6.4 by a 5-day treatment (Murata et al., 1992). The combination of the 3-day fungal treatment, alkaline extraction and hydrogen peroxide ($H_2O_2$) bleaching with 5% charge of $H_2O_2$ gave a pulp of 86.3% ISO brightness (Fujita et al., 1993). The 5-day-treated pulp was brightened

**Table 3.7.1 Bleaching conditions and optical properties of conventionally bleached and fungal-bleached hardwood pulp**

| Bleaching sequence | Dosage (% on pulp) | | | | | | Brightness (% ISO) | | |
|---|---|---|---|---|---|---|---|---|---|
| | C | $E_1$ | $D_1$ | $E_2$ | $D_2$ | As effective chlorine | Before aging | After aging[a] | PC number |
| CEDED (conventional process) | 5.0 | 3.6 | 0.8 | 0.2 | 0.3 | 7.89 | 88.8 | 84.2 | 0.78 |
| FCED (fungal bleaching) | 1.4 | 0.8 | 0.3 | — | — | 2.19 | 88.1 | 85.3 | 0.46 |

[a] At 105°C for 1 h.

Based on data from Fujita et al. (1991).

to 87.3% ISO brightness by 4% $H_2O_2$ bleaching after alkaline extraction. Optical and strength properties of OFEP-bleached pulp were comparable to those of conventional OCED-bleached pulp. Tsuchikawa et al. (1995) have reported biobleaching of hardwood pulp with lignin-oxidizing fungi *P. sordida* YK-624. When the hardwood pulp was treated with the fungus for 10 days, the kappa number was decreased from 14.4 to 5.75 and the brightness was increased to 61% ISO. If the fungal incubation was interrupted after 5 days and the pulp was extracted with alkali and treated with fungus for another 5 days, the kappa number was lowered to 4.8, and the brightness reached 80% ISO. The intermediate alkaline extraction, which was more effective than water washing, seemed to reactivate the lignin towards degradation as it does with chemical-bleaching reagents. The tensile and burst strengths of the fungus-treated pulp were almost as high as those of control pulp, but the tear strength was 34% lower.

Nishida et al. (1995) investigated the biobleaching of hardwood pulp by *P. chrysosporium* and *T. versicolor* in the solid and liquid-state fermentation systems. In the solid-state fermentation system with low nitrogen and high carbon culture medium, pulp brightness increased by 15 and 30 points after 5 days of treatment with *T. versicolor* and *P*. c*hrysosporium,* respectively. A positive correlation between the kappa number decrease and brightness increase of the fungus-treated pulp was observed.

Laccase and manganese peroxidase (MnP) enzymes were detected during biobleaching of softwood pulps with *P. chrysosporium* and *T. versicolor* (Katagiri et al., 1997). However, the enzyme lignin peroxidase (LiP) was not detected. *T. versicolor* did not delignify softwood pulp but produced laccase, whereas *P. chrysosporium* did the reverse.

Wroblewska and Zielinsk (1995) examined biodelignification of beech and birch pulp wood by selected white-rot fungi. One of the strains designated as DL-Sth-4 was found to be best for selective delignification of beech wood. About 25% of lignin was lost with very little loss in cellulose content. Pazukhina et al. (1995) used the culture filtrate of several white-rot fungi- *P. sanguinea, C. versicolor, Ganoderma applanatum* and *Trichoptum sp.* for bleaching hardwood pulp. *P. sanguinea* showed the highest selectivity in lignin degradation. Moreira et al. (1997) tested the ability of 25 white-rot fungal strains to bleach eucalyptus oxygen-delignified pulp. Under nitrogen-limited culture conditions, eight outstanding strains were identified that increased the brightness of oxygen-bleached kraft pulp (OKP) by more than 10 ISO units compared with pulp incubated in sterile control medium. The highest brightness gain of approximately 13 ISO units was obtained with *Bjerkandera* sp. strain BOS55, providing a high final brightness of 82% ISO. This strain also caused the highest delignification decreasing the kappa number of OKP by 29%. When the white-rot fungal strains were tested in nitrogen-sufficient medium, the extracellular activities of laccase and peroxidases increased in many strains; nonetheless, the brightness gains were lower than those obtained under nitrogen limitation. The best biobleaching strains were generally characterized by a predominance of MnP activity compared with other ligninolytic enzymes and by a high decolorizing activity towards the polyanthraquinone ligninolytic indicator dye-poly R-478. Moreira et al. (1998a) investigated the manganese requirement for biobleaching by *T. versicolor, P. chrysosporium, Phlebia radiata, Stereum hirsutum* and *Bjerkandera* sp. strain B0S55. When manganese was present in the medium, the pulp was bleached by all five strains. In the absence of manganese, only *Bjerkandera* sp. strain B0S 55 bleached the pulp only in the presence of organic acids. *Bjerkandera* sp. was also the only fungus that produced MnP in the absence of manganese. Fungus *Bjerkandera* sp. strain B0S 55 can be used to bleach EDTA-extracted eucalyptus oxygen-delignified pulp independent of manganese (Moreira et al., 1998b). Adding simple physiological organic acids at 1–5 mM produced 2–3 times the brightness and delignification compared to control cultures. Inorganic acids improve the manganese free biobleaching by enhancing the production of MnP and LiP. Increased physiological concentration of veratryl alcohol and oxalate were also a factor. Results indicate that MnP from *Bjerkandera* is deliberately produced in the absence of manganese and might function independently of manganese in OKP delignification. LiP might also be a contributing factor.

Iimori et al. (1994), at Nippon Paper Industries, carried out extensive screening for pulp bleaching fungi. By plating samples of decayed wood or fruit bodies directly on agar containing unbleached pulp, they isolated 1758 cultures that produced decolourization zones; 266 of these bleached oxygen-delignified hardwood pulp to 70–81% ISO brightness within 7 days of incubation under solid-state fermentation conditions. The most active isolate, SKB-1152, also brightened agitated suspensions (2% consistency) of $O_2$-delignified hardwood pulp to 80% ISO. Optimization studies, with the aim of shortening treatment time, showed that dilute pulp suspensions were brightened faster than those with higher consistency, and that inoculum-to-pulp ratio of 6% was found to be adequate. Incubation of the mycelial suspension used as inoculum in a nutrient medium for 24 h before adding it to the pulp eliminated the lag period before the onset of brightening (Iimori et al., 1996).

*P. chrysosporium* and *C. versicolor* have been successfully immobilized on polyurethane foam (Kirkpatrick et al., 1990a, b; Ziomek et al., 1991; Kirkpatrick and Palmer, 1987). Immobilized and free cultures of *C. versicolor* have been found to bleach hardwood and softwood pulp at a comparable rate and to a similar extent (Reid et al., 1990; Kirkpatrick et al., 1990a, b). The results showed that intimate contact between the fungal hyphae and pulp fibres was not required as long as the media was renewed through contact with the fungus (Archibald, 1992). Immobilization enabled the pulp to be separated from the mycelia. Another advantage of immobilization was that the same fungal biomass could be reused to treat other batches of pulp either immediately or after storage at 4°C.

Cell-free filtrates from bleaching cultures of *T. versicolor* did not cause detectable pulp brightening (Archibald, 1992). These filtrates contain laccase and MnP, which can, under appropriate conditions, delignify and brighten pulp (Paice et al., 1993). The failure to detect pulp brightening by culture filtrates can be attributed to lack of $H_2O_2$ and Tween 80 to support brightening by MnP and the absence of mediator for laccase. The ability of intact *T. versicolor* cultures to delignify and brighten pulps in the absence of a mediator for laccase or an analogue of Tween 80 suggests that the fungus produces one or more unknown enzymes that contribute to its pulp-bleaching ability. *P. sordida* YK-624 could delignify and brighten hardwood pulp separated from the mycelium by a membrane filter with 0.1 μm pores; a thin polycarbonate membrane supported more bleaching than a thicker cellulose nitrate membrane (Kondo et al., 1994). *P. chrysosporium* and *T. versicolor* could also be used through the membrane although to a smaller extent than can YK-624.

Iimori et al. (1998) have investigated the potential to biobleach unbleached kraft pulp (UKP) and OKP using culture filtrate containing MnP and LiP from *P. chrysosporium* in a short-term treatment of several hours. The brightness increase following biotreatment with MnP, LiP and cofactors was greater than that by MnP alone. There was a 7–8 points increase in brightness for UKP and OKP during the first 3h. When the 3h treatment was repeated, the brightness increase of OKP was halted at 78%.

Kondo et al. (2000) reported biobleaching of hardwood pulp by a marine fungus and its enzymes. The pulp brightness obtained by MG-60 was found to be considerably higher than that by *P. chrysosporium*. The higher MnP activity of MG-60 was observed compared with that of *P. chrysosporium* at the same conditions. Also, the MnP secreted from MG-60 demonstrated good stability against high sea-salt concentrations. It was also found that hardwood pulp was biobleached by crude enzymes secreted by MG-60 at 0 and 3% sea-salt concentration *in vitro*.

### 3.7.3 Effects on pulp properties

In order to find application in the pulp and paper industry, biological bleaching must not compromise with the quality of the pulp. Results from lab-scale fungal bleachings indicate an improvement in strength characteristics (burst factor, tear index, tensile strength, breaking length, stretch and fold) in both hardwood and softwood pulps. Jurasek and Paice (1988) suggested that the lignin may become more flexible and hydrophilic as a result of fungal enzyme action, resulting in a softer pulp with improved bonding and stronger paper characteristics. Reduced colour reversion was another benefit noted with the fungus IZU-154 (Fujita et al., 1991). Some viscosity loss, indicating limited cellulose depolymerization, has been reported as a result of fungal bleaching (Reid et al., 1990; Fujita et al., 1991). However, on the basis of experiments done with free and immobilized cultures, Kirkpatrick et al. (1990a, b) reported that upto 25% of the reduction in the pulp viscosity may be due to the presence of fungal mycelia, rather than cellulose cleavage. Although fungal bleaching is primarily an oxidative process, it appears to be more selective than oxygen bleaching at high pH and at kappa number less than 17 because there is a better retention of pulp viscosity.

### 3.7.4 Effects on effluent quality

Only few researchers have measured the impact of fungal bleaching on effluent quality. In a Japanese study, with the FCED-bleaching sequence, the COD and colour loading in the bleach plant waste water were reduced by 50% and 80%, respectively, (Table 3.7.2) (Fujita et al., 1991) assuming that the filtrate from the fungal bleaching stage was sent to a kraft chemical recovery system. Whether this could occur in practice would depend on the capacity available in the recovery furnace. The authors suggested that higher reductions could be obtained with an FED or FE$_1$DE$_2$D sequence, although there may be a slight loss in pulp yield (Fujita et al., 1991). Despite the emphasis on fungal bleaching as a means to reduce the use of chlorine and the associated formation of chlorinated organics, the effect upon chlorinated organic discharges has not been reported. As this is an important factor in the choice of any alternative bleaching sequence, quantitative information in this area is needed.

### 3.7.5 Advantages

Pretreatment with fungi has been shown to replace upto 70% of the chemicals needed to bleach kraft pulp. The usual specificity of biological reactions

**Table 3.7.2 COD and total colour loadings for conventional and fungal bleaching processes**

| Bleaching sequence | COD (kg/t of pulp) | | | | Total colour |
|---|---|---|---|---|---|
| | C | E$_1$ | D$_1$E$_2$D$_2$ | Total | (kg/t of pulp) |
| CEDED<br>(conventional process) | 10.08 | 17.64 | 3.07 | 31.42 | 38.25 |
| FCED<br>(fungal bleaching process) | 5.03 | 8.86 | 1.78 | 15.94 | 8.23 |

Based on data from Fujita et al. (1991).

and their mild reaction conditions make biological delignification an interesting alternative to bleaching with chemicals such as pressurized oxygen or ozone.

### 3.7.6 Limitations and future prospects

A serious shortcoming of the fungal bleaching process is the long incubation time required for contact with the biomass. Typical contact periods range from 5 to 14 days for both hardwood and softwood pulps. Softwood incubation periods are likely to be longer than that for hardwood pulps because softwood pulps require a longer time lag (6 days) before a kappa number reduction or a brightness increase can occur (Reid et al., 1990). Hardwood pulps generally have a lag time of 1–2 days, followed by a rapid and then slower delignification stage (Fujita et al., 1991, Kirkpatric et al., 1989, 1990c). Unfortunately, the size of the fungal bioreactor would have to be very large considering that daily production could range from 200 to over 1000 air-dried tonnes of pulp. Most researchers have performed fungal bleaching experiments at low pulp consistencies of 0.5–2% (w/v) (Tran and Chambers, 1987; Kirkpatrick et al., 1989; Kirkpatric et al., 1990a–c). Only Fujita et al. (1991) have investigated fungal bleaching at high consistency (16–24%), which would allow for a small reactor. Fungal treatment can be effected in the unbleached storage itself with minor modifications provided the treatment time is reduced to a practically feasible duration. The reaction time, required at its current stage of development, makes it economically unattractive. There is a need to identify/develop fast-growing white-rot fungal cultures that could do the job in less time.

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# Chapter 4

## ECF and TCF bleaching

### 4.1 Introduction

The focus on reduction in adsorbable organic halides (AOX) and total organic chlorides (TOCl) in bleach effluents has promoted elemental chlorine-free (ECF) and totally chlorine-free (TCF) bleaching processes (McDonough, 1995; Chirat and Lachenal, 1997; Pryke, 1995a, b, 1997, 2003; Govers et al., 1995; Moldenius, 1995, 1997). ECF bleaching is, by definition, a chlorine-free process in that no elemental (molecular) chlorine is used in the bleaching sequences. Although the term ECF does not specify it, typically, chlorine dioxide is the principal bleaching agent for these processes. Bleaching sequences that use no chlorine chemicals are termed as TCF. TCF bleaching processes significantly reduce the effluent loadings and allow total closure. TCF bleaching began to be practiced on a commercial scale basis in the paper industry beginning in the late 1980s. However, developments leading up to the various TCF technologies began much earlier in the 20th century. Actually, TCF is the culmination of several technologies involving oxygen, ozone, hydrogen peroxide, and various other peroxygens.

ECF pulp, bleached with chlorine dioxide, continues to grow and now dominates the world-bleached chemical pulp market (Fig. 4.1.1) (Pryke, 2003). Demand for ECF increased dramatically over the last decade. In 2001, ECF held the highest worldwide market share for bleached chemical pulp at greater than 75%, or more than 63 million tonnes. Market data show ECF production grew 17% in 2001. In contrast, TCF pulp production declined slightly, maintaining a small niche market at just over 5% of world-bleached chemical pulp production.

ECF production now represents 96% of North American-bleached chemical pulp production. Other regions are well on their way to replacing pulps bleached with molecular chlorine with ECF as shown in Fig. 4.1.2 (Pryke, 2003). TCF production in these regions is negligible. This trend will continue

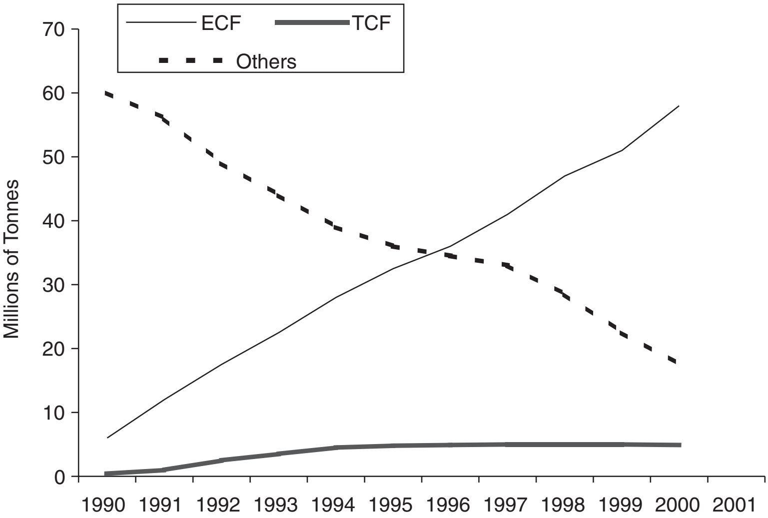
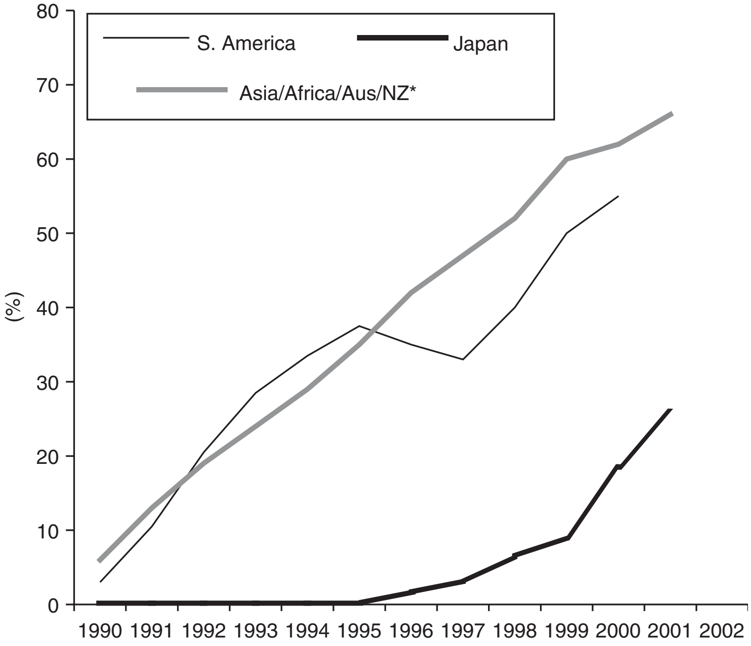


**Fig. 4.1.1. World bleached chemical pulp production: 1990–2001. (From Pryke, 2003; reproduced with permission from Miller Freeman Inc.)**



* Excludes China

**Fig. 4.1.2. Growth of ECF: 1990–2002. (From Pryke, 2003; reproduced with permission from Miller Freeman Inc.)**

as new mills planned in Germany, Chile, Brazil and Asia incorporate ECF bleaching (AIET, 2002a).

As of 2001, the amount of pulp produced in ECF sequences was 10 times the amount produced in TCF sequences. Scandinavia has the most TCF production, accounting for about one-third of total bleached kraft pulp tonnage in that region and about 58% of the world's TCF production. Recent trends suggest that worldwide growth in ECF is increasing, while TCF production has not increased substantially since 1995 (AIET, 2002a). The first true kraft TCF pulp mill was the Munksjo mill, Aspa Bruk, in Sweden. Most of the mills producing TCF chemical pulp are located in Scandinavia. Altogether, the Nordic producers generate more than half of the world's output of TCF-bleached chemical pulps. The production of chlorine bleached pulps in Scandinavia ceased altogether in 1993.

Both ECF and TCF processes are likely to yield less pulp per tonne of wood fibers than conventially bleached pulp, because the increased number of bleach/wash stages result in greater fibre loss. TCF, which has the most protracted bleached cycle has the lowest yield. Industry opinion is divided as to the relative merits of ECF and TCF processes.

Over the last decade, field studies, research and chemical analysis have demonstrated that treated wastewater from well-managed pulp and paper mills using ECF bleaching is virtually free of dioxin and persistent bioaccumulative toxic substances. The remaining chlorine containing organic substances resulting from ECF bleaching have a composition similar to those found in nature, degrade naturally and do not persist in the environment. Research shows that they present a negligible environmental risk to aquatic ecosystems (Bright et al., 2003). This research has been confirmed in ecosystem simulations by comparing wastewaters from ECF bleaching with other nonchlorine bleaching concepts, including TCF. These investigations have reached a common conclusion (Hamm and Gottshing, 2002; Tana and Lehtinen, 1996). Studies comparing ECF and TCF effluents confirmed the absence of significant differences in biological effects in the aquatic environment.

## 4.2 ECF bleaching

ECF bleaching is practiced on both conventional and reduced kappa pulps (McDonough, 1995; Chirat and Lachenal, 1997). Examples of ECF bleaching sequences are OD(EOP)D, D(EO)DD, D(EOP)D, C/D(EO)D, AD(EO) DOD (EO)DD, O(AD)(EOP)D, (EOP)D(PO)D (Pikka et al., 2000). The oxygen delignification stage can include one or two stages. An acid hydrolysis stage is especially suitable for hardwood pulps. Chemical consumption varies with wood species and mill and is especially connected to kappa number. The chemical consumption (kg/ADT) of a mill using D(EO)DD bleaching of oxygen-delignified softwood pulp from kappa number 12 to brightness 90% ISO are: $ClO_2$ (as equivalent chlorine), 44; NaOH, 15; $O_2$, 4; and $SO_2$, 1.5. Another typical ECF bleaching sequence is D(EOP)D(ED). The first D stage has a retention time of less than 1h and a temperature of about 60°C. The alkaline stage is preferably pressurized, and oxygen and hydrogen peroxide are added to boost the delignification in this stage to reduce subsequent chlorine dioxide consumption. The two final D stages normally have a retention time of 3h each, and the temperature is 70–75°C. Diffusers on top of the chlorine dioxide bleaching towers do the washing after each stage. Wash press is generally used after the EOP stage. The wash press in this position gives a higher degree of flexibility for filtrate circulations and reduction of effluent volumes. Table 4.2.1 shows typical mill data in case of DEOPDED sequence with softwood Kraft pulp of 12 kappa number. Brightness vs. consumption of active chlorine for pulps bleached in three, four and five bleaching stages is presented in Table 4.2.2. In this example, the three-stage sequence can reach a brightness target of 88% ISO. The four-stage sequence can go upto 90% ISO and the five-stage sequence upto 92% ISO.

Besides the number of bleaching stages, the amount of bleaching chemical added to the first stage (the kappa factor) also affects the brightness

**Table 4.2.1 Chemical consumption in bleaching of softwood kraft pulp[a] in D(EOP)D(ED) sequence—Mill results**

| | |
|---|---|
| Brightness (% ISO) | 89.5 |
| $ClO_2$ (kg acl/ADT) | 42 |
| $H_2O_2$ (kg/ADT) | 2 |
| COD (kg/ADT) before secondary treatment | 30 |
| AOX (kg/ADT) before secondary treatment | 0.25 |

[a] Kappa number, 12.

Based on data from Pikka et al. (2000).

**Table 4.2.2 Brightness development in different chlorine dioxide bleaching sequences**

| Chemical consumption (kg of active Cl/ODT) | Brightness (% ISO) | | |
|---|---|---|---|
| | D(EO)DED | D(EO)DD | D(EO)D |
| 20 | 81.0 | — | |
| 30 | 89.0 | 87.0 | 86.0 |
| 40 | 91.0 | 89.5 | 88.0 |
| 50 | 92.0 | 90.0 | — |

Based on data from Pikka et al. (2000).

development. Introduction of an ozone stage in a chlorine dioxide bleaching sequence means that the consumption of chlorine dioxide required to reach a certain brightness can be reduced considerably. Table 4.2.3 shows brightness vs. active chlorine charge for the sequences D(EOP)DD and Z(EO)D(ED). In the ozone sequence, filtrate from the prebleaching Z(EO) treatment can be used as wash water in oxygen delignification washing. Replacing the last (ED) stage of a chlorine dioxide bleaching sequence with a pressurized peroxide stage reduces the need for chlorine dioxide. The effect of peroxide use in a chlorine dioxide bleaching sequence is presented in Table 4.2.4. Chlorine dioxide demand can also be reduced by using ozone synergistically with chlorine dioxide.

Parthasarathy et al. (1993) have reported that conversion of a (C+D)(EOP)D sequence into ECF is technically feasible for full bleaching of both softwood and hardwood pulps. There are potentially large increases in bleaching chemical cost, however. Certain changes could minimize the cost increase: increase the first stage consistency from 3 to 12%, increase the extraction stage temperature from 75 to 95°C, operate the final D stage

**Table 4.2.3 Brightness development in a sequence replacing the first D-stage with a Z-stage**

| kg of active Cl/t | Brightness (% ISO) | |
|---|---|---|
| | D(EOP)DD | Z(EO)DnD |
| 15 | 87.0 | — |
| 20 | 89.2 | — |
| 27 | 90.0 | — |
| 35 | — | 84.2 |
| 40 | — | 86.2 |
| 47 | — | 88.5 |
| 52 | — | 89.2 |

*Note*: $O_2$-delignified pulp, kappa number, 11.1.
Based on data from Pikka et al. (2000).

**Table 4.2.4 Effect of peroxide use in a chlorine dioxide-bleaching sequence**

| Chlorine dioxide consumption (kg of active Cl/ADMT) | D(EOP)D(PO) | | D(EOP)D(ED) |
|---|---|---|---|
| | Cons. PO stage (5.5 kg) | Cons. PO stage (3.0 kg) | |
| 36 | 91.0 | 91.9 | — |
| 41 | — | — | 90.2 |
| 53 | — | — | 90.5 |
| 64 | — | — | 90.6 |

*Note*: Lab ITC$^{TM}$, $O_2$-delignified pulp; kappa number 12.0; viscosity, 1017 $dm^3/kg$.
Based on data from Pikka et al. (2000).

at high temperature and add a peroxide stage at the end of the sequence. Another short sequence, OD(EP)P, can bleach softwood kraft pulp to a brightness of 89 if chelants are added at several stages and the peroxide stage operates under severe conditions (2% $H_2O_2$, 30% consistency and 4 h at 90°C) (Desprez et al., 1993). A similar, forcing, final peroxide stage can allow full bleaching of softwood kraft pulp in the OQPDP sequence (Q = chelation stage) (Devenyns, et al., 1993). This is one step further along the road to TCF bleaching than the OQPD(EP)D sequence that has the same performance. A western Canadian mill uses the sequences DE(EO)DED and OD(EP)(EOP)DED (McKenzie, 1994). In another mill, using ozone in the OA2(EOP)D(EP)D sequence has given fully bleached pulp with properties similar to the ECF reference sequence without the ozone stage (Helander et al., 1994). Cost is similar. Market pulp quality from ECF bleaching is excellent (Moldenius, 1995, 1997). Mill studies in Canada and the United States have shown high brightness, 89–90% ISO and high strength (burst, tear, tensile and viscosity) pulps are produced with ECF (Pryke et al., 1995a, b; Wilson et al., 1992). ECF production does not require low lignin content of unbleached pulps and therefore has higher yield than today's TCF pulping and bleaching processes.

For existing mills, conversion to ECF has been relatively easy for the following reasons: many mills had existing chlorine dioxide generators that could be upgraded to the required production for relatively low capital cost; existing bleach plants were totally compatible; and bleaching cost increased modestly, 5–10%.

ECF is integral to achieving the vision of minimum impact (Haller, 1996; Axegård et al., 2003; Rennel, 1995; European Commision, 2000). A minimum impact pulp and paper mill maximizes wood yield, makes high quality paper that is easily recycled, maximizes energy production from biomass, minimizes water consumption, solid waste and air emissions, treats and disposes of waste optimally, and creates sustainable value to society (Pryke, 2003). Pulping and bleaching strategies incorporating ECF produce strong softwood fibers, minimizing the reinforcing fibre requirements for many paper grades such as lightweight coated (LWC). It has also been recognized that in combination with enhanced pulping, ECF manufacturing has a higher yield, using the least amount of wood compared with other pulping and bleaching techniques. Finally, ECF is compatible with, and at the leading edge of, so-called 'closed-loop' strategies for minimizing wastewater from bleaching (Pryke, 2003). Along with efficient wastewater treatment, closed-loop strategies are providing optimal solutions for protecting and sustaining the receiving water ecosystem (Stratton and Gleadow, 2003).

During the 1990s, governments, responding to the environmental concerns posed by persistent, bio-accumulative, and toxic compounds, developed new regulations for their respective pulp and paper industries. A common feature of many of these regulations and guidelines is the concept of 'best available technology' (BAT). Recognizing excellent performance, the US and the European Commission developed pulp and paper guidelines and regulations based on ECF bleaching as a core component of BAT (European Commission, 2000). These regulations and guidelines ensure compliance with the International Stockholm Convention on Persistent Organic Pollutants, the so-called POPs Treaty (EPA update, 2002) (Rennel, 1995). The virtual elimination of dioxin has been a key contributor to the sustainable recovery of affected aquatic ecosystems throughout the world. Fish consumption advisories downstream of pulp and paper mills are rapidly disappearing (AIET, 2002b).

