Environmentally Friendly Production of Pulp and Paper

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Pratima Bajpai

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Preface

The pulp and paper industry is large and growing, reflecting the world's demand for paper. It is a capital- and resource-intensive industry that contributes to many environmental problems, including global warming, human toxicity, ecotoxicity, photochemical oxidation, acidification, nutrification, and solid wastes. Public concern is resulting in increased pressure on industry to focus on pollution prevention rather than on end-of-pipe cleanup. Industry is responding by modifying existing production processes or developing entirely new ones to achieve cleaner production (i.e., greater energy efficiency as well as reduced emissions of greenhouse gases and toxic substances). Many companies are beginning to find that cleaner production not only reduces environmental liabilities but also reduces costs and increases both productivity and competitiveness. Minimizing or eliminating the causes of wastes and emissions makes it easier to meet existing environmental regulations and reduces the environmental impact of the mill. Cleaner production is also attractive because of concerns about the lack of effectiveness of end-of-pipe solutions. Cleaner production and related approaches will be increasingly important in environmental management in the future. The introduction of cleaner production is an ongoing process. As resource prices and disposal costs continue to rise, new opportunities arise for pollution prevention and reductions in treatment costs. For this reason, cleaner production can be linked closely with environmental management systems. This book gives updated information on cleaner production measures in pulp and paper industry. Various chapters deal with cleaner production measures in raw material storage and preparation, in pulping processes (kraft, sulfite, and mechanical), in bleaching, recovery, papermaking, in emission treatment processes, and in recycled fiber processing. In addition, it includes a discussion on newer cleaner technologies and their implementation status and benefits in the pulp and paper industry.

Chapter 1

Introduction

"Cleaner production" is an international term for reducing environmental impacts from processes, products, and services by using better management strategies, methods, and tools. It is a global movement for improving business performance and a profitable, cleaner, and sustainable future. According to the United Nations Environment Programme (UNEP) definition of "cleaner production" and the one in most common use is, "Cleaner production is the continuous application of an integrated preventive strategy to processes, products and services, to increase ecoefficiency and to reduce risks to humans and the environment" (AIT, 1999). A number of related terms are also used, including pollution prevention, low- or no-waste technologies, waste minimization, waste and emission prevention, source reduction, ecoefficiency, and environmentally sound technology. All these terms basically refer to the same concept of integrating pollution reduction into the production process and even the design of the product.

The meaning of the term "cleaner production" varies from the perspective in which it is used. For production processes, cleaner production involves conserving raw materials and energy, eliminating the use of toxic substances as much as possible, and reducing the quantity as well as the toxicity of all emissions and wastes before they leave any given process. For products, it means reducing their environmental impacts during the entire life cycle, from raw material extraction to ultimate disposal. For services, it means incorporating environmental concerns when designing and delivering services (Fig. 1.1).

The adoption of cleaner production in the industry leads to multifold advantages to an operating industry. Cleaner production leads to better efficiency of production, which means more output of products per unit input of raw materials. This helps in improving the financial performance of the mill. The ultimate goal of cleaner production is to minimize the generation of emissions and waste that needs to be treated and the associated costs. Given the increasing cost of raw materials and the growing scarcity of good-quality water, no industry can afford to use these resources inefficiently. Cleaner production measures help in overcoming constraints posed by scarce or ever-increasing costly raw materials, water, and energy.

Cleaner production minimizes the amount and toxicity of waste and emissions and renders products that are more agreeable from an environmental standpoint. The direct effect is that the pollution load on the environment is decreased and

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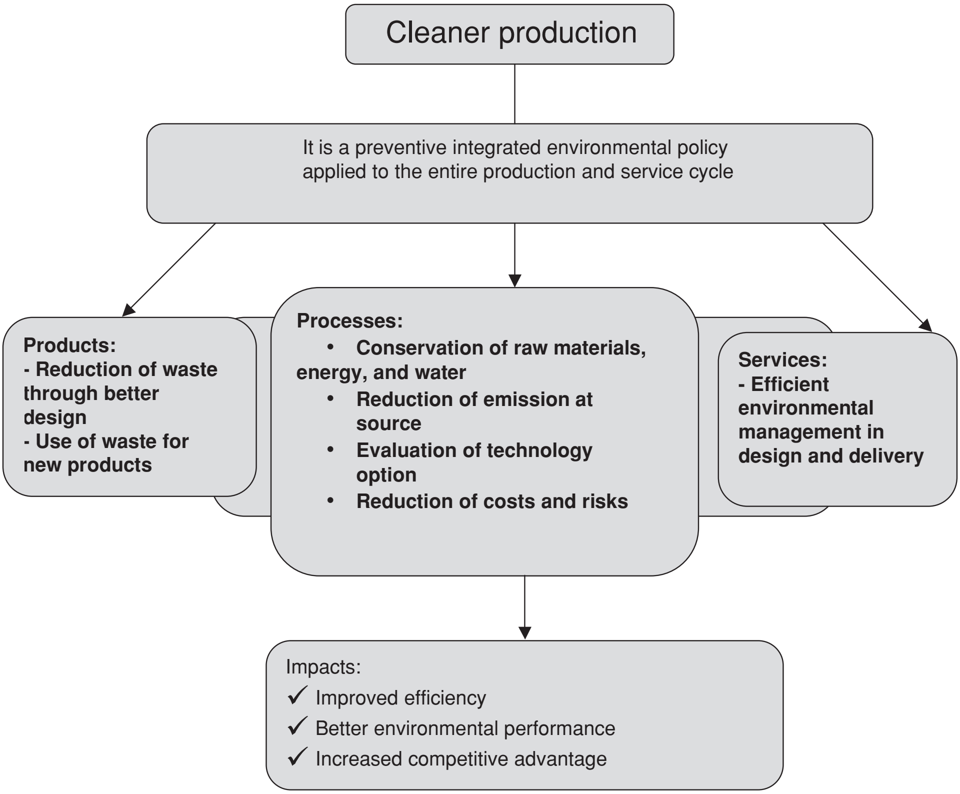

Figure 1.1 Cleaner production.

environmental quality is improved. It focuses on minimizing resource use and avoiding the creation of pollutants, rather than trying to manage pollutants after they have been created. It involves rethinking products, processes, and services to move toward sustainable development. Sustainable development concerns essential human activities, and sustainable development goals are often expected to dramatically affect both individual and public choices to modify production and consumption patterns (OECD, 2002; World Bank, 1998). Sustainable development is of critical importance for all citizens; it engages choices that will affect essential aspects of our lifestyles, and, being typically crosscutting, it should take into consideration various conflicting interests.

Consumers, suppliers, governments, and the market at large are increasingly demanding environmental responsibility by the business community. Businesses ignoring this trend and rejecting the opportunity to improve their environmental performance may find themselves left behind in the highly competitive global marketplace. Cleaner production is set to become an integral part of the business strategies of enlightened companies that want to embrace the ongoing challenges of industry leadership and continuous improvement. Cleaner production can reduce operating costs, improve profitability and worker safety, and reduce the environmental impact of our business. Companies are frequently surprised at the cost reductions achievable through the adoption of cleaner production techniques. Frequently, minimal or no capital expenditure is required to achieve worthwhile gains, with fast payback periods. Waste handling and charges, raw material usage, and insurance premiums can often be cut, along with potential risks.

On a broader scale, cleaner production can help alleviate the serious and increasing problems of air and water pollution, ozone depletion, global warming, landscape degradation, solid and liquid wastes, resource depletion, acidification of the natural and built environment, visual pollution, and reduced biodiversity.

It is proved from the past records that there lies a great potential for reduction in the pollution levels in the pulp and paper mills. From the different demonstration projects, it is established that adoption to the cleaner production has not only reduced the pollution loads but also helped in generating revenues by controlling the waste going down the drain (Nath, 1997; Radka, 1994; Satyanarayana et al., 2004).

The main difference between pollution control and cleaner production is one of timing. Pollution control is an after-the-event, "react and treat" approach, whereas cleaner production reflects a proactive, "anticipate and prevent" philosophy. Prevention is always better than cure. This does not mean, however, that "end-of-pipe" technologies will never be required. By using a cleaner production philosophy to tackle pollution and waste problems, the dependence on "end-of-pipe" solutions may be reduced or, in some cases, eliminated altogether.

Investing in cleaner production to prevent pollution and reduce resource consumption is more cost-effective than continuing to rely on the increasingly expensive "end-of-pipe" solutions. When cleaner production and pollution control options are carefully evaluated and compared, the cleaner production options are often more cost-effective overall. The initial investment for cleaner production options and for installing pollution control technologies may be similar, but the ongoing costs of pollution control technologies will generally be greater than those of cleaner production. Furthermore, the cleaner production option will generate savings through reduced costs of raw materials, energy, waste treatment, and regulatory compliance.

The environmental benefits of cleaner production can be translated into market opportunities for "greener" products. Companies that factor environmental considerations into the design stage of a product will be well placed to benefit from the marketing advantages of any future ecolabeling schemes.

Increasing consumer awareness of environmental issues has brought about a need for the companies to demonstrate the environmental friendliness of their products and manufacturing processes, particularly in international markets. By adopting the cleaner production approach, many of the market requirements are met and a company's ability to compete and get access to the "green market" increases.

Cleaner production not only improves the environment outside the mill but also improves working conditions. Keeping the mill clean and free of waste, spilled water, and chemicals not only reduces the likelihood of accidents but also motivates the workforce to control new leaks and material losses.

As public awareness of the need for environmental protection is growing each day, it becomes more and more important for the industry to respond and react to the questions and demands posed by the public. The environmental profile of a company is an increasingly important part of its overall reputation. Adopting cleaner production is a proactive, positive measure and can help the concerned company build confidence in the public regarding its environmental responsibility. Some reasons to invest in cleaner production are

- Improvements to products and processes
- Savings on raw materials and energy, thus reducing production costs
- Increased competitiveness through the use of new and improved technologies
- Reduced concerns over environmental legislation
- Reduced liability associated with the treatment, storage, and disposal of hazardous wastes
- Improved health, safety, and morale of employees
- Improved the company's image
- Reduced costs of end-of-pipe solutions

Cleaner production depends only partly on new or alternative technologies. It can also be achieved through improved management techniques, different work practices, and many other "soft" approaches. Cleaner production is as much about attitudes, approaches, and management as it is about technology. Cleaner production approaches are widely and readily available, and methodologies exist for its application. While it is true that cleaner production technologies do not yet exist for all industrial processes and products, it is estimated that more than 70% of all current wastes and emissions from industrial processes can be prevented at source by the use of technically sound and economically profitable procedures (Baas et al., 1992).

Cleaner production can contribute to sustainable development. Cleaner production can reduce or eliminate the need to trade off environmental protection against economic growth, occupational safety against productivity, and consumer safety against competition in international markets. Setting goals across a range of sustainability issues leads to win–win situations that benefit everyone. Cleaner production is such a win–win strategy—it protects the environment, the consumer, and the worker. It also improves industrial efficiency, profitability, and competitiveness.

Cleaner production can be especially beneficial to developing countries and those undergoing economic transition by planning, design, and management practices that facilitate innovative approaches to the reuse, remanufacturing, and recycling of the limited amounts of waste that cannot be avoided (Gavrilescu, 2004).

Cleaner production involves initiating steps to reduce the intensity of pollution at various levels. This can be accomplished by reducing the generation of wastes at its source and reusing and recycling the resources. Pollution prevention is of environmental and economic significance because it makes judicious use of the existing resources such as chemicals and water and eliminates the recurring costs involved in waste treatment and disposal. Most companies across the globe have charted out pollution prevention programs suitable to their industry requirements. Recent R&D initiatives undertaken by various companies include formaldehyde-free products, organic biocides, biotechnology products such as microbes, enzymes, and natural pigments.

Figure 1.2 shows the key initiatives taken by the pulp and paper industries to minimize pollution at various levels.

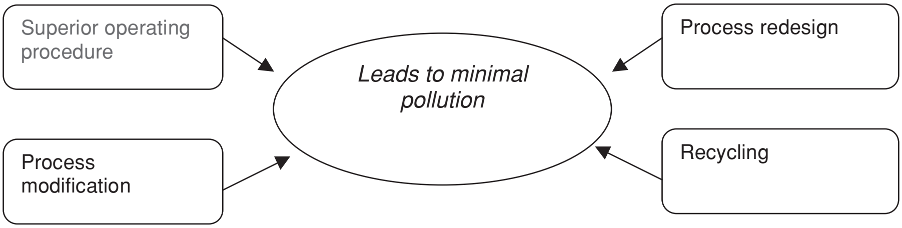

Figure 1.2 Key initiatives taken by the paper and pulp industries to reduce pollution.

1.1 SUPERIOR OPERATING PROCEDURES

The industry can implement changes in various departments such as the personnel department, inventory, waste handling department, and housekeeping units to ensure proper handling and storage of the wastes and monitoring the wastes for spills and leakages. Some of these include utilization of best available techniques such as minimizing the production of wastes and recycling of resources, separate storage and transportation facilities for nonhazardous from hazardous waste to facilitate recovery, reuse of certain chemicals and minimize the disposal costs, and conservation of water by recycling water within the industry and using the recycled water. Regular inspection of the machineries such as valves, pumps, and seals to detect leaks and spillages and the utilization of non-halogenated solvents and nontoxic cleaners during the cleaning of the machinery are required to eliminate the contamination of other materials in contact with the machinery.

1.2 PROCESS MODIFICATIONS

The existing operations can be modified to make industries more efficient and cost-effective, for example, inclusion of spill pits inside the plant to capture the leaking processed water and reusing this water in the process. About 20% of water wasted in the paper mills is due to spills, leakages, and washdowns; evaporation of black liquor to obtain concentrated solids; and modification of the system to support the usage of recycled paper in the manufacturing process.

1.3 PROCESS REDESIGN

The paper and pulp process can be modified and redesigned to accommodate the economic and environmental concerns. A few of the improved designs include dry barking of wood instead of wet to minimize the utilization of water and sludge production, wet air oxidation of wastewater sludge to obtain filler material, elimination of chlorine as a bleaching agent by using alternate bleaching agents such as ozone, and selection of additives that do not form dioxins and furans.

1.4 RECYCLING

The paper industry now utilizes certain amount of waste materials as raw materials, especially recycled fibers. Some of the key recycling procedures are utilization of filters or strainers to recycle secondary fibers, recycling, and reuse of water, and solvents used for cleaning operations can be recycled.

Tables 1.1 and 1.2 present the features of cleaner production technologies and management practices. Cleaner production technologies are related to make different changes in the process by addition of some equipment in the production processes. On the other hand, cleaner production management practices will talk of enhancing cleaner production by measures such as housekeeping and maintenance practices. The management practices will also encompass the production culture in the plant, which affects the production wastes (AIT, 1999; NPC, 1997; UNEP IE, 1996, 1997; Visvanathan et al., 1999).

Table 1.1 Cleaner Production Technologies

Concept
Involve application of a new process or equipment
Main goal is to reduce pollution and energy consumption
Involve technologies that pose lesser utilities requirements
Can be implemented in the existing system
Involve production practices that pose lesser utilities requirements

Requirements
New equipment or process
Utilities such as water, power, steam, or chemicals
Changes in the existing plant setups in a few cases
Moderate to high investments required
Vendor identification, purchasing process
Special training in the technology may be required
Continuous maintenance of new plant and machinery needed
Minor changes in the existing setups
No major utilities required
Some changes in the plant setups
No major investments required
Manageable in-house
May not require any special training
Ongoing process to get constant results

End results
Major reduction in the operating costs can be expected
Considerable enhancement in pollution standard compliance
Lesser reduction in the operating costs can be expected
Lesser effects on the pollution standard compliance

Based on AIT (1999).

Table 1.2 Cleaner Production Management Practices

Concept
Can be implemented in the existing system
Main goal is to reduce pollution and energy consumption
Involve production practices that pose lesser utilities requirements
Requirements
Minor changes in the existing setups
No major utilities required
Some changes in the plant setups
No major investments required
Manageable in-house
May not require any special training
Ongoing process to get constant results
End results
Lesser reduction in the operating costs can be expected
Lesser effects on the pollution standard compliance

Based on AIT (1999).

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Chapter 2

Overview of Pulp and Papermaking Processes

The pulp and paper industry is very diversified, using many types of raw materials to produce very different kinds of paper by different methods in mills of all sizes. Pulp and paper are manufactured from raw materials containing cellulose fibers, generally wood, recycled paper, and agricultural residues. In developing countries, about 60% of cellulose fibers originate from nonwood raw materials such as bagasse (sugarcane fibers), cereal straw, bamboo, reeds, esparto grass, jute, flax, and sisal (Gullichsen, 2000).

The paper manufacturing process has several stages: raw material preparation and handling, pulp manufacturing, pulp washing and screening, chemical recovery, bleaching, stock preparation, and papermaking (Fig. 2.1).

Paper production is basically a two-step process in which a fibrous raw material is first converted into pulp, and then the pulp is converted into paper. The harvested wood is first processed so that the fibers are separated from the unusable fraction of the wood, the lignin. Pulp making can be done mechanically or chemically. The pulp is then bleached and further processed, depending on the type and grade of paper that is to be produced. In the paper factory, the pulp is dried and pressed to produce paper sheets. Postuse, an increasing fraction of paper and paper products is recycled. Nonrecycled paper is either landfilled or incinerated.

Pulp mills and paper mills may exist separately or as integrated operations. Figure 2.2 shows a simplified flow diagram of an integrated mill. Manufactured pulp is used as a source of cellulose for fiber manufacture and for conversion into paper or cardboard.

2.1 RAW MATERIAL PREPARATION AND HANDLING

Pulp manufacturing starts with raw material preparation, which includes debarking (when wood is used as raw materials), chipping, chip screening, chip handling and storage, and other processes such as depithing (e.g., when bagasse is used as the raw material) (Biermann, 1996a; Gerald, 2006; Gullichsen, 2000).

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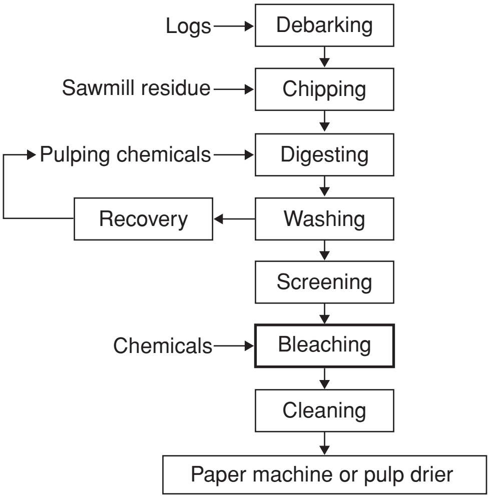

Figure 2.1 Pulp and papermaking processes.

Log debarking is necessary to ensure that the pulp is free of bark and dirt. Both mechanical and hydraulic bark removal methods are in common use. The barking drum is the most common form of mechanical debarking. Bark is removed from the logs by friction created from the rotating drum action as the logs rub against each other. In wet drumbarkers, water is added to the early solid steel portion of the drum to help loosen the bark. The remaining portion of the drum has slots to permit the

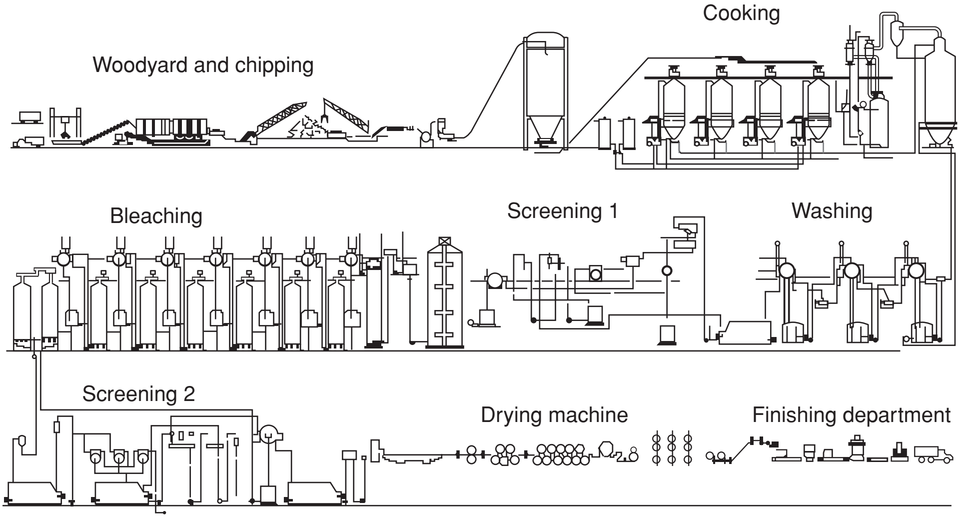

Figure 2.2 A simplified flow diagram of an integrated mill (chemical pulping, bleaching, and paper production). Based on Smook (1992b).

removed bark to fall out while the log continues on through. In dry drumbarkers, the entire length of the drum has slots for bark removal. Dry drumbarkers are longer in length and rotate much faster than wet-type drumbarkers. The bark from dry drumbarking can be fired directly into bark-burning furnaces, while bark from a wet system must be collected in a water flume, dewatered and pressed before burning. Drumbarkers usually create about 4–5% wood waste and cause broomed ends on the logs that produce inferior wood chips for pulping. They are relatively low-cost devices but have high power consumption (Russel, 2006).

After debarking, the logs (or portions of logs) are reduced to chip fragments suitable for the subsequent pulping operations. Several designs of chippers are in use, the most common being the flywheel-type disk with a series of blades mounted radially along the face. The logs are usually fed to one side of the rotating disk at an optimum angle (about 45 degrees) through a vertical directing chute. The logs can also be fed horizontally to a disk mounted at the proper angle. Generally, the horizontal feed provides better control but is less suitable for scrap wood pieces. Off-size chips adversely affect the processing and quality of pulp.

Acceptable-size chips are usually isolated from fines and oversized pieces by passing the chips over multistage vibratory screens. The oversized chips are rejected to a conveyor, which carries them to a “rechipper.” The fines are usually burned with the bark (unless special pulping facilities are available).

Conventional screening segregates chips only on the basis of chip length. More recently, the greater importance of chip thickness has been recognized, and a few recently designed screens now segregate according to this parameter. Also, new design “rechippers” that slice the chip lengthwise to reduce thickness cause far less damage to the fibers than the old-style crushers.

Within mill areas, most chips are transported on belts or in pipes, using an airveying system. Chips are readily handled by air over distances of 300–400 m, but power consumption is high and chip damage can be significant. By contrast, a belt conveyor system has a much higher initial cost. Other systems such as chain and screw conveyors are also used to move chips, but usually for relatively short distances. Bucket elevators are used for vertical movement.

Chip storage is widely utilized primarily because chips are more economical to handle than logs. Some disadvantages are apparent, for example, blowing of fines and airborne contamination, but it has been only recently that the significant loss of wood substance from respiration, chemical reactions, and microorganism activity has been quantified. It is now recognized that losses of 1% wood substance per month are typical. Considerable research has already been carried out to find a suitable chip preservative treatment, but so far, a totally effective, economical, and environmentally safe method has not been identified. In the meantime, it makes good sense to provide a ground barrier of concrete or asphalt before building a chip pile to reduce dirt contamination and inhibit the mobility of ground organisms. Chips should be stored on a first-in/first-out basis to avoid infection of fresh chips by old chips; the ring-shaped pile facilitates the complete separation of “old” and “new” chips. Wind-blown concentrations of fines should be avoided because they reduce the dissipation of heat that builds up in the pile from various causes. Thermal degradation and even spontaneous combustion can result from localized heat buildup. Optimum chip handling depends partly on pulping requirements. Because loss of extractives is high for the first 2 months of outside storage, all chips for sulfite pulping should go to storage (to reduce resin problems). If by-product recovery is important (as for some kraft pulping operations), fresh chips should bypass storage wherever possible to maximize yield.

A number of reclaiming methods are in use. Older installations employ a belt or chain conveyor along the side of the pile, which is fed by a bulldozer that pushes chips down the side of the pile onto the conveyor. This arrangement is labor-intensive (necessitating a full-time bulldozer operator) and inevitably results in damage to the chips. Modern installations work automatically, some employing augers or chain conveyors on rotating platforms at the base of the pile.

With respect to a given wood source, the quality of chips is measured by uniformity of size (i.e., length and thickness) and by the relative absence of "contaminants." All chips of 10–30 mm long and 2–5 mm thick are usually considered to be of good quality. Contaminants are considered to be oversized chips (either length or thickness), pin chips (passing 3/8 in. screen), fines (passing 3/16 in. screen), bark, rotten wood (including burned wood), and dirt and extraneous.

Oversized chips represent a handling problem and are the main cause of screen rejects in chemical pulping (Smook, 1992a). Size reduction of the oversize fraction is difficult to accomplish without generation of fines. Pin chips and (especially) fines and rotten wood cause lower yields and strengths in the resultant pulps and contribute to liquor circulation problems during cooking of chemical pulps. Bark mainly represents a dirt problem, especially in mechanical and sulfite pulping. The kraft pulping process is much more tolerant of bark because most bark particles are soluble in the alkaline liquor. Figure 2.3 illustrates the chip creation process.

2.2 PULP MANUFACTURING

The manufacture of pulp for paper and cardboard employs mechanical (including thermomechanical), chemimechanical, and chemical methods (Table 2.1).

Mechanical Pulping

There are three main categories of mechanical pulp: groundwood pulp, refining pulp, and chemimechanical pulp. Figure 2.4 shows the steps in the two first categories. In

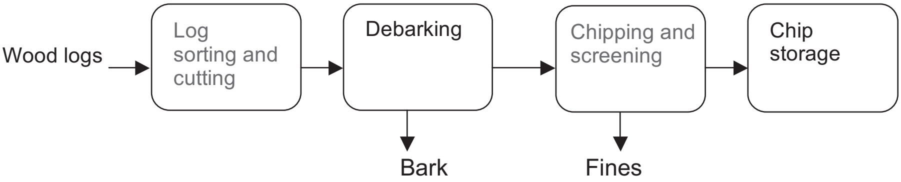

Figure 2.3 A flow diagram for wood preparation.

Table 2.1 Types of Pulping

Process	Pulp color	Yield (%)	Uses
Thermomechanical pulping	Brown	>95	Boxboard, newsprint, paper bags
Chemithermomechanical pulping	Light brown	85–95	Newsprint, specialty papers
Semichemical	Beige–brown	60–80	Newsprint, bags
Chemical—kraft, sulfite	Light brown	40–55	Newsprint, fine papers

both the grinding and refining processes, the temperature is increased to soften the lignin. This breaks the bonds between the fibers (Casey, 1983b; Gullichsen, 2000). Groundwood pulp shows favorable properties with respect to brightness ($\geq$85% International Organization for Standardization (ISO) after bleaching), light scattering, and bulk, which allows the production of papers with low grammages. Moreover, the groundwood process also offers the possibility of using hardwood (e.g., aspen) to achieve even higher levels of brightness and smoothness. Groundwood pulp has been the quality leader in magazine papers, and it is predicted that this situation will remain unchanged (Arppe, 2001). The most important refiner mechanical pulping process today is thermomechanical pulping (TMP). This involves high-temperature

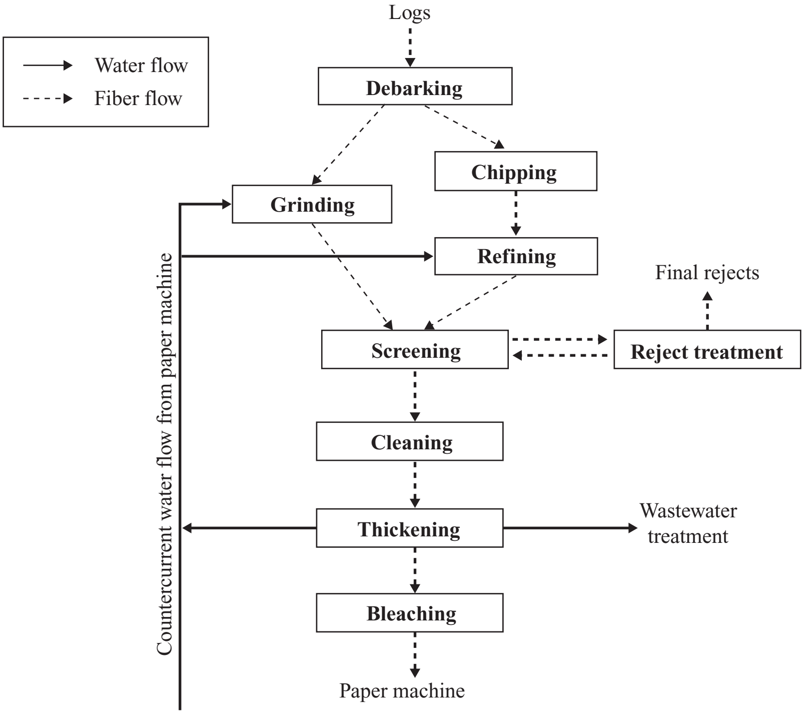

Figure 2.4 The mechanical pulping process.

steaming before refining; this softens the interfiber lignin and causes partial removal of the outer layers of the fibers, thereby baring cellulosic surfaces for interfiber bonding. TMP pulps are generally stronger than groundwood pulps, thus enabling a lower furnish of reinforcing chemical pulp for newsprint and magazine papers. TMP is also used as a furnish in printing papers, paperboard, and tissue paper. Softwoods are the main raw material used for TMP because hardwoods give rather poor pulp strength properties. This can be explained by the fact that hardwood fibers do not form fibrils during refining but separate into short, rigid debris. Thus, hardwood TMP pulps, characterized by a high-cleanness, high-scattering coefficient, are mainly used as filler-grade pulp. The application of chemicals such as hydrogen sulfite prior to refining causes partial sulfonation of middle lamella lignin. The better swelling properties and the lower glass transition temperature of lignin result in easier liberation of the fibers in subsequent refining. The chemithermomechanical pulps show good strength properties, even when using hardwood as a fiber source, and provided that the reaction conditions are appropriate to result in high degrees of sulfonation. Mechanical pulps are weaker than chemical pulps, but cheaper to produce (about 50% of the costs of chemical pulp) and are generally obtained in the yield range of 85–95%. Currently, mechanical pulps account for 20% of all virgin fiber materials. It is foreseen that mechanical paper will consolidate its position as one major fiber supply for high-end graphic papers. The growing demand on pulp quality in the future can only be achieved by the parallel use of softwood and hardwood as a raw material.

The largest threat to the future of mechanical pulp is its high specific energy consumption. In this respect, TMP processes are most affected due to their considerably higher energy demand than groundwood processes. Moreover, the increasing use of recovered fiber will put pressure on the growth in mechanical pulp volumes.

Semichemical Pulping

Semichemical pulping processes are characterized by a mild chemical treatment preceded by a mechanical refining step (Fig. 2.5) (Biermann, 1996b). Semichemical pulps, which apply to the category of chemical pulps, are obtained predominantly from hardwoods in yields of between 65% and 85% (~75%). The most important semichemical process is the neutral sulfite semichemical (NSSC) process, in which chips undergo partial chemical pulping using a buffered sodium sulfite solution, and

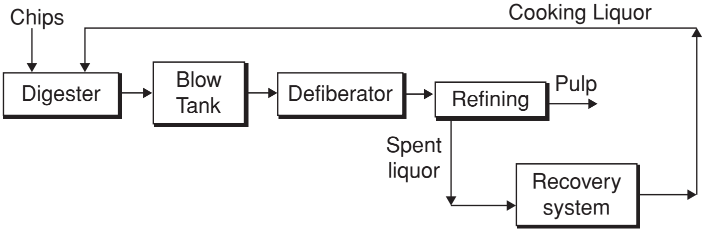

Figure 2.5 The semichemical pulping process.

are then treated in disk refiners to complete the fiber separation. The sulfonation of mainly middle lamella lignin causes a partial dissolution so that the fibers are weakened for the subsequent mechanical defibration. NSSC pulp is used for unbleached products where good strength and stiffness are particularly important; examples include corrugating medium, grease-proof papers, and bond papers. NSSC pulping is often integrated into a kraft mill to facilitate chemical recovery by a so-called cross-recovery, where the sulfite-spent liquor is processed together with the kraft liquor. The sulfite-spent liquor then provides the necessary makeup (Na, S) for the kraft process. However, with the greatly improving recovery efficiency of modern kraft mills, the NSSC makeup is no longer needed so that high-yield kraft pulping develops as a serious alternative to NSSC cooking. Semichemical pulp is still an important product category, however, and accounts for 3.9% of all virgin fiber materials.

Chemical Pulping

Chemical pulping dissolves the lignin and other materials of the interfiber matrix material, and also most of the lignin that is in the fiber walls. This enables the fibers to bond together in the papermaking process by hydrogen bond formation between their cellulosic surfaces. Chemical pulps are made by cooking (digesting) the raw materials, using the kraft (sulfate) and sulfite processes (Casey, 1983a).

Kraft Process

The kraft process produces a variety of pulps used mainly for packaging and high-strength papers and board. Wood chips are cooked with caustic soda to produce brown stock, which is then washed with water to remove cooking (black) liquor for the recovery of chemicals and energy (Biermann, 1996b). Figure 2.6 shows a simplified schematic diagram of the kraft pulping process and the corresponding chemical and energy recovery process. The kraft process dominates the industry because of advantages in chemical recovery and pulp strength. It represents 91% of chemical pulping and 75% of all pulp produced. It evolved from an earlier soda process (using only sodium hydroxide as the active chemical) and adds sodium sulfide to the cooking chemical formulation. A number of pulp grades are commonly produced, and the yield depends on the grade of products. Unbleached pulp grades, characterized by a dark brown color, are generally used for packaging products and are cooked to a higher yield and retain more of the original lignin. Bleached pulp grades are made into white papers. Nearly half of the kraft production is in bleached grades, which have the lowest yields. The superiority of kraft pulping has further extended since the introduction of modified cooking technology in the early 1980s. In the meantime, three generations of modified kraft pulping processes (modified continuous cooking, isothermal cooking, and compact cooking as examples for continuous cooking and cold blow, SuperBatch/rapid displacement heating, and continuous batch cooking for batch cooking technology) have emerged through continuous research and development. The third generation includes black liquor impregnation, partial liquor exchange, increased and profiled hydroxide ion concentration, and low cooking

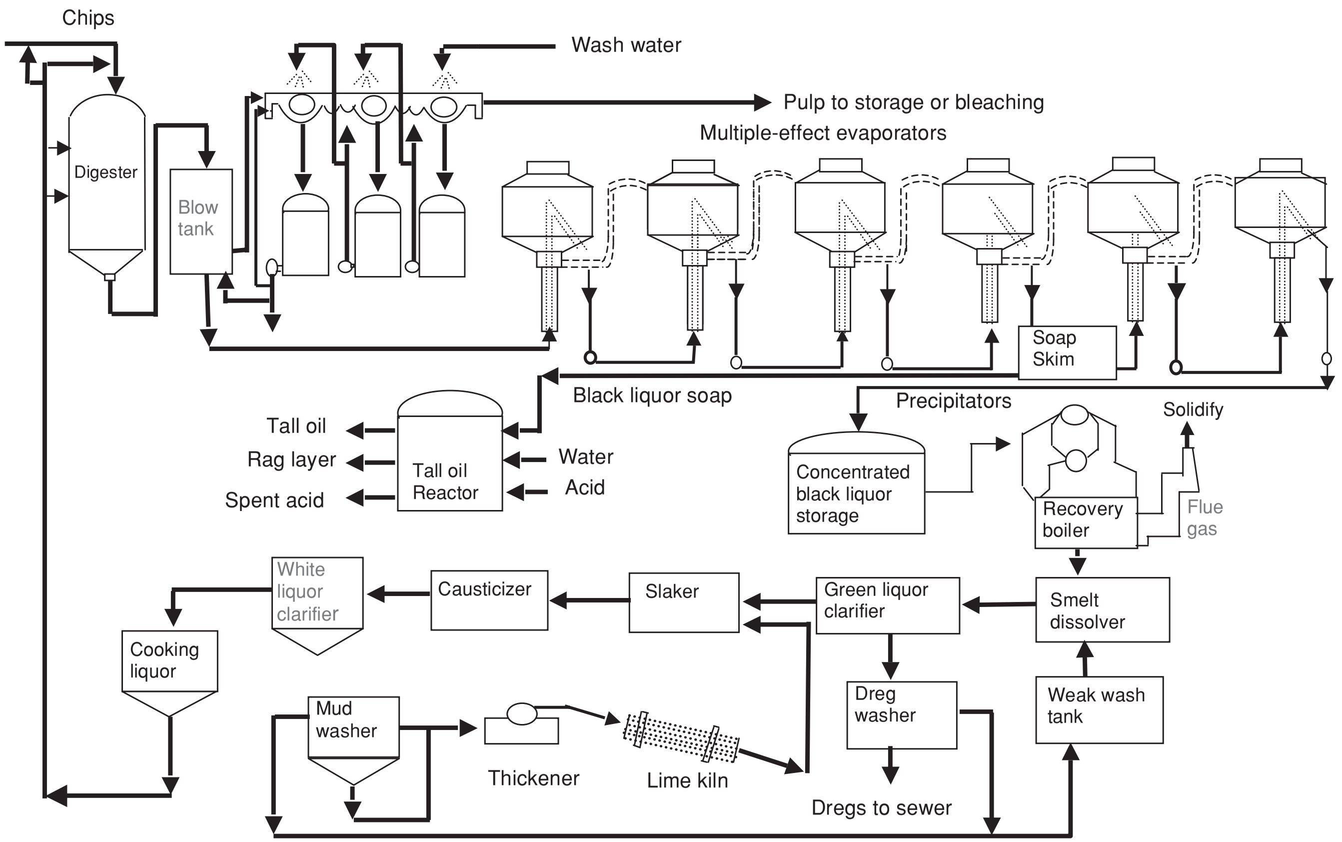

Figure 2.6 The kraft pulping process and the chemical and energy recovery cycle. Based on Smook (1992b).