Since 1990, state authorities in the United States have lifted dioxin advisories from 25 ecosystems downstream of pulp mills, representing 83% of the 30 such advisories in effect in 1990. In 2003, only 10 ecosystems remained with a dioxin advisory downstream of a bleached pulp and paper mill in the United States. The Environmental Protection Agency predicts that over time all remaining dioxin advisories downstream of US mills should be lifted following conversion to ECF bleaching. For existing mills, conversion to ECF has been relatively easy for the following reasons: many mills had existing chlorine dioxide generators that could be upgraded to the required production for relatively low capital cost; existing bleach plants were totally compatible; and bleaching cost increased modestly, 5–10%.

### 4.2.1 Modified ECF sequences

One promising trend today is the use of modified ECF sequences, i.e., sequences which still use chlorine dioxide, but not in the traditional manner of DEDED or ODED sequences (Chirat and Lachenal, 1997). The key here is to make them as efficient as chlorine-containing sequences. The use of chlorine dioxide and ozone in combination—in (DZ) or (ZD) stages—has started to appear over the past few years. Indeed, basic chemistry tells us that the reactions of these two chemicals on lignin complement each other, for example as with the case of chlorine and chlorine dioxide combinations (DC). It makes the process more efficient than DO or Z alone. The other interest in combining the use of ozone and chlorine dioxide lies in the fact that the required operating conditions (temperature, pH) are similar for the two chemicals, making it possible to run (DZ) or (ZD) stages with no intermediate washing. The criterion in the process is the replacement ratio, i.e., the amount of chlorine dioxide replaced by 1.0 kg of ozone. Ozone and chlorine dioxide (as pure chlorine dioxide) being of the same order of cost today, a replacement ratio higher than one means a reduction in chemical cost.

**Table 4.2.5 (DZ) and (ZD) treatments of an unbleached softwood kraft pulp[a]**

| Bleaching sequence | DEDED | (DZ)EDED | (ZD)EDED |
|---|---|---|---|
| $CIO_2$ (kg /ODT of pulp) | 35 | 27 | 29 |
| $O_3$ (kg/ODT of pulp) | — | 3.7 | 3.6 |
| Brightness (% ISO) | 90.0 | 90.5 | 90.3 |
| Viscosity (mPa. s) | 15.1 | 13.2 | 13.7 |
| Replacement ratio (kg $ClO_2$/kg. $O_3$) | — | 20.1 | 1.7 |
| AOX (kg/ODT of pulp) | 1.5 | 0.65 | 0.61 |

*Note*: AOX measured on the combined effluent.

[a] Kappa number, 24.

Based on data from Chirat and Lachenal (1997).

Table 4.2.5 shows an example of the (ZD) and (DZ) processes applied to a softwood kraft pulp. This type of combination has been thoroughly studied in France, both in the laboratory and at pilot scale to optimize the process. The (ZD) process is already in use in a few mills and several other projects announced recently intend to utilize it. This process provides a good example of how a relatively simple retrofit in an existing mill can meet most of the requirements described earlier.

## 4.3 TCF bleaching

In TCF bleaching, unpressurized (P) and pressurized (PO) peroxide stages, the slightly acid peracetic acid stage (Paa), and ozone stages (Z) are used. Transition metals contained in the pulp are first removed in a chelating stage (Q). Alternatively, acid hydrolysis can remove metals without the conventional chelating agent, and in a broad pH range. Oxygen delignification (often multistage) always precedes TCF bleaching. Applicable sequences are: OQ(PO)(PO), O(ZQ)(PO)(ZQ)(PO), O(Q)(PO)(ZQ)(PO), OQ(PO)(PaaQ)(PO), and OQ(EOP)(PaaQ)(PO) (Pikka et al., 2000). A high final brightness is also possible with sequences containing only alkaline bleaching stages, but these stages are most suitable as oxygen chemical sequences in fibre lines that also bleach pulp with the use of chlorine chemicals. Typical chemical consumption (kg/ADT) in oxygen chemical bleaching of softwood kraft pulp of kappa number 10 to 88% ISO brightness are: $H_2O_2$, 20; NaOH, 32; $O_2$, 6; $O_3$, 5; $H_2SO_4$, 20; and EDTA, 2.

Peroxide and oxygen are not sufficient to delignify the pulp further when the kappa number of the pulps is low. Ozone or peracids are more efficient delignifying chemicals, and can be used to reduce the kappa number to a low level before the final brightness increase in the PO stage. Chemical consumption for bleaching softwood kraft pulp of kappa number 11 to 89%

ISO brightness in Q(OP)(ZQ)(PO) sequence is shown in Table 4.3.1. The chemical charges and process conditions will obviously vary depending on wood species, degree of system closure, etc. The brightness development in TCF sequence depends on the proportions of various chemicals used. Table 4.3.2 compares the sequences (QZ)Q(PO), QpaaQ(PO), and Q(PO) for a Scandinavian softwood kraft pulp of kappa number 12. The ozone charge is 5 kg/ADT. The effect of kappa number after ozone delignification when bleaching softwood kraft pulp of kappa number 12 in a QZQQPO sequence is shown in Table 4.3.3.

TCF sequences today are less selective than ECF and consequently have been unable to retain high strength values at full brightness (Panchapakesan and Hickman, 1997). A number of studies have shown that TCF tear strength at high brightness is 10% lower than ECF and the pulps have lower fibre strength (Ek et al., 1994; Malinen et al., 1994; Moldenius, 1995, 1997; Nutt, 1995). The lower strength has implications for paper machine productivity and virgin fibre requirements in recycled grades and recyclability (Rennel, 1995). TCF production requires low lignin content of unbleached pulps and therefore has lower yield than today's ECF pulping and bleaching processes.

**Table 4.3.1 Chemical consumption in bleaching of softwood kraft pulp[a] in Q(OP)(ZQ)(PO) sequence**

| | |
|---|---|
| Brightness (% ISO) | 89.0 |
| DTPA | 2.5 |
| $H_2SO_4$ | 20.0 |
| NaOH | 34.0 |
| $H_2O_2$ | 20.0 |
| $MgSO_4$ | 2.0 |
| $O_2$ | 10.0 |
| $O_3$ | 5.0 |

[a] Kappa number, 11.

Based on data from Pikka et al. (2000).

**Table 4.3.2 A comparison of some oxygen chemical bleaching sequences applied to a softwood kraft pulp[a] when the ozone charge is 5 kg/adt**

| Peroxide charge (kg/ODT) | Brightness (% ISO) | | |
|---|---|---|---|
| | Q(PO) | QpaaQ(PO) | (QZ)Q(PO) |
| 10 | — | — | 86.5 |
| 20 | 82.0 | 84.2 | 90.0 |
| 30 | — | — | — |
| 40 | 84.2 | 88.0 | — |

[a] Kappa number, 12.0.

Based on data from Pikka et al. (2000).

**Table 4.3.3 Effect of kappa number after ozone delignification when bleaching softwood kraft pulp[a] in a Q(ZQ)(PO) sequence**

| Kappa number after Z | Brightness after (PO) (%ISO) | | |
|---|---|---|---|
| | Peroxide charge (5 kg/ODT) | Peroxide charge (10 kg/ODT) | Peroxide charge (20 kg/ODT) |
| 2.0 | 88.0 | 91.0 | 92.0 |
| 2.8 | 86.0 | 89.0 | 90.5 |
| 3.8 | 80.5 | 84.0 | 87.0 |

[a] Kappa number, 12.0.
Based on data from Pikka et al. (2000).

Studies show that TCF bleaching of 8 kappa number pulp increases overall wood consumption up to 10% when compared to an ECF bleaching of 30 kappa number pulp (Fleming and Sloan, 1994; Gullichsen, 1995; Steffes and Germgård, 1995). In a tour of Scandinavian mills, mill experience confirmed the yield loss. Wisaforest (Finland) claims it requires 6% more wood to make a ton of TCF pulp than ECF pulp. This was confirmed at the Enocell (Finland) mill. All the mills that produced any TCF pulp noted its lower strength properties (Boudreau, 1996). In North America, if the industry converted to TCF, an additional harvest of 100 million trees would be necessary to produce the same amount of pulp.

Conversion to TCF is relatively difficult for most existing mills for the following reasons: the capital cost to convert ranges from US$40–$190 million; operating costs increase US$20–$75 per tonne (Lancaster et al., 1992; Simons, 1992) and existing bleach plants have insufficient retention time for efficient hydrogen peroxide bleaching. These estimates in operating cost increases have been by mills that produce both ECF and TCF. An Austrian mill, which modernized its bleach plant to produce ECF, determined that the incremental bleaching cost for TCF would be US$60/t (Haller, 1996).

The superiority of TCF over ECF bleaching in terms of environmental impact is questionable. There are some significant disadvantages in TCF bleaching, which explains the lack of interest still being expressed by most of the pulp producers (Chirat and Lachenal, 1997). The most important of these is that bleaching a kraft pulp to high brightnesses (90% ISO) is not possible without sacrificing some strength properties. The problem of cellulose degradation during TCF bleaching has been extensively studied.

Taking an OPZ(EO)P sequence for example, it was shown that each stage might contribute to some cellulose depolymerization. One critical factor is the amount of ozone introduced in the sequence. For charges higher than 5–6 kg/t, the cellulose may be slightly depolymerized and oxidized. This last effect makes the pulp sensitive to any alkaline environment such as (EO)P, which leads to further chain cleavage by a mechanism that has already been well documented.

Consequently, despite the fact that such a sequence was close to optimum efficiency in terms of delignification (ozone is ranked in the same category as chlorine) and bleaching power, it is penalized by the occurrence of several degradation mechanisms taking place on cellulose in a synergistic way. One possible solution to the problem of cellulose degradation during TCF bleaching to 90% ISO, is to limit the charge of ozone and to introduce some nondegrading bleaching agents in the sequence. The only reagents that demonstrate this property so far are the peroxyacids (peroxyacetic, peroxymonosulphuric acids). But more research is needed to reduce the chemical cost to acceptable levels when peroxyacids are used.

TCF pulps differ qualitatively from ECF pulps (Panchpakesan and Hickman, 1997). Table 4.3.4 shows the concentrations of different sugars in the bleach plant effluent from both ECF and TCF bleaching sequences for sulphite pulps. As shown, TCF bleaching tends to dissolve more of the hemicellulose fraction, as indicated by the higher concentrations of the monomeric sugar units. The different proportions of functional groups, derived from cellulose and hemicellulose degradation, are responsible for some of the differences in chemical and physical properties between TCF and ECF pulps. The proportion of hemicelluloses retained is less in kraft pulps compared with sulphite pulps. The viscosity and degree of polymerization (DP) of TCF kraft pulps is based on the type of bleaching sequence and the operating conditions. For achieving the same brightness, TCFz pulp (OZED sequence) had a lower viscosity compared with conventional bleaching (CEDED sequence) (Nutt, 1992). TCFz pulps tend to have lower brightness and reduced strength properties compared with ECF pulps. The correlation between the chemical characteristics of TCF pulps and the lower strength properties is not well established.

**Table 4.3.4 Carbohydrates in bleach plant effluents**

| Parameters | Carbohydrates (kg/t of pulp) | |
|---|---|---|
| | ECF (ODOEDED) | TCF (OPZEP) |
| Xylose | 1.00 | 2.00 |
| Glucose | 0.75 | 1.30 |
| Galactose | 0.40 | 0.70 |
| Mannose | 0.25 | 0.40 |
| Arabinose | 0.20 | 0.20 |
| Total | 2.40 | 3.50 |

Based on data from Panchapakesan and Hickman (1997).

The refining energy (hpd/t) applied depends on the type of bleaching sequence and viscosity of pulps. The degree of refining is generally less for TCFz pulps (Panchapakesan and Hickman, 1997). This is due to the increased water-holding capacity of the pulps due to the higher proportion of carboxyl end groups. Higher viscosity in TCF pulps means a higher degree of polymerization (DP) and less number of end groups. Lower hemicellulose retention in TCF pulps also decreases the number of end groups. Reduction in the number of end groups decreases the number of active sites available for intermolecular hydrogen bonding and can result in an overall reduction in the relative bonded area. But this has to be confirmed by further experimental work.

Malinen et al. (1994) have reported that softwood TCF pulps tend to show more significant loss in strength properties compared with the hardwood TCF pulps. High consistency ozone-bleached pulps tend to have lower strength properties compared with medium-consistency pulps due to the loss in selectivity of attack by ozone and possible degradation of cellulose at higher concentrations in high-consistency bleaching.

The increase in yield from extended delignification is attributed to higher retention of $\alpha$-cellulose in RDH pulps. When extended delignification is followed by a TCF bleaching sequence, the yield advantage from higher retention of $\alpha$-cellulose is maintained through the bleaching process. Starting from the same kappa number levels, the bleaching yield in TCFz is generally lower by 0.5–1% compared with ECF bleaching processes (Panchapakesan and Hickman, 1997).

Decrease in strength properties is generally compensated by increasing the proportion of the softwood pulp in the furnish. However, the pulp mill capacity and the high cost of softwood pulp may constrain some situations. The loss in brightness and strength properties are generally less for hardwoods than for softwoods. Lower loss in strength properties for hardwoods may be due to fewer hydrophilic groups in hardwood pulps compared with softwood pulps, lower swelling ability and higher possibility of strength development by refining without losing freeness (Panchapakesan and Hickman, 1997). This must be confirmed by further experimental work. The behaviour of TCF pulps towards heat- and light-induced degradation is different than that of ECF pulps (Panchapakesan and Hickman, 1997). The higher proportion of carbonyl and carboxyl groups (photoreceptors) account for the accelerated brightness reversion characteristics of TCF pulps. Higher losses in hemicelluloses during extended delignification and TCF bleaching processes are expected to result in a pulp with lower hydrophilicity. Also, with the increased proportion of cellulosic fraction, the pulp is expected to be harder to beat. The beatability of TCF pulps is dictated by the type of bleaching sequence used and the bleached pulp viscosity. TCFz pulps tend to be more hydrophilic and easier to beat than TCFp pulps.

The higher proportion of acidic functional groups is responsible for the higher affinity to water (Table 4.3.5) (Panchapakesan and Hickman, 1997). This results in a higher water retention value for TCFz pulps. Increase in the acidic groups results in an increase in the swelling capability and decreases beating energy required for TCF pulps as compared with ECF pulps. The differences are always more significant for softwood than for hardwood pulps. Refiner plate designs may need some modifications to promote fibrillation. Wide bars may be required in place of low-width bars. The effectiveness of wet strength additives and the affinity of dye stuff also differs when changing from ECF to TCF pulps. This is due to the changes in the functional groups of TCF pulps (Panchapakesan and Hickman, 1997). The zeta potential may have been altered due to the changes in functional groups in cellulose and hemicellulose fractions. This can affect the effectiveness of chemicals, first- pass retention and some sheer characteristics. Higher swelling capacity of TCFz pulps means increased drainage resistance and water retention value. These different properties particularly affect the production of printing papers, wood-free uncoated and coated grades. Higher water retention value may be a problem in situations where forming section drainage capacity is limited. The drainage elements in such situations may need to be rearranged or additional vacuum elements may be required. In some cases, major modifications such as increasing the forming table length or providing additional top wire dewatering may be required. First-pass retention is generally expected to increase for $TCF_Z$ pulps due to less refining, better fibre swelling ability and, hence, lowest production of fines.

Due to the increased hydrophilicity of the pulp, problems may be encountered in the saveall, especially if the saveall is hydraulically limited (Panchapakesan and Hickman, 1997). Optimizing furnish refining and

**Table 4.3.5 Changes in carboxyl group content in pulp by different bleaching agents**

| | mmol of –COOH/100 g of cellulose |
|---|---|
| Unbleached | 0.08 |
| Ozone | 0.45 |
| Chlorine (2% as $ClO_2$) | 0.10 |
| Chlorine (4% as $ClO_2$) | 0.15 |
| Oxygen | 0.28 |
| Chlorine (2% as $ClO_2$) | 0.33 |
| Chlorine (4% as $ClO_2$) | 0.38 |
| Peroxide | 0.26 |

Based on data from Panchapakesan and Hickman (1997).

adjusting drainage elements in the forming section will help improve first-pass retention and also lower the amount of fines circulating in the white-water system. Decreasing the fines content helps improve the filtration rate in the saveall and also reduces the sweetener requirement. Increased swelling capacity of fibre results in an increase in the amount of bound water. This can limit water removal in the press section. Modifications required in the press section may include increased press loadings, upgrading the vacuum systems and major changes in press section configuration. Higher press loads may also be necessary to control sheet bulk. Lower strength properties may mean increased sheet breaks in situations where significant open draw exists between the dryer sections. This may require modifications to support the control sheet caliper. However, no significant changes should normally be required in the calendar section.

## 4.4 Conclusions

ECF bleaching based on chlorine dioxide is a technology choice for sustainable pulp and paper manufacturing. Papermakers and paper users alike desire ECF's excellent product quality, resource conservation attributes, and compatibility with sustainable minimum impact-manufacturing. Government organizations increasingly recognize and document ECF's proven pollution prevention record, its contribution to sustainable ecosystem recovery and its position as a core component of BAT. Fueled by continued strong government support and proven environmental integrity, new paper mills throughout the world are incorporating ECF-based bleaching to produce quality products with sustainable manufacturing technologies.

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# Chapter 5

## Chlorine-free bleaching of secondary fibres

### 5.1 Introduction

The galloping rises in price of fibrous raw materials and waste disposal problems are leading paper producers throughout the world to increase their use of secondary fibres for paper products. The percentages of secondary fibre in almost every grade of paper and boards and particularly in printing and writing papers has more than doubled in the past decade, and is expected to triple or quadruple in the next 10–15 years. Earlier, paper recycling was done mainly because it made economical sense to do so, whereas now it has been driven more by a collective environmental mandate of sorts. The marketplace for secondary pulps and papers continues to develop and mature, but is still very much in fluctuation and confusion, as deinked speciality market pulp mills continue to start-up and shut down in rather disordered order. This huge secondary paper undertaking is primarily aimed at reducing volumes of wastepaper in the world's growing landfill sites. But, from the perspectives of various environmentalists, recycling also helps to preserve and economize scarce forest resources, minimize environmental pollution and contribute to water and energy conservation. Since recycling has such an obvious environmental attachment, it follows that the processes used to produce deinked fibres, especially the bleaching process, should have come very much under inspection in recent years. Hydrogen peroxide has been mainly used for bleaching of secondary fibres, at least during the last quarter century. However, various reducing agents and chlorine containing compounds have been also used. The pressure on modern secondary fibre mills to produce a chlorine-free product are now as strong as those directed toward virgin bleached kraft pulp mills. This is especially true considering that, in the United States and in other countries, the federal government and states and provinces are specifying secondary papers for use by their many branches of government.

Chlorine-free bleaching of secondary fibres is carried out with oxidative (hydrogen peroxide, oxygen, ozone) and reductive (sodium dithionite and formamidine sulphinic acid) bleaching chemicals (Ackermann, 2000; Renders, 1992, 1995; Renders and Hoyos, 1994; Renders et al., 1995; Magnin et al., 2000; Muguet and Sundar, 1996; Patt et al., 1993; Matzke and Kappel, 1994; Suss, 1995; Fluet, 1995; Gangolli, 1982; Kronis, 1992, 1997). Hydrogen peroxide bleaching is theoretically efficient for bleaching wood-containing pulp but is also often used (with success) to improve the brightness of wood-free deinked pulp (Hemling, 1986). Ozone and oxygen have been also used for bleaching or decolourizing secondary fibres. The oxygen-bleaching stage is usually supported with hydrogen peroxide. Its use has become more common in commercial application. Ozone is the only chlorine-free bleaching chemical that can almost completely destroy optical brighteners in deinked pulps. However, the use of ozone has not played any significant role in the bleaching of secondary fibres. Peracids have been reported for laboratory-scale treatment but there are no industrial applications. Sodium dithionite and formamidine sulfinic acid (FAS) are used industrially in some cases to bleach deinked pulps containing mechanical pulp. They are also used for decolourizing dyed brokes or deinked pulp resulting from mixtures containing dyed papers. Lachenal (1994) has classified these chemicals into two categories: the nondegrading and degrading agents. Hydrogen peroxide, sodium hydrosulphite and FAS belong to the category of nondegrading agent. Their action is limited to the destruction of carbonyl groups (and azo groups for the reductive agents). Coloured organic molecules are modified into colourless molecules. Pulp yield is not considerably affected. Oxygen and ozone belong to the category of degrading agents. They can destroy phenolic groups, carbon–carbon double bonds and conjugated aromatic structures. Chromophore groups are dissolved away from the fibre structure and then removed. Pulp yield is significantly affected. When high brightness is required, combinations of oxidative and reductive bleaching are sometimes used.

## 5.2 Bleaching with hydrogen peroxide

Hydrogen peroxide has the advantage of being compatible with the environment, as it decomposes to water and oxygen. Therefore, strong environmental concerns make the product more attractive as a bleaching agent for secondary fibres. Hydrogen peroxide is the most frequently used chemical for high-yield pulp bleaching when high brightnesses are required. For a mixed wastepaper furnish of old newsprint (ONP) and old magazines (OMG), bleaching has some similarity to mechanical pulp bleaching.

However, most of the secondary fibres have been bleached before and so they will not necessarily respond in the same way to the bleaching stage as virgin pulps. The chemistry of hydrogen peroxide bleaching is reviewed by Renders (1995) and Ackermann (2000). The bleaching effect uses the dissociation of hydrogen peroxide in water to form a hydronium ($H_3O^+$) and a perhydroxyl ion ($HO_2^-$):

$$H_2O_2 + H_2O \rightleftharpoons HO_2^- + H_3O^+$$

The perhydroxyl anion acts as a nucleophilic bleaching agent. Increasing its concentration is necessary to achieve a high bleaching effect. This is possible by increasing the hydrogen peroxide concentration and by addition of sodium hydroxide. The following is activation of the hydrogen peroxide:

$$H_2O_2 + OH^- \rightleftharpoons H_2O + HO_2^-$$

Table 5.2.1 shows the effect of hydrogen peroxide/sodium hydroxide dosage on brightness development (Helmling et al., 1985). At low dosages of sodium hydroxide, the hydrogen peroxide bleaching liquor does not have sufficient activation. In the highly alkaline range, a loss of brightness occurs with additional sodium hydroxide. This is due to the increased yellowing reactions of excessive hydroxide ions on the lignin structures of mechanical fibres. With hydrogen peroxide/sodium hydroxide proportions at which optimum bleaching occur, the ratio between the rates of bleaching and yellowing reactions is most favourable. Residual hydrogen peroxide content at the end of the bleaching process is a sign of an optimum hydrogen peroxide activation. If the residual hydrogen peroxide is less than 10% of the original hydrogen peroxide dosage, the yellowing reactions dominate over the bleaching reactions. So, hydrogen peroxide bleaching is an excess bleaching reaction. Higher brightness is obtained with increasing dose of hydrogen peroxide (Table 5.2.1). The required amount of sodium hydroxide to obtain the maximum bleaching effect also increases. An increase in the amount of hydrogen peroxide from 1.5 to 3.0% requires a 0.2% increase in the amount of sodium hydroxide. Bleaching should be conducted under optimum hydrogen peroxide/sodium hydroxide conditions for economic reasons. The chemical oxygen demand (COD) load of the process water increases with increasing alkalinity, so it is important to keep the alkali amount to a minimum (Berndt, 1982; Putz and Gottsching, 1982). The solubility of oxidized lignin or hemicelluloses increases with increasing pH. This is particularly true when processing wood-containing pulp. Bleaching is improved with addition of hydrogen peroxide. Brightness does not increase indefinitely because hydrogen peroxide reacts only with certain chromophores. Table 5.2.2 shows the brightness development with increasing dose of hydrogen

**Table 5.2.1 Effect of $H_2O_2$/NaOH dosage on brightness**

| $H_2O_2$ (%) | NaOH (%) | Brightness (% ISO) |
|---|---|---|
| 0.25 | 0.0 | 56.9 |
| | 0.5 | 58.1 |
| | 0.7 | 58.3 |
| | 1.0 | 57.5 |
| | 1.5 | 55.9 |
| | 2.0 | 54.8 |
| | 2.5 | 53.9 |
| | 3.0 | 53.3 |
| 0.50 | 0.0 | 57.3 |
| | 0.5 | 58.5 |
| | 0.8 | 59.0 |
| | 1.0 | 58.8 |
| | 1.5 | 57.4 |
| | 2.0 | 56.3 |
| | 2.5 | 55.2 |
| | 3.0 | 54.6 |
| 1.0 | 0.0 | 57.5 |
| | 0.5 | 58.8 |
| | 1.0 | 60.5 |
| | 1.1 | 60.6 |
| | 1.5 | 59.6 |
| | 2.0 | 58.1 |
| | 2.5 | 56.6 |
| | 3.0 | 55.7 |
| 1.5 | 0.0 | 56.9 |
| | 0.5 | 58.8 |
| | 1.0 | 61.0 |
| | 1.3 | 61.9 |
| | 1.5 | 61.7 |
| | 2.0 | 60.0 |
| | 2.5 | 58.5 |
| | 3.0 | 57.3 |
| 3.0 | 0.0 | 56.4 |
| | 0.5 | 59.1 |
| | 1.0 | 62.3 |
| | 1.5 | 64.0 |
| | 1.6 | 64.0 |
| | 2.0 | 61.4 |
| | 2.5 | 61.0 |
| | 3.0 | 59.5 |

Based on data from Helmling et al. (1985).

peroxide (Helmling et al., 1985). The maximum increase occurs with hydrogen peroxide additions of less than 1.5%. Higher doses lower the gradients of the brightness development significantly. Hydrogen peroxide dosage of more than 2% are not recommended for economic reasons. The presence of heavy metal ions or enzymes—catalases in secondary pulp slurries—can

**Table 5.2.2 Effect of hydrogen peroxide dosage on brightness by optimized NaOH addition**

| $H_2O_2$ (%) | NaOH (%) | Brightness (% ISO) |
|---|---|---|
| 0.25 | 0.7 | 57.6 |
| 0.50 | 0.9 | 58.9 |
| 1.0 | 1.2 | 60.4 |
| 1.5 | 1.4 | 61.8 |
| 3.0 | 1.6 | 63.6 |

Based on data from Helmling et al. (1985).

cause decomposition of the hydrogen peroxide. This causes loss of the activation energy required to break the oxygen–oxygen bond. Hydroxide radicals form that decompose into water and oxygen via a chain reaction.

$$H_2O_2 \rightarrow 2HO^{\cdot} \rightarrow H_2O + \frac{1}{2}\,O_2 \quad \text{or}$$

$$H_2O_2 \rightarrow H^{\cdot} + {}^{\cdot}OOH \rightarrow H_2O + \frac{1}{2}\,O_2$$

These reactions are undesirable and occur very slowly, but increased temperature, high alkalinity and catalysts can speed up these reactions. Besides the economically inefficient hydrogen peroxide consumption, oxidative damage to the fibres are due to the radicals formed at the time of decomposition. For stabilization of the hydrogen peroxide, it is necessary to deactivate the catalytic substances in the secondary pulp slurry.

Bleaching results are significantly affected by the process parameters such as stock consistency, temperature, reaction time and the chemicals used (Ackermann, 2000; Renders, 1992, 1995). Table 5.2.3 shows the effect of pulp consistency on brightness development (Helming et al., 1985). Brightness is higher at higher pulp consistency. This is due to two main reasons: a higher consistency gives a higher relative concentration of bleaching chemicals that come into direct contact with the fibres; the displacement of the aqueous phase also eliminates dissolved matter that can unfavourably affect the bleaching reaction. Mixing problems are encountered when the pulp consistency is above 30%. The bleaching chemicals do not mix homogeneously into the pulp without the use of highly effective mixing methods. This increases the leveling of brightness. For this reason, the consistency is mainly limited to 25% in separate bleaching stages. Because hydrogen peroxide is also used in other stages of secondary fibre processing such as during slushing, the application cannot always occur under optimum conditions. The consistency at bleaching usually is in the range 10–25%. No practical or acceptable alternatives to high consistencies exist for economic

**Table 5.2.3 Effect of pulp consistency on brightness**

| Consistency (%) | Brightness (% ISO) |
|---|---|
| 5 | 56.8 |
| 10 | 59.4 |
| 15 | 61.0 |
| 25 | 62.3 |
| 30 | 63.0 |

Based on data from Helmling et al. (1985).

reasons. However, temperature, reaction time and alkalinity can optimize the reaction. There is a close relationship in chemical reactions between the reaction time essential to obtain the reaction product and the temperature at which the reaction components interact. In many applications, a high temperature is therefore useful to speed up the reaction. This applies for also bleaching with hydrogen peroxide. The temperature cannot increase indefinitely because unwanted secondary reactions such as yellowing reactions or hydrogen peroxide decomposition occur more rapidly. If bleaching occurs at extremely low temperatures, then long reaction time is required to obtain similar bleaching results. The temperature should therefore be in the range of 40–70°C for economic reasons. Typical reaction times are in the range of 1–3 h when bleaching occurs in a separate process stage. A lower dose of sodium hydroxide is required at higher temperatures for optimum hydrogen peroxide activation. Helmling et al. (1985) have reported that the alkalinity must be reduced by about 0.1% with a temperature increase of 10°C to ensure optimum matching of temperature activation and alkali activation. In contrast, the effect of the stock consistency on the hydrogen peroxide and sodium hydroxide relationship is unimportant.

Although bleaching with hydrogen peroxide is less efficient for secondary fibre than for virgin fibres, careful control of some process parameters can help to maximize the brightness gain. The easiest way to detect poor hydrogen peroxide efficiency is to determine, in parallel with the brightness, the hydrogen peroxide consumption. Generally, a total hydrogen peroxide consumption means a significant loss of the hydrogen peroxide efficiency. Some of the important parameters causing this hydrogen peroxide decomposition are discussed in the following sections:

Trace metals catalyse the decomposition of hydrogen peroxide. Such metals include iron, manganese and copper, which are normally found in virgin pulps (Kutney et al., 1985a) as well as aluminium which is introduced in the paper-making process (Galland et al., 1989). An acid wash at pH 2 is found to be effective in removing transition metal ions for chemical pulp bleaching. Such a pretreatment before a hydrogen peroxide stage has been applied successfully on waste paper containing 40% newsprint and 60% magazines; a temperature beyond 70°C simultaneously destroys catalase (Patt et al., 1993). But according to Renders (1995) and Renders et al. (1995), this approach does not appear to be suitable for secondary fibres since filler material such as calcium carbonate can greatly increase the acid demand. Chelating agents and sodium silicate are commonly used in case of secondary fibres to deactivate the heavy metal ions that contribute to the wasteful decomposition of hydrogen peroxide. The role of a chelant is to form soluble complexes with heavy metal ions. The more commonly used chelating agent is DTPA. The need for chelating agents will depend on the contamination of the pulp. Some researchers have used chelation treatment under extreme conditions in case of bleaching mixed office waste (Sharpe, 1995). Treatment was performed with 1% DTPA at a pulp consistency of 10% and temperature of 90°C for 60 min. Bleaching of the pulp, with 3% hydrogen peroxide after this treatment, reduced the metal concentrations. The decomposition of hydrogen peroxide reduced and the brightness increased. The brightness of chelated pulp was 12.3 ISO points higher as compared to 9.6 ISO points for unchelated pulp. In case of other furnishes, the addition of DTPA did not show any positive results (Patt et al., 1996). The heavy metal and the filler contents of the grades were too high. The complexing agents chelated other metal ions on a stoichiometric basis. Similar observations were made by other researchers (Renders, 1992, Renders, 1995 and Renders et al., 1995).

Sodium silicate is found to chelate metal ions and so it is able to reduce the hydrogen peroxide decomposition. Silicate is also a source of alkalinity and silicate added in the pulper helps in ink removal by flotation (Renders, 1992). Table 5.2.4 shows the increase in brightness and the reduction of consumed hydrogen peroxide with increasing dosage of silicate for a 50/50 mixture of newsprint and magazines (Renders and Hoyos, 1994). Kutney (1985b), Renders (1995) and Renders et al. (1995) have reported that sodium silicate is the most efficient for stabilization of hydrogen peroxide. Tables 5.2.5 and 5.2.6 show the comparison of the effects of chelating agents

**Table 5.2.4 Effect of sodium silicate dosage on brightness and consumed hydrogen peroxide**

| Sodium silicate (%) | Brightness (% ISO) | | $H_2O_2$ consumption (%) |
|---|---|---|---|
| | After disperger | After post-flotation | |
| 0 | 56.0 | 58.8 | 100.0 |
| 1.6 | 59.5 | 65.0 | 97.5 |
| 3.4 | 62.0 | 67.5 | 65.0 |

*Note*: Pilot plant optimization—50/50 newsprint/magazine mixture, 70°C, 1% $H_2O_2$, 1% total alkalinity. Based on data from Renders and Hoyos (1994).

**Table 5.2.5 Hydrogen peroxide stabilization for ONP/OMG bleaching**

| Stabilization | Brightness (% ISO) | $H_2O_2$ consumption (%) |
|---|---|---|
| No stabilization | 58.9 | 100 |
| 1.0% DTPA | 63.6 | 92 |
| 1.0% DTPMP | 63.9 | 90 |
| 2.5% silicate | 66.0 | 80 |
| 5.0% silicate | 67.2 | 67 |
| 2.5% silicate + 1.0% DTPA | 66.7 | 78 |
| 2.5% silicate + 1.0% DTPMP | 67.8 | 67 |

Based on data from Robberechts et al. (2000).

**Table 5.2.6 Hydrogen peroxide stabilization for bleaching of mixed office waste**

| Stabilization | Brightness (% ISO) | $H_2O_2$ consumption (%) |
|---|---|---|
| No stabilization | 70.8 | 100 |
| 1.0% DTPA | 72.6 | 97 |
| 1.6% DTPMP | 72.6 | 98 |
| 2.5% silicate | 73.7 | 75 |
| 2.5% silicate + 1.0% DTPA | 73.7 | 73 |
| 2.5% silicate + 1.6% DTPMP | 73.1 | 68 |

Based on data from Robberechts et al. (2000).

(DTPA and DTPMP-sodium salt of diethylene-triamino-pentamethylene phosphonic acid) and sodium silicate in post-deinking bleaching on two types of furnishes (ONP/OMG mixture and MOW) (Robberechts et al., 2000). Results show that sodium silicate is more effective than the chelating agents. Increase in brightness is more with sodium silicate. The positive effect on brightness with chelating agents is more distinct on ONP/OMG mixture. DTPA or DTPMP in addition or in replacement of sodium silicate has practically no effect on the final brightness of mixed office waste. Silicate is generally used at a dose level of 2–3%. Beyond this level, scaling and fouling problems of machine clothing and reduced efficiency of the retention aids can occur at the paper machine. To reduce the dosage of silicates, chelating agents can be added simultaneously.

An uncontrolled decomposition of hydrogen peroxide is initiated by catalase. Catalase is an enzyme which is produced by all aerobic microorganisms and animal and vegetable cells. In the cell, they act as protective enzymes against the hydrogen peroxide and some other substances produced in the respiratory chain. Hydrogen peroxide has a strong toxic effect on the cell. The cell therefore tries to destroy the hydrogen peroxide by the catalase as quickly as possible. Accordingly, catalases are also specific peroxidases that suppress an overproduction of hydrogen peroxide and therefore prevent the destruction of the cells (Aebi, 1987). This natural reaction process can determine the microbial activity in pulp slurries or filtrates. After an excess dosage of hydrogen peroxide, the rate of decomposition is measured. This indirectly provides information about the presence of microorganisms (Prasad, 1989).

The main known sources of catalase-forming microorganisms are the wastepapers and the slime in the wastewater from the paper machine which is sent back to the deinking plant. The presence of catalase can be easily detected: the addition of a known concentration of hydrogen peroxide to the filtrate containing the catalase results in a quick decomposition of the hydrogen peroxide with the formation of oxygen bubbles, with total decomposition being reached after 15 min (Galland, 1989). The destruction of catalase by a thermal treatment ($> 70°C$) has also been described. Although this treatment is efficient, it is not suitable for all stages in a deinking line. In the pulper, for example, the temperature is limited to 50–55°C, above which stickies start to melt and cause serious problems. An alternative solution is the application of a biocide, such as a peroxygen compound, peracetic acid. The catalase-forming microorganisms are killed by the application of peracetic acid, and catalase formation is also inhibited. Peracetic acid is injected into the white-water circuit. As with all biocides, peracetic acid has to be applied in 'shock doses,' due to its powerful nature and its lack of residual activity. Within 24 h, and with four different shock doses of peracetic acid, the water circuit of a deinking plant can be disinfected. The hydrogen peroxide stability in the deinking circuits can thus be restored and normal brightness gains are observed. An increase in the hydrogen peroxide introduction rate in the pulping stage has been proposed to prevent catalase formation (Brauer et al., 1995; Keegan and Cairns, 1995; Ng and Davis, 1995). Glutaraldehyde has also been proposed for catalase deactivation. It has been used successfully in several mills (Salzburger, 1996; Ben and Rivals, 1998).

Sodium dithionite is sometimes used in combination with hydrogen peroxide in a two-stage bleaching of deinked pulp for colour removal. Residual amounts of hydrosulphite in the water circuit can cause a loss of hydrogen peroxide efficiency. Moreover, dithionite by-products, such as sodium bisulphite and sodium thiosulphate, have both a hydrogen peroxide and caustic soda demand. This means that not only must the initial level of hydrogen peroxide be increased to destroy residual dithionite, but also that the caustic soda demand can vary in a deinking or bleaching line when applying both reductive and oxidative bleaching chemicals. This has to be considered in the optimization of both caustic soda and hydrogen peroxide levels.

For the utilization of hydrogen peroxide in a deinking line, several addition points can be considered, as follows: in the pulper; in the dispersion unit; and as post-bleaching at the end of stock processing line. The use of hydrogen peroxide in the pulping stage is not a perfect solution since ink and contraries present in the pulper reduce the bleaching efficiency of hydrogen peroxide. Its main advantage is that no additional equipment is required. Pulping of secondary fibres is generally performed under alkaline conditions which induce yellowing of the mechanical pulp contained in secondary fibres. Hydrogen peroxide in pulping is mainly used to prevent this harmful effect. The main reasons in favour of using hydrogen peroxide at this stage are the already existing alkaline conditions, the presence of sodium silicate and the temperature. In the conventional pulper, consistency used is low which prevents an optimum use of the bleaching chemicals. Now medium consistency or drum pulpers are available. The increase of pulp consistency to 15–18% create more favourable conditions for the use of hydrogen peroxide, but other conditions such as pulping time prevent an optimum use of the bleaching agent. The average pulping time of 15 min is not sufficient to obtain maximum brightness increase. The presence of a wide range of different impurities, including printing ink, also catalyses the undesired peroxide decomposition. This results in an increased addition of stabilizing chemicals such as water glass and possibly chelating agents. Kneaders and dispergers are used in deinking plants in order to detach residual ink after a deinking stage or for fragmentation of visible contaminants in secondary fibre pulp. Mechanical dispersion of the primarily dark particles usually occurs with a loss of brightness. Recycled pulp is dispersed with high consistencies of 25–30% and temperatures of 60–95°C. These process conditions and the high shear environment are perfect for admixing of peroxide. The dispersion bleaching acts against the graying of the pulp, resulting from the dispersion of the ink particles, by improving the brightness of the fibre furnish if only by a few points. Carre et al. (1995) have reported that hydrogen peroxide bleaching can compensate for the loss of brightness caused by dispersion. Presently, bleaching stage in a disperser is proposed between two flotation stages: hydrogen peroxide is added at high temperature (70–95°C) and high consistency (25–30%), and mixing is performed in fractions of a second in the disperser. After dilution to 12%, the stock is fed into a bleaching tube or a tower with the help of a medium consistency pump. The bleaching reaction is carried out at 60–65°C and the reaction time is approximately 30 min. In newer installations there is no dilution after the disperger and screws are used for stock transport. In this way, the whole bleaching stage can be operated at high consistency. After thickening and often after hot dispersion, the chemicals are mixed with the pulp, steam is introduced (if a hot dispersion stage is not implemented) and the pulp is stored in a bleaching tower at 60°C for 1–3 h at 15% consistency.

In hydrogen peroxide bleaching there is a trend toward even higher consistencies up to 40% (ultra-high consistency) (Matzke and Keppel, 1994). Benefits are reduced steam consumption, reduction in chemical consumption, lower COD load due to reduced alkali application and less anionic trash in the stock due to better loop separation. The reaction time is reduced by 50% when bleaching is done at a consistency of 30% instead of 10% (Sharpe, 1995).

Hydrogen peroxide is a highly effective bleaching chemical for improving the brightness of deinked pulp. The bleaching result is sufficient for many applications for using deinked pulp to satisfy the optical requirements of the paper produced. A prerequisite for successful bleaching is stabilization of the hydrogen peroxide to the reactions that cause its decomposition. The effects on chromophores of the lignin that use oxidative reactions are limited. If higher optical quality demands are made on the deinked pulp, additional bleaching with reductive bleaching chemicals will be necessary.

Ackermann (2000) has summarized diverse experiences on hydrogen peroxide bleaching of secondary fibres : Bovin (1984) and Blechschimdt and Ackermann (1991) have recommended separate bleaching with hydrogen peroxide after a deinking process (flotation or washing). The increase in brightness in this case is higher when compared with those obtained by hydrogen peroxide bleaching before a deinking stage (Tables 5.2.7 and 5.2.8) (Putz, 1987; Bovin, 1984). Alkaline yellowing during pulping due to the absence of hydrogen peroxide is compensated by bleaching after deinking. The addition of hydrogen peroxide in the pulping stage is found to be essential only in the case of high proportions of mechanical fibres in the pulp. In this case, even small amounts of hydrogen peroxide lead to brightness stabilization. Increasing the dose of hydrogen peroxide beyond 2% (on

**Table 5.2.7 Effect of hydrogen peroxide on brightness at different pulp consistencies**

| $H_2O_2$ (%) | Brightness (% ISO) | | | |
|---|---|---|---|---|
| | Before flotation | | After flotation | |
| | 4% consistency | 25% consistency | 4% consistency | 25% consistency |
| 0.0 | 45.0 | 45.5 | 51.5 | 52.2 |
| 0.5 | 45.5 | 50.0 | 55.2 | 58.5 |
| 1.0 | 46.8 | 51.2 | 57.5 | 60.7 |
| 2.0 | 48.0 | 51.1 | 58.8 | 62.0 |

Based on data from Putz (1987).

o.d. pulp) to obtain higher increase in brightness is not recommended. Improvement in bleaching is obtained by splitting the dose of hydrogen peroxide before and after flotation (Melzer, 1985). Most deinking plants take advantage of the synergistic effects of flotation and bleaching by adding hydrogen peroxide during pulping and during dispersion or post-bleaching. Ackermann et al. (1992) and Helming et al. (1986) have reported that a prerequisite for maximum brightness gain at the post-bleaching stage is the optimum removal of ink particles at the deinking stages. A higher content of ink particles actually gives a inferior bleaching effect. Table 5.2.9 presents the conditions for hydrogen peroxide bleaching.

**Table 5.2.8 Brightness gain in a flotation deinking process using different ways for bleaching (75% old newspaper, 25% old magazines)**

| Processes | | Brightness (% ISO) |
|---|---|---|
| I | (P–D) | |
| | P (1% $H_2O_2$) | 51.7 |
| | D | 57.3 |
| II | (P–Bl–D) | |
| | P (0% $H_2O_2$) | 47.6 |
| | Bl (1% $H_2O_2$) | 53.3 |
| | D | 57.7 |
| III | (P–D–Bl) | |
| | P (0% $H_2O_2$) | 46.9 |
| | D | 51.4 |
| | Bl (1% $H_2O_2$) | 58.9 |

*Notes*: P, Pulping; D, Deinking; Bl, Bleaching.
Based on data from Bovin (1984).

**Table 5.2.9 Bleaching conditions for hydrogen peroxide**

| Parameters | Values |
|---|---|
| Hydrogen peroxide dose (%) | 0.5–3 |
| Sodium hydroxide dose (%) | 0.5–2.0 |
| pH | 9–11 |
| Time (min) | 30–90 |
| Pulp consistency (%) | 10–15 (medium consistency)<br>25–30 (high consistency) |
| Temperature (°C) | 60–90<br>100°C for wood-free papers |
| Stabilizers | Silicate 1–3%<br>DTPA 0.1–0 .3% |

Based on the data from Renders (1995) and Ackermann (2000).

## 5.3 Bleaching with dithionite

Sodium dithionite is a reductive bleaching chemical. It is also known as sodium hydrosulphite. Reductive bleaching is especially essential not only for bleaching, but also for removing colour from coloured recovered paper and carbonless paper (Hache et al., 1994; Dumont, 1994; Fluet and Shepperd, 1997). Many dyes used to colour paper can be effectively destroyed by reductive bleaching chemicals. Sodium dithionite is known to be effective for colour stripping and can remove many types of dyes. Most of the acidic and direct dyes are permanently decolourized by sodium dithionite because it breaks the azo groups. Some of the basic dyes are temporarily decolourized. Dithionite is sometimes used in combination with an oxidizing agent, since some dyes which are not reactive with oxidizing chemicals can react with some reducing agents.

Sodium dithionite decomposes rapidly when exposed to air. When exposed to water, the solid form liberates sulphur gases, which are corrosive to equipments and buildings. The aqueous solution is typically stored in closed tanks with a nitrogen pad. Sodium dithionite is generally supplied as dry powder. These commercial products may contain stabilizers, buffers (phosphates, carbonates), and chelates.

Dithionite was produced for the first time in 1906 by BASF in Germany in powder form. Initially, the product was obtained by the zinc dust process. Zinc is first converted into zinc dithionite in an aqueous solution with sulphur dioxide and then by sodium hydroxide to sodium dithionite and zinc oxide. Later on, a process was developed which uses the sodium amalgam from the mercury cell electrolysis of sodium chloride solution and converts this directly into sodium dithionite with sulphur dioxide. This process produces a material which is free of heavy metals and so it is stable. Chlorine-alkali electrolysis in Europe is changing from the amalgam process to the diaphragm process due to the mercury content of the wastewater. BASF later developed the formiate process in which sodium formiate is converted with bisulphite into sodium dithionite. Sodium formiate is produced from carbon monoxide and sodium hydroxide. Dithionite can also be produced on-site using Borol by the Ventron process. Borol is a mixture of 12% borohydride ($NaBH_4$), 40% sodium hydroxide ($NaOH$) and 48% water. Dithionite is produced by the reaction of Borol with aqueous sulphur dioxide or sodium bisulphate. The reaction is as follows:

$$NaBH_4 + 8NaHSO_3 \rightarrow 4Na_2S_2O_4 + NaBO_2 + 6H_2O$$

Sodium dithionite is present in the bleaching solution with about 85% active substance. Sodium bisulphite and sodium perborate are also produced in the reaction. The process has been patented by Rohm and Hass Company. In this process solutions of sodium bisulphite and sodium borohydride, as Borol solution, are added sequentially and directly into a secondary paper pulp stream in medium or high-consistency mixing equipment at high temperature. This process shows better performance when compared to sodium dithionite bleaching (Meyers et al., 1999; Hache et al., 2001). It also offers economic advantages. The advantage of *in situ* production is that the preparation of the bleaching solution can be controlled. So, there is no loss of active substance due to the transport and storage of the naturally unstable dithionite solution.

Dithionite was used for the first time for bleaching of mechanical pulp in the 1930s. Initially sodium dithionite was used in small amounts as a powder. The bleaching effect was limited because the bleaching time and the temperatures were too low. Good results were obtained when atmospheric oxygen was excluded. With the introduction of continuous bleaching processes such as tower bleaching, the use of solutions of dithionite proprietary blends became necessary to ensure their homogeneous mixing with stock. Another option is the use of cooled, alkalized solutions of sodium dithionite. At temperatures below 10°C, these solutions are so stable that they can be stored for long periods. This eliminates the complicated process of dissolving the powder.

Dithionite is a stronger reducing agent in alkaline media as seen from the following redox potential. However, in some pulp and paper bleaching applications, acid pH is preferred.

$$HS_2O_4^- \rightarrow H_2SO_3,\ E^0 = -\ 0.07\ \text{V}\ \ \text{(in acid)}$$

$$S_2O_4^{2-} \rightarrow SO_3,\ E^0 = -\ 1.13\ \text{V}\ \ \text{(in base)}$$

Sodium dithionite undergoes three competing reactions in the pulp system:

$$Na_2S_2O_4 + H_2O + \text{pulp} \rightarrow \text{bleached pulp} + NaHSO_3 + H_2O \tag{5.3.1}$$

$$Na_2S_2O_4 + H_2O + O_2 \rightarrow NaHSO_3 + NaHSO_4 \tag{5.3.2}$$

$$Na_2S_2O_4 + H_2O \rightarrow Na_2S_2O_3 + NaHSO_3 \tag{5.3.3}$$

Reactions (5.3.2) and (5.3.3) are the wasteful side reactions. Reaction (5.3.2) with oxygen consumes dithionite with no bleaching effect. Reaction (5.3.3) forms thiosulphate, which can cause pitting corrosion. Formation of thiosulphate can be minimized by adding only the amount of dithionite needed, mixing the dithionite and pulp efficiently, and maintaining the process pH at the highest practical level.

Heavy metal ions such as iron and copper have a harmful effect on bleaching. Treatment of the pulp with chelating agents such as EDTA and DTPA has a favourable effect on bleaching efficiency (Melzer and Auhorn, 1981). Chelating agents are often premixed dry with the sodium dithionite by the supplier.

Reducing dithionite has a higher kinetic reaction rate as compared with hydrogen peroxide. Reaction time is significantly shorter in dithionite bleaching. Studies have shown that the bleaching reaction takes a few minutes. Bleaching is good at higher temperatures that favour diffusion of the dithionite ions into the fibre cell wall (Melzer, 1985). Due to the sensitivity of dithionite to oxygen, a separate bleaching stage is essential. So, a combination with the pulping stage of the stock processing operation is not possible as in case of hydrogen peroxide bleaching. Dithionite bleaching is usually performed at low pulp consistencies, because at low consistency air is low. The optimum consistency in case of dithionite bleaching is in the range of 3–5%. The bleaching chemicals are mixed and the pulp is directed into an upflow bleach tower so that the fibres reacting with the dithionite do not come into contact with the atmospheric air. At the top of the tower, the ambient air can react with unutilized dithionite and convert it into bisulphate and bisulphite. The homogeneous mixing and distribution of the bleaching chemicals in the pulp are very important because of the short reaction time. Good mixing reduces decomposition of dithionite through exposure to air. Low-consistency mixers and fluidizing MC pumps, which empty the air from the pulp slurry and simultaneously mix the bleaching chemicals, are standard components in the dithionite-bleaching process. By shifting the stock consistency into the more economical MC range, dithionite bleaching became a common practice in secondary fibre pulp processing. Dithionite bleaching is an important system in the deinking process when a colour correction by stripping dyes is necessary in addition to fibre brightening. Higher brightness is obtained at higher temperature. Brightness gain is more at temperatures beyond 60°C (Table 5.3.1) (Putz, 1987). At longer reaction time the stability is reduced as no residual is left. Thermal reactions then dominate and lead to yellowing of the pulp. At higher temperatures, brightness reversion is observed particularly for furnishes with a higher mechanical fibre content. Dithionite also converts into thiosulphate very rapidly at temperatures above 80°C accompanied by sulphur precipitation. For these reasons, the reaction times in dithionite bleaching of wood-containing DIP are usually short. A reaction temperature of about 60°C is common to reduce the energy consumption. Putz (1987) has reported that higher temperatures offer additional brightness advantages especially with dithionite dosages of more than 1% on o.d. pulp (Table 5.3.2). The brightness differences of recovered pulp treated at 40–80°C are lesser below dithionite dosage of 1%.

**Table 5.3.1 Effect of reaction time at different temperatures on brightness**

| Reaction time (min) | $\Delta R_{457}$ (% ISO) at different temperatures | | | | |
|---|---|---|---|---|---|
| | 25°C | 40°C | 60°C | 80°C | 95°C |
| 15 | — | — | — | 7.1 | — |
| 30 | 3.9 | 5.4 | 7.8 | 8.0 | 7.4 |
| 60 | 4.6 | 6.2 | 8.0 | 8.4 | 8.2 |
| 120 | — | 6.9 | 8.2 | 8.1 | 7.3 |
| 180 | 4.9 | 5.3 | — | 7.9 | 6.4 |

*Notes*: $Na_2S_2O_4$, 1%; pH 8.4, and consistency, 3%.
Based on data from Putz (1987).

**Table 5.3.2 Effect of dithionite dosage at different temperatures on brightness**

| $Na_2S_2O_4$ (%) | Brightness (% ISO) at different temperatures | | | | |
|---|---|---|---|---|---|
| | 25°C | 40°C | 60°C | 80°C | 95°C |
| 0.5 | 59.4 | 58.6 | 59.4 | 60.4 | 60.3 |
| 1.0 | 60.3 | 62.9 | 63.6 | 64.0 | 63.6 |
| 1.5 | 60.7 | 63.9 | 64.6 | 65.9 | 64.7 |
| 2.0 | 61.6 | 64.5 | — | 67.1 | 66.3 |
| 2.5 | — | — | 64.9 | 66.9 | — |
| 3.0 | 62.6 | 64.4 | 65.6 | 67.5 | 66.4 |

*Notes*: Reaction time, 60 min; pH 8.4; consistency, 3%.
Based on data from Putz (1987).

Bleaching results are lower compared with values at 80°C after a reaction time of 1 h at approximately 95°C. This is attributed to heat-yellowing and fast dithionite reaction. Polcin (1973) has suggested reducing the reaction time to 5–10 min at such high temperatures to prevent brightness reversion. pH is an important process variable in dithionite bleaching. Best results are obtained at initial pH of 6–7 with a dithionite dosage of 1% depending on the reaction temperature (Table 5.3.3) (Putz, 1987). Maximum increase in brightness is obtained at about pH 7.0 and above a temperature of 60°C. Higher dose of dithionite and higher reaction temperatures require higher initial pH (Table 5.3.4) (Putz, 1987). Because of the interaction between high temperatures and added amounts, the pH drops rapidly and therefore prevents an optimum reaction. The optimum pH range in the dithionite bleaching of secondary fibre pulp is in the neutral to weakly alkaline range, whereas in case of mechanical pulp the optimum pH is in the acidic range. Under practical operating conditions, the dosage of dithionite used in bleaching deinked pulp is in the range of 0.5–1% on o.d. pulp. Brightness gain of 4–7% ISO in wood-containing deinked pulp is obtained in case of medium-consistency bleaching. Better results are obtained in case of

**Table 5.3.3 Effect of pH at different temperatures on brightness**

| pH | $\Delta R_{457}$ (% ISO) at different temperatures | | | |
|---|---|---|---|---|
| | 25°C | 40°C | 60°C | 80°C |
| 4.0 | 4.2 | 5.5 | — | — |
| 5.0 | 5.9 | — | 8.0 | 8.6 |
| 6.0 | 7.0 | 8.5 | 9.3 | — |
| 7.0 | 5.5 | — | — | 9.8 |
| 8.5 | 4.5 | 7.4 | 9.2 | 9.0 |
| 10.0 | 2.3 | 5.4 | 8.2 | — |
| 11.0 | — | — | — | 5.2 |

*Notes*: $Na_2S_2O_4$, 1%; reaction time, 60 min; consistency, 3%.
Based on data from Putz (1987).