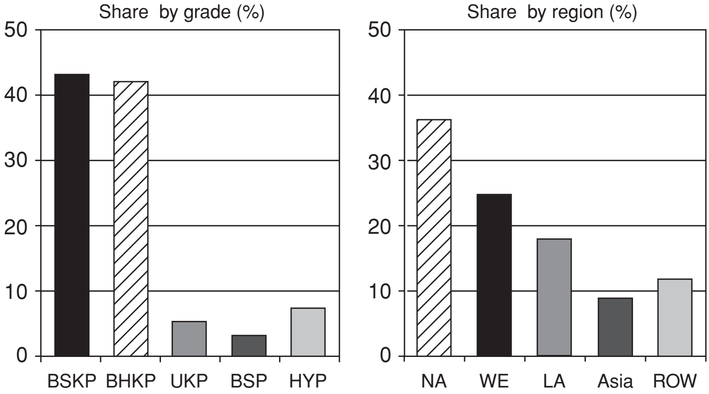

Figure 2.7 Global market pulp capacity of bleached kraft pulp: percent share by grade and percent share by region (Johnson et al., 2008). Reproduced with permission from Beca AMEC.

temperature (elements of compact cooking); also the controlled adjustment of all relevant cooking conditions in that all process-related liquors are prepared outside the digester in the tank (as realized in continuous batch cooking). However, the potential of kraft cooking is not exhausted by far. New generations of kraft cooking processes will likely be introduced, focusing on improving pulp quality, lowering production costs by more efficient energy utilization, further decreasing the impacts on the receiving water, and recovering high-added-value wood by-products (Annergren and Lundqvist, 2008; Marcoccia et al., 2000; McDonald, 1997).

In 2005, the global market pulp capacity was approximately 54 million tonnes; bleached kraft pulp accounted for 85% of capacity (Johnson et al., 2008). North America has the majority share by region, followed by Western Europe and Latin America (Fig. 2.7). Bleached hardwood kraft pulp capacity has grown at a faster rate than bleached softwood kraft pulp.

Many of the developments in kraft pulp production have been driven by severe environmental concerns, especially in Central Europe and Scandinavia during the 1980s and 1990s. Increasing pulp production resulted in increasing effluent loads. The need to reduce the amount of organic material originating mainly from bleach plant effluents was most pronounced in highly populated countries, where filtered river water was used as a source of drinking water. The biodegradability of the bleach plant effluents, particularly from the chlorination (C) and extraction stages (E), turned out to be very poor due to the toxicity of halogenated compounds. Finally, the detection of polychlorinated dioxins and furans in chlorination effluents and even in final paper products during the 1980s caused a rapid development of alternative, environmentally benign bleaching processes (Bajpai, 2005a). The initial intention was the complete replacement of all chlorine-containing compounds, resulting in totally chlorine-free (TCF) bleaching sequences. This could be easily accomplished with sulfite pulps due to their good bleachability. Kraft pulp mills have been converted dominantly to elemental chlorine-free (ECF) bleaching rather than to TCF bleaching because the latter, by using ozone or peracids to yield high brightness, deteriorates pulp quality. ECF bleaching, comprising chlorine dioxide (D)-containing bleaching sequences, such as DEOpDEpD, is acknowledged as a core component of the best available technology, since numerous field studies have shown that ECF bleaching is virtually free of dioxin and persistent bioaccumulative toxic substances. ECF pulp, bleached with chlorine dioxide, continues to dominate the world bleached chemical pulp market (Pryke, 2003). In 2007, ECF production reached more than 88 million tonnes, totaling more than 89% of world market share. Total ECF production increased by 12.6 million tonnes compared to 2005 levels (AET, 2007). In contrast, TCF production continued to decline, maintaining a small niche market at less than 5% of world bleached chemical pulp production.

Sulfite Process

This process uses different chemicals to attack and remove lignin. Compared to kraft pulps, sulfite pulps are brighter and bleached more easily, but are weaker. Sulfite pulps are produced in several grades, but bleached grades dominate production (Sixta, 2006). Yields are generally in the range of 40–50%, but tend toward the lower end of this range in bleached grades. Compared to the kraft process, this operation has the disadvantage of being more sensitive to species characteristics. The sulfite process is usually intolerant of resinous softwoods, tannin-containing hardwoods, and any furnish containing bark. The sulfite process produces bright pulp, which is easy to bleach to full brightness, and produces higher yield of bleached pulp, which is easier to refine for papermaking applications.

The sulfite process is characterized by its high flexibility compared to the kraft process, which is a very uniform method, which can be carried out only with highly alkaline cooking liquor. In principle, the entire pH range can be used for sulfite pulping by changing the dosage and composition of the chemicals (Biermann, 1996b; Smook, 1992b). Thus, the use of sulfite pulping permits the production of many different types and qualities of pulps for a broad range of applications. The sulfite process can be distinguished according to the pH adjusted into different types of pulping. The main sulfite pulping processes are acid (bi)sulfite, bisulfite (Magnefite), neutral sulfite (NSSC), and alkaline sulfite.

A typical sulfite pulping process is shown in Fig. 2.8 (Smook, 1992b). The sulfite cooking process is based on the use of aqueous sulfur dioxide and a base—calcium, sodium, magnesium, or ammonium. The specific base used will impact on the options available within the process in respect of chemical and energy recovery system and water use. The dominating sulfite pulping process in Europe is the magnesium sulfite pulping, with some mills using sodium as a base. Both magnesium and sodium bases allow chemical recovery. The lignosulfonates generated in the cooking liquor can be used as a raw material for producing different chemical products.

2.3 PULP WASHING AND SCREENING

After pulp production, pulp processing removes impurities, such as uncooked chips, and recycles any residual cooking liquor via the pulp washing process (Smook,

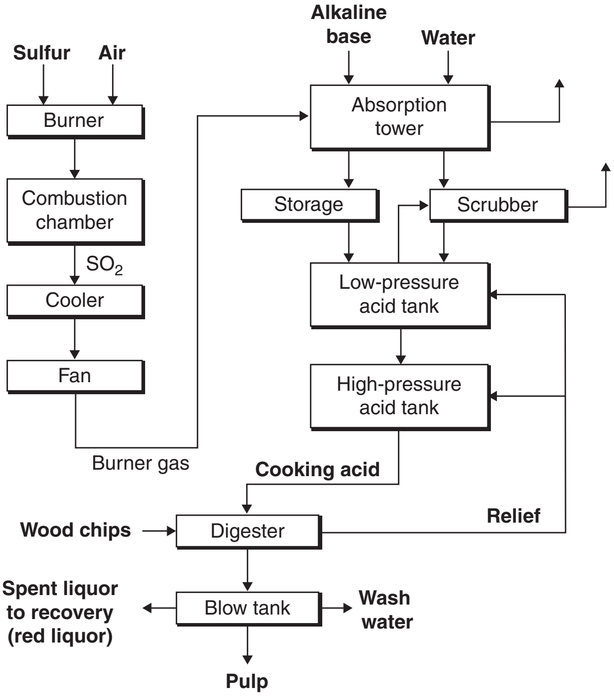

Figure 2.8 The sulfite pulping process. Based on Smook (1992b).

1992b). Pulps are processed in a wide variety of ways, depending on the method that generated them (e.g., chemical and sulfite). Some pulp processing steps that remove pulp impurities include screening, defibering, and deknotting. Pulp may also be thickened by removing a portion of the water. At additional cost, pulp may be blended to ensure product uniformity. If pulp is to be stored for long periods, drying steps are necessary to prevent fungal or bacterial growth. Residual spent cooking liquor from chemical pulping is washed from the pulp using pulp washers, called “brown stock washers” for kraft and “red stock washers” for sulfite. Efficient washing is critical to maximize return of cooking liquor to chemical recovery and to minimize carryover of cooking liquor (known as washing loss) into the bleach plant because excess cooking liquor increases consumption of bleaching chemicals. Specifically, the dissolved organic compounds (lignins and hemicelluloses) contained in the liquor will bind to bleaching chemicals and thus increase bleach chemical consumption. In addition, these organic compounds function as precursors to chlorinated organic compounds (e.g., dioxins and furans), increasing the probability of their formation.

The most common washing technology is rotary vacuum washing, carried out sequentially in two, three, or four washing units. Other washing technologies include diffusion washers, rotary pressure washers, horizontal belt filters, wash presses, and dilution/extraction washers. Pulp screening removes remaining oversized particles such as bark fragments, oversized chips, and uncooked chips. In *open* screen rooms, wastewater from the screening process goes to wastewater treatment prior to discharge. In *closed-loop* screen rooms, wastewater from the process is reused in other pulping operations and ultimately enters the mill's chemical recovery system. Centrifugal cleaning (also known as liquid cyclone, hydrocyclone, or centricleaning) is used after screening to remove relatively dense contaminants such as sand and dirt. Rejects from the screening process are either repulped or disposed of as solid waste (Gullichsen, 2000).

Brown Stock Washing

The objective of brown stock washing is to remove the maximum amount of liquor-dissolved solids from the pulp while using as little wash water as possible. The dissolved solids left in the pulp after washing will interfere with later bleaching and papermaking and will increase costs of these processes. The loss of liquor solids due to solids left in the pulp means that less heat can be recovered in the recovery furnace. Also, makeup chemicals must be added to the liquor system to account for lost chemicals (Gullichsen, 2000).

It would be easy to achieve very high washing efficiencies if one could use unlimited amounts of wash water. As it is, one has to compromise between high washing efficiency and a low amount of added wash water. The water added to the liquor during washing must be removed in the evaporators prior to burning the liquor in the recovery furnace. This is a costly process and often the bottleneck in pulp mill operations. Minimizing the use of wash water will therefore decrease the steam cost of evaporation.

In dilution/extraction washing, the pulp slurry is diluted and mixed with weak wash liquor or freshwater. Then, the liquor is extracted by thickening the pulp, either by filtering or pressing. This procedure must be repeated many times in order to sufficiently wash the pulp.

In displacement washing, the liquor in the pulp is displaced with weaker wash liquor or clean water. Ideally, no mixing takes place at the interface of the two liquors. In practice, however, it is impossible to avoid a certain degree of mixing. Some of the original liquor will remain with the pulp, and some of the wash liquor will channel through the pulp mass. The efficiency of displacement washing then depends on this degree of mixing and also on the rate of desorption and diffusion of dissolved solids and chemicals from the pulp fibers.

All pulp washing equipment is based on one or both of these basic principles. Displacement washing is utilized in a digester washing zone. A rotary vacuum washer utilizes both dilution/extraction and displacement washing, while a series of wash presses utilize dilution\extraction. Most pulp washing systems consist of more than one washing stage. The highest washing efficiency would be achieved if freshwater were applied in each stage. However, this approach would require large quantities of water and is therefore not used. Countercurrent washing is the generally used system design. In countercurrent washing, the pulp in the final stage is washed with the cleanest available wash water or freshwater before leaving the system. The drained water from this stage is then sent backward through each of the previous stages in a direction opposite to the pulp flow (Smook, 1992b).

Screening

Screening of the pulp is done to remove oversized and unwanted particles from good papermaking fibers so that the screened pulp is more suitable for the paper or board product in which it will be used (Biermann, 1996b; Ljokkoi, 2000). The biggest oversized particles in pulp are knots. Knots can be defined as uncooked wood particles. The knots are removed before washing and fine screening. In low-yield pulps they are broken down in refiners and/or fiberizers; they are also removed in special coarse screens called "knotters."

The main purpose of fine screening is to remove shives. Shives are small fiber bundles that have not been separated by chemical pulping or mechanical action. Chop is another kind of oversized wood particle removed in screening. It is more of a problem when pulping hardwoods because it originates mostly from irregularly shaped hardwood vessels and cells. Chop particles are shorter and more rigid than shives. Debris is the name for shives, chop, and any other material that would have any sort of bad effect on the papermaking process or on the properties of the paper produced.

2.4 PULP BLEACHING

Pulps prepared by most pulping processes are too dark 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 sulfite processes are lighter in color and can be used in products such as newsprint. The sulfite process produces chemical pulps with the lightest color (Smook, 1992c). 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. Technical Association of the Pulp and Paper Industry (TAPPI) or (General Electric) GE brightness is measured with an instrument in which the illumination of the sample is directional, oriented at 45 degrees to the surface. The most common standard, developed by the 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 percent GE and percent 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 sulfite 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 fiber 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 practiced based on the reasoning that not all products require high brightness.

The papermaking properties of chemical pulps are changed after bleaching. Removal of the residual lignin in the pulp increases fiber flexibility and strength. On the other hand, a lowered hemicellulose content results in a lower swelling potential of the fibers and a reduced bonding ability of the fiber surfaces. If bleaching conditions are too severe, there will be fiber 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 brightness level (Farr et al., 1992; Fredette, 1996; McDonough, 1992; Reeve, 1989, 1996a). Bleaching is carried out in a multistage process, that is, 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 multistage 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 and Strumila, 1979; Reeve, 1996a).

The introduction of Cl_2 and ClO_2 in the 1930s and early 1940s, respectively, increased markedly the efficiency of the bleaching process (Rapson and Strumila, 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 the lignin, allowing much of it to be washed out and removed with the spent liquor by subsequent alkaline extraction. The resulting brownish kraft pulp eventually required additional bleaching stages to increase brightness, which led to the development of the multistage process. Chlorine dioxide, a more powerful brightening agent than hypochlorite, brought the kraft process efficiency one step further (Rapson and Strumila, 1979; Reeve, 1996a). Between the 1970s and 1990s, a series of incremental and radical innovations increased again the efficiency of the process, while reducing its environmental impacts (Reeve, 1996b). Development of oxygen delignification, modified and extended cooking, improved operation controls, for example, improved pulp and chemical mixing, multiple split chlorine additions, and pH adjustments increased the economics of the process and led to significant reduction of wastewater (Malinen and Fuhrmann, 1995; McDonough, 1995). In addition, higher ClO_2 substitution brought down significantly the generation and release of harmful chlorinated organic compounds. Table 2.2 details different considerations 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-degree 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 further reducing the amount of bleaching chemicals needed. Under tightening regulations and market demands for chlorine-free products, the industry eventually accelerated the implementation of ECF and 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 (Bajpai, 2005a; McDonough, 1995).

2.5 STOCK PREPARATION

Stock preparation is conducted to convert raw stock into finished stock (furnish) for the paper machine. The pulp is prepared for the paper machine including the blending of different pulps, dilution, and the addition of chemicals. The raw stocks used are the various types of chemical pulp, mechanical pulp, and recovered paper and their mixtures. The quality of the finished stock essentially determines the properties of the paper produced. Raw stock is available in the form of bales, loose material, or, in case of integrated mills, as suspensions. Stock preparation consists of several process steps that are adapted to one another as fiber disintegration, cleaning, fiber modification, and storage and mixing. These systems differ considerably depending on the raw stock used and on the quality of furnish required. For instance, in the case of pulp being pumped directly from the pulp mill, the slushing and deflaking stages

Table 2.2 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	Achieve high brightness without pulp degradation, good particle bleaching	Expensive, must be made on-site
P	H_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, provide chlorine-free effluent for recovery	Expensive, poor particle bleaching
E	NaOH, 5–10% solution	Hydrolyze and solubilize lignin	Effective and economical	Darken pulp

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

are omitted. The following operations are practiced in the paper mills (Biermann, 1996e; Paulapuro, 2000):

- Dispersion
- Refining
- Metering and blending of fiber and additive

A number of new concepts have been introduced by Kadant Lamort with regard to virgin pulp stock preparation.

Dispersion

Pulpers are used to disperse dry pulp into water to form a slush or a slurry. The stock in the pulper is accelerated and decelerated repeatedly, and hydrodynamic shear forces are produced by the severe velocity gradients. The resulting forces serve to loosen fibers and reduce any flakes into individual fibers.

Beating/Refining

Pulp produced in a mill without mechanical treatment is unsuitable for most paper grades. Paper made from unbeaten virgin pulp has a low strength, is bulky, and has a rough surface. In good-quality paper, the fibers must be matted into a uniform sheet and must develop strong bonds at the points of contact. Beating and refining are the processes by which the undesirable characteristics are changed (Baker, 2000).

Mechanical treatment is one of the most important operations when preparing papermaking fibers. The term “beating” is applied to the batch treatment of stock in a Hollander beater or one of its modifications. The term “refining” is used when the pulps are passed continuously through one or more refiners, whether in series or in parallel. Refining develops different fiber properties in different ways for specific grades of paper. Usually, it aims to develop the bonding ability of the fibers without reducing their individual strength by damaging them too much, while minimizing the development of drainage resistance. So, the refining process is based on the properties required in the final paper. Different types of fiber react differently because of differences in their morphological properties (Baker, 2000, 2005). The refining process must take into account the type of fibers.

Most of the strength properties of paper increase with pulp refining because they rely on fiber–fiber bonding. However, the tear strength, which depends highly on the strength of the individual fibers, decreases with refining. After a certain point, the factor limiting the strength is not the fiber–fiber bonding, but the strength of the individual fibers.

Refining beyond this causes a decrease in other strength properties besides tear. Refining a pulp increases the fibers’ flexibility and results in denser paper, which means that bulk, opacity, and porosity values decrease during the process (Lumiainen, 2000). Mechanical and hydraulic forces are employed to alter the fiber characteristics. Shear stresses are imposed by the rolling, twisting, and tensional actions, occurring between the bars and in the grooves and channels of the refiner. Normal stresses (either tensional or compressive) are imposed by the bending, crushing, and pulling/pushing actions on the fiber clumps caught between the bar-to-bar surfaces. During beating and refining, fibers randomly and repeatedly undergo tensile, compressive, shear, and bending forces. They respond in three ways

1. Fibers develop new surfaces externally through fibrillation and internally through fiber wall delamination.
2. Fibers deform, resulting in changes in their geometric shape and the fibrillar alignment along their length. Overall, the fibers flatten or collapse. Fiber curl changes and kinks are induced or straightened. On the small scale, dislocations, crimps, and microcompressions are induced or diminished.
3. Fibers break, resulting in changes in length distribution and a decrease in mean fiber length. A small amount of fiber wall material also dissolves. All

> these changes occur simultaneously and are primarily irreversible. The extent of the changes depends on the morphology of the fibers, the temperature, the chemical environment, and the treatment conditions. The conditions depend on the design of the equipment and its operating variables such as the consistency, intensity, and amount of treatment. Each pulp responds differently to a given set of conditions, and not all fibers within it receive the same treatment (Lumiainen, 2000).

As different types of fibers have different lengths and cell wall thicknesses and also vary in the width of their central lumen (canal), some fibers are fibrillated more by one kind of beating than another. Fibers that have thick cell walls and narrow central canals, such as linen, are less prone to cutting but readily fibrillate. So, choosing the right type of fiber to produce the refining effect appropriate to the desired paper properties is important. The problem in producing paper with the required properties is that cutting and fibrillation are not independent of one another. Cutting is necessary to produce smaller fibers that pack to give a good, smooth paper, while fibrillation is required for strength. The degree to which each of these is achieved depends on the characteristics of refining. Moreover, increasing fibrillation to impart strength and stiffness also increases the surface area of the fiber mat and reduces permeability.

The characteristics built into a paper by refining are a compromise. Cutting is different from fibrillation. Beating the fiber in an aqueous environment forces water into the cell walls. This is necessary for fibrillation. However, cutting does not require the cell walls to be swollen and should be conducted early in the refining process so that it does not introduce additional fibrillation–-too much water retention by the fiber may result in drainage difficulties. While cutting can be distinguished from fibrillation in the refining process, fibrillation cannot be achieved without cutting some fibers.