**Table 5.3.4 Effect of pH and dithionite dosage on brightness**

| pH | Brightness (% ISO) at different $Na_2S_2O_4$ dosages | | |
|---|---|---|---|
| | 0.5% | 1.0% | 2.0% |
| 4.0 | 59.9 | — | — |
| 5.0 | — | 63.1 | 61.6 |
| 6.0 | 62.6 | 64.0 | 63.9 |
| 7.0 | — | — | 64.6 |
| 8.0 | 61.7 | 63.9 | 64.8 |
| 10.0 | 59.5 | 63.2 | 64.1 |

*Notes*: Temperature 80°C; reaction time, 60 min; consistency, 3%.
Based on data from Putz (1987).

wood-free deinked pulp if coloured paper is part of the pulp. Fluet (1995) has reported that in case of mixed office waste, brightening and colour-stripping efficiencies are better at temperature of 80–100°C, pH of 7–8 and medium or high consistency. When temperature and consistency are both in the higher range, the retention time is short. There is some brightness reversion if the retention time is too long and the temperature is high. Kaichang et al. (2000) have reported that some detergents can enhance the efficiency of dithionite. Brightness reversion is more in case of dithionite when compared to FAS (Putz, 1987). Better results with dithionite are obtained in laboratory when compared to the mill (Fluet, 1994). Presence of air in the pulp slurry; poor mixing efficiency of the bleach liquor with the pulp particularly at high consistency in the mill environment; presence of metal ions such as iron and aluminium, presence of residual chemicals due to carryover especially of hydrogen peroxide; and unstable dithionite liquor could be some of the reasons for obtaining poorer results in mill. Conditions for dithionite bleaching are summarized in Table 5.3.5.

**Table 5.3.5 Bleaching conditions for sodium dithionite**

| Parameters | Values (range) | |
|---|---|---|
| | Low consistency | Medium consistency (or high consistency, disperger) |
| Dose (%) | 0.2–2.0 | 0.2–2.0 |
| Time (min) | 60–120 | 30 |
| Consistency (%) | 3–5 | 10–15 (30) |
| pH | 6–8 | 7–8 |
| Temperature (°C) | 60–80 | 80–100 |

Based on, the data from Ackermann (2000).

## 5.4 Bleaching with formamidine sulphinic acid

FAS has become a key chemical used for brightening and colour stripping of secondary fibres. The ability of FAS to effectively colour strip results in a substantial reduction in the filtrate colour as well. Different types of application such as in pulper, bleaching tower or disperser have been described (Fig. 5.4.1) (Kronis, 1997). FAS is a low-odour, crystalline reducing agent and can be used on all types of wastepaper. Its use is particularly recommended when using a furnish containing dyed paper. Its use as bleaching agent was first proposed in the textile industry. Process patented by Suss and Kruger (1983) proposes bleaching conditions for mechanical pulp and secondary fibre pulp that can apply in a single- and a two-stage process with other bleaching chemicals. FAS contains thiocarbamide sulphur dioxide according to the X-ray structure analysis. The material forms at low temperatures under acidic to neutral pH conditions in a reaction from two hydrogen peroxide molecules and one thiocarbamide molecule. FAS is a white to slightly yellow powder, odourless, and non-flammable. FAS is also known as thiourea dioxide. FAS is oxidized by atmospheric oxygen like all reducing bleaching chemicals, but compared to dithionite it is considerably less prone. This allows a wider range of application possibilities for bleaching not only as a separate bleaching stage, but also in combination with other stages of the stock processing operation. FAS also has a lower sulphur content compared to dithionite. This has an positive effect on the sulphate load of the white-water loop. The sulphate level in the bleaching effluent can be reduced by as much as 75%. As a result, the corrosion susceptibility of the equipment and instruments is lower. Also, the production of unpleasant odours due to hydrogen sulphide is lower.

FAS is slightly soluble in water and under alkaline conditions the solubility increases. Only about 27 g/L enter the solution as sulphinate, the solubility under alkaline conditions increases up to 100 g/L. The alkaline solutions of FAS has a higher solubility, but its aqueous solution decomposes very

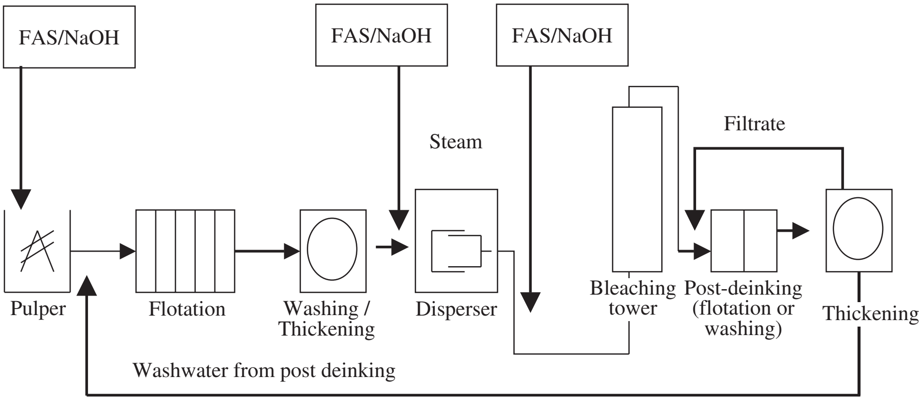
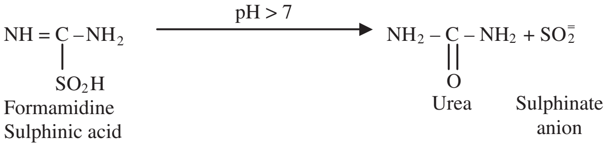


**Fig. 5.4.1. Opportunities for application of FAS in a deinking process. (From Kronis, 1994; reproduced with permission from Miller Freeman Inc.)**

rapidly. For this reason, alkaline bleaching solutions are prepared shortly before their addition in a continuous process. Consumption must then occur as soon as possible. FAS hydrolyses to the sulphinate anion and urea under heat and alkaline conditions as follows:



$$NH=\underset{\displaystyle SO_2H}{\underset{|}{C}}-NH_2 \xrightarrow{pH > 7} NH_2-\underset{\displaystyle O}{\underset{\|}{C}}-NH_2 + SO_2^{=}$$

The sulphinate anion has a high negative redox potential and is responsible for reductive bleaching (Fallon, 1994). Compared to dithionite, FAS has a slightly higher reductive potential when both chemicals are under alkaline conditions.

Important parameters for FAS bleaching include temperature, time, alkalinity and consistency. Consistency, in the case of FAS, is important only to the extent of the increased possibility of air entrapment in the pulp at the higher consistencies that would decrease the efficiency of FAS. Also of prime importance in determining the feasibility of using FAS is the furnish type and the degree of brightening or colour stripping required. With regard to the furnish, factors include the type of paper and the amount of wood-containing fibres; the amount of coloured grades used; the amount of ink blanketing on the fibre and the nature of the dyes present. Sodium hydroxide is commonly used as alkaline source. Most important process parameter of FAS bleaching is the reaction temperature, which is the most effective means of controlling the bleaching reaction. Kronis (1992) has reported that increasing the reaction temperature from 40 to 90°C almost doubled the bleaching result of a wood-free deinked pulp after a reaction time of 30 min (Table 5.4.1). At lower temperatures, increasing the reaction time is necessary for developing brightness. Increasing the reaction time alone is insufficient to compensate fully for the lower brightness level that occurs with lower temperatures. Only small quantities of FAS are necessary to perform effective bleaching if the temperature is set at an optimum value (Table 5.4.2) (Kronis, 1992). A brightness of about 72% ISO is obtained at a temperature of 80°C with only 0.2% FAS, whereas at a temperature of 50°C three times more FAS is required to attain the similar brightness.

Kang et al. (1999) and Taylor and Morrison (1999) have explored the possibility of using sodium silicate instead of sodium hydroxide and they have also examined the effect of chelating agents on FAS bleaching. Sodium silicate improves FAS bleaching by efficiently deactivating transition metals. Addition of chelating agents to the FAS stage in a FP sequence improved the bleaching of the FAS stage and also the subsequent hydrogen peroxide stage

**Table 5.4.1 Effect of temperature and retention time on brightness in post-bleaching of wood-free deinked pulp**

| Time (min) | Brightness (% ISO) at different temperatures | | | |
|---|---|---|---|---|
| | 40°C | 50°C | 70°C | 90°C |
| 0 | 65.0 | 68.0 | 70.0 | 70.8 |
| 15 | 71.2 | 74.2 | 77.9 | 79.6 |
| 30 | 73.3 | 76.0 | 79.2 | 80.6 |
| 60 | 75.8 | 77.7 | 80.4 | 81.9 |
| 90 | 76.7 | 78.3 | 80.8 | 82.5 |
| 120 | 77.1 | 78.8 | 80.8 | 82.3 |

*Notes*: FAS, 0.4%; NaOH, 0.2%; consistency, 4%.
Based on data from Kronis (1992).

**Table 5.4.2 Effect of temperature on brightness in post-bleaching of deinked pulp with different amount of FAS**

| Temperature (°C) | Brightness (% ISO) at different doses of FAS | | | |
|---|---|---|---|---|
| | 0.2% | 0.4% | 0.6% | 0.8% |
| 50 | 65.2 | 68.4 | 72.6 | 73.8 |
| 60 | 68.2 | 71.8 | 74.0 | 75.7 |
| 70 | 71.1 | 72.6 | 74.5 | 75.7 |
| 80 | 72.3 | 73.8 | 74.9 | 75.7 |

*Notes*: FAS NaOH = 2:1; brightness, Unbl. DIP = 55.0% ISO.
Based on data from Kronis (1992).

(Table 5.4.3) (Kang et al., 1999). This can be explained by the increased removal of transition metals from the pulp and reduced hydrogen peroxide decomposition. An additive effect is observed when both chelating agent and sodium silicate are added to the FAS treatment in a FP sequence. Significantly higher brightness can be achieved at higher temperatures. At lower temperature longer times are necessary for developing brightness. FAS performs very well in a hot disperser application because it operates at high temperature. Hot dispersing unit combines the benefits of high-intensity mixing with high temperature (90–120°C). In a hot dispersing unit, FAS is metered along with sodium hydroxide into the heating screw of the dispersing unit at a high consistency of 25–30%. The retention time in hot dispersing unit is up to 2 min. This is followed by a subsequent reaction at a lower consistency with minimum 15 min retention time. If the disperser is followed by a chest, a special bleaching tower is not required. For post- bleaching, FAS is added in a medium consistency pump and fed into a bleaching tube, in a tower or in a chest. The Works of Fluet (1995), Johnson (1997) and Kronis (1992) show that results are comparable with sodium dithionite and FAS. Kronis (1992) has reported that with coloured paper, FAS and Y provide comparable results and the economics slightly favour FAS. Fluet (1995) has reported that Y performs similarly to FAS on the same dosage basis on mixed office waste but at a lower cost. Compared to dithionite, the sulphate levels in the bleaching effluent are lower in case of FAS (Kronis, 1992). The formation of FAS *in situ* in the presence of pulp by consuming the residual hydrogen peroxide of a P stage is presented as a potentially cost-effective process (Fallon, 1994) but the safe handling of thiourea, which is a potential carcinogen, must be seriously considered. In this process, the residual

**Table 5.4.3 Effect of silicate and DTPA on FAS and FAS+P bleaching**

| Stage or sequence | Brightness (% ISO) | *B** value | Residual $H_2O_2$ of P stage (% on pulp) |
|---|---|---|---|
| F | 61.4 | 10.0 | — |
| $F_Q$ | 62.3 | 10.8 | — |
| $F_{Q+Si}$ | 62.7 | 10.6 | — |
| FP | 76.0 | 6.0 | 0.12 |
| $F_{Si}P$ | 77.5 | 5.7 | 0.18 |
| $F_QP$ | 78.1 | 5.3 | 0.32 |
| $F_{Q+Si}P$ | 78.6 | 5.3 | 0.37 |
| $F^*_{Q+Si}P$ | 79.4 | 5.1 | 0.42 |

*Notes*: F: 0.5% FAS, 0.25% NaOH, 90°C, 1 h; $F_Q$: 0.5% FAS, 0.2% DTPA, 90°C, 1 h;
$F_{Q+Si}$: 10% pulp consistency, 0.2% DTPA, 1% $Na_2SiO_3$, 0.5% FAS, initial pH 9.6, 90°C, 1 h;
$F^*_{Q+Si}$: 10% pulp consistency, 0.2% DTPA, 1% $Na_2SiO_3$, 0.5% FAS, initial pH 9.6, 90°C, 1 h, pulp slurry was acidified to pH 5 before washing.
Based on data from Kang et al. (1999).

hydrogen peroxide from a tower stage is acidified and thiourea is added. Then alkaline conditions allow the FAS bleaching to take place.

When both hydrogen peroxide and FAS are used in a deinking line, it is necessary to recognize that a residual of hydrogen peroxide will consume FAS, and vice versa (Kronis, 1997). This is especially important if FAS treatment immediately follows a hydrogen peroxide bleaching stage because of the significant hydrogen peroxide residual that normally results and the more expensive FAS that could be consumed. Conversely, a residual of FAS prior to hydrogen peroxide is normally not of concern because of the low levels of FAS applied and the negligible amounts remaining at the end of an FAS stage.

The reaction of hydrogen peroxide with FAS is shown below:

$$2H_2O_2 + NH_2C(NH)SO_2H + NaOH \rightarrow NH_2CONH_2 + NaHSO_4 + 2H_2O$$

For example, a residual hydrogen peroxide of only 0.05% on pulp can consume theoretically a minimum of 0.08% FAS on pulp, or 0.5 kg hydrogen peroxide can consume a minimum of 0.8 kg FAS. So, it is important to destroy or reduce the residual hydrogen peroxide prior to the FAS treatment. Thought should be given to having a post-flotation stage between the hydrogen peroxide and FAS. Dilution that occurs after the hydrogen peroxide treatment before flotation, followed by thickening of the deinked stock before the FAS stage, would ensure a negligible hydrogen peroxide residual. When hydrogen peroxide is used in pulper and FAS is used downstream, then there is little chance that hydrogen peroxide will exist until the FAS stage. If a residual of hydrogen peroxide needs to be destroyed immediately before FAS treatment, then bisulphite can be used. Bisulphite reacts with hydrogen peroxide according to the following equation:

$$NaHSO_3 + H_2O_2 \rightarrow NaHSO_4 + H_2O$$

Therefore, a residual of 0.05% on pulp would be destroyed with a minimum of 0.15% $NaHSO_3$ on pulp. Some important factors to consider based on the results indicated the following: applying hydrogen peroxide in the pulper and FAS in post-bleaching was favoured over both chemicals used in sequential post-bleaching; the alkalinity requirement for FAS in mill needs to be determined on a case-by-case basis because of the unique buffering capacity of a particular furnish; in the case of processing office wastepaper, chemical treatments alone do not appear to be as effective for brightening as having the capability of ink removal; a particular furnish mix should be examined on a case-by-case basis, although there may be a general trend developing favouring P-FAS over FAS-P as the wood-containing content of

**Table 5.4.4 Bleaching conditions for FAS**

| Parameters | Values |
|---|---|
| Dose (%) | 0.3–1.0 |
| pH | 8–11 pH is adjusted with 1 part FAS. 0.5 part NaOH |
| Pulp consistency (%) | 12–15 (medium consistency) 25 - 30 (high consistency) |
| Temperature (°C) | 80–120 |
| Time (min) | 15–90 |

furnish increases; and hydrogen peroxide alone is not as widely effective at colour stripping as FAS (Kronis, 1997). Conditions for FAS bleaching are summarized in Table 5.4.4.

## 5.5 Bleaching with oxygen

Oxygen bleaching of secondary fibres was reported for the first time in the mid-1980s. Improved pulp cleanliness is the most important benefit that can be achieved with oxygen bleaching of secondary fibres. This can be attributed to delignification of wood derived dirt, dispersion of hot-melts and wax, and the solubilization of binders that hold together flakes of coating, wet strength paper and ink. The brightness gains depend on the grade of secondary fibre. Putz (1995) has reported an alkaline yellowing of the pulp if there is a high groundwood content and the application of oxygen alone on a wood-containing pulp is not appropriate. Oxygen treatment is used for the production of writing and printing papers with high standards of optical quality or in processing wood-free deinked pulp as a chemical pulp substitute. In most cases, mixed office waste largely consisting of wood-free bleached fibres is used. Depending on the quality of sorting, this can be contaminated to some degree with coloured papers, unbleached fibres and other impurities. The oxygen bleaching of widely varying pulp compositions then levels the varying optical properties of the deinked pulp (Gehr and Borschke, 1996). Use of the oxygen stage for high-quality paper depends to a considerable degree on economic criteria. In North America particularly, the operation of the appropriate plants shows that their profitability links with the costs of cleaning, screening and bleaching and the treatment of the resulting residues. Industrially, the efficiency is in doubt. The market situation of virgin hardwood pulp also has a main influence since both types of fibre compete as the raw material for the production of wood-free paper grades. The success of the process is therefore linked to some degree to the political pressure for using secondary fibres. Oxygen bleaching represents an effective process step within secondary fibre processing, especially in cases where unbleached fibres influence negatively the optical cleanliness of wood-free deinked pulp. With increasing contents of unbleached fibres in recycled pulp, the advantage of the hydrogen peroxide-supported oxygen stage compared with hydrogen peroxide bleaching grows in importance.

Oxygen treatment is conducted at medium consistency (12–15%), high pressure 100 psi (7 bar), alkaline pH (9.5–10.5) and high temperature (100–110°C). The reactions of the oxygen bleaching process are very fast radical chain reactions. These reactions are called autooxidation and are responsible, particularly for degrading lignin and for forming hydrogen peroxide with the participation of the oxygen and its radical reaction products. The brightness increase that accompanies bleaching is due to the subsequent, relatively slow reactions of the hydrogen peroxide with the chromophores. Fig. 5.5.1 presents the reactions in oxygen bleaching. Several electrophilic (radical) and nucleophilic (ionic) reactions occur (Ackermann, 2000; Gratzl, 1992). These reactions result in the formation of many heterolytical and homolytical fragmentations and hydroperoxides. The hydroperoxides finally decompose. Gratzl (1992) has reported that homolytical reactions for other oxygen chemical bleaching stages such as hydrogen peroxide bleaching are unusable because they result in the decomposition of the bleaching agent, but processes involving radicals are absolutely essential at the oxygen stage. The electrophilic character of oxygen is very weak due to its very low reduction and oxidation potential. Increasing the temperature or activating the system using a base such as sodium hydroxide is necessary to initiate a reaction. The activation involves an ionization of functional groups, especially phenolic structures and structures with acidic hydrogen such as quinone methide in

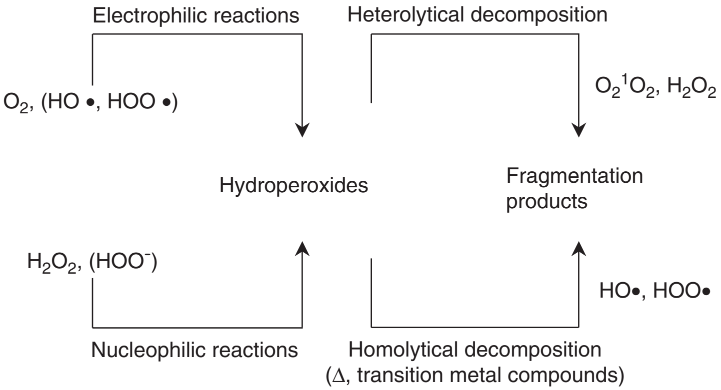


**Fig. 5.5.1. Reactions in oxygen bleaching. (From Ackermann, 2000; reproduced with permission from Fapet OY, Finland.)**

the lignin. Temperatures higher than 80°C are necessary to achieve feasible reaction times. Reactions on the contaminants, introduced with the secondary fibres in the oxygen treatment of deinked pulp besides those on the chromophores of the lignin, occur. This is in contrast with chemical pulp bleaching. This results in improved pulp cleanliness. Markham and Courchene (1988), Thomas et al. (1995a, b), Magnotta and Elton (1983) and Patt et al. (1996) have reported that following effects are important in this background: colour stripping of water soluble dye; delignification of wood-derived dirt particles; detackification of stickies; wet strength resin removal; improvement of laser and xerographic ink removal; fragmentation of adhesives such as hot melts and waxes; and solubilization of binders that hold together flakes of coating wet strength papers and inks.

Several researchers have studied the bleaching of secondary fibres with oxygen (Economou et al., 1996; Duxbury et al., 1995; Darlington et al., 1992; Kulikowski, 1991; Patt et al., 1996; Strasbourg and Kerr, 1998; Putz, 1995; Suss, 1995; Marlin, 2001, 2002a, b; Magnin, 2000). The optical effect improves as the oxygen content increases (Ackermann, 2000). Higher increase in brightness along with improved pulp cleanliness is obtained. Higher oxygen concentrations produce a stronger optical homogeneity, particularly for pulp mixtures having greatly fluctuating proportions of contaminants. Large gas bubbles are formed with large oxygen quantities particularly in medium consistencies. Some pulp is dragged along by their uncontrolled movement so the retention time is difficult to control. The pressure is often increased to keep the gas bubbles small. The most effective method is to ensure an optimum distribution of the oxygen in the pulp with suitable mixing units. Oxygen levels of 5 kg/t pulp will then be sufficient to provide the desired bleaching effects. Oxygen bleaching of secondary fibres with low mechanical pulp content (16%) has been examined by Economou et al. (1996). The furnish contained 40% kraft bags, 40% old corrugated containers, 10% coloured ledger and 10% newspapers. It was found that bleaching improved when the pulp consistency was increased to 25%. The dose of the sodium hydroxide was found to be the most important parameter. Increasing the dose of sodium hydroxide, reduced the kappa number by up to 56% and increased the brightness of the oxygen bleached pulp by up to 12.7 ISO points. When the amount of sodium hydroxide was increased beyond 6% (w/w), a noticeable drop in selectivity was observed while there was no change in the breaking lengths of the bleached pulp. The increase of oxygen partial pressure reduced the kappa number and increased the brightness. Breaking length of the handsheets improved slightly. Increase of oxygen pressure beyond 6 bar, reduced the selectivity of delignification and the tear properties. Ackermann et al. (1996) observed that oxygen treatment can cause a dramatic loss in brightness in the bleaching of wood containing deinked pulp due to yellowing of the mechanical fibre component. Only the addition of hydrogen peroxide can prevent this brightness loss. Air products has developed high-efficiency process under the trade name OXYPRO ($O_R$) for oxygen bleaching of secondary fibres (Duxbury et al., 1995). This process is found to be very efficient for bleaching and also very effective in removing the colour (Darlington et al., 1992). The colour-stripping is through the formation of various different oxidant species which may include some or all of superoxide radical ion, hydrogen peroxide ion, hydroperoxide ion, hydroperoxyl and hydroxyl radicals and also small amounts of hydrogen peroxide (Darlington et al., 1992). Depending on the furnish composition, the $O_R$ stage may also contain hydrogen peroxide. This treatment is found to be equal or exceed the colour stripping and brightening ability of sequences containing H, P, Z, Y and FAS. The $O_R$ stage is reported to improve optical homogeneity by removing the colour from dyed and brown fibres. Kulikowski (1991) has found that the treatment is effective for removing contaminants such as stickies, speck dirt, laser printed inks and wet strength resins. Duxburg (1995) has reported the optimization of the $O_R$ system for brightnening, colour stripping and cleaning of mixed office waste. Sodium silicate is found to have the most beneficial effect on the brightness. The incorporation of the $O_R$ stage in a mill deinking line (Weir, Scotland) has been successful. The $O_R$ stage can deal with high quantities of groundwood. Hydrogen peroxide was found to be very effective in increasing the brightness of high groundwood (20–30%) pulp. Patt et al. (1996) and Magnin et al. (2000) have reported that OP treatments are more effective than conventional P stages. The optical homogeneity is considerably better although the increase in brightness is little. The mottled appearance of mixed recovered papers containing brown fibres is found to be more effectively reduced. Duxbury et al. (1995) have found that the difference in brightness between P and OP stage becomes more distinct with increasing amounts of unbleached kraft fibres in a wood-free pulp (50% white ledger and 50% coloured ledger). Hydrogen peroxide bleaching under oxygen pressure OP in the case of pulp containing bleached chemical pulp and 10% brown fibres from kraft envelopes was studied by Marlin et al. (2001). Brightness difference between OP and P was found to be always positive (up to 10 points). It increased with temperature and with an increase in sodium hydroxide dose particularly at high temperature. The reason could be attributed to higher reactivity of oxygen with lignin at high temperature and high alkalinity. It was also found that the superiority of OP versus P is governed by the amount of oxygen and not by the pressure. Study on the bleaching kinetics of P and OP stages and O+P sequence revealed that at similar hydrogen peroxide consumption, the OP stage reached higher brightness value than P stage, indicating that oxygen had an additional action on the lignin when introduced into a P stage. Oxygen and hydrogen peroxide had an additive effect since the O+P sequence reached the same brightness as that of OP stage but the kinetics of OP was much faster than that of O+P. Strasbourg and Kerr (1998) have reported the use of oxygen in a deinking line that uses mixed office waste in a North American mill. This technology was found to be better for handling unbleached and semi-bleached fibre commonly present in mixed office waste furnishes. Without the oxygen, even a relatively small amount of unbleached fibre was evident in the final stock, whereas, with oxygen, it was possible to have up to 3% unbleached fibres in the furnish. Other studies (Putz, 1995; Suss, 1995; Marlin, 2001; Magnin, 2000) did not show any improvement by using oxygen in a hydrogen peroxide stage. According to Putz (1995), the bleaching results of an OP stage correspond to a P stage on a wood-containing pulp. An additional detachment of residual ink from the fibres is affected by mechanical forces in the high-shear mixer but not by an oxygen treatment. Hydrogen peroxide bleaching of a pulp mixture composed of 70% refined bleached chemical pulp and 30% refined unbleached mechanical pulp at various temperatures and various dose level of sodium hydroxide was investigated under oxygen pressure (Marlin et al., 2001). The additional brightness gain was by one point only at lower dose of sodium hydroxide (Table 5.5.1). The addition of a reductive stage after P or OP stage did not increase the brightness difference between OP and P stages. The inferior effect of oxygen in the case of mechanical pulp could be attributed to the creation of coloured quinone groups on TMP lignin during the oxygen treatment and due to the poor delignifying action of oxygen because of the higher molecular weight of TMP lignin and its lower amount of free phenolic groups (Marlin, 2002a). The efficiency of OP stage seems to depend on the composition of the waste papers, and on the process conditions.

**Table 5.5.1 Brightness after P and (OP) stages on fully bleached chemical pulp contaminated with 30% unbleached mechanical pulp**

| Temperature (°C) | Brightness (% ISO) | | | | | |
|---|---|---|---|---|---|---|
| | 1.5% NaOH | | 1.0% NaOH | | 0.5% NaOH | |
| | P | (OP) | P | (OP) | P | (OP) |
| 70 | 71.7 | 70.2 | 74.7 | 74.5 | 75.1 (68.7)[a] | 76.2 (59.3)[a] |
| 80 | 70.6 | 69.7 | 73.4 | 74.7 | 76.0 (76.4)[a] | 77.1 (78.4)[a] |
| 90 | 70.6 | 68.4 | 74.6 | 74.0 | 76.2 (69.8)[a] | 77.0 (66.1)[a] |

[a] Consumption of $H_2O_2$/ initial $H_2O_2$ (%).
Based on data from Marlin et al. (2001).

**Table 5.5.2 Effects of oxygen bleaching on deinked pulps**

| | | |
|---|---|---|
| Bleaching condition | High alkali application<br>High temperature | Low alkali application<br>Low temperature<br>Hydrogen peroxide addition |
| Wood-containing DIP | High delignification<br>High COD load<br>Loss of brightness | Low delignification<br>Relatively low COD load<br>Increase of brightness |
| Wood-free DIP | Delignification<br>High COD load<br>Low brightness increase | Low delignification<br>Relatively low COD load<br>High brightness increase |

Based on data from Gehr and Borske (1996).

Table 5.5.2 presents the effects of the oxygen treatment on deinked pulps (Gehr and Borscke, 1996). Best results are obtained with low dose of alkali with the simultaneous application of hydrogen peroxide at a temperature of 80°C. COD load is also reduced. The increase in brightness is usually 4–8% ISO points and even 12% ISO points in some cases.

## 5.6 Bleaching with ozone

Ozone is well known as a powerful oxidizer. It is also the only oxygen-based bleaching chemical able to destroy optical brighteners that enter the secondary fibre pulp primarily via wood-free writing and printing papers. Ozone transforms dyes into colourless compounds as a result of its high reactivity towards conjugated bonds (Karp and Trozenski, 1996). Ozone bleaching of secondary fibres has been studied by several researchers (Castillo, 1995; Muguet and Sunder, 1996; Kogan et al., 1994, 1995; Gangolli, 1982; Patt et al., 1996; Magnin et al., 2000; Roy, 1994; Abadie-Maubert and Soteland, 1995; van Lierop and Liebergott, 1994; Karp and Trozenski, 1996). A two-year cooperation between Ponderosa fibres and Air Liquide has resulted in the first commercial application of ozone for bleaching of secondary fibres (Muguet and Sunder, 1996). This proprietary bleaching process was started about a decade ago.

Ozone is a powerful oxidizer, second only to fluorine (oxidative potential: $O_3$, 2.07V; $F_2$, 3.03V and $Cl_2$, 1.36V). It oxidizes organic compounds containing mainly $>C=C<$ linkages which are oxidized to carbonyl groups $>C = 0$. Ozone also attacks the aromatic groups. Fig. 5.6.1 shows the scheme of reactions in ozone bleaching (Ackermamm, 2000; Gratzl, 1992). Ozone is a very strong oxidizing agent and owing to its mesomeric nature, oxygen can react with different ionic mechanisms. The heterolytical decomposition of ozone in which different polyoxide stages occur results in the splitting of $C=C$ bonds. The carboxyl and carbonyl groups are formed simultaneously.

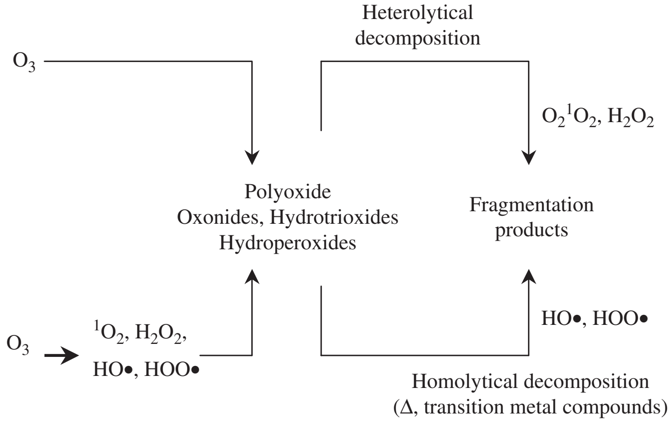


**Fig. 5.6.1. Reactions in ozone bleaching. (From Ackermann, 2000; reproduced with permission from Fapet OY, Finland.)**

Oxygen and hydrogen peroxide are formed *in situ* as part of this process. Aromatic and especially phenolic structures are also attacked by ozone and are decomposed into simple aliphatic acids. These reactions are not selective and last only a few seconds. Ozone has a limited stability in aqueous systems that leads to homolytical decomposition. This is one of its drawback. Decomposition of ozone is catalysed by the presence of even the negligible amounts of transition metal compounds, heavy metals or base ($pH > 3$). The radical reactions also result in degradation of carbohydrate structures, which is not desirable besides forming hydrogen peroxide and oxygen. Treatment with ozone also negates the effectiveness of various substances contained in the secondary fibre pulp (Ackermann, 2000).

Ozone is usually generated by corona discharge in pulp and paper applications. Ozone is a relatively unstable, reactive gas, and must be generated at site. The formation of ozone from oxygen is shown below:

$$O_2 + e^- \rightarrow 2O + e^-$$

$$O + 2O \rightarrow O_3 + O_2$$

Ozone bleaching is commonly carried out at high consistency. Medium consistency can be an alternative. Castillo (1995) has studied the effect of several process variables on bleaching. The effects of ozone dose (0.2–1%), temperature (25–45°C) and pulp consistency (30–45%) on brightness development were studied. Brightness depended linearly on ozone charge and pulp consistency. Low consistency decreased the final brightness due to the reaction of ozone with water. Temperature had no effect. Usually, acidic conditions are used for ozone bleaching of virgin fibres since metals ions accelerate ozone decomposition and a pH of 2.5 helps to solubilize and remove these ions. Chelating agents can also be used for inactivation of the detrimental ions. Some reports in the literature show that ozone can efficiently remove the dyes under neutral or alkaline pH also (Kogan et al., 1994). Study by Kogan and Muguet (1994) show that the radical reactions of the ozone caused by the increased concentration of OH ions can also lead to colour stripping of dyes although less effectively than at a low pH. Acidic conditions actually have many disadvantages such as the need for an acid, pH shock-inducing stickies problems, risk of $CaSO_4$ deposits, loss of $CaCO_3$, etc. (Muguet and Sundar, 1996). But in case of bleaching pulp for tissues, acidic conditions can be justified because low levels of ash are required for tissues. Highest increase in brightness was observed in case of fibre furnish containing either unbleached or semi-bleached chemical fibres. Very little or no bleaching effect was observed in case of secondary fibres containing high content of mechanical fibres. However, improvement of mechanical properties was noted (Gangolli 1982). Treatment of mechanical pulp with ozone affects the optical properties through both the light adsorption and light-scattering ability. Ozone bleaching is greatly influenced by the composition of the deinked pulp. Abadie-Maubert and Soteland (1985) and van Lierop and Liebergott (1994) have reported that improvement of mechanical or optical properties depends on the composition of wastepapers. Higher content of mechanical fibres exceeding 20% prevent any optical gain (Table 5.6.1) (Muguet and Sundar, 1996). This table also shows that higher brightness is obtained when ozone is used in combination with hydrogen peroxide. A larger proportion of mechanical fibres is beneficial for the development of strength characteristics. As a result of the formation of new carboxyl groups, an increase in fibre bonding accompanies the ozone treatment. This results in a significant increase in strengths such as tensile index and burst index. This effect does not occur with wood-free deinked pulps (Kogan and Muguet, 1994; Kappei and Matzke, 1994; van Lierop and Liebergott, 1994).

**Table 5.6.1 Effect of added mechanical pulp content on brightness development (MOW)**

| Total mechanical pulp content (%) | Brightness (% ISO) | | |
|---|---|---|---|
| | Control | Z[a] stage | ZP[b] stage |
| 5 | 65.0 | 72.6 | 77.7 |
| 10 | 64.0 | 69.1 | 75.0 |
| 20 | 62.3 | 64.0 | 70.5 |
| 30 | 60.9 | 61.9 | 67.2 |

[a] Z stage, 1.6% $O_3$.

[b] P stage, 1% $H_2O_2$.

Based on data from Muguet and Sundar (1996).

Several reports in the literature show that ozone is able to destroy fluorescence (Patt et al., 1996; Magnin et al., 2000; Kogan et al., 1994, 1995). Brightness increases (UV excluded or UV included) with increasing ozone dosage, but fluorescence decreases and 80% of the fluorescence is found to be removed at 1% ozone on a mixed white/coloured paper (Muguet and Sundar, 1996) (Table 5.6.2). Magnin et al. (2000) have reported that on DIP produced from 100% white office papers free of coloured papers, nearly 70% of the fluorescence can be destroyed with ozone. Due to the great number of the multiple bonds in dye structures and the high reactivity of ozone on these multiple bonds, ozone is considered to be an efficient chemical for colour stripping of dyed paper. Karp and Trozenski (1996) found that ozone exhibits similar bleaching characteristics to that of sodium hypochlorite when applied to a wide spectrum of colourants used to dye paper.

Air Liquid has developed the Redoxal process which is an ozone-based reductive/oxidative process combining Z, P and Y or FAS. ZP is found to be effective in bleaching a large range of furnish. Excellent optical properties, high colour removal and acceptable yield are obtained (Kogan et al., 1995; Muguet and Sunder, 1996). Hydrogen peroxide is used after ozone without washing to stabilize the previously achieved brightness, protecting the pulp from the brightness reversion. Other researchers have also obtained good results with ZPY combination in bleaching wood-free secondary fibres containing coloured papers (Magnin et al. 2000).

Ozone treatment allows almost complete destruction of optical brighteners. This is particularly important for using deinked pulps in papers used for food applications. For such applications, no chemical substances can transfer to the foodstuffs regardless of whether they represent a potential health risk. Considering the considerable costs involved, this effect may not offer sufficient reason to introduce an ozone stage within secondary fibre processing. Roy (1994) has reported that by using chemical quenchers, achieving a

**Table 5.6.2 Effect of ozone charge on the brightness development of mixed paper (white/ coloured ledger)**

| Ozone consumption (%) | Brightness (% ISO) | |
|---|---|---|
| | Without UV | With UV |
| 0.00 | 60.8 | 70.9 |
| 0.20 | 65.8 | 71.1 |
| 0.45 | 69.9 | 73.6 |
| 0.50 | 72.4 | 75.9 |
| 0.85 | 74.0 | 76.5 |
| 1.20 | 76.5 | 78.6 |

Based on data from Muguet and Sundar (1996).

**Table 5.6.3 Effect of ozone on brightness of wood-containing grades based on 50% old newspapers and 50% magazines**

| Ozone charge (%) | Brightness (% ISO) | |
|---|---|---|
| | Pulp A | Pulp B |
| 0.0 | 58.8 | 58.2 |
| 0.5 | 57.9 | 57.3 |
| 1.0 | 57.4 | 57.0 |
| 1.5 | 57.0 | 56.9 |
| 2.0 | 56.9 | 56.6 |

Based on data from Kappel and Matzke (1994).

comparable effect is possible in which the fluorescent materials are masked and therefore made ineffective. Kappel and Matzke (1994) have reported that the higher ozone content can even cause a small loss of brightness in case of deinked pulps produced from old newspapers and magazines (Table 5.6.3).

## 5.7 Bleaching with peroxyacids

Peroxyacids have been studied only on a laboratory scale for bleaching of secondary fibres (Kappadia et al., 1992; Thorp et al., 1995; Szegda, 1994; Walsh et al., 1993; Tschirner and Segelstrom, 2000; Dubreuil, 1995; Magnin et al., 2000). The most commonly reported peroxyacids are peracetic acid and peroxymonosulphuric acid (Caro's acid). Dubreuil (1995) has reported that at a temperature of 60–80°C, peracetic acid and Caro's acid react as electrophiles. They hydroxylate aromatic agents to facilitate the nucleophilic oxidative degrading in the subsequent bleaching stages. They are able to destroy optical brighteners like ozone or chlorine and chlorine dioxide. In addition, peracids oxidize alcohols and aldehydes to carbonic acids and can hydroxylate double bonds. This destroys the conjugation in chromophores. The disadvantages are the acidic reaction conditions that cause gypsum to form and reduce the pulp yield when carbonate is present. Potassium permonosulfate which is the salt of permonosulfuric acid has been proposed for the removal of colour (Kappadia et al., 1992). It was found to work well at alkaline conditions (pH 9–11) and a temperature of 70°C. This chemical has been proposed to replace sodium hypochlorite for repulping wet strength papers (Kappadia et al., 1992). It has been found that activated alkali metal persulphates repulp neutral/alkaline wet strength broke and decolourize certain dyes and optical brighteners more effectively than nonactivated persulphates (Thorp et al., 1995).

Mixture of peracetic acid and permonosulphuric acid (Pxa) has been found to be very effective for bleaching of secondary fibres (Szegda, 1994). This mixture is obtained by addition of acetic acid to Caro's acid. Pxa increases both brightening and colour removal of reductive bleaching agents used in the same sequence beyond the ability of hydrogen peroxide. Combination of Caro's acid and sodium chloride was used by Walsh et al. (1993) for removal of colour in wood-free papers. Caro's acid oxidizes the halide to the halogen which in turns removes the colour. Significant effect on lignin removal, ink removal and brightness improvement for low grades of secondary fibres having high lignin content was observed by peracid pre-treatment (Tschirner and Segelstrom, 2000). Better results are obtained when the mixture of peracetic acid and peroxymonosulphuric acid are used. Bleaching response in the subsequent alkaline hydrogen peroxide stage is significantly improved. The effects of peracids on deinking of mixed office waste are found to be less pronounced. Dubreuil (1995) and Magnin et al. (2000) have found that fluorescence can be destroyed by the use of peracetic acid, Caro's acid and potassium permonosulphate under acidic conditions. The considerable costs for the bleaching agent and the unsuitable pH conditions for deinked pulp are the most important reasons negating industrial application of peracids.

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# Chapter 6

# Closed-cycle bleach plant

## 6.1 Introduction

Environmental considerations, market demands and government legislation are forcing the pulp and paper industry to reduce its impact on the environment. Closed-cycle mills are a major step in this direction. A closed-cycle mill (i) offers more flexibility in the siting of new mills, including consideration of mill locations with limited fresh water resources, (ii) offers increased opportunities to maintain or expand production in environmentally sensitive locations, (iii) offers more favourable market and environmental evaluation of products including the provision of a more durable solution to future environmental standard, (iv) drastically reduces or even eliminates liquid discharges and the associated water quality problems, (v) separates and recycles valuable resources, (vi) preserves energy that can be used to reduce cost of production and amortize capital costs, (vii) saves on capital and operating costs for effluent treatment in addition to savings on chemicals and heat and (viii) reduces use of fresh water.

These prospects encourage the emergence of new and innovative zero liquid discharge or closed-cycle systems that when implemented in a mill, will enable the recovery of clean process water from the effluent and recycle it back into the mill. For many years, the pulp and paper industry has been in pursuit of a closed-cycle pulp mill. The driving forces behind this prolonged effort vary from company to company. It appears that one of the overriding goals has been to leave at least one environmental stage altogether, and to perhaps get government regulatory compliance agencies and environmentalists off the industry's back once and for all. In recent years, several economic driving forces have also emerged. Many companies are investigating effluent closure or at least minimum impact possibilities because they offer several economic benefits. For the most part, mills working towards minimum impact or bleach plant filtrate closure have not attempted to take advantage of this approach in the market place. Several mills in Scandinavia have placed totally effluent-free (TEF) or minimum impact mill (MIM) products on the market seeking premiums, but have not achieved any significant success. But effluent closure or minimum impact could become a fairly significant marketing tool for the pulp and paper industry in the 21st century.

The effluent-free concept, first proposed by Rapson in 1967 and pioneered by Great Lakes Forest Products Ltd., Thunder Bay, Ontario in 1978, involves the internal cycle of all the contaminated process streams to eliminate all pulp mill effluents (Reeve et al., 1979). Any closed-cycle technology must use a process for the removal of problematic compounds from the system. Industrial waste streams are very often complex aqueous mixtures of inorganic and organic solubles and then purification requires a combination of technologies with different specificities.

The closed-cycle or zero effluent mills is an attractive concept, since it responds to short-term environmental legislation as well as future legislation that could regulate additional effluent parameters and require tertiary effluent treatment systems, extensive testing of effluent contaminations, testing of effects on receiving waters, etc. Purification of industrial waste waters for process water reuse represents a major step in water savings and in closing the chemical processes. In view of the increasingly higher demands on the quality of mill effluent discharge, it appears advantageous to upgrade the secondary effluent by a suitable tertiary polishing stage and reuse the tertiary effluent in mill operations. This concept of effluent management might lead to complete closure of the effluent cycle in certain mills.

In the interest of reducing the environmental impact of pulp mill effluents, many companies are examining ways to modify effluent composition and reduce effluent volume. In the extreme, reduced effluent volume means a closed effluent-free pulp mill operation. The best and lowest-cost closed-cycle configuration is specific to every mill. However, in all cases, it is necessary to determine the appropriate combination of in-mill and ex-mill measures to achieve zero discharge at minimum cost. The ultimate goal of a closed-cycle mill is to have minimal impact on the environment.

## 6.2 In-mill and ex-mill measures to achieve mill closure

There is no single workable approach for mill closure nor is it likely. The optimum closure strategy for a given mill depends on the type of pulping and bleaching process employed. Kraft mills utilizing ECF bleaching sequences will have much more difficulty achieving closure and, of course, effluent-free ECF mills will still carry the stigma of producing pulp containing traces of organic chlorides. Several viable strategies are being proposed today for closing up ECF bleach plants depending on the amount of chlorine dioxide charged and the degree of washing in the bleach plant: (i) recycle of untreated alkaline effluent to the recovery loop and reuse of treated acid effluent to the recovery loop, (ii) recycle of untreated alkaline effluent to the recovery loop and evaporation of acid effluent with disposal of concentrate and (iii) evaporation of combined bleach plant effluent with disposal of concentrate. Table 6.2.1 presents the impact of each of these options on mill costs and operations (Ricketts, 1994).

The combined effluent evaporation approach is being promoted by Zerotech, a joint venture of Miller Western and NLK (Manolescu et al., 1994). Jaakko Poyry and Eka Nobel have also a joint project in collaboration with the Nordic forest products industry that presumably uses a similar approach for ECF mill closure (Anonymous, 1994a). With concentrate disposal, this scheme has the advantage of minimal impact on existing fibrelines and chemical recovery systems. The other two ECF closure strategies are similar in many respects. Both involve the following elements: (i) efficient bleach plant washing, (ii) increased evaporation requirements, (iii) increased solid loads to the recovery boilers and (iv) replacement of bleach plant caustic with oxidized white liquor to maintain sodium–sulphur balance. Reuse of acid effluent will probably require an additional metals removal process, since the acidic bleach plant effluent is the primary purge point for metal contaminants such as iron, manganese and others that are introduced with fresh water and raw materials. In addition, provision must be made for chloride ion removal somewhere in the liquor loop. This approach is being used by Champion International for closure of ECF bleaching kraft mills (Maple et al., 1994a, b). All closed-cycle ECF schemes that do not involve complete recovery of all bleach plant effluents must deal with the issue of dissolved solids disposal. If chlorinated organics were not a concern, the dissolved solid could be rendered inert and then landfilled. For bleached kraft mills using chlorine dioxide, the dissolved solids will most likely be incinerated with most of the chlorides removed as sodium chloride ash. This step in the ECF closure process is bound to receive close scrutiny by the EPA as an outgrowth of its regulation of chlorinated organics from municipal waste incinerators (Anonymous, 1994b). Before incineration, the effluent must be concentrated to support economical burning and

**Table 6.2.1 Impact of ECF closure strategies on mill costs and operation**

| Strategy | Operating costs | Capital costs | Increased risk of scale/ corrosion | Increased recovery load |
|---|---|---|---|---|
| Alkaline recycle/acid reuse | L | L–M | L–M | M |
| Alkaline recycle/acid disposal | M | M–H | L | L–M |
| Combined alkaline/acid evaporation and disposal | H | H | None | None |

*Notes*: L = low haze, M = moderate, H = high.
Based on data from Ricketts (1994).

to maximize water recovery. Mechanical separation (e.g. ultrafiltration (UF)) will only remove suspended solids (SS), not dissolved solids. Reverse osmosis will remove dissolved solids after most of the SS have been removed. This technology, however, may require prior biological treatment to remove organics. Evaporation of effluent using waste heat from incineration seems to be the most promising technology for concentrating dissolved solids. Several methods have been proposed for concentrating bleach plant effluents. These effluents streams pose particularly difficult problems when evaporated. At the higher temperatures associated with multiple-effect evaporation or even mechanical vapour recompression evaporation, organics are volatilized, contaminating the distillate with biological oxygen demand (BOD). The distillate cannot be reused without further treatment typically stream stripping, biological treatment or both. In addition, acidic effluents become increasingly corrosive at higher temperatures, requiring the use of expensive materials of construction. Alternative materials, such as plastic-lined carbon steel are being evaluated for this service and may offer significant capital cost savings. The freeze crystallization process offers some real advantages in that its low operating temperatures reduce corrosion rates and the release of volatiles (Patel, 1992). This technology is based on the Chetwynd mills experience. It must overcome some technical obstacles before being widely accepted. Until this happens, the technology of choice for effluent concentration probably will be mechanical vapour recompression evaporation followed by conventional multiple-effect evaporation.

TCF mills will be able to closeup their bleach plants by recycling the effluent directly to the chemical recovery loop. Most unbleached mills probably will develop closure strategies based on minimization of water usage using conventional technology with treatment of effluent for recovery and reuse using technology similar to that already in place at few high-yield mills.

A key element in progressing towards either a closed-cycle or effluent-free mill lies in reducing effluent volume to permit the economical treatment of process streams (Gleadow and Hastings, 1991). Considerations for decreasing process water use include: (i) the effect of washing and bleaching equipment, (ii) the reuse of evaporator condensates and machine white-water, (iii) the recovery of heat and water from process vents, (iv) the effect of debarking technologies and (v) the influence of water reduction measures on effluent treatment requirement and costs. Decreasing non-process water use, particularly for cooling service, dictates the separation and recycle of these streams. This requires attention to equipment specification and design, overall mill heat balances, process heating and cooling demands, requirements for cooling towers/surface condenser arrangement and control of cooling loads.

It is feasible to make the entire pulping and chemical recovery operation effluent-free. Systems closure in existing mills may be approached in stages. Steps to move progressively towards reduced effluent operation could include (i) brown line closure, (ii) liquor and chemical cycle spill control and pick up, (iii) separation of process and non-process waters, (iv) rationalization and mill-wide integration of the hot, warm cold and cooling water systems, (v) use of filtrate for wire-cleaning purposes, (vi) spill recovery for filtrate and fibre, (vii) use of medium-consistency (MC) bleaching stages, (viii) increased delignification before bleaching and (ix) installation of wash presses at the end of brownstock and use first bleaching stage filtrates for post-press dilution. These could be followed by partial and then full closure of the bleach plant. The approach taken would depend on the bleaching technology employed and how the bleaching effluent is taken particularly with reference to how the brownstock filtrate is treated. Almost universally, brownstock and post-oxygen filtrates are counter-currently washed, concentrated in black liquor evaporators and burnt in recovery boilers. Taking water use reduction, a step further, direct recycle of part of the alkaline extraction stage effluent from modern chlorine compounds containing bleaching sequences could be feasible if recovery boiler precipitator catch is sewered or leached to control chloride and potassium levels in the chemical recovery system. This would eliminate half or more of the COD and most of the colour discharged from the bleach plant.

The collection, concentration and combustion of bleach effluent in a separate dedicated system, can also be done separately. Conceptually, this is appealing. The existing chemical recovery processes are left undisturbed and this type of installation could be applied equally well in green field or existing mills. Technically, this option is considered a zero-effluent solution as opposed to a closed-cycle option. These ‘concentrate and burn schemes’ have the added advantage of removing from the closed-cycle, not only chloride ions but also potentially troublesome cations such as K, $S_1$, Al, Mn, Ca and Mg. The principal disadvantage is the additional capital cost of the separate bleach plant filtrate processing system and the additional operating cost for fuel consumed by the incinerator and the energy consumed by the bleach filtrate evaporator. An additional cost may be incurred for handling or disposing of the ash generated by the incinerator.

The only way of decreasing the amount of effluent is to replace fresh water by already used so-called ‘whitewater’ treated or not. The reuse of process water is, in most cases, possible without any treatment and this kind of recycling is a normal routine in all pulp and paper mills.

The basis for selection of an adequate treatment system is good knowledge of the process, as well as of the raw materials and their influence on the water to be treated. In addition, the result of the treatment has to be defined clearly taking into account how the different components react to different treatment methods and which components are to be separated from the water to make it reusable.

The method for water treatment has to be chosen based on the quality demands of the treated water. For example, is it necessary to remove SS, SS and colloids or all components? A coarse treatment classification can be made from the kind of treatment result achieved. These are the separation of (a) fibre, leaving pigments and other fines in the water, (b) SS, giving clear water, (c) colloidal substances, (d) dissolved substances and (e) inorganic salts. In principle, the water-treatment methods available to achieve the established goal are: (i) mechanical separation which can be amplified by using chemical coagulation and flocculation, (ii) biological treatment, (iii) membrane filtration and (iv) evaporation, distillation, and crystallization (freeze concentration).

Internal treatment of whitewater was originally introduced to retain otherwise lost fibre and filler which had a positive effect on the process economy. Later on, the separation of the solids from the water led to high-quality clear filtrate which could be used in showers on the wire part of the paper machine. In the case of several paper machines in a mill, the water savings can be phenomenal. Over and above, energy is also saved as the temperature is maintained. However, one has to be careful. Clear whitewater contains organic substances which act as carbon sources for bacterial growth. Elimination of primary SS does not eliminate the possibility of secondary SS. The bacterial growth (slime) can be very harmful as it can cause spray nozzles to become plugged. Slime problem can be taken care of by using chemicals, biocides, dispersants, etc. It can also be controlled by increasing the temperature of the system to higher than 50°C or maintaining a pH of 8.5–9, but both these methods are not possible in many cases.

Internal whitewater treatment must be economically feasible. Earlier, the recovery of valuable solids justified a simple so-called save-all treatment. But now, the price of water has increased as stringent rules and limitations are applied on effluent quality and the demand on fresh water quality has increased. Water used for cooling and sealing purposes should be kept clean but the situation is often the opposite. Whitewater is allowed to intrude the system and the water is rejected as waste. In this case, it is easy to find the reason of pollution and take the necessary preventive measures. Clean cooling water can be reused. The retention disturbing compounds should not be allowed to enter the paper machine system. In order to restrict the amount of disturbing components like anionic trash in the paper machine system in combination with low fresh water usage, it is necessary to isolate the pulping department from the paper mill. This can be achieved by high-consistency pulp transfer in combination with indirect heat transfer. The filtrate from pulp dewatering is treated for efficient removal of dissolved and dispersed substances in the first place. The counter-current principle need to be applied. This means that the clean (or treated) water is used on the paper machine and that excess, preferably clarified water is pumped to the pulping department. The pulp is transferred to the paper machine at high consistency (15–35%) in order to reduce the transportation of disturbing agents. The most polluted water should be collected at the pulping department and if so decided, treated biologically for reuse. While implementing this scheme, it is important to take care of the energy distribution through the production line. Pulp at high consistency does not transfer heat, but water does. The even distribution of energy has to be taken care of by heat exchangers, making it possible to maintain the correct temperature on the paper machine.

In cases, when water has to be free from SS, both particle size and concentration have to be defined as according to the definition, all particles above the size of 1–5µm are SS. Separation of SS is dependent on the technique employed. *Screening* is used when coarse material has to be separated whereas clarification is used when small particles are also to be separated. *Sedimentation* is the widely used clarification method. However, care has to be taken not to overload the system. Particles settle according to Stoke's law, in the gravity field at a certain velocity depending on their size and density. In order to achieve good results, flocculation aids are used. Floatation is feasible if the solids to be separated have a lower density than water or when small amounts of oil-like droplets have to be eliminated from the water. Clarification by floatation is achieved by the rising force of air bubbles attached to the particles.

Water containing SS can be filtered using a well-defined mesh or fine screen. The filtrate quality depends on the mat of fibres formed and usually water of different degrees of clarity is obtained from a drum filter or disc filter. Utilizing a bed of sand or a combination of different materials of different particle sizes, it is possible to effectively separate SS from water. However, this kind of filtration needs backwashing because the capacity of this type of systems for solid accumulation is limited. Sometimes, the use of semi-permeable membranes, especially the microfilters, are helpful in separating very fine suspended particles.

For removal of colloidal and dissoived substances, one of the methods is chemical precipitation. By applying certain poly-valent metal ions like $Fe^{2+}$, $Fe^{3+}$, $Al^{3+}$, $Ca^{2+}$, $Mg^{2+}$, it is possible to destabilize a part of the colloids and achieve coagulation which leads to adsorption on solids. Formation of metal-hydroxide enhances the separation and resulting solids are separated in conventional ways. The efficiency is dependent on the process behind the water to be treated. Lignin and fat-type colloids are partially separated but carbohydrates remain in solution. Efficiency, measured by COD or BOD, shows great variations. The application of metallic cations for coagulation is disturbed by complexing agents such as EDTA or DTPA used in the bleaching process.