There is a difference in drainage properties between cut and fibrillated fibers. Because of the difference, papermakers use the terms "free beaten" and "wet beaten," respectively. The difference in papermaking properties between the free-beaten and wet-beaten are

- Wet-beaten produces strong, dense, less porous, less absorbent, and dimensionally unstable papers.
- Free-beaten produces weak, bulky, porous, absorbent, and dimensionally stable papers.

The swollen cell walls in wet-beaten stock will collapse and shrink when the final paper is dried. However, if they come into contact with water again, such as in the lithographic printing process, they will readily reswell because damage to the cell walls makes them susceptible to water ingress. Wet-beaten stocks experience a large shrinkage in web width on drying but quickly expand again, which may cause registration problems during printing on rewetting. However, maximum burst tensile and fold strength can only be achieved by extended refining. This causes swelling and fibrillation at the cost of stability and bulk.

The degree of fibrillation imposed during refining also affects the rate at which the dilute suspension of pulp dewaters on the machine. The rate of dewatering is important because once the wet paper web has been formed, water must be removed as quickly and efficiently as possible (starting from 99% water in the pulp fed on to the papermaking wire down to about 7% in the finished paper). The freeness of the pulp is important to the papermaker, with the rate of drainage giving an indication of the degree of beating or refining. The freeness is a measure of intentional beating and of any changes in fiber morphology during the mixing and dispersion of fibers.

Different refiners are used in refining and these differ in their design and operating conditions (Bajpai, 2005b; Baker, 2000; Biermann, 1996d; Stevens, 1992). While machine configurations have undergone changes, all have a similar action and work by an arrangement of cutting edges, brushing surfaces, contact pressures, and peripheral speeds. Within certain limits, when a refiner is properly applied, there is not a great difference between the ability of conical and disk refiners to develop fibers. A fiber is only aware of how many times it is hit and how hard it is hit.

The first refining machine was a Hollander beater. It was invented in the 1700s and operates in a batchwise mode. It was phased out in the late 1970s because it is slow and expensive to run. These days it is only used in small mills and in special applications, for example, cutting long cotton/rag fibers before the refining process. The Hollander beater comprises a large open vessel, a rotating bar-equipped drum, and two or three bar-equipped counter bed plates. It is energy-intensive, but produces a gentle and quite uniform treatment. Its refining energy and intensity can be independently controlled, which is an advantage. The beater suits small-capacity mills and short runs and is more versatile than other refiners, because different treatments can be obtained by changing the pressure during the beater cycle.

Two types of continuous refiner are used for stock preparation: conical refiners and disk refiners. Conical and disk refiners have almost completely replaced beaters in stock preparation systems. They occupy less space at similar levels of production and are more efficient in developing fiber strength. Conical refiners can be split into low-angle types (Jordan) and high-angle types (Claflins). They have been manufactured in a range of sizes and capacities. Their operation is similar to that of a disk refiner, except in geometry. In conical refiners, the refining surfaces are on a tapered plug. These surfaces consist of a rotor that turns against the housing and the stator, both of which contain metal bars mounted perpendicularly to rotation. The Jordan refiner, patented by Joseph Jordan in 1858, is a low-angle conical refiner. It achieves different levels of refining by moving a rotating plug into a stationary shell to change the distance between the two surfaces. There are many sizes and capacities of this type of refiner. The Jordan refiner is still found in many fine paper mills but has a number of shortcomings when compared to the more modern conical and double-disk refiners (Lumiainen, 2000). The no-load power is high, which equals low operating efficiency; typically, in many installations the efficiency is less than 50%.

The next conical-type refiner is a wide-angle refiner with a 60-degree angle rather than 16 degrees. The most widely used version of this type of refiner is the Bematec Clafin refiner (Bajpai, 2005b). These refiners operate with a large working area at low speeds, having relatively little power installed for the throughput capacity. Fillings are available that produce anything from extreme cutting to almost pure fibrillation and do so, without sacrificing efficiency. Wide-angle refiners are adaptable and work economically under a variety of conditions. This type of refiner is found in many mills and has a deserved reputation for robustness and long filling life. Another type of conical refiner is the shallow-angle refiner, for example, Conflo. It is well established worldwide. The advantages for this refiner are a low no-load power and a long refining zone (Lumiainen, 1991). The shallow-angle refiner is an energy-efficient replacement for older types of low-angle conical refiners and offers a range of fillings suitable for softwood and hardwood pulps.

In the mid-1990s, Pilao S.A. of Brazil, a manufacturer of disk-type refiners, began a project to improve on the available designs of conical refiners (Anonymous, 1998a, b). The goals were to develop a unit that combined the fiber development and reduced energy characteristics of the new conical refiners with higher capacity and energy efficiency. The result of the project was a conical refiner with three refining cones. The refining system is a wide-angle, double-flow conical refiner with a double-sided conical rotor and two conical stators. Like a double-disk refiner, the rotor floats and is balanced by stock flow and hydrodynamic pressure on both sides. In concept, the refiner can be thought of as a double-disk refiner folded back over itself. The new type of conical refiner provides more complete and homogeneous fiber treatment and improved fiber development. The hydrodynamic forces in a conical refiner may force more fibers across the bar intersections.

Disk refiners also operate continuously. These refiners became available for papermaking in the 1930s, after the conical refiners. Disk refiners are able to operate at high consistency, which favors fiber fibrillation with minimal fiber cutting. They have lower no-load energy requirements (an indication of energy that does not contribute to refining), are more compact, and are easier to maintain. The disk refiner group comprises three types: single-disk, double-disk, and multi-disk-type refiners. Single-disk refiners are almost entirely used only in high-consistency refining because their efficiency in low-consistency refining does not meet today's requirements. Multi-disk refiners are intended for very low-intensity refining with extremely fine plate pattern and are most suitable for the postrefining of mechanical and hardwood pulps (Baker, 2005).

Another type of refiner is cylindrical refiner called the "Papillon" developed by Andritz (Gabl, 2004; Lankford, 2001). It incorporates the Hollander beater principle—which integrates the production engineering requirements of a continuous refining process to some advantage. The pulp is refined on one-cylinder level, which yields the following advantages: the pulp transport and refining processes operate independently of one another. This means that refining conditions can be properly targeted over the entire refining gap. Same refining speed over the entire refining gap results in improved technological values and net energy consumption for refining, as well as a significant reduction in the no-load power compared to conventional refining units. The concept of the new refiner is based on market requirements in terms of improved use of the fiber strength potential available.

DoubleConifiner and ConiDisc are two advanced refiners available from Aikawa Iron Works KK (Aoshima, 2002). Both possess the combined characteristics of the double-disk refiner and conical refiner. DoubleConifiner achieves sufficient refining without causing damage to the pulp fibers, resulting in improvements in stretch resistance and intralayer strength. Thune Myren medium-consistency refiner developed by Thune Myren, in conjunction with PFI, operates at between 10% and 22% consistency. The refiner is screw-fed, and the removed water can be re-added after refining or into the refiner casing (the preferred method).

The changes that take place in fibers during beating profoundly affect the character of the paper, which can be made from them. Some of the changes can be seen when the fibers are examined under a microscope, but in many instances, there is a marked change in the papermaking properties with no commensurate visible change. In general, it may be said that the outer surface of a fiber consists of a network of fibrils, while the inner, secondary wall has parallel bundles of fibrils of the same general dimensions. Beating tends to remove that portion of the outer surface which remains after the processes of cooking, bleaching, and purification. As beating proceeds further, the inner wall of the fiber starts to swell and disintegrate. Beating for most grades of paper involves only the first of the process, but for glassine papers it goes nearly to completion.

Blending/Chemical Addition

The various fibrous and additive components are combined and blended to make the furnish (Biermann, 1996e; Paulapuro, 2000). The pulp components are supplied from a high-density storage tower. Therefore, a series of controlled dilution steps and mixing stages are necessary to achieve a uniform consistency. Accurate proportioning of pulps and additives into a blend is the major task of this stage. Many chemical additives are added to the stock at different points before the paper machine. The chemical additions are made at points right up to the wire, known as “stock additives” or “wet-end additives.” For the majority of these additives, there are alternative points of addition, but some are much more effective if added at the right place. Routine additions at the beater or paper machine wet-end stage include sizing agents, mineral fillers, starch, and associated products and dyes (Krogerus, 2007; Smook, 1992d). Chemicals to give special effects, for example, wet strength, and to control such machine problems as foam, slime, and pitch. Fillers, or loading materials, were originally considered as adulterants used chiefly to cheapen the paper. It was not long, however, before they were recognized as serving perfectly legitimate purposes by increasing the opacity of the paper, aiding in obtaining a good finish on calendering, and improving printing qualities by reducing “showthrough” and “strikethrough” of the ink. Today, fillers are used in the great majority of printing papers, though there are some bulky papers and specialties in which they are not employed. Fillers increase the weight more than the bulk of a paper; they also affect adversely the strength of the paper and make it much more difficult to size with rosin. These facts must be remembered when setting specifications for a paper. Commonly used fillers are discussed in the following sections (Biermann, 1996e; Krogerus, 2007).

China Clay

China clay has the benefit of being chemically inert and therefore can be used in its natural state with any type of sizing agent, acidic or alkaline. Commercial quantities are available in a wide range of particle sizes and brightness levels, the finer and brighter grades being used in high-quality papers. The use of china clay provides a smooth receptive surface that easily accepts printing ink, and although not as opaque as some more expensive fillers, it is satisfactory for many types of paper.

Chalk

Naturally occurring chalk tends to be of coarser particle size than china clay; hence, it increases matt surface to the paper. However, as it reacts with the acidic alum used in conventional sizing, its use as a filler is restricted. Commercially, calcium carbonate is available to the papermaker as ground, naturally occurring calcium carbonate or as synthetically prepared "precipitated calcium carbonate." The precipitated calcium carbonate is produced in various ways, most common being the passing of carbon dioxide through milk of lime (calcium hydroxide) or by the reaction of soda ash (sodium carbonate) with milk of lime. Another source of calcium carbonate is from the alkali recovery stage in the sulfate process. These so-called protected chalks are coated with starch and a polymer. As chalk is inexpensive compared to china clay, and with the introduction of "neutral" or "alkaline" sizing, this has led to an increased use of chalk as a filler.

Titanium Dioxide

Titanium dioxide with its high refractive index provides excellent opacity and brightness to paper, especially useful for thin bible papers, laminate base papers, and waxed papers. Titanium dioxide is also used in combination with other fillers, such as china clay, whereby in order to reduce costs, the proportion of titanium dioxide is kept to a minimum. Thus, a typical addition to a white lining for boxboards is 10% china clay, 3% titanium dioxide. The use of fillers in such liners is to make the brown shade of inner piles of waste paper from which the board is formed. The comparatively high cost of titanium dioxide has led to the use of synthetically prepared fillers, for example, sodium aluminum trihydrate. These can be used to replace a proportion of the titanium dioxide with virtually no loss of opacity, thereby reducing costs. They are however not suitable for such partial substitution of titanium dioxide in waxed papers. Titanium dioxide absorbs ultraviolet radiation to a much greater extent than other fillers. It is therefore not economical to use fluorescent brightening agents in papers in which titanium dioxide is the only filler. The synthetically prepared fillers referred to above are often incorporated with titanium dioxide in such cases, because by reducing the absorption of the ultraviolet radiation they enhance the effect of the brightening agent.

Other Additives

Other additives used are slimicides, antifoaming agents, filler retention aids, pitch control agents, and wet-strength agents (Krogerus, 2007). Urea-formaldehyde and melamine formaldehyde resins are commonly used wet-strength agents and have a range of qualities, most of which require curing on the machine and running under acid conditions. Other chemical types can operate under neutral conditions, for example, in tissues, such as, polymide resins, modified starches, and emulsified elastomers. It is important that the correct agent is used for particular papers.

Sizing Agents

Chemicals that are used in the process of sizing are known as sizing agents. The process of sizing can be accomplished in two principal ways: (1) internal sizing and (2) surface sizing (Davison, 1992; Hodgson, 1997; Latta, 1997; Luukkonen et al., 1995; Neimo, 2000; Roberts, 1996, 1997). Internal sizing plays an important role in controlling the absorption and penetration of liquid such as water and ink into the paper, paperboard, and sheet material. The purpose of internal sizing is to inhibit penetration of liquids into the internal structure of paper. Internal sizes are introduced at the wet end of the papermaking system, usually as colloidal suspensions, which are retained in the fiber network during sheet formation. Adequate sizing maintains consistent runnability through the size press and helps to provide uniform printability in uncoated papers. For coated paper base stock, adequate sizing helps to control binder migration. Many factors influence the degree to which paper will resist penetration by liquids. These may include such paper properties as porosity and hydrophobicity (Bajpai, 2004).

Internal sizing agents are hydrophobic substances, which must attach to the paper (through the use of an appropriate functional group) to present a hydrophobic surface. On the basis of the pH, the internal sizing can be categorized into three types: (1) acid sizing, (2) neutral sizing, and (3) alkaline sizing. The three most common internal sizing agents currently being used are rosin systems, alkene ketene dimers (AKD), and alkenyl succinic anhydrides (ASA). A papermaker chooses the appropriate sizing agent by observing the processing conditions in the wet end of the paper machine and the particular grade being produced. For paper being made with acidic conditions in the wet end, a papermaker would choose to use a rosin size as an internal sizing agent. In the past, mills used to prepare their own rosin size. But nowadays, readymade fortified rosins either in powder or in liquid form are available for use. In acid sizing, the alum chemistry plays a very important and critical role in imparting sizing property to the paper/board. At low pH (<4.0), the aluminum exists as a soluble ionic species, but as the pH is raised, a colloidal hydroxylated alum floc forms. At higher pH values (>7.0), the alum flocs tend to redissolve and soluble aluminate is formed. As alum floc is a cationic material, it has affinity for anions such as anionic rosin particles, and fiber, fines, and fillers. Thus, alum serves as a precipitating and anchoring agent for the size and also serves as a retention aid for fine fillers, and dyes, improves drainage etc. Extensive studies have been carried out on rosin sizing at neutral/alkaline pH, which include substitution of alum by other chemicals or with other retention aids. For effective sizing, alum may be replaced with polyaluminum chloride, which increases the efficiency of rosin sizing significantly at pH greater than 5.5. Some polyaluminum phosphate sulfate compounds can get good sizing results using rosin size at neutral/alkaline pH. Similarly, polyamines are known to improve rosin-sizing efficiency at neutral/alkaline pH because of their large charge densities in the neutral region and high molecular weight.

For neutral/alkaline paper machines, a papermaker would prefer to use a synthetic sizing agents such as AKD and ASA. AKD is used as a sizing agent in pH range of 6–9 that is both in neutral and alkaline media. Internal sizing at neutral/alkaline pH gives the possibility to use calcium carbonate as a filler. Another benefit that neutral/alkaline sizing gives is that the paper gains an improved storage durability compared to rosin-sized paper, for example, archive papers. ASA is another type of cellulose-reactive sizing agent that has found wide domestic acceptance in recent years due to its advantages. ASA is preferred for many grades because of its on-machine sizing and size press holdout. Sizing with ASA is typically 80% to 100% developed on the machine, and paper can immediately be converted and shipped. ASA is found to be more reactive than AKD. ASA is typically used as an internal sizing agent for alkaline papermaking in the pH range of 7–9 with good sizing efficiency. The ASAs are quite reactive molecules and can promote sizing without heating. Therefore, alkaline papermaking with an ASA size offers the papermaker an opportunity for enormous saving in raw materials and production cost. AKD use is more common in Europe, while in the United States the application of ASA is growing and today surpasses that of AKD.

Several other compounds have been investigated for alkaline paper sizing and found to be successful at least on a laboratory scale. Some of these alternative chemistries include various forms of acid chlorides, acid anhydrides, enol esters, alkyl isocyanates, and rosin anhydrides (Hodgson, 1997). Polymers and copolymers of styrene and acrylates exhibit great promise as both an internal and surface sizing agent and offer some interesting effects from economic and technical aspects. The use of these products makes it possible to create a hydrophilic/hydrophobic matrix on the paper surface that improves copy, ink-jet, laser-jet, and offset printing results.

There seems to be some advantage to be gained in some grades of paper by using mixed sizing systems. A combined sizing system of AKD and a cationic rosin size used in conjunction with alum gives a synergistic improvement when used in liquid packaging board. Combinations of AKD and ASA when used in full or pilot-scale production of fine paper containing precipitated calcium carbonate have also been shown to give a better sizing response, less size reversion, and allowed the use of higher filler levels with higher specific surface area. There was also less migration, higher frictional resistance, and better ink-jet printability.

Nearly every paper contains coloring matter of some sort. Coloring is usually done by adding the necessary material to the stock in the beater. Even white papers generally contain small amounts of blue and pink to offset the naturally yellow tone of the fibers, and to give the blue tone, which is generally considered to be "white." Soluble dyes are used more generally than pigment colors and are always added to the stock after dissolving. Such dyes are of three types: the so-called acid, basic, and "direct" dyes, which have to be handled differently in the beater and which impart different characteristics to the paper. Acid dyes need to be applied on sized stock as they do not take well on unsized fibers. They give even colors of good fastness to light, but are not so intense or brilliant as the next class. Basic dyes give much brighter colors of greater depth, but most of them are not very fast to light, so are seldom used where great permanence of color is needed. Direct dyes take well on unsized fibers, but are not of great brilliance, and are used only where that property is unimportant. Different fibers take up the coloring matter differently, and if the fiber furnish contains both bleached and unbleached fibers uneven dyeing may result, some fibers being much more deeply colored than the rest.

Another characteristic that is developed by adding certain materials to the stock in the beater is known as "wet strength." A number of resins will cause this, among them being those formed from melamine and formaldehyde, or urea and formaldehyde, and others for the same purpose are being introduced frequently. These resins attach themselves to the fibers, and once the paper is dried it no longer becomes as weak when soaked in water as the untreated paper would be. While a paper with no resin will retain almost none of its dry strength on soaking, one treated to develop wet strength and correspondingly soaked may retain 30–40%. This difference is very appreciable in the use of the paper and makes it much more serviceable for blue prints, military maps, and all purposes where it might become wet.

2.6 PAPERMAKING

A flow diagram for a typical papermaking process is shown in Fig. 2.9. The actual papermaking process consists of two primary processes: dry-end and wet-end operations. In wet-end operations, the cleaned and bleached pulp is formed into wet paper sheets. In the dry-end operations, those wet sheets are dried and various surface treatments are applied to the paper. The traditional Fourdrinier machine is still widely used but for many paper grades has been replaced with twin-wire machines or gap formers and hybrid formers (Atkins, 2005; Buck, 2006; Ishiguro, 1987; Lund 1999; Malashenko and Karlsson, 2000). Twin-wire formers have become the state-of-the-art design (Malashenko and Karlsson, 2000). In twin-wire formers, the fiber suspension is led between two wires operating at the same speed, and is drained through one or both sides. There are different types of twin-wire formers (e.g., gap formers). In gap formers, the diluted stock is injected directly into the gap between the two wires, and combinations of Foudrinier and twin wires (hybrid formers). Multiply papers can be made on a variety of formers, but recently two and three ply papers and liners are being made on multi-Fourdrinier wet ends. Whatever the forming device, the wet paper web is passed through presses to remove as much water as possible by mechanical means. More moisture is removed by evaporation on multiple drying cylinders.