Colloidal and dissolved substances can partially be removed from wastewater by *membrane filtration*, known as micro-, nano- and ultrafiltration. The efficiency, measured as COD and TOC removal, depends on the membrane quality (its material and openness) and volume reduction factor, among other parameters. Following are the general observations about the performance of membrane filtration processes. (i) typical flux for UF is 5–10m$^3$/m$^2$/day at a pressure of 1–5 bar, and for nanofiltration (NF), it is 1.5–2.5m$^3$/m$^2$/day at 10–15 bar, (ii) reductions of dissolved COD by UF is 10–50% depending on the source of whitewater or effluent; the corresponding TOC reductions are 15–50%, (iii) applying NF on the UF permeate, the reductions in COD and TOC are 65–95% and 70–90%, respectively of the original values and (iv) NF, also called as 'loose reverse osmosis', removes inorganics which is indicated by a reduction in specific conductance in the range of 40–85%. Thus, membrane filtration seems to be feasible as part of an internal water treatment system. UF has successfully been implemented for the recovery of pigment and binder in connection with coating of board and paper. Several types of whitewater and effluent have been studied on a pilot plant in connection with the Eureka project on 'Improved water reuse in pulp and paper industry' (Gartz, 1993).

It has been demonstrated that the biological treatment of whitewater improves the clarification considerably. The reason for the same is that the organic compounds stabilizing the fines in suspension are consumed by the bacteria present in the bioreactor. The primary carbon sources are the carbohydrates and extractives, the group responsible for poor first pass retention, poor dewatering on the wire and bad smell in the product. The introduction of internal biological treatment will improve the efficiency of conventional wastewater treatment systems. In addition, it will eliminate the possibility of secondary solids, as the carbon source is consumed in the bioreactor. However, the clear filtrate from the pulping has to be cooled before biological treatment if the temperature exceeds 30–35°C, supplemented with phosphorous and nitrogen and the pH has to be adjusted to neutral (7.0 ± 0.5). Several types of bioreactors and methods are available and the selection of optimum technology (aerobic or anaerobic) will depend on a case-by-case evaluation. In many mills, biological effluent treatment is already implemented which can be easily utilized for the same.

In order to make the biologically treated water useful in the process replacing fresh water, SS and possible colour have to be removed. This is most efficiently achieved by UF. It has been experienced that the flux through the UF membrane increases considerably compared to water prior to biological treatment which enables higher capacity for a given filtration area at constant pressure drop and temperature. The bacterial biomass partially binds chlorides which has been shown by the fact that the amount of chloride in dry matter was found to be 1500–3000ppm for biomass grown in a whitewater where the chloride concentration was 20–40ppm. However, under the conditions prevailing in biological treatment, heavy metals are normally precipitated as hydroxides, provided that the complexing additives like DTPA and EDTA are not used in excess. The biodegradability of these substances still remains questionable which can be evaluated using the existing bioreactors.

With the combination of biological and efficient after-treatment (membrane or chemical precipitation), it is possible to replace fresh water in the process. However, there are few important requirements that need to be considered. For example, (i) bioprocesses need nutrients in the form of nitrogen and phosphorous. These elements have to be added before the biological treatment in such a manner that the concentration in the treated water is lower than the incoming wastewater; (ii) biological process takes place at neutral pH and (iii) the after-treatment is needed in order to separate secondary SS (bacterial cells). With proper operation, the treated water will be free from components causing biological activity, retention and dewatering disturbances and thus be of acceptable quality for recycling.

The above referred treatments do not remove inorganics from the water and the overall salt content, measured as specific conductivity must be kept at, or below an acceptable limit by extracting part of the treated water as effluent. If waste heat of sufficient temperature is available, partial evaporation at low pressure can be feasible. The resulting salt solution has, of course, to be disposed of in a acceptable way. Alternatively, the inorganic rich stream may be cooled to crystallize out the salts.

## 6.3 Development of mill closure process

### 6.3.1 For kraft mills

There are several kraft pulp mills throughout the world that are actively involved in the development of closed-cycle technology, and some of these are already operating closed cycle (Gleadow et al., 1996, 1997, 1998; Albert, 1995; Gleadow and Hastings, 1995). Most notable among these being Champion International's bleach filtrate recycle (BFR) process, first put into commercial operation at the company's Canton, NC, mill in the mid-1990s, and Union Camp's C-free process at Franklin, VA, and elsewhere.

In addition to Champion and Union Camp, several mills around the world have made considerable progress in reducing effluent discharge per tonne of pulp production. Some mills are down to single-digit m$^3$ of effluent volume per tonne of production. These pioneer mills include the SAPPI Ngodwana mill in South Africa, the Metsa Rauma greenfield mill in Finland that started up in 1996, the Modo Husum mill in Sweden, Metsa Botnia in Kaskinen, Finland, the Munksjo Mill, Aspa Bruk (10 000 TCF), in Sweden, Sodra Cell at Monsteras, Sweden, the UPM Kymmene mill in Wisaforest, Finland, and the SCA Ostrand mill in Sweden, which is using a modified version of C-free. Other mills have also made progress towards effluent closure, but certainly these mills are among the world's leaders. Most of these mills are using ozone bleaching. All are recycling significant volumes of bleach plant filtrate. For example, SCA has been operating at around 5 m$^3$ of effluent discharge per tonne and is approaching total closure, and the Modo Husum mill is near 50% closure, with the remaining production at or below 5 m$^3$ / t. Aspa Bruk has been running at about 75% closure for some time with plans for total closure in the near future. Sodra has announced plans for closed-loop bleaching at all three of its mills (Johnson et al., 1996).

The first attempt to eliminate effluent from a commercial chlorine-based bleached kraft pulp mill (BKPM) was at the Great Lakes Paper Company's mill at Thunder Bay, Ontario, Canada, during the period 1979–1985. The operation was not successful, but this pioneering work identified many of the problems that must be solved to achieve bleach plant closure. Following a consideration of the Thunder Bay experiences, Reeve has outlined some of the developments required to eliminate discharge of effluent from a BKPM (Reeve, 1984). The corrosion caused by high concentrations of chloride in the chemical recovery cycle was a major problem in the Thunder Bay mill. This was one factor that influenced subsequent work on closure of bleach plants, with most of the effort being directed towards TCF bleaching sequences. However, there are two current developments that use ECF sequences. Commercially proven bleaching technologies and the high quality of the bleached pulp were reasons for the interest in these sequences. Moreover, there are a large number of ECF bleach plants throughout the world that may be able to retrofit the technology.

A joint venture between the Jaakko Poyry and Eka Nobel companies has developed a process for the closure of a bleach plant employing a D(EO)DD sequence (Myreen and Johansson, 1996). The acidic filtrates are circulated within the bleach plant and then taken to a novel treatment process. Some of the alkaline (EO) stage filtrate is added to the pulp mill recovery system, and the remainder is combined with the acidic filtrates. The combined filtrates are concentrated to a 50% solids content and oxidized with pure oxygen in a specially designed reactor. The alkaline brine from the reactor contains all the inorganic components present in the bleach plant filtrates. The heavy metals precipitated as carbonates are imbedded in the insoluble calcium carbonate.

The insoluble material is separated from the brine, and it is claimed that there are no problems with its disposal in an ordinary landfill. The condensate from concentration of the filtrates contains methanol. If this is removed, the condensate can be used as process water in the bleach plant. The process has been tested successfully on a large pilot plant scale at the Gruvon mill in Sweden.

The second approach is the BFR™ process (Fig. 6.3.1) that has been developed by Champion International Corporation (Canovas and Maples, 1995,1997). This process, which is based on a D(EOP)D sequence, uses an ion exchange procedure to remove nonprocess elements such as calcium and transition metals from the first D stage filtrate. The purified filtrate and the EOP filtrate are added to the chemical recovery system. Potassium and chloride are removed from the system by means of the preferential accumulation of these elements in the precipitation dust from the recovery boiler. Sodium sulphate and sodium carbonate are selectively crystallized from a solution of the dust and returned to the recovery boiler. Potassium and chloride salts are left in the filtrate for disposal. The second D stage filtrate has not been included in the recycling system so far, but it is claimed that this can be done by minimizing the additional chloride load with extended delignification or other measures, if needed (Maples et al., 1994a, b). The BFR process is being demonstrated on a commercial scale at the Champion mill in Canton, NC.

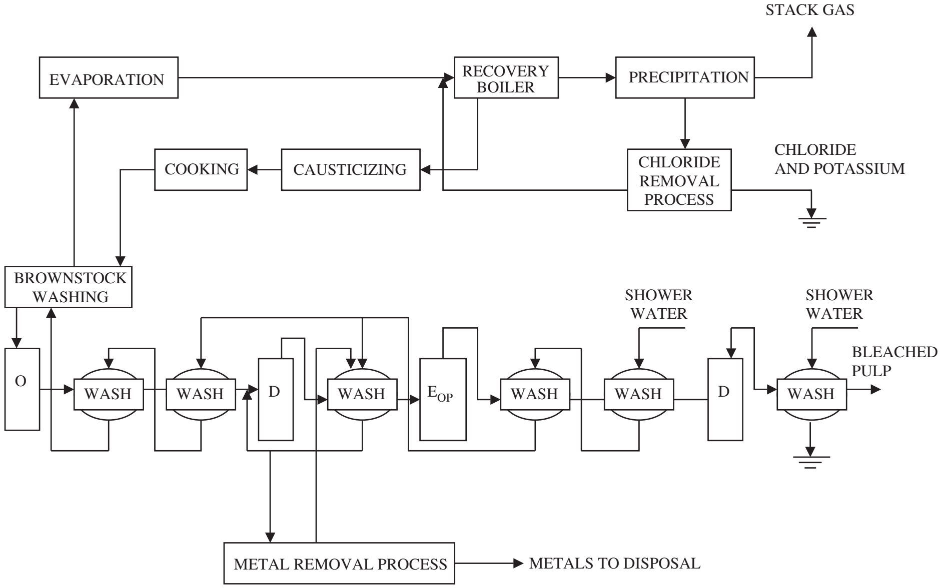

**Fig. 6.3.1. Overview of the Champion BFR$^{TM}$ process. (From Canvos and Maples (1997); reproduced with permission from Miller Freeman Inc.)**

Husum mill of MoDo paper AB, Sweden produces 690 000 ADI (air-dried tones) per year of kraft pulp on hardwood and softwood lines. It has looked towards in-plant process changes, as opposed to external treatment of effluents (Johnson et al., 1996) to meet effluent standards. Some development highlights with alkaline effluent recycle are as follows, (i) from 1983 to 1985, E, stage effluent was recycled from the softwood bleach line, which had been rebuilt as a D/CE$_{OP}$DED sequence with two wash filters after the E$_{OP}$ stage. This was stopped due to concerns over corrosion, as a new ultra-washer with a steel band was installed for brownstock washing, (ii) full-scale operation with UF was carried out from 1988 to 1992, with 40% of the E$_1$ stage effluent treated and (iii) TCF was developed for the hardwood mill with oxygen delignification installed in 1990 and ozone bleaching in May 1993. This enabled the mill to recover a large portion of the bleach plant effluent with close-up trials starting in the fall of 1993. Anticipated problems included increased solid wastes, difficulty in maintaining the soda–sulphur balance, increased black liquor evaporation requirement, slightly increased load to the recovery boiler and build-up of extractives in the birch line. During 1993, bleach plant effluent was reduced from 60 to 20m$^3$/t, (iv) initial trials with closure of the entire TCF bleach plant were held in 1993 and 1994. Further investments were made to improve control of the water balance, a major portion of which included a 2500m$^3$ filtrate tank, the same size as the post-oxygen storage tower and (v) the Husum mill began trials with closed prebleaching for hardwood in 1993, and now regularly produces hardwood pulp in a closed-loop fashion, marketed as MoDO balans. Bleach chemicals used include oxygen, ozone and peroxide, and the sequence currently includes 3–5kg ClO$_2$/ADT to decrease kappa number variations. Recycle of the ZP filtrates to brownstock results in increased chemical consumption during bleaching. Direct counter-current filtrate recirculation is used in the bleach plant, with fresh caustic used in the E$_o$ and P stages. At this time, the first two stages of bleaching are closed, with filtrate sewered from the last two bleaching stages, for regular hardwood production. For approximately 25% of the time, the line is run counter-currently, with no filtrate sent to sewer. The hardwood line averages 5m$^3$/ADT effluent, on a monthly basis. With closed–cycle operation, scaling problems have resulted in reduced productivity. The scaling problems are addressed through intensive mechanical cleaning.

The majority of the kraft mills developing closed-cycle technology are using TCF bleaching sequences with an ozone stage. Hydrogen peroxide stages are used in all of these sequences. Most mills are recycling the filtrates from the alkaline stages, but all or part of the filtrates from the acidic stages are excluded. These stages contain most of the heavy metals removed from the pulp and present the greatest challenge for final closure of the bleach plants.

The first step taken by the National Swedish Environmental Protection Board towards a closed kraft mill was oxygen bleaching, along with other internal measures, such as screen room closure, improved washing, condensate stripping and increased chlorine dioxide substitution (Albertsson and Bergkvist, 1973). Swedish pulp mills are currently recycling the E stage liquor to the recovery cycle. With $O_2$ prebleaching and high chlorine dioxide substitution in the chlorination stage, E stage effluent with and without membrane treatment has been burnt in the recovery furnace (Albertsson and Bergkvist, 1973). Chlorine was expelled from the system by liquor losses and flue gases to such an extent that accumulation never occurred. No corrosion effect was observed. The only problems experienced were the deposit and plugging in the recovery boiler and dilution to black liquor.

Andersson (1997) and Lindberg and Lund (1980) reported a nonpolluting bleach plant by counter-current washing and decolourizing and reusing the extraction stage effluent as wash water in the chlorination stage. The entire effluent flow was treated by ion-exchange resin and the condensate was stripped. The system reduced 90% of the effluent COD and colour, 60% of the BOD and significantly removed chlorinated phenols and guaiacols. The treatment system required half of the energy cost needed for an aerated lagoon treatment. A full-scale installation for a 250t /day kraft bleach plant has been in operation since 1973.

Dorica et al. (1986) proposed a complete effluent recycling system based on UF and reverse-osmosis membrane techniques. The concept was based on $E_1$ effluent colour removal by UF, chloride removal from the ultrafiltration filtrate and C-stage effluent by reverse osmosis, and separation of chloride from the UF/reverse osmosis concentrates by diafiltration or reverse osmosis. The chloride-lean $E_1$ filtrate and C-stage effluents were recycled. The chloride-rich diafiltration filtrate had the potential to be used for generation of sodium chlorate and chlorine dioxide, whereas the organic material in the concentrate could be incinerated. The cost of UF and reverse osmosis was higher than that of the Rapson and Reeve closed-cycle bleach plant.

In Sweden, research studies on bleached kraft mill systems closure have been initiated by the Swedish Pulp and Paper Research Institute in Stockholm (STFI), and by pulp and paper companies, equipment suppliers and consultants. Details of most of the research are not generally available because the TEF or closed–loop bleaching (CLB) issue is seen as a competitive one because it is believed that TEF pulp mills naturally supersede TCF pulp in the western European marketplace. Many of the leading Swedish bleached kraft pulp manufacturers are planning and have been conducting mill trials with recycled alkaline stage filtrates ($E_{0P}$ and P stages). There has also been a number of mill trials with peracetic acid or ozone-free TCF bleaching and a growing recognition that ozone may neither be necessary nor desirable for high strength and brightness TCF bleaching. The cooling of interest in ozone has been enabled by advances in peroxide and oxygen bleaching and extended pulping technologies. Since 1994 Aspa has been running trials with peracetic acid, involving a secret pretreatment stage followed by PaaQP stages. Use of Paa allows the production of fully bleached pulps without the strength loss associated with ozone. The Paa stage is in a milder pH range than an A or Z stage, and thus recycle of filtrates is possible without metal deposition common to an acid–base–acid filtrate recycle arrangement. Since 1993, Aspa has been recycling all of the alkaline nitrates to brownstock washing and has been experimenting with using some of the Q-stage filtrate in recausticizing. The points of filtrate addition include lime mud dilution, mud washing and the smelt dissolving tank (Johnson et al., 1996).

Union Camp Corporation (Franklin, VA) has selected an OZ($E_O$)D sequence over an ODED sequence as the former met the needs for effluent recycle (Johnson et al., 1996). With this sequence, Union Camp pioneered and installed a high-consistency ozone bleaching line designated C-free. Both the O and Z stages are at high consistency and an 84.5 GE brightness pulp is produced. Filtrates from O, Z and $E_o$ stages are sent back to the recovery via counter-current washing with a bleed of part (2.1m/t) of the Z stage to prevent scaling. The final D stage (7.3m/t) is open to sewer. The mill can run up to 88 GE brightness. Fig. 6.3.2 shows the Franklin Fibreline. Union Camp has conducted many trials while the acid (Z) purge is reduced or eliminated using three strategies: (i) modification of the chemistry; (ii) use of additional processes; and (iii) manipulation of the internal filtrate flow configuration.

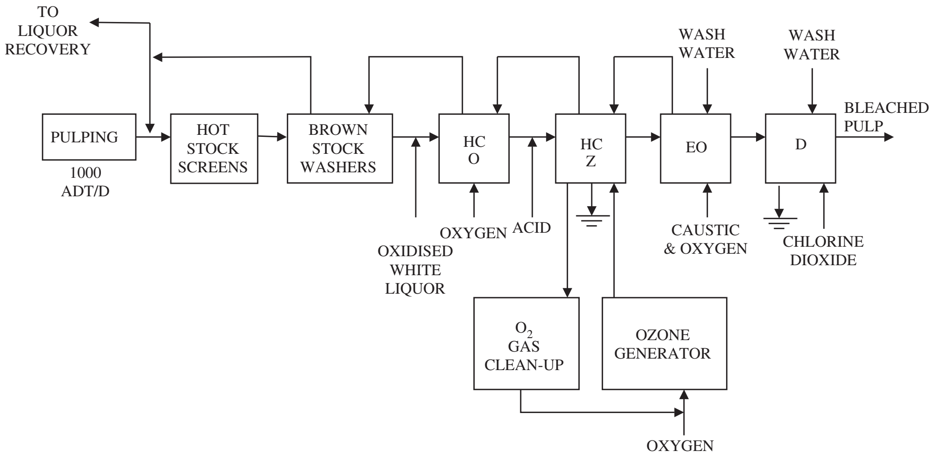

**Fig. 6.3.2. Union Camp Franklin Fibreline. (From Johnson et al., (1996); reproduced with permission from Appita.)**

Weyerhaeuser Paper Company (Tacoma, WA), which is the world's largest producer of market pulp, is supporting the demonstration of technology that may be useful in closed-cycle implementation (Johnson et al., 1996). This includes pilot operation of the MTCI pulsed bed black liquor gasifier at their New Bern, NC, kraft mill. Weyerhaeuser's minimum impact mill model is one that has accepted full accountability for the impact of its operations on the environment, is committed to continuous reduction of air, water and solid waste discharges, achieves discharge levels that are recognized as being minimum impact using sound science and maintains product performance and purity. In order to monitor and benchmark performance towards a minimum impact mill, over 30 parameters relating to water, air and solid waste discharges are used. The concept is shown in Fig. 6.3.3.

Louisiana-Pacific (LP) Corporation (Samoa, CA) is unique in North America in its Swedish style embrace of in-plant TCF and closed-loop bleaching technologies, instead of external treatment as the means to satisfy environmental needs (Johnson et al., 1996). The LP mill was exempted from the clean water act requirement that bleached kraft mills install external effluent treatment, and proceeded with the in-plant modifications to reduce effluent parameters. The mill has an extensive liquor spill collection and recovery system. Since January 1994, Samoa has produced only TCF pulp and demolished its chlorine dioxide generators. Samoa uses a continuous digestor, built in 1965, with a 700/day capacity by use of soluble

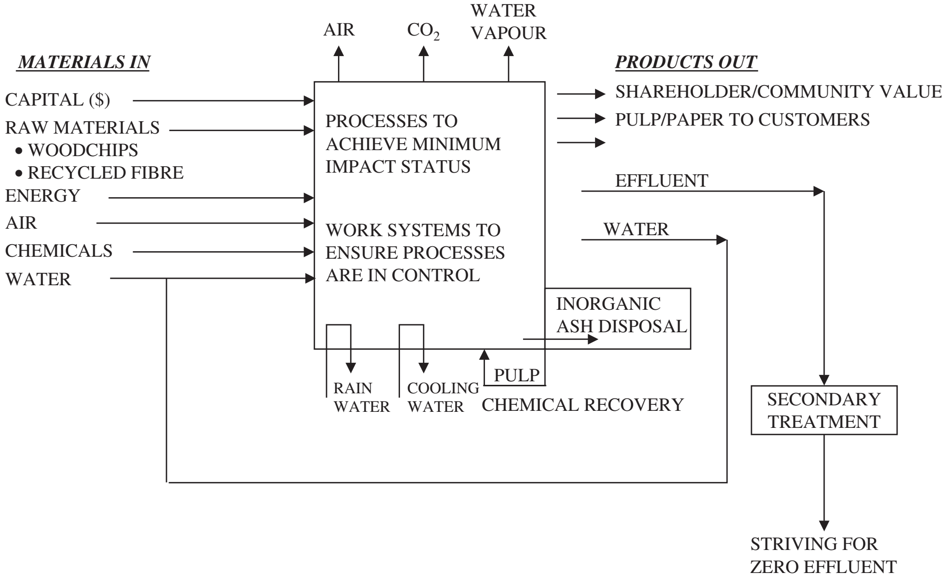

**Fig. 6.3.3. Weyerhaeuser minimum impact mill model. (From Johnson et al., (1996); reproduced with permission from Appita.)**

anthraquinone (AQ) and a retrofit to Lo-solids consistently to achieve a softwood kappa of 16. The stock is washed in three vacuum filters, followed by closed screening installed in 1987, and MC single-stage oxygen delignification to kappa 8–10. Oxygen delignification is followed by a CB filter and vacuum washer. The bleach plant uses towers originally designed for a CEDED sequence and runs using a $QE_{OP}PPP$ sequence. The mill has a new low-odour boiler, installed in 1990, which meets all mill steam and electric power demands and exports both steam and electricity to neighbouring domestic and manufacturing users. Steam stripping of foul condensates is used and, on start-up of this system in 1994, the mill COD was halved. The mill has an advanced noncondensable gases (NCG) collection system with co-firing of NCGs in the lime kiln, and a dedicated incinerator with the ability to transfer load without venting, should either combustion source fail. The only bleach plant effluent discharged is from the chelation stage and this was determined to be 6.76m$^3$/t. This is the lowest known bleach effluent flow for a continuously operating bleach plant. Fig. 6.3.4 shows filtrate recycle in the LP bleach plant.

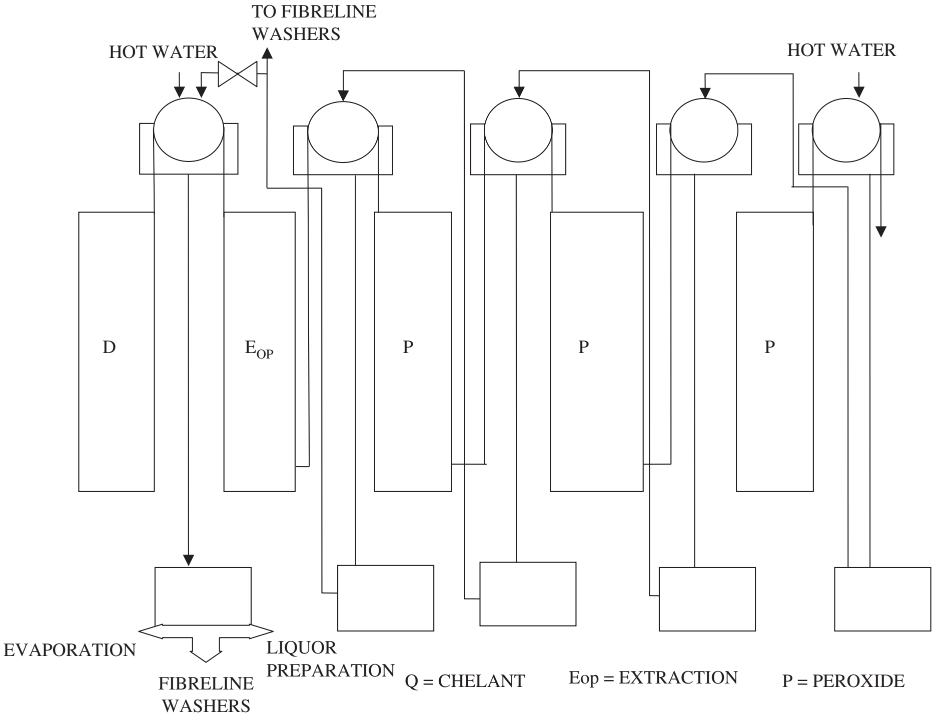

**Fig. 6.3.4. Louisiana–Pacific bleach plant filtrate recycle. (From Johnson et al., (1996); reproduced with permission from Appita.)**

Canadian pulp and paper companies, in conjunction with the Canadian Government, announced a 5 year C$88 million research project with the goal of creating commercially viable closed-loop mill technologies designed to reduce wastewater effluents and air emissions in October 1996 (Ferguson and Finchem, 1997). According to a CPPA statement, the programme shifts the research focus from pollution treatment at the end of the pipe to pollution prevention inside the mill. Mills will, therefore, be able to recover trace chemicals, raw materials and water from the waste stream and reuse them.

Ahlstrom Corporation has undertaken parallel development of closure technologies for both bleaching strategies—ECF and TCF (Ferguson and Finchem, 1997). They have looked at cooking, washing, bleaching and chemical recovery issues. Scaling had been the major obstacle for most mills. In fact, several mills that are progressing well in their closure efforts are sewering effluents to manage scaling. This could actually reduce effluent discharges without affecting product quality, except for the scaling problems. The overall result of all of Ahlstrom's efforts is the start-up of a Finnish softwood TCF market pulp mill that has a bleach plant effluent discharge of 5m$^3$/metric ton of pulp and total mill discharge of 15m$^3$/metric ton—among the lowest in the world. Their drum displacement washer technology, which effectively splits bleach plant filtrates, allows for very selective filtrate reuse. One of the other challenges Ahlstrom is addressing is evaporator condensate cleanliness. They have also developed a stripper technology which, combined with the company's evaporator technology, is capable of reducing condensate BOD by 98%. Although they have not demonstrated this combined technology in a full-scale mill setting, the combination has important implications for reducing the fresh water demand of a mill. Ahlstrom think that it may be possible to use some condensates on pulp drying machines, which is a major step towards reducing the effluent volume. They have also developed technologies to precipitate and filter NPE from bleach plant process streams; improve green liquor filtration; and separate mill sulphur process streams, converting reduced sulphur compounds into oxidized sulphur compounds and ultimately to sulphuric acid for use in the bleach plant. Parts of these technologies are present in different mills. At the moment, no single mill has all of the technologies, but this is expected to happen soon.

Over the past few years, Sodra Cell has made a concerted effort to achieve its goal of becoming 100% TCF at all three of its bleached kraft mills (Johnson et al., 1996). Sodra has an 8-day aerated lagoon for effluent treatment at its Monsteras mill, and primary clarifiers at its Morrum and Varo mills. Monsteras has a capacity of 335 000 ADT/year and produces ozone-based TCF softwood and hardwood pulps in campaigns on one line. Monsteras started its ozone bleach plant in September 1992. Sodra is expanding production capacity at Monsteras by 60% for a daily production capacity of 1700 t. Sodra is rebuilding its Morrum mill for TCF and expanding production by 44 000 ADT to 415 000 ADT/year. The Varo mill has a capacity of 315 000 ADT/year softwood pulp, produced on one line. Varo currently produces TCF without ozone using a sequence based on hydrogen peroxide. Varo is installing increased evaporation capacity to boost capacity from 345 to 385 t/h of evaporation and solids from 68% to 75%.