The Fourdrinier papermaking machine is composed of three main sections: the forming section, the press section, and the drier section (Fig. 2.10). A paper slurry consisting of about 0.5–1.0% fiber is pumped into a box where it flows out through a slot onto a moving wire belt. Once on the belt, the water is removed by draining and suction, leaving the fibers to form a very wet and weak paper. The paper is then pressed, heated, and dried, resulting in a continuous roll or "web," which can be further finished as desired or required (Biermann, 1996f; Smook, 1992e).

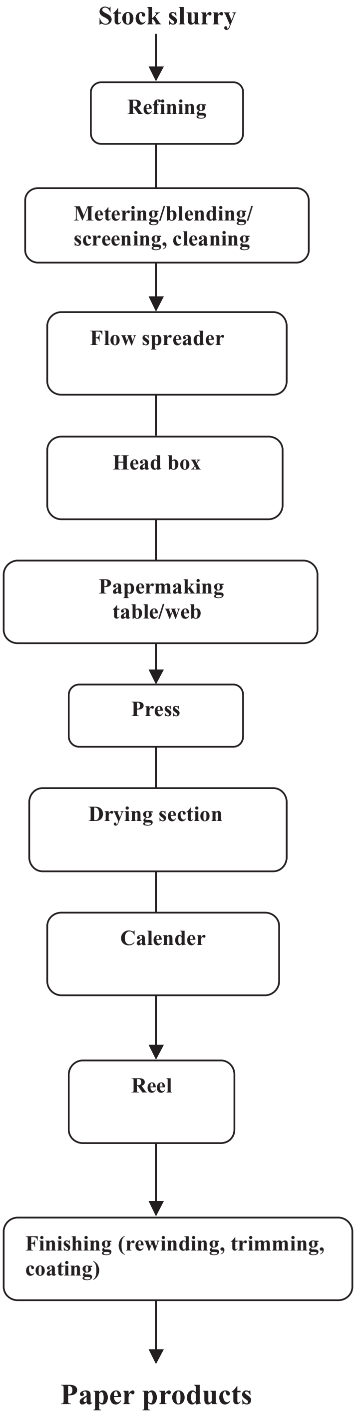

Figure 2.9 A typical papermaking flow diagram.

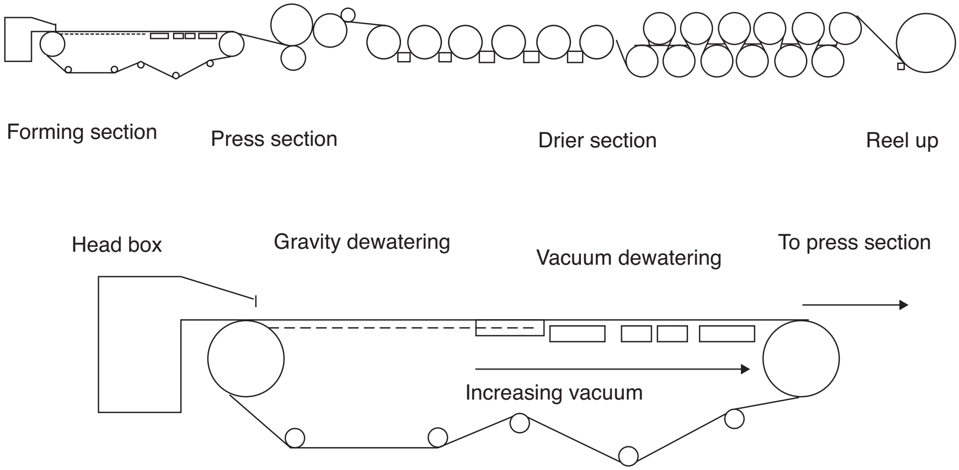

Figure 2.10 A schematic diagram of a paper machine with a Fourdrinier forming section. Based on Smook (1992e).

Forming

The forming section of the Fourdrinier constitutes what is called the wet end of the machine. This section consists of the head box, the forming wire, foils, suction boxes, couch roller, breast roller, and dandy roll (Buck, 2006; Smook, 1992e). Pulp is pumped from the machine box through the screens and cleaners to the head box. The purpose of the head box is to deliver a uniform slurry to the forming wire. There are several different designs, but all incorporate a method to induce turbulence (deflocculation), while preventing crosscurrents, which would inhibit the uniformity of the stock. The simplest design is the gravity-fed head box. It uses height/weight-level difference to force the pulp through several baffles and a through a perforated rotating cylinder, before flowing through the apron and slice. A gravity-fed head box can deliver an 8 in.-stock depth at a rate of 400 ft/min. If faster production speeds are required, the stock must be fed under pressure. These machines can operate at speeds greater than 4000 ft/min. The pressurized head boxes are usually hydraulic, and the stock is forced through conical injectors, through a perforated plate and through a horizontally split apron and the slice. The apron height and the slice height, which control the jet of pulp, can be independently adjusted by hydraulics.

The pulp flowing onto the forming wire is approximately 0.5–1.0% fibers, with the makeup consisting of water. As the water is removed from the slurry, the fibers settle onto the surface of a traveling wire, forming a wet mat of paper. Therefore, the main objective of the forming section is the controlled removal of water. Originally, gravity allowed the water to drain through a brass forming wire 60–70 meshes/in., 40–50 ft length and 70–90 in. in width. But as production speeds increased, more efficient methods were developed. The forming wire, now a fine polymer screen with about 65 meshes/inch, carries the paper slurry over table rolls, foils, and suction boxes, providing precise control over drainage and agitation control. As the slurry exits the slice onto the wire, the water starts draining from the suspension. Water jets are positioned over the edges of the forming wire to control the width of web, creating what is called the deckle edge. The first fibers forming the mat on the wire are oriented in the direction of the machine; this is, the wire side of the paper. If the rest of the fibers in the slurry were allowed to orient themselves in the same direction, the paper would have poor tear resistance and surface properties. If gravity was the main method of dehydration, the machine would have to be run at low speeds to overcome the orientation problem; the alternative is to remove the water quickly while the fibers are still agitated from the effects of the head box.

The first set of dewatering elements is a bank of table rolls. In earlier designs, table rolls were a series of small solid rollers. Now, they are much larger and are used as only the first water removal step. The rotation of the roll in contact with the covered wire causes a vacuum to form between the two, which pulls the water from the web.

With increasing speeds, the table rolls cause problems with paper uniformity and are not able to remove enough water before the presses. Foils have replaced most, if not all of the table rolls. Foils remove water using a doctor blade at the bottom of the forming wire. The blade causes a difference in pressures, which draws water from the web behind the blade. This method allows for more control over the removal process and is not significantly affected by machine speeds.

Water removal can be further enhanced by placing a vacuum on the foil drainage system. After the foils, water is further removed using flat suction boxes. The suction boxes remove the majority of the water, changing the stock consistency from 2% to 20% fiber content. Above the first couple of suction boxes, a skeleton roll covered with wire may ride at the top of the paper mat. This roll called a “dandy roll” compresses the paper, releasing any trapped air and improving the surface. The dandy roll can be covered with various wire patterns, which may simulate the forming wire and may have recessed or raised element designs, imparting a watermark onto the paper. In areas where the watermark elements, usually a wire design, are above the surface of the dandy roll, fewer fibers are allowed to settle, and the paper appears light. If the watermark elements are below the dandy roll surface, more fibers are allowed to settle than in the rest of the paper, and the paper appears darker in these areas. An alternative to using a dandy roll to create watermarks is the Molette. The Molette is a rubber stamp roll located before the wet press of the machine. This type of watermark actually embosses the paper and squeezes the fibers to the edges of the stamp.

A variation on the Fourdrinier was developed in the 1960s and employed the use of two forming wire, allowing the paper mat to be dried from both sides simultaneously. First, twin-wire machines were constructed so that the head box sprayed a vertical stream between the forming wires at the nip of twin breast rolls (Malashenko and Karlsson, 2000). The paper web was then further drawn vertically, while vacuum boxes operate from both sides. Newer designs returned to a horizontal feed system with both forming wires traveling horizontally and vacuum boxes drawing suction from below and above the web. Another variation is the use of a dewatering mat above the suction boxes on a Fourdrinier; this is referred to as a hybrid twin-wire machine.

In 1809, in England, John Dickinson invented another mechanical method of manufacturing paper, the cylinder mold machine (Smook, 1992e). Instead of pouring fibers through the forming wire, his machine dipped the forming wire into a vat, much in the same manner as handmade paper. This allowed him to create watermarks and four-sided deckled edges comparable to hand-couched paper. The modern cylinder mold machine, also known as "cylinder vat" or "mold made," is used to make fine bond paper with shadowed watermarks, currency and security papers, art papers, extremely heavy stock, corrugated cardboards, and multi-ply papers. The key to the cylinder mold machine is the use of a cylinder wire covered by the forming wire (now called the "cylinder blanket" or "cover"), partially submerged in a vat full of pulp. As the cylinder rotates into the paper stock, the slurry flows onto the surface of the cylinder, and the water flows through the wire cover to the inside of the cylinder where it is discharged. The fiber mat that accumulates onto the cylinder surface is removed or "couched" by a traveling felt belt. This traveling felt, "the cylinder felt," is sometimes referred to as the forming wire, even though the paper is already formed by the cylinder. If multiple-layer paper is desired, several vats and cylinders can be placed in series with the paper web acting as the cylinder felt for the additional paper mat. There are two main cylinder vat designs: contraflow and direct flow; and the cylinder felt can be above or below the drying stock.

Pressing

When the paper leaves the couch roll, it contains 80–85% of water, is very easily damaged, and will support its own weight for only a very short distance. It is therefore transferred to a traveling woolen felt, which supports it through the first of a series of presses whose function is to remove more water by squeezing and at the same time make the sheet denser and smoother. Two or three presses are used in series, and the paper may go directly through, or it may pass under one press and be reversed through its rolls so that the two sides of the sheet may be more nearly alike. The top roll of the press stands vertically over the lower roll, and it is connected with compound levers and weights, which permit regulation of the pressure applied and a maximum pressure much greater than that supplied merely by the weight of the top roll. Each press has a separate felt to carry the web, and just before the web reaches each set of rolls, the felt often passes over a suction box to aid in water removal. All felts are kept taut by a series of stretch rolls as they return to the point at which they picked up the paper web. Transferring the web from the couch to the first felt is done when starting by cutting a narrow strip by means of the squirt on the wire and blowing it onto the felt by an air blast; in slow machines it may be done by picking it off the couch by hand and lifting it onto the felt. At each press the web sticks to the top roll and has to be transferred to the next felt by hand or by air blast. After leaving the last press to go to the driers, the sheet will still contain about 71–74% of water, but it has gained enough in strength so that it can be handled to the driers without difficulty (Biermann, 1996f).

Many modern machines are equipped with a smoothing press whose function is not to remove water, but to smooth and flatten the sheet after it comes from the true presses and before it goes to the driers. This aids in removing wire and felt marks and produces a superior paper, both for smoothness and for strength.

The felts used on the wet end of the paper machine are not true felts, which are made without weaving, but are actually heavy blankets woven from very high-grade woolen yarns. They must be strong to withstand the pull of the machine, but also of a texture loose enough to pass water readily. They are made in great variety to suit the speed of the paper machine and the grade of paper being made, and the surface of the paper is considerably influenced by the length of nap and the fineness of weave of the felt. Felts are easily damaged and must be handled carefully both off and on the machine.

Drying

After leaving the presses, the paper goes to the dry section of the machine, the purpose of which is the removal of the water, which cannot be taken out by pressing and which amounts to about 70% of the weight of the wet paper at this point (Biermann, 1996f). A paper machine drier is a cast iron drum with closed ends, very carefully made so that it may be in good running balance and supplied with a steam inlet and a device to remove condensed water continuously and without loss of pressure. The outer surface is turned and polished as smooth as possible. Driers are usually mounted in two rows, one above the other, but staggered, so that an upper drier is over the space between its two neighbors in the bottom row. At the back, end of each drier is a gear, which meshes with the gears on two driers in the row above or below, so that all turn at the same speed. A row of driers is usually broken into two banks with approximately an equal number of drums, and each bank is driven independently of the other. In some machines the driers are driven by an endless roller chain instead of gears; this is simpler in some respects and is desirable on high-speed news and kraft machines.

When the driers are arranged in two rows, each row usually has a long felt, which covers about one-half the surface of each drier and is kept tight by means of stretch rolls. These felts are also not true felts, and most of them are not wool, but a kind of heavy cotton duck; some are made of cotton and asbestos to withstand better the deterioration caused by the heat of the driers, which gradually rots the cotton. The purpose of the felts is to hold the paper firmly against the surface of the driers, except where it passes from one drum to the next, and thus produce a smooth sheet without cockles. The wet web is carried from the last press to the first drier and then in turn to the others until it emerges in a dry condition at the end of the two banks.

In passing the driers, about 2 lb of water must be evaporated for each pound of paper made. In cold climates, if this is allowed to escape directly into the room, it causes condensation on the ceiling and water drops all over the machine, so it is customary to cover the drier section with a hood from which the vapors are removed by fans.

From the driers the paper generally goes through calenders that consist of rolls of cast iron, chilled on the surface to make them hard, and ground and polished to a very smooth surface. A machine calender stack may have as many as 11 rolls, all mounted in a housing at each end of the rolls, and all driven from the bottom roll by friction. The paper is fed in at the top, passes down through the stack and out at the bottom to the reel, where it is wound into large rolls, which are then rewound at full width or through slitter knives which allow the preparation of rolls of other desired sheet widths. The machine calender is designed to compact the sheet and give it a better finish. If this is not desired, the sheet coming from the driers may bypass the calender and go directly to the reel. Some paper machines use two calender stack sets so that the sheet passes the first one and then the other.

There are various modified paper machines for special purposes and products, but these need only brief mention. The "Yankee machine" dries the paper against a highly polished, single-drum drier, and this may be combined with the wet part of either a Fourdrinier or a cylinder. This produces the paper sometimes called "machine glazed." A modified Fourdrinier, known as the Harper machine, was built to handle very thin tissues, which were too light to be passed from the couch to the wet felt. Other modifications combine portions of the Fourdrinier and cylinder machines into various assemblies.

Finishing

After the drying section, the web is subjected to several finishing steps prior to shipping it as a final product. The web can be sized, giving the paper surface resistance, or if other properties are needed, the web can be surface-coated. The web can also be supercalendered, giving the surface a very smooth, uniform surface. In the final stages, the web is rewound and slit into two or more rolls and if needed sheeted.

Sizing

Sizing imparts resistance to liquids on the paper surface, a property necessary for paper used for writing or printing. Without external sizing, ink would bleed and feather. External or surface sizing can be performed either on the paper machine or on a stand-alone unit (Smook, 1992e). Machine sizing can be performed either by running the web through a size vat or by running the web through a size press. In the case of the size vat, the web, after exiting the drier section, is directed down into a vat and through another set of drying cans. Size presses are located after between the two drier sections and apply a coat of sizing by transference from rollers, and the metering is accomplished by the nip. The most common types of sizing consist of pigments and starches, although animal glue and glycerin can also be used (art and banknote papers).

Coating

Coating paper may be desirable or necessary to improve optical, printing/writing, and/or functional properties. Functional properties can be for protection from liquids, oils, gases, and chemicals, improve adhesion characteristics, improve wear, or some other property. Coatings can be classified as aqueous, solvent, high solids, or extrusion. Aqueous coatings, used for commodity papers, contain water-soluble binders and are applied as a liquid. Common aqueous binders are casein, starch, protein, acrylics, and polyvinyl acetates. Solvent coatings are used in situations where the binders are not soluble in water and are used with specialty papers. High-solid and extrusion coatings are used for specialized papers, where chemical, gas, or liquid resistance is necessary. High-solid coatings are applied as a coating of monomers and are polymerized by UV or electron curing. Extrusion coatings are applied as a molten film of wax or polymer.

Supercalendering, Cockling, and Embossing

After the chemical processes have been completed, physical processes, such as supercalendering, cockling, and embossing, can be used to create the desired surface texture to the paper (Smook, 1992e). Supercalendering uses friction and pressure to create a very smooth and glossy paper surface. The supercalender consists of a stack of rollers having surfaces alternating between steel and cotton in construction. There is enough pressure between the steel and cotton rollers to slightly compress the cotton surface causing a drag. The difference in surface speed on either side of the nip creates friction, which polishes the paper surface. The cockle finish on many bond writing papers is created by the vat, sizing the web, then subjecting it to high-velocity air driers under high tension, and then under low tension. The finished paper is usually heavily sized and has the characteristic rattle associated with high-quality bond paper. Embossing is achieved by running the web through an off-line press, where it is subjected to an engraved cylinder. The concept is similar to the dandy roll, but because the paper fibers cannot be redistributed, the surface of the paper is raised or depressed.

Slitting, Sheeting, and Shipping

Once the paper roll (machine log) is reeled from the paper machine, it is removed and transferred to a rereeler or a machine winder (Biermann, 1996f). A rereeler unreels the web from the mandrels to create a full log. During this process any defects can be removed and the web spliced. A machine winder is similar to the rereeler, but is able to slit the web into multiple, narrower rolls. These rolls can be further finished by supercalendering, embossing, etc., sheeted or wrapped and shipped. If the finished product is sheeted paper, the rewound rolls are transferred to machines known as cutters. The cutters can slit the web to form multiple narrower webs and cut across the web creating sheets. The paper rolls are placed onto a stand at one end of the machine. As the web unwinds, it can be slit either adjusting the web width or creating several parallel webs. After the slitters, the web travels under a revolving knife, which cuts the web into sheets. After being cut, the sheets are jogged through an online inspection system, which checks caliper and dimensions. If the sheet does not conform, it drops down into a sheeter for recycling as broke. After the cutters, the paper stacks are placed into guillotine trimmers, where the edges receive their final trim.

After trimming, paper rolls have inner headers (circular disks) applied to the ends, wrapped with a heavy moisture-resistant paper or plastic and sealed with outer headers. The sealed rolls are then placed flat, to prevent flat spots from forming, and shipped. Sheeted paper can be prepared for shipping in various ways depending on the size of the finished product. If the finished sheets are small, such as 8 1/2 in. × 11 in., the sheets are stacked in junior cartons, cross-stacked on pallets, strapped and wrapped. Similarly, larger sheets can also be carton-packaged, strapped and wrapped. Large orders, such as those for printers, can be bulk-packed on skids (slightly different dimensions and design than a pallet), wrapped, and strapped.

2.7 CHEMICAL RECOVERY

The chemical recovery system is a complex part of a chemical pulp and paper mill and is subject to a variety of environmental regulations. Chemical recovery is a crucial component of the chemical pulping process: it recovers process chemicals from the spent cooking liquor for reuse. The chemical recovery process has important financial and environmental benefits for pulp and paper mills. Economic benefits include savings on chemical purchase costs due to regeneration rates of process chemicals approaching 98%, and energy generation from pulp residue burned in a recovery furnace.