Beloit Corporation and its acquisition—IMPCO—has a long history of effluent reduction efforts (Ferguson and Finchem, 1997). Some of these efforts date back to the late 1960s, with technologies for nitrate recirculation and returning effluent back to the recovery. Some of this work included the use of nonchlorine options such as oxygen, ozone and peroxide. In 1973, IMPCO worked with Scott Paper to jointly pilot the first ozone-based sequence, a 10 t/day project that produced 2 $m^3$/t of effluent. Beloit has done extensive pilot scale work on the alkaline sulphite, anthraquinone, methanol (ASAM) pulping process at a pilot facility in Bainfurt, Germany. The process has been combined with a TCF bleaching sequence and full countercurrent recirculation of effluents. This pilot plant work has confirmed an effluent volume of 2 $m^3$/t. Based on laboratory and pilot plant work with its RDH cooking technology, Beloit has teamed with Sodra's mill at Morrum, Sweden, to build a very low-effluent flow fibreline. The RDH system cooks softwood to kappa 12–13 instead of the original kappa 28–30 the mill had prior to installation of the RDH system. The oxygen system further reduces the kappa to 9–10 entering the bleach plant. At the same facility, hardwood is now cooked to kappa 12–13 instead of the orginal 18–20. The oxygen system on the hardwood line further reduces the kappa number to an average of 8 entering a TCF bleach plant. The bleach plant has an effluent discharge of less than 4$m^3$/metric t of pulp. The combination of RDH cooking, $O_2$ delignification and peroxide bleaching allows Morrurn to produce a 90% ISO pulp. The key to closure of this system has been increased yield in the cooking system and bleaching with only peroxide. Beloit also provides several other components to reduce effluent volume, including multistage oxygen delignification based on the two-phase kinetics of oxygen and a high-temperature peroxide process (called PHT) jointly developed with Paprican. This hot peroxide technology is easy to retrofit with existing peroxide stages and, in conjunction with an ECF sequence, dramatically reduces the amount of peroxide needed for efficient bleaching. In addition, Beloit has installed ozone systems—one for chemical pulp and one for secondary fibres—and promotes both medium- and high-consistency ozone depending on specific mill needs—as a supplement to ECF and TCF bleaching sequences.

Eka Nobel has initiated a joint project to demonstrate technical solutions for eliminating bleach plant effluent in mills using chlorine dioxide based

ECF bleaching processes (Johansson et al., 1997). Results are encouraging, indicating a strong potential for success with no corrosion problems and a reasonably low-energy demand for the process. TCF advocates often argue that chlorides formed from chlorine dioxide in bleaching prevent recirculation of bleach plant process water. If not managed, chlorides can accumulate in the mill's recovery system and ultimately lead to severe corrosion and operating problems. However, there are realistic options to avoid these problems. Bleach plant filtrates need not be recirculated into the mill's chemical recovery system. They can be treated separately. Thus, no change in processing conditions prior to the bleach plant are required. With separate treatment, other problems are also solved. In both ECF and TCF bleaching, non-process elements brought in with the wood are dissolved in the pulp slurry. These elements include silica, aluminium, manganese and potassium and must be balanced. Eka Nobel's TEF bleach plant approach involves the following process steps: (i) water volume reduction, (ii) the method and cost of evaporation of bleach plant waste liquors, (iii) purification of evaporator condensate before reuse in the mill and (iv) electrodialysis to purge chlorides and recycle them back to the chemical recovery system. Eka Nobel estimates that it is necessary to reduce process water volume to less than 15 $m^3$/t of pulp before evaporation and electrodialysis become economically feasible.

Stora Billerud is working generally in the area of water reduction and closing the water cycle in all of their mills (Johnson et al., 1996). The Gruvon mill of Stora bleaches part of their production with a DEDED sequence and has reportedly reduced its bleach effluent flow to ~12 $m^3$/ADT. Gruvon is also using carbon dioxide addition in the brownstock line to improve washing of both COD and soap. The Skoghall mill has a pilot plant pressurized Chemrec gasifier located on-site and also has pilot plant facilities for a cooperative research programme. The programme focus is on the ECF closed-cycle and partners in the research include Jaakko-Poyry, Eka Nobel, Metsabotnia and Kymmene. The approach used consists of evaporation of bleach plant effluents to optimum concentration, purification of the condensates so that they can be used as process water, incineration or thermal oxidation of the remaining solids in an acceptable way, and final treatment of the inorganic slag obtained by incineration. The pilot plant includes evaporation, thermal oxidation, flocculation and an electrodialysis unit. The pilot evaporator utilized is a plastic-filmed desalination style unit and is supplied by Hadwaco. Another mill of Stora-Vallvik in Sweden is installing a pressurized peroxide stage for 800 ADT/day softwood to make full brightness TCF. The mill has shown some interest in water systems closure and has been performing trials using peracetic acid in bleaching.

The Finnish industry has adopted efficient effluent treatment technologies and is also competing with Sweden's in-plant and TCF technologies, predominantly for market reasons (Johnson et al., 1996). Metsa-Rauma (MR) has constructed a new 500 000 ADT /year TCF softwood pulp mill in southern Finland. MR expects the TCF sequence to offer advantages both in the marketplace and in reducing bleach plant flows. The mill has incorporated Sunds super-batch digesters and an Ahlstrom oxygen delignification system. Bleaching uses oxygen, peroxide and MC ozone bleaching technology. Metsa Botnia mill has been steadily increasing TCF production at both Kemi and Kaskinen mills since first producing TCF in 1991 with enzymes, oxygen and peroxide at 82% ISO brightness for softwood and 85% ISO for hardwood. Kaskinen's objective is to develop a completely closed cycle. Total mill effluent flow is around 50 $m^3$/ADT and, over the last 10 years, the COD, BOD and AOX loads have been reduced by 50–90%. Partial return of alkaline filtrates was achieved in 1992. There are ongoing trials towards achieving closed cycle both for Kaskinen and to support the development of the new Rauma mill. Kymmene, Wisforest capacity is 580 000 ADT/year bleached hardwood and softwood pulps, of which TCF capacity is 280 000 ADT/year. It has secondary treatment and was the first mill in Finland to implement both oxygen delignification and ozone bleaching. It has been reducing its bleach nitrate effluent streams over the past several years and current process water use is 25 $m^3$/ADT. The mill would like to cut this to half. The ECF/TCF fibreline uses six conventional and two super-batch digesters followed by oxygen delignification. The ECF bleach sequence used is $O(ZD)(O/E_0)(ZD)(EPD)$ and the TCF sequence is O(ZQ)(OP)(ZP). Process water use averages 25 $m^3$/ADT. While on TCF production, the mill uses 15 $m^3$/ADT and is trying to attain a level of 10 $m^3$ /ADT. The mill is also working towards closure of air emissions, with all strong odours and 85% of weak odours collected. The target for sulphur dioxide emissions was 0.15 kg/ADT and the total of all gaseous sulphur compound emissions was less than 0.3 kg/ADT by the end of 1995.

Mills in South Africa and Australia have been leaders in low water use due to the arid climates of these countries (Johnson, 1996). There is active closed-cycle research in New Zealand and Australia. The new Chilean and Brazilian mills' environmental performance is world class. Specifically, environmental performance at the Brazilian mills Riocell and Bahia-Sul is among the world's best (Johnson, 1996). In South Africa, Sappi's pulp paper and board mill, Ngodwana, Transvaal has been at the forefront of efforts to reduce water use for the last 15 years. It is located in an arid area and stores water for up to a year before use. Effluent cannot be discharged back into the river because of sensitive agricultural uses downstream. The mill irrigates all of its effluent on pastures. The mill manufactures 1500 t/day of final product. This comprises bleached pulp, unbleached pulp, newsprint and liner board. Kraft pulping capacity is 1220 ADT/day and bleaching capacity is 550 ADT/day. The mill water use is 33 million L/day and effluent flow to irrigation is 24 million L/day (16 m/t of product). Concern for the long-term viability of irrigating chloride-containing effluents initiated an extensive research programme into alternatives. These include investigation into the Rapson–Reeve concept and a number of other closed–cycle processes. Sappi developed a bleach effluent recovery process suitable for chlorine and chlorine dioxide containing bleach sequences, based on separate effluent concentration and incineration using a magnesium-based recovery process. This process can offer a positive return on investment because of the recovery of bleach plant chemicals.

Solvay Interox, a hydrogen peroxide producer, is pursuing technology to improve the effectiveness of peroxide bleaching (Ferguson and Finchem, 1997). The success could give mills the opportunity to choose either very efficient pressurized peroxide bleaching, or using their recovery cycle effectively to manage metals in their bleach plant filtrates as they move towards closure. Of course, as the bleaching power of pressurized peroxide stages is substituted for chlorine dioxide, both organic and inorganic chloride levels can be reduced, making filtrate recovery less complicated. Controlling the presence and behaviour of transition metals is the key to optimizing the performance of hydrogen peroxide–based delignification and bleaching stages. Under alkaline pH conditions, kraft pulps have a stronger chelating affinity for transition metals than do standard chelating agents such as aminocarboxylates. As a result, metals control with aminocarboxylate chelants is efficient in only slightly acid to neutral pH conditions. It was recognized that metal control was going to be a key issue in effectively bleaching with peroxide. Solvay Interox's researchers demonstrated that metals had a decided preference for attaching themselves to kraft pulps. They theorized that either precipitated or undissolved manganese salts were somehow bound to the fibre or that there was some other factor, perhaps uronic acid groups, that somehow developed chelating ability. The breakthrough in understanding the precise chemical nature of uronic acids in pulp came in 1995. The work reported by Finnish research groups identified hexenuronic acid as a uronic acid subclass, formed under alkaline cooking processes. The researchers reported that hexenuronic acids could be removed in a hot acid hydrolysis stage. Once the hexenuronic acid was removed, chelants seemed to be much more effective in removing metals and became effective across a wide range of pH. It has been found that chelation might be possible well in the alkaline range. This in turn might allow a mill to send all of the removed metals to the recovery boiler, keeping them out of the bleach plant entirely. Researchers at Solvay Interox were also excited about the impact of the hot acid hydrolysis followed by chelation process on the efficacy of subsequent hydrogen peroxide bleaching stages. They were able to take some extended cooked, oxygen delignified pulp to fully bleached brightness in a single peroxide bleaching stage. The new strategy has been effective in bleaching hardwoods, softwoods and eucalyptus kraft pulps. The bleached pulps have a better brightness stability. Reducing the concentration of transition metals, which interfere with the stability of peroxide, may allow mills to move towards high-temperature pressurized peroxide bleaching stages with confidence. These developments should make hydrogen peroxide an even more cost-effective and efficient bleaching chemical for kraft chemical pulp processing.

Eka Chemicals is excited about the opportunities that 'Smart Chemistry' offers to mill closure efforts (Ferguson and Finchem, 1997). Smart Chemistry, which separates alkaline and acidic effluent streams—processing the acidic streams through the waste treatment plant and recycling the alkaline streams through the liquor cycle—is held by the company to be a cost-efficient method for minimizing bleach plant effluents. The improvements in the case of ECF bleaching can be significant (Table 6.3.1). As researchers have investigated various bleaching strategies (and their effluent implications), TCF bleaching—once thought to be the linchpin of mill closure—has lost some of its appeals. TCF bleaching is sensitive to the transition metal concentrations, which can build-up as effluent systems are moved towards closure. Both TCF and ECF present their own challenges to closure. One of ECF challenges—chloride removal from the liquor cycle—is the target of one of Eka Chemicals' developments—the precipitator dust recovery (PDR) process. Improvements in mill operations during the last decade have led to increasing levels of NPE in kraft chemical recovery cycles. Purging the NPE, particularly potassium and chloride, remains a major stumbling block in effluents closure efforts because of their effect on recovery boiler reliability and performance. The PDR process is a method of selectively removing potassium and chloride from the liquor cycle. The process is also capable of recovering sodium and sulphur which would otherwise be lost. The primary components of recovery boiler electrostatic precipitator (ESP) dust are sodium, sulphur, carbonate, potassium and chloride. The dust probably also

**Table 6.3.1 The effects of partial closure on ECF bleaching**

| Effluent type | $BOD_5$ (kg/t) | AOX (kg/t) | COD (kg/t) | Colour (kg/t) |
|---|---|---|---|---|
| Combined bleach plant effluent | 11 | 1.04 | 62 | 51 |
| Alkaline effluent | 6 | 0.15 | 38 | 36 |
| Acid effluent (to waste treatment) | 5 | 0.9 | 24 | 17 |
| Acid effluent after secondary treatment | 0.2[a] | 0.2 | 12 | 22 |

[a] Separation of alkaline and acid effluents enhances the treatability of the acid stream.
Based on data from Ferguson and Finchem (1997).

contains lower but not insignificant concentrations of calcium, silica, magnesium and manganese, and traces of heavy metals. After dissolving ESP dust in water, the PDR process concentrates and selectively crystallizes the valuable components (sodium, sulphur and carbonate) as burkeite ($2Na_2SO_4 \cdot Na_2CO_3$). The remaining crystallizer solution is rich in both potassium and chloride. Careful choice of the crystallizer purge rates boosts process efficiency by favourably shifting solution equilibria. Eka Chemicals' work has demonstrated excellent potassium and chloride removal efficiencies—90% or better—if solution concentrations are properly managed. At the same time, the PDR system is capable of recovering 60–80% of the sodium and sulphur in the ESP dust. The operating cost implications of these efficiencies make the process quite attractive to mills. Another challenge that ECF bleaching presents is reclaiming or disposing of the saltcake, primarily sodium sulphate by-product from the mill's chlorine dioxide generators. The first prong of the challenge is that reclaiming saltcake through the liquor cycle competes with incremental production from recovery boiler capacity. The second prong is that as a mill reduces its process losses, while continuing to reclaim saltcake through the liquor cycle, the sulphidity of the liquor cycle increases. This leads to totally reduced sulphur (TRS) emission problems that may in future reduce a mill's liquor burning capacity. In extreme cases, high liquor sulphidities can also be detrimental to pulp quality. Eka Chemicals has developed a new technology that may help reduce sulphidity build-up while avoiding the high capital or operating costs associated with other low by-product generation technologies. The new Generator Liquor Splitter approach takes the liquor from a chlorine dioxide generator operating in a 'noncrystallizing mode' and passes it through a two-compartment electrolytic cell. The cell products are a concentrated acid–sulphate mixture which is returned to the generator, and a membrane-grade caustic solution, which has a high chloride content. With this cell configuration and a newly developed cell membrane with a 2 year life, the cell can be operated very economically.

Mannisto et al. (1995) have examined the technical and economic consequences of converting to low-effluent pulp production for three hypothetical bleaching kraft mills: (i) an old mill; (ii) a modern mill and (iii) a greenfield mill. Although liquid effluent-free production of bleached kraft mills was found to be technically possible, it was expensive. It was found that the total cost of converting a mill into low-effluent production would increase the cost of the pulp manufacture by US$5O–15O /ADT. In the case of a greenfield mill designed for liquid effluent-free operation, the cost of producing a ton of air dried pulp is expected to be US$20–60 higher than for a conventional greenfield mill. Development of new technologies may reduce these cost differences. It was suggested that if the liquid effluent-free bleached kraft mill is to become a reality, the industry will need to focus its efforts on several key areas. These include: (i) improving the quality of non-chlorine bleach sequences; (ii) developing methods for removing and managing NPE (chloride, metals and nutrients); (iii) minimizing increases in solid waste generation and air emissions; (iv) managing the mill chemical balance; (v) managing upset conditions and (vi) developing design standards.

Brooks et al. (1994) used process simulation and mill data from Louisiana-Pacific's Samoa, CA, market pulp mill, to evaluate the conversion of a conventional oxygen-delignified softwood bleach plant into TCF bleaching based on hydrogen peroxide. During a recent mill TCF close-up run, substantial reductions were made in water use, steam consumption and sewer loading. Thirty-one percent of the bleach plant organic dissolved solid material, normally lost to the sewer during conventional chlorine bleaching, was recycled to the recovery boiler. An economic evaluation comparing the TCF process, conventional chlorine bleaching and 100% $ClO_2$, substitution was made. TCF bleaching costs were found to be about US$26–29 /air dried metric ton pulp more than ECF bleaching.

Studies by Prasad et al. (1996) have shown that high kappa kraft pulping coupled with multiple oxygen stages and TCF bleaching can be used to close a pulp mill without overloading the recovery system and with a production increase under certain circumstances. When compared with a conventional kraft pulp (kappa number 30) followed by one oxygen stage and ECF bleaching, pulp produced at a kraft kappa number of 40–50 followed by multiple oxygen stages and TCF bleaching, showed a similar or lower cost and a lower boiler throughput at constant production. Under constraints of limited digester capacities or limited boiler thermal capacity, production can be increased with a multiple oxygen/TCF closed system relative to a conventional kraft oxygen system.

Covey and Nguyen (1996) have shown that a direct alkali recovery system (DARS) process can be integrated with a chlorine-based bleach plant for waste treatment and recovery of active chemicals, which can be reused in the pulping or bleaching process. It is possible to treat the effluent from an ECF bleach sequence with the DARS fluidized-bed reactor by providing means to extract and discharge chloride from the chemical cycle. At the typical operating temperature of the DARS process, sodium chloride is volatile and accumulates mainly in the dust of the reactor. The chloride can be leached and separated from the other useful chemicals by evaporative crystallization. This approach can maintain the chloride in the liquor circuit at a tolerable level.

Techniques of NF and electrodialysis have been shown to be techno-economically feasible to purify the $E_1$ effluent and recycle it as process water (de Pinho et al., 1995). The Selenga Pulp & Paper Company in Russia is the world's first zero discharge unbleached kraft mill (Kenny et al., 1995a). Zero discharge was accomplished by employing activated sludge, chemical precipitation and re-aeration waste treatment methods. The mill produces 173 000 t/year of unbleached kraft pulp, of which approximately 11 000 t is sold as market pulp. The 10 batch digesters, each with a capacity of 140 $m^3$, feed seven pulp drying machines. One machine produces corrugated paper and two paper board machines produce linerboard. Internal mill measures were adopted to reduce water discharges. These included: (i) spills control; (ii) in-mill recycling; (iii) installation of heat exchangers; (iv) improved communication between the treatment plant and the mill; and (v) monetary awards.

Saunamaki (1995) compared the biodegradability of wastewaters from TCF bleaching with those of wastewaters from chlorine gas (CG) bleaching and ECF bleaching. Activated sludge treatment of TCF wastewaters reduced COD by 55–65% compared with 34–45% for wastewater containing chlorine compounds. Chemical flocculation of biologically treated TCF wastewaters with aluminium sulphate resulted in 85% total removal of COD. TCF wastewaters were very light in colour, in contrast to wastewaters from CG bleaching. Combined biological and flocculation treatments of TCF wastewaters reduced phosphorus by 97–99%. Nitrogen in TCF wastewaters was high because of the presence of EDTA. Activated sludge treatment did not remove EDTA, but addition of aluminium sulphate to treated wastewaters reduced EDTA by 65%. Residual peroxide in TCF wastewaters made them highly toxic, although biological treatment removed this toxicity. Treated TCF wastewaters had higher levels of heavy metals and NPE than did CG and ECF wastewaters.

The Russians have developed tertiary treatment systems to minimize the impact of effluent on receiving waters (Kenny et al., 1995b). Tertiary treatment at Baikalsk Pulp & Paper Co. and Svetogorsk Pulp and Paper Co. are examples of effective tertiary treatment technology unique to the pulp and paper industry. The Baikalsk three-stage, biological, chemical and sand filtration treatment is highly effective in reducing BOD, SS and colour. Svetogorsk's sand filtration/flotation tertiary technology is effective in removing SS and BOD.

A variety of process condensates is generated within the digester and liquor evaporation areas of a kraft process. These condensates contain various concentrations of reduced sulphur compounds, terpenes and related wood derivatives, black liquor carryover and semi-volatiles such as methanol, acetone and methylethylketones (MEK). Reuse of condensate is an important component of water usage and heat conservation programmes in a kraft mill operation. Increasing the quantity of condensates reuse and, for some reuse applications, improving the quality of condensates via treatment, offers the potential for (i) further reduction in water usage rates and (ii) reductions in atmospheric emissions of volatile organic compounds such as methanol from unit process at which condensates are reused. It is probably that present limitations on the quantity of condensates used in a mill are, in part, related to the quality of the remaining available condensates. Thus, further reuse of condensates may require some part of pretreatment.

### 6.3.2 For sulphite mills

Closure of bleach plants in sulphite mills has been more successful than in kraft mills. In Germany, the mills switched from bleaching sequences using traditional methods with elemental chlorine, chlorine dioxide and hypochlorite, to sequences without elemental chlorine and low in active chlorine (Suss, 1986a, b). Since 1991, TCF bleaching of sulphite pulps with oxygen and hydrogen peroxide has become state of the art (Nimmerfroh and Suss, 1991). Five of the six German sulphite pulp mills are processing 100% of their capacity TCF and only one mill is bleaching pulp for specialities with the aid of chlorine dioxide.

Under TCF conditions, the idea of a closed-cycle mill attracted new interest. However, there was one limiting factor: standard TCF bleaching uses caustic soda as the source of alkali in the oxygen and hydrogen peroxide stages. Although the recovery boilers of magnesium-based sulphite mills can tolerate small amounts of sodium ions, mill scale experience at PWA Waldholf, Mannheim, with the counter-current washing of $E_{OP}$ filtrates caused difficulties (Nimmerfroh et al., 1995). These consisted of swings in pH values and a resulting precipitation of alkaline lignins, as well as depression of the melting point by sodium in the magnesium oxide in the combustion furnace. For these reasons, it is advantageous to substitute all the caustic soda with magnesium oxide. Hydrogen peroxide-reinforced oxygen delignification with magnesium oxide offers the following advantages over caustic soda applications: (i) unburdening of the wastewater treatment plant as the dissolved organic compounds are returned to the recovery cycle; (ii) generally lower COD load due to lesser release of hemicellulose; (iii) lower COD load per decreased kappa unit; (iv) lower costs for the alkali or no costs for the alkali at all; (v) higher pulp yield due to lower loss of lignin and hemicellulose and (vi) improved pulp strength as more hemicellulose is retained in the pulp. When three stages of bleaching (OPMgO–P–P) were replaced by a single-stage bleaching (OPMgO), the system required higher dosing of MgO and the modifications in the bleaching conditions. The essential prerequisite for the success of the single-stage bleaching process, implemented at PWA Waldholf (Fig. 6.3.5), is a very high washing efficiency after the cooking process. The COD carryover from the cooking has a clearly negative influence on the bleaching process with regard to selectivity and hydrogen peroxide consumption. The washing system, the bleaching system and the

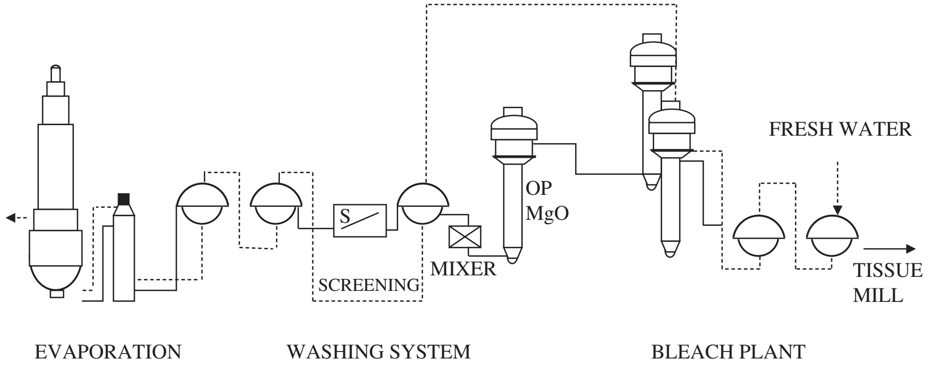

**Fig. 6.3.5. Flowsheet of Kamyr line at PWA Waldholf. (From Nimmerfroh et al., (1995); reproduced with permission from Pulp and Paper Technical Association of Canada.)**

unbleached pulp washing system must be considered as one unit. Fresh water is added only as washing water at the end of the bleaching process. As a result of using a complete counter-current flow of water, starting from the washing after the bleaching stage via pulp washing filters and the pressure diffuser into the Kamyr digester, the effluent volume to the evaporator did not increase dramatically (Nimmerfroh et al., 1995). However, there was an increase in the dirt count of the pulp from approximately 1200–1500 specks/m$^2$. Most of these impurities are tiny pieces of incompletely bleached bark, although they are hardly visible in the final tissue product. There was not much difference in the paper-making properties on the tissue machines, with the exception of beatability. The single-stage bleached pulp needs a distinctly higher beating energy compared with two-stage bleached pulp. When a closed-cycle condition was reached, the COD load at the entrance to the bleaching equipment rose from 105 to 150 kg/t. This high COD level caused only a slight decrease in the delignification efficiency compared with open conditions. The demand for oxygen and hydrogen peroxide was not significantly increased. However, it became essential to decrease the pH to 4 by addition of sulphuric acid at the second to last washing stage following the OPMgO stage. This ensures that nonhydrated magnesium oxide is dissolved and not transferred with the pulp to the machines, since magnesium oxide particles affect the coating process on the Yankee cylinder. The effluent from the modified Kamyr line includes the stream of condensates from the spent liquor evaporation, which is processed in a two-stage anaerobic and aerobic biological wastewater treatment. The effluent loads after biological treatment are given in Table 6.3.2 along with the minimum requirements set by the authorities for pulp and recycling mills, for comparison.

**Table 6.3.2 Effluent loads**

| | COD (kg/t) | BOD (mg/L) | AOX (kg/t) |
|---|---|---|---|
| 1. Current PWA situation (with Kamyr line) | 9 | $< 15$ | 0 |
| 2. Legal minimum requirements | | | |
| (a) Pulp | 70 | 25 | 1.0 |
| (b) Recycling mill | 5 | 25 | 0.1 |
| 3. On improved washing | 5 | $< 15$ | 0 |
| 4. On precipitation after biological treatment | 2 | $< 10$ | 0 |

Based on data from Nimmerfroh et al. (1995).

Domsjo sulphite mill in Sweden modified their sodium-based sulphite pulping and bleaching process to reduce the environmental impact and ultimately close the water cycle while maintaining high quality of the pulp (Nordberg et al., 1991). The fresh spruce chips are cooked in the batch digesters. The cook consists of two stages: a neutral impregnation stage followed by an acid delignifying stage. This two-stage cook makes it possible to reach a very low kappa number (<8) and still maintain a high yield (54%) after the cook. The old bleaching sequence $C_D$EpD has been replaced by $E_{OP}$P. After digestion, the pulp is washed and fed to the first extraction stage, which is also an internal deresination of the pulp. The alkali stage is reinforced with oxygen and peroxide, which results in a more even kappa number before the peroxide stage. Also, the wash liquor is deresinated to ensure a low resin content both in the pulp and in the system. Bleaching with peroxide only would mean that the old bleach plant equipment could be used with minor modifications, and also that the effluent would be free from chlorine compounds. This would make a complete close-up of the bleach plant possible. The filtrates can be sent to the recovery. The goal of modifying the bleach plant was to reach brightness $> 88\%$ ISO by using only oxygen and peroxide as bleaching chemicals and at the same time closing up the washing system. The main physical modifications were as follows: (i) A MC pump with capability to pump and mix chemicals at 18% pulp consistency was installed before the peroxide stage, (ii) the peroxide stage was moved one step backwards, which gave one more washing stage after bleaching with peroxide and (iii) the washing system was rebuilt so that a complete close-up should be possible. Full-scale trials were started in spring 1990 and showed that brightness greater than 85% ISO was possible with peroxide only. After start-up of the modified bleach plant, addition of bleaching chemicals was increased in the hope of reaching brightness $> 88\%$ ISO by using only oxygen and peroxide as bleaching chemicals. By adding around 5 kg $H_2O_2$ /t pulp in the reinforced extraction stage and up to 25 kg in the peroxide stage, the target of $> 88\%$ ISO brightness, and even $> 90\%$ ISO, was reached. The addition of NaOH was adjusted to give an initial pH of

11.5 in both stages. The total charge of $H_2O_2$ seems rather higher than expected. The $BOD_7$ figures from the bleach plant decreased from 6 to 1.5 t/day and there was no problem in the recovery system. Another advantage from bleaching with peroxide is an AOX-free effluent as well as a product that contains no AOX. Condensates and spills from the unbleached part of the production are treated in the anaerobic and aerobic process, together with the CTMP effluent and effluents from three chemical plants on-site. The CTMP effluent is first treated in an ultraffltration step for removal of extractives. The biological treatment has a capacity of 50 t of BOD/day and the reductions of $BOD_7$ and COD are 95% and 70%, respectively. During 1990, the recovered biogas could replace 5 000 $m^3$ oil and the recovered sulphur amounted to 1000 t. The above-mentioned measures have reduced the $BOD_7$ to the recipient from 50 to 12 t/day, and the COD from 160 to 55 t/day. Extractives (8–12t) are burnt in the boiler house, which means a lot for reduction of toxicity in the effluents. The old bleaching technique gave a bleach plant effluent of 20 000 $m^3$/day, with 6 t BOD/day (Table 6.3.3). In theory, the new bleaching technique and closing up the bleach plant eliminate that completely. In practice, however, it is realistic to expect around a 70–95% reduction. The effluent flow has reduced to 5 000 $m^3$/day, with a $BOD_7$ load of only 1–2 t/day (Table 6.3.4). Thus, the total amount of $BOD_7$ from the pulp mill to the recipient has been reduced from 12 to 7.5 t/day. Moreover, the important aspects of the papers produced, such as yellowing, strength characteristics and optical properties did not change on switching

**Table 6.3.3 Characteristics of bleach plant effluent**

| Parameter | Old bleaching | Modified bleaching |
|---|---|---|
| Flow ($m^3$/day) | 20 000 | 5 000 |
| $BOD_7$ (t/day) | 6 | 1–2 |
| COD (t/day) | 25–30 | 5 |
| AOX (t/day) | 1.7 | 0.0 |

Based on data from Nordberg et al. (1991).

**Table 6.3.4 Estimation of operating cost for bleach plant closure**

| Item | Amount per ton pulp | Unit price ($/kg) | Cost ($/t pulp) |
|---|---|---|---|
| Additional $O_3$ | 0.3 kg | 1.8 | + 0.54 |
| Additional $H_2O_2$ | 2.0 kg | 1.1 | + 2.20 |
| Additional NaOH | 3.0 kg | 0.3 | + 0.90 |
| Reduced water | 11 $m^3$ | 0.06 | − 0.66 |
| Effluent treatment | | | − 1.50 |
| Net balance | | | + 1.48 |

Based on data from Krotscheck et al. (1994).

over to the new process (Nordberg, 1991). As part of a move towards TCF bleaching, the ability of magnesium oxide to replace sodium hydroxide as the alkali source was investigated by Johansson et al. (1996) in a sulphite mill. The aim was to allow partial or total effluent closure yet still maintain high brightness and viscosity levels of the pulp. Results indicate that magnesium oxide can be partially substituted for sodium hydroxide in the sequence (OPMg)QP. Complete substitution would, however, significantly reduce brightness. Adding a Paa stage improved the final brightness but not to the same level as (OPMg)QP. The introduction of a high-temperature peroxide stage resulting in the final bleaching sequence (OPMg)Paa(PMg + Q,O), produced a high brightness level and enhances the potential for effluent closure.

The change-over to TCF bleaching at the Hallein Mill in Austria has also been reported (Reisner and Schloffer, 1996). The integrated sulphite mill has a capacity of 120 000 t/annum. In 1991, the mill changed from CEHH to $E_{OP}$PP bleaching by installing a new $E_{OP}$ bleaching stage. Between 1991 and 1994, the process was improved, bringing bleaching costs to the same levels

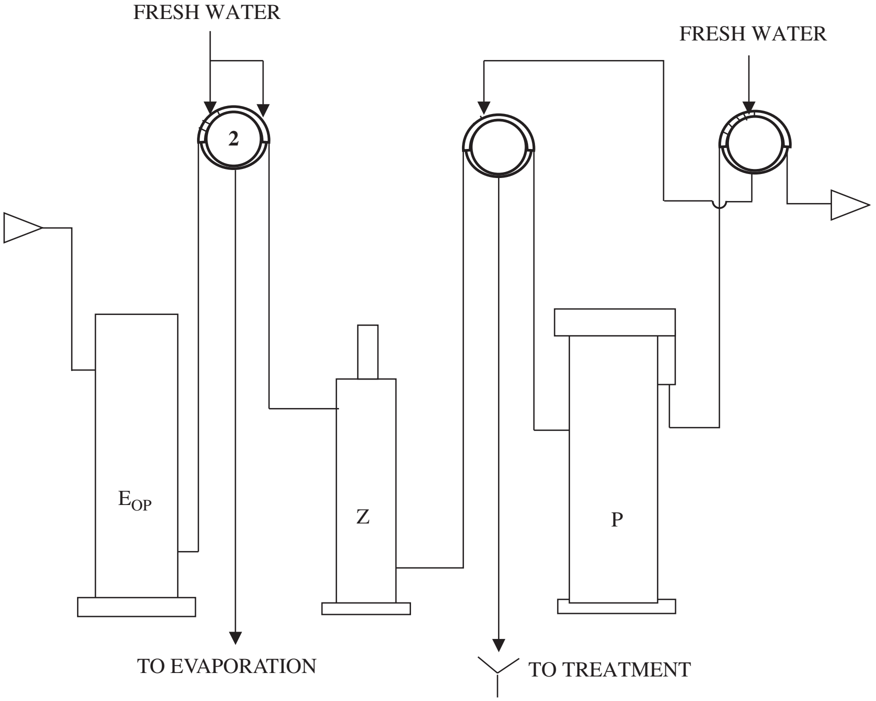

**Fig. 6.3.6. Simplified flow scheme of the Lenzing bleach plant showing current liquor management. (From Krotscheck, (1994); reproduced with permission from Miller Freeman Inc.)**

as chlorine bleaching. The steps involved in the change-over include oxygen delignification, TCF bleaching, changing to MgO in the delignification stage, and closing up the bleach plant. By changing the $E_{OP}$ stage to OPMgO and closing the loop to the recovery plant, a 50% reduction in COD for the bleach plant filtrates has been achieved.

Lenzing AG in Austria has been producing 135 000 t/year sulphite dissolving pulp from beech wood (Krotscheck et al., 1994). Since 1992, their whole production has been TCF with a bleaching sequence of $E_{OP}$ZP, following installation of the world's first ozone stage in the bleaching line. The final pulp brightness was 90% ISO. Most of the effluent from the bleach plant is completely recycled as shown in Fig. 6.3.6. Fresh water is used on the extraction and peroxide stage washers as well as for pulp dilution in the extraction stage washer screw. Peroxide stage filtrate is recycled to the ozone stage washer. Recycling of the $E_{OP}$ filtrates to the magnesium-based recovery cycle was not possible because of high caustic load. Therefore, Lenzing has installed a separate evaporation and combustion system where $E_{OP}$ filtrates are disposed of together with alkaline effluent from viscose fibre production. Only the Z stage filtrate is discharged to the effluent treatment

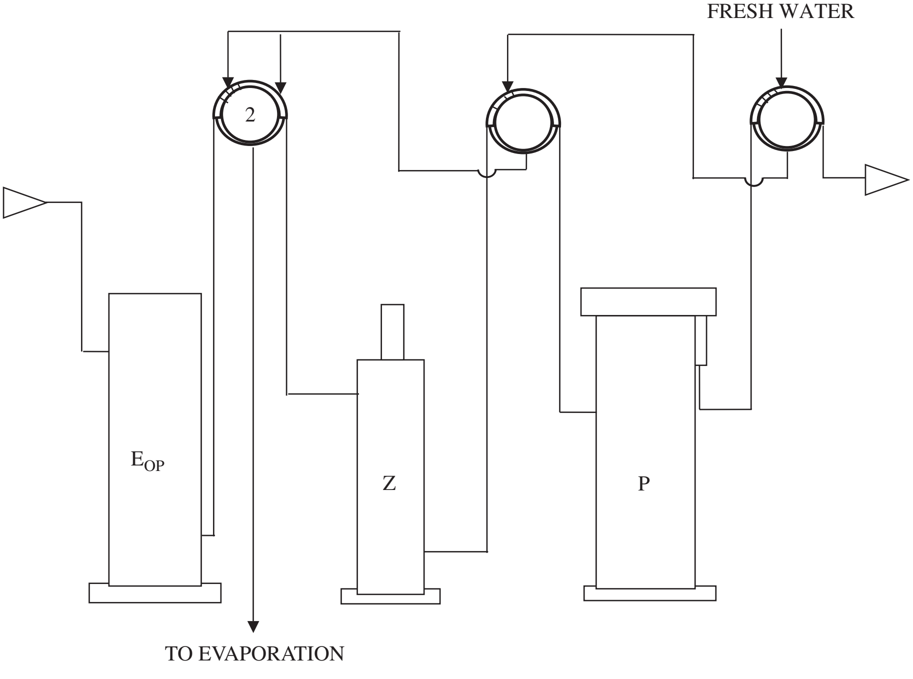

**Fig. 6.3.7. Simplified flow scheme of the Lenzing bleach plant showing closed operation mode. (From Krotscheck, (1994); reproduced with permission from Miller Freeman Inc.)**

system. However, complete closure of the bleach plant means elimination of the Z-stage effluent. The closed operation set-up provides for the desired closure of the bleach plant by replacement of the fresh water used for showers, and dilution at the extraction stage washer with ozone stage filtrate as shown in Fig. 6.3.7. Based on the bleach plant model configuration, the Z-stage filtrate stream is connected to the $E_{OP}$, shower and dilution water streams in the simulation system. The liquor concentrations generally increase as confirmed by laboratory experiments, simulation and plant trials. The organics concentration in the Z stage would be 10 times higher than in normal operation, and lies between the $E_{OP}$ and P filtrates. As a consequence of closure, the final brightness falls behind (up to 1.5% ISO) normal operation brightness for a given ozone charge. Even though bleaching selectivity is not affected, it is necessary to increase both ozone and peroxide charges so that the final brightness target can be met. There was also an indication of increase in manganese concentration after closure. For evaluation of the feasibility of bleach plant closure, a rough operating cost was estimated (Table 6.3.4), which indicates that closure means a drawback in economic efficiency. The mill has reported that it is well on its way to complete closure.

## 6.4 Some practical considerations

For all the closed-cycle kraft mills, corrosion will be the major problem. The problem will be greater for mills that do not bleach with a TCF sequence, because of the chloride ion content of the bleached plant effluent recycled to the chemical recovery loop. The mills must be prepared to spend the time and money to develop and maintain an ongoing corrosion monitoring programme. There is no need to eliminate all of the chlorides, as demonstrated by coastal mills, which may have NaCl levels as high as 20–25 g/L and are still able to operate relatively free of trouble. The best method for removing chlorides will be by dumping a portion of the recovery boiler precipitator catch. The ash can be treated to recover sodium as saltcake and remove the chlorides as sodium and potassium salts. Controlling chloride levels by this method would reduce the risk of corrosion and would also reduce recovery boiler pluggage from sticky saltcake. The latter is known to be a problem for mills with high black liquor chloride and potassium levels.

Mills that recycle all or most of the bleach plant effluent will have problems due to build-up of inerts. In the case of mills that bleach with peroxide, transition metals such as iron, manganese and copper must be purged to avoid peroxide decomposition. These metals are reported to have an adverse effect on chlorine dioxide and also to promote the catalysis of highly oxidative free radicals, which attack cellulose. Under certain conditions, multivalent nontransition metals such as calcium, magnesium and aluminium can form precipitates, which may lead to scale formation in process equipment (Jayawant, 1994). Several techniques have been proposed for selectively removing these metals from the acidic bleach plant effluent. The closed-cycle mills must establish an ongoing programme for monitoring metal concentrations at key points in the process. Metals intrusion must also be minimized by efficient debarking and other means.

Full or partial recycle of excess bleach filtrates to the chemical recovery system would mean increased dissolved solids load and, in most cases, increased evaporation load. For fully closed TCF mills with peroxide and ozone bleaching, the increased organics and inorganics load will be similar to that resulting from an oxygen delignification stage (Shackford and Foelkel, 1994). The excess water in the recycled effluent can be handled either by increasing the capacity of the existing multiple-effect evaporator or by installing a dedicated evaporator set to concentrate recycled effluent.

Recycle of alkaline effluent to the post-oxygen washers will increase the total dissolved solids carried into the bleach plant. The highly oxidized organics in the carryover will increase the bleach chemical requirement for both ECF (chlorine dioxide) and TCF (ozone) sequences, although the increase is expected to be modest (Maples et al., 1994a, b). Brightness development and bleached pulp physical properties are not expected to be significantly affected by bleach plant closure.

Bleach plant closure will have major effect on sodium–sulphur balance. Most ECF and TCF bleach sequences will require the addition of sulphuric acid and caustic which, when recycled, will add significant amounts of sulphur and sodium to the liquor loop. In order to control sodium and sulphur levels, it may be necessary to replace caustic with oxidized white liquor and periodically to purge sulphur from the liquor system (Shackford and Foelkel, 1994).

The so-called closed-cycle mill will never actually be completely closed. In fact, a ‘zero discharge’ mill is a technical impossibility since there will always be the need for a continuous purge of dissolved solids as well as more conventional solid wastes such as ash, dregs and slaker grits. Even a zero liquid discharge mill will present serious technical challenges to prevent a build-up of undesirables, which would encourage corrosion or deposition. Process upsets will occur in a closed-cycle facility just as surely as they do in a conventional mill. To be truly closed-cycle, the mill must have the capability for containment and storage of all process spills, as well as the means for either returning the liquor or filtrate to the process or sending it on to waste treatment. State-of-the-art process controls and information systems will be mandatory for proper monitoring of critical process variables in a closed-cycle mill.

## 6.5 Economic considerations

Although there is still considerable debate over the most cost-effective and reliable process design for closed-cycle facilities, particularly for non-TCF bleached kraft mills, most of the studies indicate that there is no significant increase in the capital cost associated with designing a new facility for full-scale closure (Gleadow et al., 1993; Norrstrom et al., 1993; Albert, 1994). This is mainly due to offsetting the cost of additional evaporation, cooling and spill protection/surge capacity, with savings resulting from considerably downsized water and wastewater treatment systems. However, 7–9% higher capital costs for the closed cycle mills (1500 t/day bleached eucalyptus kraft mill) have been estimated by Gleadow et al. (1993). These estimates assume an ideal location adjacent to a source of water, both for the mill and to disperse effluent. If water supply dams and water or effluent pipelines are required, the closed-cycle case would incur lower off-site costs. For a severe site, this may result in similar overall project capital costs. These mills may have a competitive disadvantage compared with those better located. For example, capital costs for a 1000 t/day BKPM are estimated to be $40 million less for a TCF/effluent-free BKPM than for a new ECF BKPM as shown in Table 6.5.1. Principal incremental savings arise from elimination of the waste treatment plant and chlorine dioxide plant. Principal incremental costs arise from the larger evaporator system, and cooling tower.

With regard to the operating costs, the picture was not quite clear although it appeared that a closed-cycle mill may offer some manufacturing cost advantages. These costs are very site-specific and need to be evaluated on a case-by-case basis. There are indications that the costs are similar for both open and closed cycles (Gleadow et al. 1993). No conclusions regarding the costs of ECF compared with TCF bleaching can be drawn, as the plantation wood has different yields and chemical requirements, and consequently different equipment requirements than those for mature wood. Operating costs are reported to be $35/t pulp less for a TCF effluent-free BKPM than for a new ECF BKPM (Albert, 1997). Principal savings are for bleaching chemicals, make-up cooking chemicals and the effluent treatment plant operation (Table 6.5.2). On the other hand, the operating costs of a closed-cycle sulphite mill in Austria, producing dissolving pulp, were reported to be slightly higher ($1.48/t pulp) than the open-cycle operation. The bleaching sequence followed is $E_{OP}ZP$ (Krotscheck, 1994).

From a practical standpoint, the greatest hurdle for widespread implementation of closed-cycle technology will be the capital costs associated with closure of existing mills. Estimated capital costs for the retrofit of closed-cycle into existing mills are highly variable, depending to a large degree on the capacity and capability of existing equipment, and the product

**Table 6.5.1 Comparison of capital costs for the reference BKPM and effluent–free BKPM ($ millions)**

| Cost item | Effluent-free BKPM | Reference BKPM | Net cost savings in effluent free |
|---|---|---|---|
| Site | 4.0 | 5.0 | 1.0 |
| Site development | 11.5 | 13.0 | 1.5 |
| Water treatment | 5.0 | 14.5 | 9.5 |
| Wood preparation | 40.0 | 40.0 | |
| Pulping | 57.0 | 55.0 | (−)2.0 |
| Evaporation | 33.5 | 28.5 | (−)5.0 |
| Recovery boiler | 110.0 | 105.5 | (−)5.0 |
| Power boiler and turbine | 125.0 | 125.0 | |
| Recausticizing | 46.0 | 40.0 | (−)6.0 |
| Oxygen delignification | 24.0 | 24.0 | |
| Bleaching | 60.0 | 65.5 | 5.5 |
| Chlorine dioxide | 0.0 | 12.0 | 12.0 |
| Bleach chemical preparation | 0.5 | 2.5 | 2.0 |
| Bleach vent system and scrubber | 0.5 | 2.5 | 2.0 |
| Pulp dryer | 57.0 | 55.0 | (−)2.0 |
| Effluent treatment | 0.0 | 34.0 | 34.0 |
| Cooling towers | 7.0 | 0.0 | (−)7.0 |
| Environmental studies and engineering for effluent treatment | 0.0 | 3.5 | 3.5 |
| Contingency | 4.0 | 0.0 | (−)4.0 |
| Total direct costs | $ 585.0 | $ 625.0 | $ 40.0 |

Based on data from Albert (1997).

**Table 6.5.2 Operating costs in ($/t) of the bleach plants**

| Operating cost item | Effluent–free BKPM | Reference BKPM |
|---|---|---|
| Cooking chemicals make-up | | |
| Saltcake | — | 6.37 |
| Sulphur | 1.16 | — |
| Steam for black liquor evaporation (additional for effluent–free) | 3.92 | — |
| Bleaching chemicals | 49.17 | 52.26 |
| Steam for bleaching | 3.75 | 4.37 |
| Effluent treatment plant | — | 9.00 |
| Subtotal | 58.00 | 72.00 |
| Incremental capital cost | | |
| $40 × $10^6$ amortized 15 years at 10% | — | 15.00 |
| Maintenance cost for incremental equipment | — | 6.00 |
| Total cost per ton | 58.00 | 93.00 |

Based on data from Albert (1997).

qualities being sought. For bleached chemical pulp mills, the cost of conversion is primarily a function of: (i) existing fibreline configuration; (ii) bleach sequence and bleach chemical costs; (iii) utility (power and steam) costs; and (iv) waste treatment costs.

In general, mills faced with high waste treatment costs and low unit costs for steam and power would have most to gain from closure. With any operating cost savings offset by the substantial depreciation costs of the capital expenditures required for closure, it is doubtful that there will be a compelling economic incentive for converting any bleached pulp mill to closed-cycle operation. Some existing mills such as Lenzing in Austria, SAPPI's Ngodwana in South Africa, and Union Camp (at Franklin, VA) in the USA have made major strides towards full or partial closure because of extremely tight limits on allowable effluent discharge rates. For these mills, economics were not the primary consideration. Without regulatory or market pressures, however, most existing mills may never convert to closed-cycle operation unless there is a strong economic incentive. The overall economics depend on (a) capital costs of new equipment, (b) impact of nitrate recycling on bleaching, (c) final quality versus bleaching cost and (d) market reaction.

Three case studies have been reported regarding the retrofitting of closed-cycle designs into existing Canadian-bleached kraft mills (Gleadow et al., 1998). These studies were based on a 4-year research programme carried out jointly by H.A. Simons Ltd., the Pulp and Paper Research Institute of Canada and several Canadian mills. The objective of this programme was to provide technically and economically feasible solutions to enable bleached kraft mills to be designed and operated with increasing levels of bleach plant filtrate recycle. The study had three main directions: (i) process simulations and case study development (based on mill sampling); (ii) laboratory and pilot plant process studies; and (iii) corrosion studies and testing. Development of these case studies indicated that implementation of closed-cycle operation in existing mills may involve substantial costs, with the case study estimates at C$75–90 million (in 1995 dollars) per mill or US$216–415 per annual ADT. For these case studies, the increase in operating costs was generally that required for serving the cost of capital, as other operating costs remained similar. Closed-cycle operation appears feasible, although several technical issues are still to be resolved.

Ultimately, all process industries in developed countries will be required to operate in a closed-cycle mode. Widespread closure of paper industry mill water systems will probably occur within the few years or so. However, producers of all pulp, paper and board grades will be affected. Bleached chemical pulp mills will be converted after the industry has already invested millions of dollars in existing mills to minimize or eliminate chlorinated organic discharge and after more cost-effective processes for treating pulp and paper mill waste streams have been developed. The greatest technical hurdles towards closure will then be cleared, although the economic hurdles may still be present for existing mills.

## 6.6 Conclusions

The optimum closure strategy for a given mill depends on the type of pulping process employed: unbleached kraft, bleached kraft, bleached sulfite, etc. In general, most unbleached mills probably will develop closure strategies based on minimization of water usage using conventional technology with treatment of effluent for recovery and reuse technology similar to that already in place at high-yield mills like Meadow Lake and Chetwynd. At present, evaporation is the only industrially proven technology. The strategy must (1) not have a negative effect on pulp quality, (2) not cause losses in pulp production, (3) have operating cost competitive to biological secondary effluent treatment system and (4) minimize use of treatment chemicals to ensure purity of smelt and ash for potential recovery and to avoid effect on other unit's operations.

Extensive closure of a TCF bleach plant is very demanding and requires extremely good washing of the pulp between the stages. However, kraft mills utilizing TCF bleaching sequences will be able to close up their bleach plants by recycling the effluent directly to the chemical recovery loop. ECF-BKPMS will have much more difficulty achieving closure and, of course, effluent-free ECF mills will still carry the stigma of producing pulp containing traces of organic halides.

Most early closed-cycle implementations will be in existing mills in North America, Sweden, and Finland. Many mills are positioned to reduce bleach plant effluent to the level at which complete recycle is economically feasible and to consider recycling alkaline effluent to the recovery cycle. The closed-cycle pulp mill is a part of the ultimate strategy for a holistic approach to the environment. The driving forces are moving the industry in the long term to achieve environmental harmony and looking at the total impact on the environment. Coupled with sustainable, recyclable, biodegradable nature of the products, a closed-cycle process where no process effluent are released into the receiving water is the long–term solution.

Closed-cycle bleached kraft mill appears to be technically feasible. The challenge is to optimize process choice to give good economics. The choice of closed-cycle should be based on market demands and sound economics and should not be imposed by regulations.

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# Abbreviations

| | |
|---|---|
| A | acid treatment |
| ABTS | 2,2′-azinobis (3-ethylbenzthiazoline-6-sulfonate) |
| ADT | air dried tonne |
| AIET | alliance for environmental technology |
| Al | aluminium |
| AOX | adsorbable organic halides |
| AP | acidic peroxide |
| AQ | anthraquinone |
| ASAM | alkaline sulphite, anthraquinone, methanol |
| BAT | best available technology |
| BFR | bleach filtrate recycle |
| BKPM | bleached kraft pulp mill |
| BOD | biochemical oxygen demand |
| C | chlorination |
| Ca | calcium |
| $Ca(OCl)_2$ | calcium hypochlorite |
| $CaCO_3$ | calcium carbonate |
| $CaSO_4$ | calcium sulphate |
| CD | treatment by mixing chlorine and chlorine dioxide simultaneously (C proportion is higher than D) |
| CG | chlorine gas |
| $CH_3CO_3H$ | peracetic acid |
| $Cl_2$ | chlorine |
| CLB | closed-loop bleaching |
| $ClO_2$ | chlorine dioxide |
| CMC | carboxymethyl cellulose |
| COD | chemical oxygen demand |
| CPPA | Canadian Pulp and Paper Association |
| CTMP | chemithermomechanical pulp |
| Cu | copper |
| D | chlorine dioxide treatment |
| D/C | sequential bleaching with chlorine dioxide and subsequent chlorination without washing between the addition of chemicals |
| DARS | direct alkali recovery system |

| | |
|---|---|
| DC | sequential bleaching with chlorine dioxide and subsequent chlorination without washing between the addition of chemicals |
| DED | chlorine dioxide, extraction, chlorine dioxide |
| DIP | deinked pulp |
| DMD | dimethyldioxirane |
| DMSO | dimethyl sulfoxide |
| DP | degree of polymerization |
| DTPA | diethylenetriamine pentaacetic acid |
| DTPMP | diethylene-triamino-pentamethylene phosphonic acid |
| E | alkaline extraction |
| $E_1$, $E_2$ | first and second alkaline extractions, respectively |
| ECF | elemental chlorine-free |
| EDTA | ethylenediaminetetraacetic acid |
| Eo | oxidative extraction |
| $E_{OP}$ | oxidative extraction in presence of hydrogen peroxide |
| EOX | extractable organochlorine |
| Ep | alkaline extraction in the presence of hydrogen peroxide |
| EPA | environmental protection agency |
| ESP | electrostatic precipitator |
| F | fungal treatment |
| FAS | formamidine sulphinic acid |
| Fe | iron |
| G | gram |
| GE | brightness measurement using general electric test |
| H | hypochlorite stage |
| $H_2O_2$ | hydrogen peroxide |
| $H_2SO_4$ | sulfuric acid |
| HBT | hydroxybenzotriazole |
| $HCO_3H$ | peroxyformic acid |
| HPA-5 | heptamolybdopentavandophosphate heteropolyanion |
| HWKP | hardwood kraft pulp |
| ISO | International Organization for Standardization |
| K | potassium |
| kg/tp | kg/ton of pulp |
| KP | kraft pulp |
| LiP | lignin peroxidase |
| LMS | laccase-mediator system |
| LP | Louisiana-Pacific |
| LWC | light weight coated |
| MC | medium consistency |
| MCC | modified continuous cooking |

| | |
|---|---|
| MEK | methyl ethyl ketones |
| MFO | mixed function oxygenase |
| Mg | magnesium |
| MgO | magnesium oxide |
| $MgSO_4$ | magnesium sulfate |
| MIM | minimum impact mill |
| Mn | manganese |
| MnP | manganese peroxidase |
| MOW | mixed office waste |
| MR | Metsa-Rauma |
| Na(OCl) | sodium hypochlorite |
| $Na_2O_2$ | sodium peroxide |
| NaCl | sodium chloride |
| NADPH | nicotinamide adenine dinucleotide phosphate (reduced form) |
| NaOH | sodium hydroxide |
| NCASI | National Council for Air and Stream Improvement |
| NCG | non-condensable gases |
| NF | nanofiltration |
| NHAA | *N*-hydroxyacetinalide |
| $NO_2$ | nitrogen dioxide |
| NPE | non-process elements |
| O | oxygen-delignification/bleaching |
| $O_2$ | oxygen |
| $O_3$ | ozone |
| o.d | oven dry |
| ODL | oxygen delignification |
| ODT | oven-dried ton |
| OMG | old magazines |
| OKP | oxygen-delignified kraft pulp |
| ONP | old newsprint |
| Or | OXYPRO |
| OXYTRAC | Two-stage oxygen-delignification system |
| P | hydrogen peroxide treatment |
| Pa | peracetic or peroxyacetic acid |
| PDR | precipitator dust recovery |
| PFA | peroxyformic acid |
| PO | pressurized peroxide bleaching stage |
| POPs | persistent organic pollutants |
| Px, Pxa | peroxymonosulphuric acid, permonosulphuric acid |
| RDH | rapid displacement heating |
| S | sulfur |

| | |
|---|---|
| $SO_2$ | sulphur dioxide |
| SS | suspended solids |
| STFI | Swedish Pulp and Paper Research Institute, Stockholm |
| SWKP | softwood kraft pulp |
| TAED | tetra acetyl ethylene diamine |
| TAPPI | Technical Association of Pulp & Paper Industry |
| TCDD | tetrachlorobenzo-*p*-dioxin |
| TCDF | tetrachlorodibenzofuran |
| TCF | totally chlorine-free |
| TEF | totally effluent-free |
| TIS | Tappi information sheet |
| TMP | thermomechanical pulp |
| TOC | total organic carbon |
| TOCl | total organochlorine |
| TOX | total organic halides |
| tpd | tons per day |
| TRS | total reduced sulphur |
| UF | ultrafiltration |
| UKP | unbleached kraft pulp |
| W | water soak stage |
| X | xylanase enzyme treatment |
| Y | dithionite |
| Z | ozone stage |

# Index

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