Environmental benefits include the recycle of process chemicals and lack of resultant discharges to the environment. The kraft and sulfite pulping processes use chemical recovery systems of some form; however, the actual chemical processes at work differ markedly.

Chemical Recovery (Kraft)

Although newer technologies are always under development, the basic kraft chemical recovery process has not been fundamentally changed since its patent issue in 1884. The stepwise progression of chemical reactions has been refined; for example, black liquor gasification processes are now in use in an experimental phase.

The schematic diagram of the kraft pulping process and the corresponding chemical and energy recovery process is shown in Fig. 2.6. The primary operations of the kraft recovery process are (Vakkilainen, 2000)

- Concentration of black liquor by evaporation.
- Combustion of strong black liquor to give the recovered inorganic chemicals in the form of smelt. The smelt, sodium sulfide, and sodium carbonate, dissolved in water, give green liquor.
- Causticizing sodium carbonate to sodium hydroxide, using calcium hydroxide that is recovered as sodium carbonate.

- Recovery of by-products such as tall oil, energy, and turpentine.
- Regeneration of calcium carbonate to calcium hydroxide in a limekiln.

Evaporation is done to produce black liquor of sufficiently high concentration with minimum chemical losses. Washing separates pulp and black liquor. The resulting weak black liquor contains 12–20% organic and inorganic solids. Burning this weak black liquor would require more heat than it would produce. The black liquor must therefore undergo concentration for efficient energy recovery. The evaporation of black liquor has following main unit operations: (1) separation of water from black liquor to generate concentrated black liquor and condensate, (2) processing of condensate to segregate clean and fouled condensate fractions, and (3) separation of soap from black liquor.

To decrease black liquor viscosity, a liquor processing stage such as a liquor heat treatment (LHT) unit can also be present. The LHT ensures high dry solids even with high-viscosity liquors. The LHT process treats the liquor at elevated temperature for an extended period, when high-molecular-weight polysaccharides and lignin are broken down and viscosity is permanently reduced (Rauscher et al., 2006). Another possible component could be a black liquor oxidation stage. Possible advantages to black liquor oxidation include improvement in multiple-effect evaporators through reduced scaling on heat transfer surfaces, reduced corrosion rates of metal evaporating surfaces, possible increases in tall oil yield, reduced chemical makeup requirements for Na_2SO_4 and CaO, increases in yield from higher white liquor sulfidities in the digester, and reduced total reduced sulfur emissions. In modern high solids evaporators, the mixing of recovery boiler electrostatic precipitator ash occurs with 30–45% dry solids black liquor. Noncondensable gases from evaporation require collection for processing. When using a direct-contact evaporator stage, efficient oxidation of black liquor is necessary to suppress release of odorous gases into the flue gas stream. Evaporation of black liquor uses direct or indirect heating and flashing of black liquor. Most industrial evaporators are the multiple-effect, steam-heated-type. Vapor recompression evaporation is often a component in the first stage of evaporation of weak black liquor as a capacity booster.

The properties of black liquor vary from mills to mills depending on many factors, including mill location, digester conditions, pulp yield, wood species, white liquor properties, chemicals-to-wood ratio, and brown stock washing efficiency. In general, hardwood pulping requires less chemicals, has a higher pulp yield, and consequently, generates less black liquor solids than softwood pulping (Tran, 2007). Harwood black liquor generally contains less organics, tall oil, and soap, and has a lower heating value (~5% lower) than softwood black liquor. In Brazil, Chile, and tropical countries, eucalyptus is the dominant wood species used in kraft pulping. Because the properties of eucalyptus black liquor are similar to those of other types of hardwood black liquor, the chemical recovery process in eucalyptus kraft mills is essentially the same as others.

When processing nonwood black liquors, small mills use direct-contact evaporation. Hot flue gas from the recovery boiler heats a film or spray of black liquor. This technique can only evaporate to a maximum 65% dry solid content due to the sharply increasing liquor viscosity at higher dry solid contents. Unoxidized black liquor releases organic sulfur compounds on contact with flue gases. Oxidation of weak black liquor can partly avoid this. Economics favors the installation of indirect heating as unit size increases. Then, all flue gas heat generates steam and electricity.

Concentrated black liquor contains dissolved wood residues (organic) and inorganic cooking chemicals. Combustion of the organic portion of liquor produces heat. The organic compounds in black liquor serve as a fuel for the production of steam, which is used to generate electricity. The heat released as a result of black liquor combustion is recovered as high pressure/temperature superheated steam in the recovery boiler. The efficiency in converting the fuel value in kraft black liquor (13,000–15,000 kJ/kg) to steam is typically lower than for fossil fuel combustion, because of the heat used to evaporate the water entering with the black liquor, the heat of reaction consumed in producing Na_2S, and the heat carried out with the molten smelt. The amount of steam produced is typically about 3.5 kg per kilogram of black liquor solids, but can range from 2.5 to about 3.8 kg steam per kilogram of black liquor solids, depending on the thermal efficiency of the recovery boiler (Tran, 2007). The high-pressure steam is passed through a steam turbine to generate electricity. Depending on the quality of the steam and the type of the turbine, a 1000 t/day kraft pulp mill can generate 25–35 MW of electricity by burning 1500 t/day black liquor dry solids in its recovery boiler. The lower pressure steam exiting from the turbine is used in various processes in the mill.

Combustion in the recovery furnace needs careful control. High concentration of sulfur requires optimum process conditions to avoid production of sulfur dioxide and reduced sulfur gas emissions. Besides environmentally clean combustion, efficient reduction of inorganic sulfur must occur in the char bed.

The process of the recovery boiler includes several unit processes: (1) combustion of organic material in black liquor to generate steam, (2) reduction of inorganic sulfur compounds to sodium suifide, (3) production of molten inorganic flow consisting primarily of sodium carbonate and sodium suifide, (4) recovery of inorganic dust from flue gas, and (5) production of a sodium fume to capture combustion residues of released organic sulfur compounds (Bajpai, 2008; Biermann, 1996c; Reeve, 2002; Vakkilainen, 2000).

A limekiln calcines lime mud to reactive lime (CaO) by drying and subsequent heating. The calcining process can use a rotary furnace or a fluidized-bed reactor (Adams, 1992; Biermann, 1996c; Venkatesh, 1992). The main unit processes of the limekiln are the following: drying of lime mud and calcining of calcium carbonate. Some additional operations can also be present. The limekiln combusts small amounts of odorous noncondensable gases. The limekiln process produces dust that requires capture. For larger amounts of oxidized sulfur gases, flue gas scrubbers are necessary. The drying of lime mud and the calcining of calcium carbonate to calcium oxide require heat. This heat comes from burning oil or natural gas in the limekiln. The limekiln can also use other fuels such as gasified biomass.

The causticizing process converts sodium carbonate in green liquor to caustic soda. The unit operations in causticizing include dissolving molten smelt to weak white liquor to produce green liquor, green liquor clarification or filtration, mixing green liquor and lime in a slaker to form sodium hydroxide and lime mud with subsequent completion of the causticizing reaction in reaction tanks, white liquor clarification and filtration for lime mud separation, and lime mud washing (Arpalahti et al., 2000; Biermann, 1996c).

Molten smelt from the recovery boiler contains small amounts of unreacted carbon and nonprocess elements. The small undissolved particles in green liquor require separation for disposal. Separation can use settling or filtration. Washing the dregs minimizes chemical losses.

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Chapter 3

Environmental Issues of the Pulp and Paper Industry

The pulp and paper industry is a capital and resource-intensive industry that contributes to many environmental problems, including global warming, human toxicity, ecotoxicity, photochemical oxidation, acidification, nutrification, and solid wastes. The most significant environmental impacts of the pulp and paper manufacture result from the pulping and bleaching processes: some pollutants are emitted to the air, others are discharged to the wastewaters, and solid wastes are generated as well (Bajpai, 2001).

Much research has focused on the bleaching technology employed because this component of the production process has historically been associated with the formation of chlorinated dioxins and other chlorinated organic chemicals. These pollutants are toxic, nonbiodegradable, and tend to contaminate food chains through bioaccumulation. The dioxins are known for their extreme toxicity and are believed to be carcinogenic. Bleaching technology is also a key determinant of the potential for the closure of mill process circuits to achieve zero-effluent operation (Bajpai, 2001; Bajpai and Bajpai, 1996).

There is a development to close up water circuits in pulp and paper mills, and a further reduction of discharges can be expected (toward effluent-free mills). However, today, there are no kraft mills operating full-time, which completely recover all bleach plant effluent. Few chemithermomechanical pulp mills, sodium-based sulfite pulp mills, and a few producers of corrugating medium and Testliner using recycled fiber have realized zero effluents to water.

There is a debate about minimum-impact pulp manufacturing in the recent past. This minimum-impact mill stands for a concept with a broader range of issues and challenges covering minimization of resource consumption and emissions, minimizing crossmedia effects, taking into account economic aspects and working environment (Elo, 1995; Hanninen, 1996).

The pulp mills caused serious emissions of sulfur in the past, but in the recent years especially the sulfur air emission has been reduced considerably, which could be attributed to advancement of process technology. In most countries, the recycling

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Environmentally Friendly Production of Pulp and Paper, by Pratima Bajpai

of fibers of used paper has reached a quite advanced level and for some paper grades a further increase may be expected. The recovery of energy from wastes and from pulp and paper manufacturing processes (rejects, sludge) is possible, thereby avoiding a waste disposal problem. But in this respect there is still a high potential for increased use of efficient on-site techniques. For chemical pulping, no external energy is needed but the total demand of process energy is still on a high level. Mechanical pulping is the most energy-intensive process because of the electricity demand of the refiners. Also, recovered paper processing and papermaking are energy-intensive processes. This is caused by the fact that for papermaking the solid content of a dilute suspension of fibers and possibly fillers has to be brought to about 95% solids as a typical dry solid content in finished papers by means of pressing and drying.

During the period before the 1970s, the pulp and paper industry caused substantial wastewater discharges into receiving waters. The effects observed were sometimes of dramatic character with oxygen depletion and fish kills. From the end of the 1970s until recently, the main emphasis was put on the role of chlorinated substances formed in the bleach plant. Dioxins and furans had been detected in some effluents of pulp mills, and the public discussion focused on the harmful effects of chlorine bleaching. The public concern about the potential environmental hazard imposed by the use of chlorine in the bleach plants has brought about a drastic decrease in the use of molecular chlorine as a bleaching chemical during the last decade (Bajpai, 2001).

Increasing awareness of environmental consequences of bleach effluent has led to stringent environmental regulations. Prior to 1985, there were prescribed limits for only conventional parameters such as chemical oxygen demand (COD), biological oxygen demand (BOD), and total suspended solids (TSS). But now, most nations have imposed limits on adsorbable organic halides (AOX) of the effluents. In some nations, limits have also been set on individual chlorinated organic compounds of bleach effluents, namely, 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF). A reduction of AOX has been achieved by a combination of several measures. The use of molecular chlorine has largely been replaced by chlorine dioxide and introduction of other oxygen-containing chemicals such as molecular oxygen, peroxide, and ozone. Due to the strong reduction of the chloride content of the effluents, a closure of the mill system and recycling of the bleach plant effluent back to the chemical recovery system of the mill have been made possible. The reduction of both chlorinated and non-chlorinated organic substances in the effluents of pulp mills has been achieved to a large extent by in-process measures, for example, increased delignification before the bleach plant by extended or modified cooking and additional oxygen stages, spill collection systems, efficient washing, and stripping and reuse of condensates. Another contributing factor to the decreased emissions of AOX and non-chlorinated toxic organic compounds into receiving waters was the installation of external treatment plants of different designs (Bajpai and Bajpai, 1996).

The current trends within the pulp and paper industry is toward increased closure of the bleach plants by using either elementary chlorine-free (ECF) or totally chlorine-free (TCF) bleaching of pulp (Bajpai, 2005; Chirat and Lachenal, 1997; McDonough, 1995; Pryke, 2003). In paper mills, an increased reuse of treated process waters by

Table 3.1 Chlorinated Organic Compounds in Bleach Plant Effluents

Type	Number of varieties	Amount (g/t pulp)
Chlorinated phenolics	40	Up to 100
Chlorinated aldehyde, ketones, and lactones	45	500
Chlorinated acids	40	Up to 500
Chlorinated hydrocarbon	45	—
Chlorinated ether	20	—
High molecular mass	—	Up to 4 kg Cl

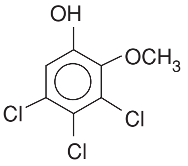
implementing production-integrated advanced wastewater treatment systems will be allowed. Wastewater discharges, environmentally friendly handling of wastes, energy saving and recovery, and locally smell from kraft pulp mills are expected to remain future priorities of environmental actions in the pulp and paper industry.

3.1 EFFLUENT TOXICITY

Of the different wastewaters generated by the pulp and paper industry, bleach plant effluents are considered to be the most polluting. About 300 different compounds in bleached pulp mill effluents have been identified. About 200 of them are chlorinated organic compounds, which include chlorinated resin acids, chlorinated phenolics, and dioxins. The main compounds, by general type, are listed in Table 3.1. Pollutants such as chlorinated phenolics and dioxins are toxic, nonbiodegradable, and tend to contaminate food chains through bioaccumulation. The dioxins are known for their extreme toxicity and are believed to be carcinogenic (Bajpai, 2001). Table 3.2 shows

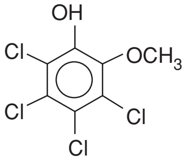
Table 3.2 Polychlorinated Phenolic Compounds Selected by US EPA for Regulation

Polychlorinated phenols	Minimum level, ppb (μg/L)
Pentachlorophenol	5.0
2,3,4,6-Tetrachlorophenol	2.5
2,4,5-Trichlorophenol	2.5
2,4,6-Trichlorophenol	2.5
3,4,5-Trichloroguaiacol	2.5
3,4,6- Trichloroguaiacol	2.5
4,5,6-Trichloroguaiacol	2.5
3,4,5-Trichlosyringal	2.5
3,4,5,6-Tetrachlorocatechol	5.0
3,4,6-Trichlorocatechol	5.0
3,4,5-Tetrachlorocatechol	5.0
3,4,5,6-Tetrachloroguaiacol	5.0



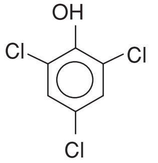
345-TCG

3,4,5-Trinchloroguaiacol



TeCG

Tetrachloroguaiacol



246-TCP

2,4,6-Trichlorophenol

Figure 3.1 Specific compounds discharged from bleached pulp mills. Based on Gavrilescu (2006) and Liebergott et al. (1990).

the list of 12 polychlorinated phenolics selected by Environmental Protection Agency (EPA) for regulation.

The most common chlorinated phenolics in bleached kraft pulp mill effluents are tri- and tetrachloroguaiacols (Fig. 3.1) (Liebergott et al., 1990). The substitution of chlorine dioxide for chlorine in the bleaching stage also alters effluent composition. For example, catechols and guaiacols together include 77% of the total chlorinated phenolic content when chlorine is alone used in the bleaching stage. When a 70:30 ClO_2/Cl_2 ratio was used in the first stage, the catechol and guaiacol portion decreased to 46%, and at 100% chlorine dioxide substitution, only 10% of the chlorinated phenolics were of the catechol and guaiacol-type (Liebergott et al., 1989).

Bleached kraft mill effluent is a complex mixture of chlorinated and non-chlorinated products of lignin and/or extractives of wood that imparts dark color to the effluent. Colored effluent may result in the following detrimental effects upon receiving the water body.

1. Color, derived from lignin, is an indicator of the presence of potentially inhibiting compounds.
2. Color reduces the visual appeal and recreational value of the water.
3. It affects downstream municipal and industrial water uses, and increases the cost and difficulty of pretreatment for industrial processes.

4. It retards sunlight transmission, thus reducing the productivity of the aquatic community by interfering with photosynthesis.
5. Color-imparting substances form complexes with metal ions, such as iron, or copper, and form tar-like residues. These residues may have direct inhibitory effects on some of the lower organisms in the food chain.
6. Color bodies exert long-term BOD (20–100 days) that cannot be measured in terms of 5-day BOD.

Bleached kraft mill effluent can affect the biological quality of the receiving water. Disappearance of benthic invertebrates, high incidence of fish diseases, and mutagenic effects on the aquatic fauna are some of the consequences of the disposal of bleach effluents into surface waters (Sodergren et al., 1993; Sundelin, 1988). Bleached kraft and bleached sulfite mill effluents have been demonstrated to impair the functions of liver, enzyme systems, and metabolic cycles in the exposed fish. Furthermore, such exposures have been demonstrated to increase the incidence of spinal deformities and reduced gonad development. The low-molecular-weight fraction of bleach effluent contains potentially problematic (toxic) compounds. These have the ability to penetrate cell membranes and tend to bioaccumulate. Low-molecular-weight chlorinated organic compounds significantly affect the life of aquatic ecosystems.

A major part of the organically bound chlorine (80%) is believed to be heterogeneous material of relatively high-molecular-weight compounds (Fig. 3.2). These compounds apparently contribute little to the effluent BOD and acute toxicity. Their major contribution is toward color, COD, and chronic toxicity. Ecological/natural processes, such as sedimentation, biodegradation, and bioaccumulation, are apparently correlated with the molecular size and hydrophobicity of the compounds. Highly polar and high molecular mass constituents are responsible for the toxicity of the bleach effluents during early-life stages of marine animals and plants (Higachi et al., 1992). Chlorocymenes and chlorocymenenes in the bleach effluent have been reported to bioaccumulate in fish and mussels (Suntio et al., 1988).

Chlorinated dioxins, which are present in very low concentrations in the bleach plant effluent (usually in parts per trillion levels), account to a 10-billionth of the total AOX discharged. About 210 different dioxins, belonging to the two families, namely polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), have been reported in the bleach effluents. 2,3,7,8-TCDF and 2,3,7,8-TCDD are especially toxic, carcinogenic, and bioaccumulable. The structures of the most toxic forms of dioxin and furan molecules are shown in Fig. 3.3 (Rappe and Wagman, 1995). A dioxin molecule is bonded by two oxygen atoms and a furan molecule by a single oxygen atom and a direct bond. Under standard atmospheric conditions, all dioxins are solid and are characterized by low vapor pressure and limited solubility in water. Polychlorinated dioxin toxicity depends on the location and the number of additional chlorine atoms attached to the benzene rings. PCDD/PCDF that have four chlorine atoms substituted in positions 2, 3, 7, and 8 are considered to be the most toxic (Rappe and Wagman, 1995). The major

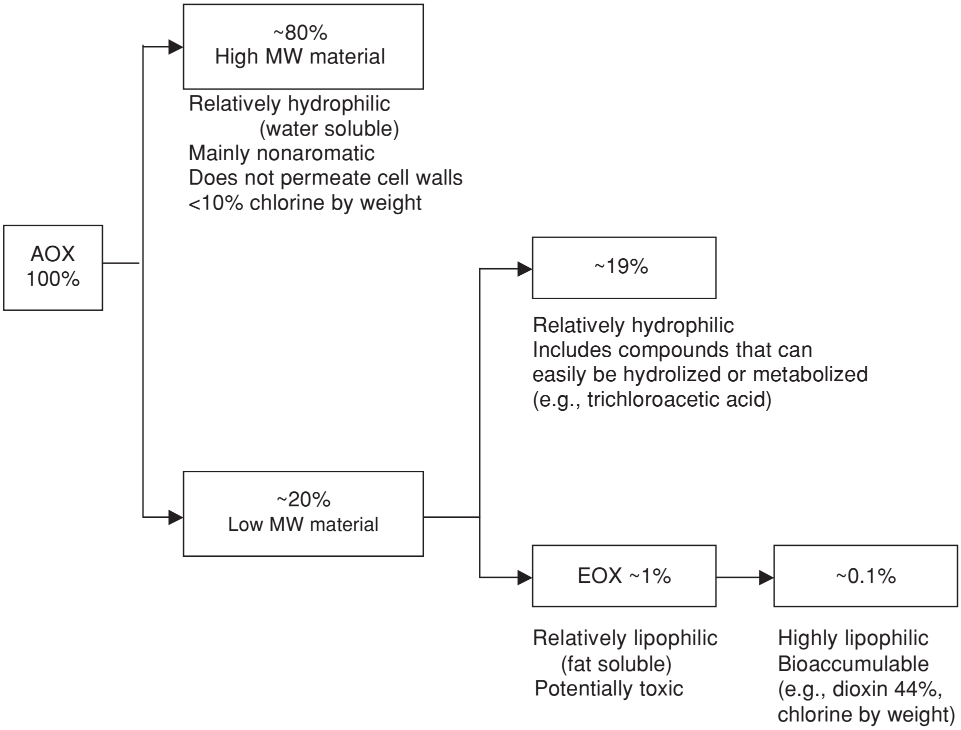


Figure 3.2 The character of AOX in the effluent from conventionally pulped and bleached kraft pulp. Based on Bajpai and Bajpai (1996) and Gergov et al. (1988).

source of dioxins in the pulp and paper industry is the bleaching process in which chlorine is used as a reagent. It was found that the pulp chlorination stage is the first point where dioxins are generated (McKague and Carlberg, 1996). The chlorinated pulp contains the largest concentration of dioxins that are solubilized in the next alkaline extraction stage. The quantity of dioxins in the bleaching effluents is very

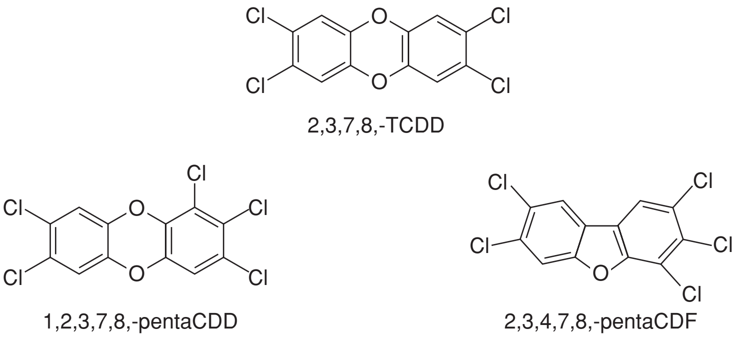


Figure 3.3 Most toxic isomers of polychlorinated dioxins and furans. Based on Gavrilescu (2006) and Rappe and Wagman (1995).

low; normally these compounds cannot be determined even with the best analytical techniques.

Dioxins are almost insoluble in water. They tend to enter the food chains and accumulate in high concentrations in predators, such as fish-eating birds (McCubbin, 1989; McCubbin et al., 1990). Adverse effects of dioxins have been observed in almost all species tested. According to an EPA report (Anonymous, 1994), human beings lie somewhere in the middle of the sensitivity range (from extremely responsive to extremely resistant) for dioxins. Even in trace amounts, dioxins may cause a wide range of adverse health conditions, such as disruption of regulatory hormones, reproductive and immune system disorders, and abnormal fetal development (Bajpai and Bajpai, 1996).

Some data suggest that the toxicity of treated effluent from advanced ECF mills can be similar to treated TCF effluent (Verta et al., 1996). The most advanced TCF effluents generally show the lowest toxic effects for effluents tested using standardized techniques. Moreover, many studies continue to suggest that even the most advanced ECF mills produce effluent with a higher toxicity than do TCF mills (Cates et al., 1995; Kovacs et al., 1995; Rappe and Wagma, 1995; Rosenberg et al., 1994; Vidal et al., 1997). Some of these studies also suggest that formation of bioaccumulative dioxins and furans, while indeed greatly reduced in mills using ECF processes, continues to occur. This is most probably due to the partial dissociation of chlorine dioxide to produce elemental chlorine, throwing some doubt on the accuracy of the term “ECF” (Johnston et al., 1996). Research has been conducted on ecosystem integrity and biodiversity in waters, which receive treated effluent from ECF mills in British Columbia, Canada. These mills meet some of the strictest existing standards in the world. The data continue to show a strong correlation between exposure to the effluent and severe ecosystem disturbance (Bard, 1998).

In general, treatment of effluent reduces toxicity in the case of all effluents (Verta et al., 1996), although toxicity of the effluent can itself influence the effectiveness of biological treatment processes. There are indications that TCF effluents may be simpler to treat. For example, reduction of AOX and chlorate, which are only generated in ECF, but not TCF, bleaching (Germgard et al., 1981), requires anaerobic conditions, while COD and BOD, produced in both ECF and TCF mills, are most effectively removed in aerobic conditions (Duncan et al., 1995). Because TCF mills do not produce AOX and chlorate, the treatment systems needed are, therefore, likely to be less complex. A study, which contradicts assertions that ECF and TCF effluents have a similar toxicity, demonstrates that ECF effluents are more toxic to methanogenic organisms than are TCF effluents. A greater potential for anaerobic biodegradation was also demonstrated for TCF effluent (Vidal et al., 1997) as might have been expected from these results. Nonetheless, certain types of chronic toxicity do appear in both the treated ECF and TCF effluents (Stauber et al., 1995).

Despite the general reductions in toxicity, which have been achieved for pulp effluents, certain biologically active chemicals present in the wood furnish can pass through treatment plants without being degraded. Hence, impacts on fish populations have been detected following exposure to a wide variety of mill effluents employing various bleaching processes (Johnston et al., 1996). Research from British Columbia has shown that dilute concentrations as low as 2% of treated bleach effluent from kraft mills with 100% ClO_2 substitution can cause actual, physical genetic damage to salmon (Easton et al., 1997). This research needs to be replicated for the effluents of the most advanced ECF mills, as well as TCF mills. Indeed, these observations have provided a compelling argument for developing totally effluent-free mills.

In addition to the identified problems of chemicals in the wood furnish, alternative bleaching processes require changes in process chemicals. A group of chemicals that have given rise to concerns are the chelating agents (ethylenediamine tetraacetic acid (EDTA) and diethylenetriamine pentaacetic acid (DTPA) are examples). Such agents are used to remove metallic contaminants in the pulp before bleaching with peroxide and are employed in most currently operating TCF mills as well as in some ECF mills with peroxide stages. Metallic contaminants would otherwise reduce the efficiency of the peroxide (Södra Cell, 1996). These chelating agents are currently discharged to effluent treatment and appear to be relatively resistant to degradation. At present, there does not appear to be an efficient decomposition pathway for the chelants EDTA and DTPA, and their presence may initially inhibit the efficiency of activated sludge secondary treatment (Larisch and Duff, 1997). However, treatment with aluminum sulfate can result in a 65% EDTA reduction in treated effluent, and photochemical degradation is known to be a possibility (Saunamaki, 1995). While most toxicity studies seem to support the claim that any chelants and metals coming through treatment and/or the final effluent are not a significant environmental problem (Saunamaki, 1995), this issue needs to be more specifically studied in relation to aspects other than direct toxicity. In particular, the ability of chelating agents to mobilize metals after discharge, and the potential consequences of this for natural systems, requires comprehensive evaluation.

Some studies suggest that efficient acid washing of the pulp before bleaching can eliminate the need for chelating agents (Bouchard et al., 1995), but this may be very dependent on furnish. Moreover, acid wash strategies that can fully eliminate the need for chelants may cause unacceptable viscosity loss in the pulp. Metal removal treatments using acid washing need to be further developed into processes that avoid degradation of the final product quality (Lapierre et al., 1997). Alternative chelants are being investigated. Hydroxycarbolates (glycolate and galactarate) have been shown to act as effective complexing agents in closed TCF process simulations (Gevert and Lohmander, 1997). Moreover, research has led to the identification of chelants that may be used to control process metals and which appear to be readily biodegradable (Lockie, 1996). While these initiatives show promise, the usefulness, degradability, and toxicity of such alternative chelating compounds require exhaustive evaluation. It is inevitable that some of these chemicals will be purged from pulp production systems as a result of the need to control the buildup of nonprocess elements, particularly in the bleach lines. The purging of nonprocess elements from pulp production systems is therefore an issue of some importance in relation to the potential for full mill closure and zero-effluent operation in both TCF and ECF systems.

3.2 AIR EMISSIONS

Air emissions from chemical pulp mills are primarily made up of particulates, hydrogen sulfide, oxides of sulfur, and oxides of nitrogen. Micropollutants include chloroform, dioxins and furans, other organochlorines, and other volatile organics. As with liquid effluent discharges, the levels of emissions are highly dependent on the type of process technology employed and individual mill practice. Another important factor is the fuel type and quality. While older mills caused severe air pollution, mitigating technology now exists to eliminate most harmful gas and particulate emissions. Whether this technology is utilized depends on local factors such as legislation, company and mill policy, and proximity to populated areas.

The contribution of the paper industry to global warming has been an ongoing debate for several years, with some suggesting that the absorption of carbon dioxide by plantation forestry more than offsets the emissions of greenhouse gases caused during the production, transportation, and disposal of pulp and paper products. A study by the International Institute for Environment and Development dismisses this argument, concluding that the paper cycle results in the net addition of about 450 million CO_2 equivalent units per year.

While the advantages of in-mill process changes with respect to the use of water resources and concomitant impacts on receiving aquatic systems are well documented, the implications of changes in air emissions (principally from recovery boiler systems) as a result of closed-loop operation have been less well explored (Caron and Delaney, 1998).

Södra Cell has reported occasional increases in NO_x emissions at its low-flow TCF plants located at Värö and Mörrum, but these have been reduced and attributed to the numerous mill start-ups and shutdowns as the various processes were refined (Södra Cell, 1996). The company is considering additional technological controls to reduce NO_x emissions to 1 kg/t of pulp or less. The increased quantity of organic matter reaching the recovery boiler from recycling of effluent has increased the amount of electricity the mill is capable of generating for itself. As a source of energy from combustion, recovery boilers are regarded as preferable to hog fuel boilers in terms of the relative amount of air pollutants generated (Luthe et al., 1997). Information contained in the annual environmental reports from mills in Scandinavia producing both advanced ECF and TCF pulp suggests that overall releases of NO_x, total reduced sulfur (TRS), SO_2, and particulate matter are similar for both production processes (Södra Cell, 1996). While NO_x (nitrous oxides), CO_2 (carbon dioxide), TRS/SO_2 (total reduced sulfur/sulfur dioxide), and PM (particulate matter) continue to be important, there are other emissions that must be considered.

The potential for products of incomplete combustion and other hazardous compounds, including chemicals such as the chlorinated dioxins, from ECF mills is an obvious concern (Environment Canada, 1998). Polychlorinated biphenyls, dioxins, and furans have been found in fly ash from the burning of sludge from kraft mills (Kopponen et al., 1994), raising concerns that substantial quantities may be emitted to atmosphere. One study from British Columbia, Canada, suggests that the flue gas from recovery boilers with high chloride loading due to salt-laden wood does not represent a major source of dioxin/furan emission to air; however, levels of these persistent organic pollutants have been observed in other recovery boiler emissions (Luthe et al., 1997).

In addition, some of the hazardous air pollutants (HAP) or trace air contaminants and total reduced sulfur compounds such as methyl mercaptan, chlorine dioxide, formaldehyde, and chloroform are a priority for individual regulation and control, particularly with respect to their potential to compromise mill worker health and safety. Accordingly, one mill has installed a “light stripper” for cleaning the less polluted condensates in the evaporator stage. The aim is to eliminate emissions of polluted condensates and reuse them in the process. This company has also installed the first weak gas system in Sweden (Södra Cell, 1996). The weak gas system is able to collect malodorous gases and combust them in the recovery boiler. This limits malodorous discharges and aerial emissions of process sulfur (Södra Cell, 1996). Both of these systems were added at the Värö Bruk mill. This mill already uses TCF bleaching and generates bleach plant effluent of between 10 and 15 m^3/ADt.

Hydrogen chloride and methanol are other major air pollutants of concern produced in recovery boilers (Andrews et al., 1996). Older, direct-contact evaporator recovery boilers emit greater quantities of these pollutants, as well as generating significant sulfur emissions. Accordingly, upgrading of mills to closed-loop operation should ideally include installation of nondirect-contact, low-odor recovery boilers (Simons, 1994). This type of recovery boiler should be fitted at newly constructed mills. In addition to reducing environmentally significant air emissions, these recovery boilers also allow the firing of black liquor solids (BLS) at greater concentrations (up to 80% BLS) than direct-contact units. In turn, this increases recovery boiler capacity and generally reduces emissions of TRS and SO_2 (McCubbin, 1996).

Methanol and a wide range of other HAPs and volatile organic compounds (VOCs) are also generated in the process lines and vented from oxygen delignification systems and white liquor oxidation systems (Crawford et al., 1995; NCASI, 1994). Methanol, especially, may be generated in large quantities. Reducing the methanol content of the final post-oxygen washer shower water is likely to have a significant positive impact on emissions of methanol from oxygen delignification systems (Crawford et al., 1995). It is not clear from the literature if this measure will also lower the concentrations of the other HAP and VOC present. Hence, the US EPA cluster rules outline techniques for these gaseous streams to be collected and introduced into the fire zone of the recovery boiler (US EPA, 1998). It has also been pointed out (Crawford et al., 1995) that there is a need to routinely monitor the areas around the oxygen delignification system for HAPs and VOCs.

The question of precisely what to monitor in the way of air emissions from pulping operations is an important one. The US EPA suggests that methanol is an acceptable surrogate target compound for monitoring and regulation of gas-phase HAP compounds. This assertion is however somewhat difficult to verify. A wide range of HAPs and VOCs have been detected in studies of pulp mill air emissions (NCASI, 1994). Moreover, it appears that no direct correlation exists between reduction in emissions of methanol and reduced emissions of other pollutants such as methyl mercaptan and chlorobenzene among the variety found in actual working mill environments. Phenols, as well, do not appear to be reduced proportionally to methanol (Simons, 1994). This is of significance in terms of potential long-term, low-level worker and community exposure to the other compounds. It implies that monitoring needs to be extended in scope and should encompass not only recovery and power boiler stacks but also cooling towers, process vents from oxygen delignification, washers, and chemical generation processes. Additionally, internal mill working areas need to be subjected to monitoring as well as external environments. In bleaching operations, TCF mills emit no chlorinated compounds, which are generated in ECF mills by bleaching or chlorine dioxide manufacture. Chloroform, dichloroacetic acid methyl ester, 2,5-dichlorothiophane, and other volatile organochlorine compounds have been found in the vent gases of mills using 100% chlorine dioxide substitution. These compounds have also been found to volatilize from the treatment ponds of these mills, but were almost nonexistent when investigated in a TCF mill (Juuti et al., 1996). Side reactions during chlorine dioxide bleaching lead to the formation of chloroform, chlorinated phenolics, and other chlorinated organics, as well as phenol and methanol (Simons, 1994). The precursors for the chlorinated organic chemicals are not present in TCF bleach plants. While the concentrations of chlorinated compounds have decreased markedly from levels generated by mills employing elemental chlorine as a bleaching agent, they have not been eliminated by the use of chlorine dioxide. These chemicals are of environmental significance because they are released into the local environment and may also be transported over large distances from the mill (Calamari et al., 1994; Juuti et al., 1996). Chlorine dioxide itself is an air pollutant of great concern, especially in relation to the possibility of leaks and fugitive emissions in the plant (Simons, 1994). The US EPA has recognized the major benefit that TCF systems are not expected to produce HAPs in the bleach plant (US EPA, 1998). For the most part, there are overall positive environmental benefits in relation to air emissions from the use of modern mill technology and additional benefits for non-chlorine chemical bleach sequences. Nonetheless, the implications of technology and process change on this aspect of pulp mill operations have not been exhaustively explored. There is a need to generate comparative information from advanced mill operations in order to assess the nature and scale of likely atmospheric emissions under closed-loop mill operations in order to establish, as a minimum, that improvement in effluent quality is not at the expense of air quality.

Solid Waste

Solid waste from paper manufacture ranges from 10 to 250 kg/t (dry equivalent). Disposal is usually to landfill, although incineration is becoming increasingly widespread. Other experimental disposal techniques include using the waste as a soil improver, but, as with all disposal options, there is some concern about possible dioxin and heavy metal contamination. Solid waste disposal issues significantly decrease in a perfect closed-loop mill. However, the need to control the nonprocess elements will require purge points to prevent upsets in bleaching and recovery chemistry, and minimize corrosion of mill equipment (Gleadow et al., 1997). Given that there will continue to be some sludge and solid waste produced, the quality of these wastes becomes of considerable concern. This is particularly the case because, increasingly, land spreading is being promoted as a means of disposing of these wastes. Uncontaminated sludge could prove to be a beneficial resource. Composting of properly treated sludge could facilitate the reuse of otherwise nonrecyclable wastes. The use of pulping and bleaching wastes as raw materials for other processes may also be a desirable goal.

However, there is a need to carry out long-term studies on the feasibility and safety of composting and reusing waste solids from either ECF or TCF mills. In practice, sludge is increasingly being fed into mill recovery boilers. While current evidence suggests that both ECF and TCF mills increasing their burn volume in the recovery boiler are maintaining compliance with air quality regulations, this must be continuously monitored as the move to full effluent loop closure proceeds. As noted above, current air monitoring obligations are demonstrably deficient. Increased combustion of sludge provides a further imperative for developing the scale and scope of air monitoring programs.

Sludge from bleached kraft pulp mills contains a wide variety of chemicals of both natural origin and originating de novo from pulping and bleaching activities. The commonly tested regulatory chemical parameters include chlorinated dioxin congeners and heavy metals, together with agriculturally orientated parameters such as carbon/nitrogen ratio and salt content (O'Connor, 1995; Rabert and Zeeman, 1992). While all these parameters continue to be important, improvements to secondary treatment and the move toward complete chlorine dioxide substitution have revealed new compounds that need to be addressed. Plant sterols, resin acids, phthalates, chlorinated and non-chlorinated alcohols (phenols, guiacols, catechols), terpenes, and benzene have been detected in ECF kraft mill secondary sludge (Brezny et al., 1993; Fitzsimons et al., 1990; Kookana and Rogers, 1995; Martin et al., 1995; O'Connor and Voss, 1992). These studies primarily address sludge from mills at, or approaching 100% chlorine dioxide substitution. The concentrations of chlorinated, bioaccumulative compounds found in these studies vary. Some debate has taken place concerning the best sampling and testing methods for low levels of these compounds, as well as on their origin: from the breakdown of chlorolignin or through a sorption–desorption pathway (Martin et al., 1995; O'Connor and Voss, 1992).

Regardless of the origin of such substances in mill sludge, it is clear that long-term studies under realistic conditions, backed by comprehensive chemical analysis, are necessary before large-scale land-spreading of kraft mill sludge can be justified (Kookana and Rogers, 1995). Additionally, the extreme variability in sludge indicates a need for continuous testing at each mill before sludge can be spread on land (Aitken, 1995). This has been emphasized by the New Hampshire Department of Environmental Services following experiences in New Hampshire, USA. This body considers that the inherent variability in sludge composition necessitates extensive testing and monitoring prior to spreading on land. This followed the discovery of VOCs during postapplication testing in landfill groundwater where short paper fiber sludge had been used for remediation purposes. The potential for this problem was not identified through preapplication tests.

The process changes adopted by the industry are known to have resulted in qualitative changes in the sludge. For ECF sludge, closing the loop is resulting in increased disposal of sulfur chemicals from the ClO_2 generator (Paleologou et al., 1997) because sulfate compounds are by-products of ClO_2 generation and often used as makeup chemicals in bleaching and pulping. Increased chlorine dioxide production for ECF and increased filtrate recycling heighten concentration of sulfur chemicals in process circuits. Because increased sulfur becomes a concern for nonprocess element control in closed-loop designs, this increase necessitates disposal of excess sulfates. These eventually end up in effluent treatment in many current mills. Under anaerobic conditions, certain bacteria can reduce sulfate, leading to increased bacterial growth, corrosion problems, and increase in treated effluent toxicity. TCF sludge has not been commonly tested. Because many of the TCF mills in the world are in the forefront of effluent recycling technology, it is likely that issue of waste fiber sludge disposal will progressively diminish in importance. The impacts of burning this material must be continuously evaluated, and opportunities for more beneficial reuse sought out.

Assertions that increased effluent recycling will lead to an eventual doubling of lime muds, dregs, precipitator ash, and other purge streams must be viewed with some concern (Ryynänen and Nelson, 1996). It has been estimated that, on average, grits, dregs, and ash currently comprise about 3% of the dissolved material resulting from pulping and bleaching operations. While closed-loop operations may double that figure to 6%, this must be weighed against the complete elimination of liquid effluent discharge and of dissolved waste fiber and spent liquors going to aquatic or land-based discharge.

Processes that allow for a maximum of nonpolluting and worker-safe reuse of pulping and bleaching by-products are needed.

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Chapter 4

Emissions from Pulp and Papermaking

4.1 KRAFT PULPING

The most important emissions from kraft pulping can be categorized into the following groups (Pöyry, 1998; Saarinen et al., 1998; Salo, 1999; Stora Enso, 2003; Suhr, 2000):

Water

- Organic substances—chemical oxygen demand (COD) and biological oxygen demand (BOD)
- Extractive compounds such as resin acids
- Chlorinated organics (adsorbable organic halides—AOX), chlorate
- Nitrogen, phosphorus
- Suspended solids
- Metals, salts
- Colored substances

Air

- NO_x, SO_2, CO, CO_2, dust
- Malodorous total reduced sulfur (TRS) compounds, for example, methyl mercaptan and dimethyl sulfide
- Hydrogen sulfide, volatile organic compound (VOC), chlorine compounds

Solid waste

- Boiler ashes
- Dregs, lime mud
- Sand and stones
- Green liquor sludge
- Wood waste, bark, rejects

Environmentally Friendly Production of Pulp and Paper, by Pratima Bajpai

- Primary and biosludge
- Cleaning and mixed household-type waste
- Small amounts of hazardous waste

Wastewater Emissions

Different types of wood species are used as raw material in the kraft pulping process. The pulp yield is dependent on the selectivity in delignification and bleaching (Biermann, 1996a; Smook, 1992). The wood required for manufacturing 1 tonne of chemical pulp is normally between 4 and 6.6 m^3.

Emissions to water from a kraft pulp mill originate from different stages (Fig. 4.1). They also include accidental spills. Emissions to water mostly include oxygen-consuming organic substances measured as COD and BOD. Effluents from bleach plant using chlorine contain organically bound chlorine compounds (Das and Jain, 2004; Kirkpatrick, 1991; UNEP, 1987). Some compounds leached from bark in the wood handling (extractives such as resin acids) show toxic effects on aquatic organisms. Emissions of colored substances may affect the living species in the recipient

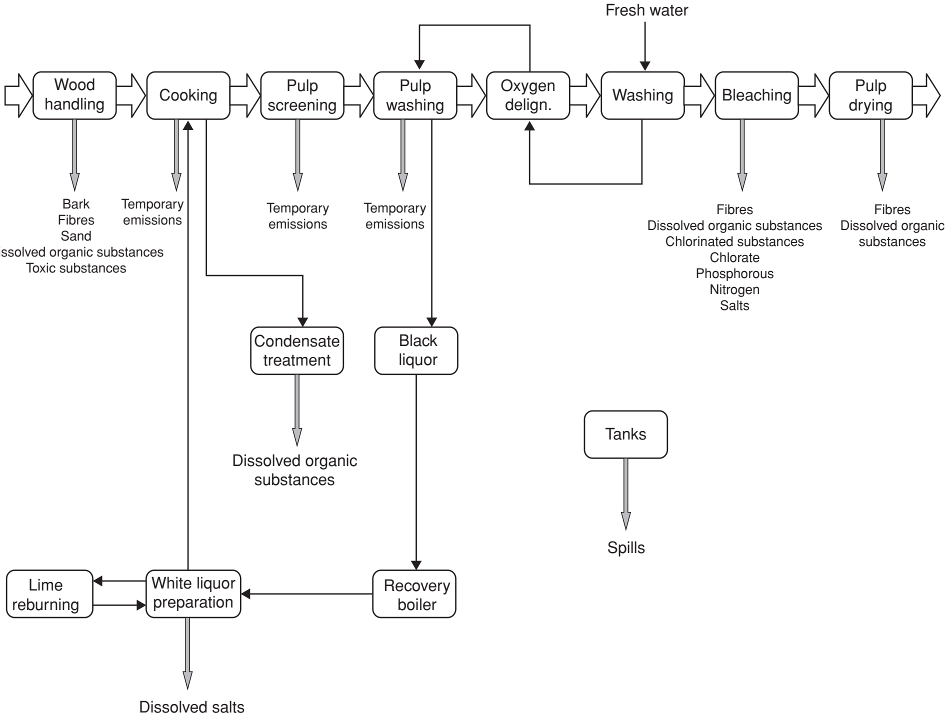

Figure 4.1 Emissions to water from kraft mills. Reproduced with permission from European Commission (2001).

negatively, because the water transparency is decreased (Bajpai, 2001). Emissions of nutrients have a negative impact due to eutrophication. In lower concentration, individual metals extracted from the wood can be determined in the effluents.

The water consumption varies significantly between different mills. Water consumption can be reduced in a pulp and paper mill by increasing internal water recirculation. In a kraft pulp mill, it can be achieved by

- Transferring wet debarking to dry debarking
- Changing over to more efficient washing equipment
- Recycling alkaline bleach filtrate
- Using the condensates from evaporation
- Closing the screen room with respect to water (European Commission, 2001)

There is a difference in water management between integrated and nonintegrated pulp mills. In an integrated mill, the pulp comes from the pulping process to the papermaking process at about 4% consistency and wastewater from pulping and from papermaking is usually treated in one single treatment plant. In nonintegrated pulp mills, the market pulp is dewatered and dried. The volume of water used is closely linked to the wastewater load, discharged from the mill. The pollution depends mainly on the design and operation of the processes that cause the major part of discharges and on the degree of closure of the mill (Biermann, 1996b; Gullichsen, 2000). The main sources of wastewater are from

- Wood handling
- Condensates from cooking and evaporation
- Spills from different process stages/sections
- Black liquor residues from unbleached pulp
- Discharges from the bleach plant

Debarking plant is the major source of pollution in wood handling. It consumes water and generates an effluent containing nutrients, fibers, and oxygen-consuming organic compounds such as resin acids and fatty acids that are toxic to aquatic life before treatment (Kostinen, 2000). Biological treatment has proved to be very efficient in reducing/eliminating toxicity. In a transfer from wet to dry debarking, water consumption and discharges are reduced. The dryness of the removed bark is however only slightly affected. This is because dry debarking means that water is recycled, not that water is not used. In wet debarking, 0.6–2.0 m^3 of water is used per solid cubic meter of wood. Dry debarking still uses 0.1–0.5 m^3 water per cubic meter of wood to wash the logs, and some organics are dissolved but to a lesser extent compared to wet debarking. Dryness of the bark can be increased by pressing or drying the bark. An increase in dryness will improve heat generation but result in an increased pollution load. Table 4.1 shows the pollution load of debarking effluent before biological treatment (Finnish BAT Report, 1997).

Table 4.1 Pollution Load of Debarking Effluent before Biological Treatment

Effluent properties	Wet debarking and press	Dry debarking and press
Effluent volume (m^3/m^3 wood)	0.6–2	0.1–0.5
BOD5 (kg/m^3 wood)	0.9–2.6	0.1–0.4
COD (kg/m^3 wood)	4–6	0.2–2
Total phosphorus (g/m^3 wood)	5–7	2–4

Based on data from Finnish BAT Report (1997).

The solid content in the bark is normally 35–45%. After normal wet or dry debarking, the bark is about 30–35% dryness. This can be increased to 40–45% in a press, but then there is an additional press effluent to consider. Bark press effluent is toxic and high in COD (20–60 kg/m^3). It could be dealt with at a chemical pulp mill by feeding it to the digester with the chips for subsequent evaporation and burning of the concentrate in the recovery boiler. In northern countries, during the wintertime, the frozen logs and snow are melted before debarking. This is done in the debarking drum with hot water or steam or on special type of conveyors before the debarking drum. At any given installation, the water consumption and discharges from dry debarking will increase and will then be in the middle to upper range as shown in Table 4.1.

Process vapors from digesters and the evaporation plant generate condensates (Gullichsen, 2000; Hynninen, 1998). Approximately 8–10 m^3/ADt of total condensates are produced with a COD load of about 20–30 kg/t and 7–10 kg/ADt of BOD5. The COD is mainly methanol (5–10 kg/ADt) with some ethanol and a number of organic sulfur compounds (1–2 kg/ADt TRS), 1–2 kg turpentine, and inorganic nitrous compounds. In the foul condensate, ketones, terpenes, phenolics, resin and fatty acids, and various dissolved gases are found. A large proportion of nitrogen discharged from a kraft pulp mill is found in condensates. About 1 m^3 of condensate per tonne of pulp has a COD concentration of 10–20 kg/m^3. The level is higher in condensates from hardwood pulp than from softwood. These strong condensates are normally treated in a stripper where the removal efficiency for most compounds is over 90% depending on the pH. Stripping systems usually remove malodorous gases (TRS) and COD-contributing substances at the same time. Stripped condensates after treatment can be fed to the stripper column. Energy-saving techniques enable lowering steam consumption from 0.2 tonne steam per tonne of condensate down to 0.02–0.04 tonne steam per tonne of condensate. The stripped gases are either incinerated in a dedicated burner with subsequent SO_2 scrubbing or burned in the limekiln.

About 7–9 m^3 of weaker condensates are produced with COD ranging from 0.5 to 2.0 kg/m^3, containing a total of about 8–12 kg of COD/t of pulp. These condensates do not contain metals and very useful for washing in the bleach plant when aiming at closing up this part of the process. They can also be reused as scrubbing liquor for limekilns or as white liquor makeup water. This means that some condensates will be used in closed parts of the process and not discharged to waste. Other condensates will be used in open parts, for example, the bleach plant, and end up in the effluent together with those condensates, which are not reused but discharged directly to waste. The total discharges of condensates to effluent are normally about 4–8 kg COD/t of pulp, which is mostly biodegradable. Alternatively, moderately contaminated condensates can be stripped in a system linked to the evaporation plant, thereby affecting treatment without any substantial additional use of energy. In this way the total COD load before any reuse is reduced to about 5 kg/t, a reduction of about 50% compared to only treating the most contaminated condensates.

Spillage of fibers and black liquor takes place in the digestion and screening plant, evaporation plant, and from tanks and during washing (Gullichsen, 2000). Spillage of white liquor, weak liquor, lime, etc., takes place during causticizing. Most spills can be collected and recycled if adequate buffer volumes are used and appropriate procedures employed. Leakage from mechanical components such as pumps can be reduced by choosing the right seals. The conductivity of individual outflows of wastewater is normally checked in order to decide which liquids spilled are recycled in the process and which are directed to waste. Improved collection of spillage can be achieved if clean water, such as cooling and sealing water, is piped off separately. The remaining spillage water can then be more easily recycled in the appropriate part of the process. Discharge of organic matters in spills is normally between 2 and 10 kg/t pulp. The lower figure is achieved using sufficiently large buffer volumes and proper supervision procedures. In principle, it should be possible to reduce discharges of spills to zero if clean cooling and sealing waters are piped off separately, sufficient buffer volumes are in place, and good housekeeping practiced. Improved collection of spillage not only reduces discharges to water but also reuses of valuable resources such as chemicals, fibers, and energy.

Pulp washing recovers as much as possible cooking chemicals and dissolved organic substances. By using press washing in the final stage, the amount of water can be reduced from 6–10 m^3/t of pulp to 2–3 m^3/t of pulp. This increases the amount of chemicals and contaminants eventually burned in the recovery boiler. The reduction of contaminants in the pulp is however less than the reduction of flow indicates. Washing is not 100% efficient, so a certain amount of chemicals and pollutants is transported with the pulp to the bleaching stage where it consumes bleaching chemicals and enters the effluent. For measuring this carryover, standardized methods are available. Washing losses are currently typically 5–10 kg of COD/t for softwood and 7–12 kg of COD/t for hardwood.

Most of the pollutants are generated in the bleach plant (Bajpai, 2005; Bajpai and Bajpai, 1996). If the bleach plant can be partly or fully closed, this would result in substantial reductions in discharges of water containing organic substances, nutrients, and metals (Bajpai and Bajpai, 1996, 1999; Gavrilescu, 2006). Wastewater quantities from a bleach plant are generally in the range of 20–40 m^3 water per tonne of pulp. Some mills have tried to increase the degree of closure of the bleach plant by reducing the water volume. Partial closure of the bleach plant is now achieved at both elemental chlorine-free (ECF) and totally chlorine-free (TCF) mills. Compared to open bleach plant, the reduction in COD load has been 25–50% and the reduction in flow even higher or down to 5–10 m^3/t pulp compared to the more normal 25 m^3/t pulp. The emissions from the bleach plant depend on a number of factors (Bajpai and Bajpai, 1996; Gullichsen, 2000):

- Degree of delignification achieved before the pulp enters the bleach plant
- Washing loss
- Bleaching sequences chosen and bleaching chemicals used
- Type of wood
- Final brightness of the bleached pulp to be attained
- Degree of closure of the bleach plant

Table 4.2 shows COD generated during bleaching using various delignification methods. The calculation for the discharge of residual lignin in kilogram COD/t pulp assumes a discharge of approximately 2 kg COD per kappa unit and a pulp to be bleached to full brightness. However, where the kappa number is less than 10, the discharge of COD is closer to 1.5 kg/kappa unit (OSPAR, 1994).

Organic chlorine compounds have been a matter of concern in the pulp and paper industry for more than two decades (Bajpai and Bajpai, 1996; Claeys et al., 1979; Sprague and Colodey, 1989; Suntio et al., 1988). These are produced mainly by the reactions between residual lignin present in the fiber and chlorine used for

Table 4.2 Discharges of COD from Bleaching of Hardwood and Softwood Pulp Using Different Delignification Methods

		Hardwood pulp		Softwood pulp	
Delignification method	ODL/ozone bleaching	Kappa	COD (kg/ADt)	Kappa	COD (kg/ADt)
Conventional cooking	—	18	38	30	63
Conventional cooking	ODL	13	27	15	32
Modified cooking	—	16	14	20	42
Modified cooking	ODL	10	15	12	25
Further modified cooking	—	13	26	15	30
Further modified cooking	ODL	10	15	10	15
Conventional cooking	ODL + ozone	No information available	3	No information available	6

Based on data from OSPAR (1994).
ODL, oxygen delignification.

bleaching. A different perception of the impact of chlorinated compounds in the public enhanced the environmental pressure on pulp mills, and thus, a change in the marketing concepts of the mills virtually stopped the use of molecular chlorine for bleaching of pulp (Bajpai and Bajpai, 1996). This means that the formation of chlorinated dioxins and dibenzofurans has virtually ceased and the degree of chlorination of the remaining chlorinated substances has declined. At the same time, the composition of AOX formed has undergone a change, parallel with the reduction of AOX discharges from pulp mills. For example, phenolic compounds with 3–5 chlorine atoms in the atomic ring, that is, the phenolic compounds that degrade most slowly and are most toxic, have decreased significantly below 1 g/t air dry pulp. In recent years, following market demands, some mills have completely eliminated the use of bleaching chemicals containing chlorine by combining oxygen delignification with an ozone stage and/or a peroxide stage.

Table 4.3 shows discharge of AOX during bleaching of softwood and hardwood pulps in different sequences. Pulps entering the bleach plant with low kappa numbers

Table 4.3 Discharges of AOX during Bleaching of Softwood and Hardwood Pulp in Different Sequences

Softwood pulp				
Delignification techniques	Bleaching sequences	Kappa	ClO_2 (kg/t)	AOX (kg/t)
Conventional cooking	D(EOP)DED	30	95	2.0
Conventional cooking + oxygen delignification	D(EOP)DED	16	60	0.8
Modified cooking + oxygen delignification	D(EOP)D(EP)D	10	30	0.3
Conventional cooking + oxygen delignification	ZD	No information	10	0.1
Modified cooking + oxygen delignification	ZP	No information	0	0
Hardwood pulp				
Cooking techniques	Bleaching sequences	Kappa	ClO_2 (kg/t)	AOX (kg/t)
Conventional cooking + oxygen delignification	D(EO)DED	13	40	0.5
Modified cooking + oxygen delignification	D(EOP)DED	10	30	0.3
Conventional cooking + oxygen delignification	ZD	No information	5	0.1
Modified cooking + oxygen delignification	ZP	No information	0	0

D, chlorine dioxide; E, extraction; O, oxygen; P, peroxide; Z, ozone.
Based on data from OSPAR (1994).

Table 4.4 Discharges of COD from Kraft Mills before Treatment

COD (kg/ADt) in different stages					
Wood handling	Condensates	Spillage	Washing loss	Bleaching	Total from mills
1–10	2–8	2–10	6–12	15–65	31–105

Based on data from CEPI (1997), OSPAR (1994), and Finnish BAT report (1997).

require less bleaching chemicals. If the kappa number is below 10, the need of chlorine dioxide as active chlorine can be limited to about 30 kg/t for softwood pulp, equivalent to about 6 kg chlorides. Another 1 kg chloride per tonne comes with the wood. The amount of chloride resulting from bleaching stages with chlorine-containing chemicals is of concern. These chlorides cause corrosion in the process equipment if they cannot be expelled in the effluent.

Table 4.4 summarizes the volume and total load of organic substances of effluents discharged from different process steps after primary treatment. At present, the lowest total discharges after primary treatment in bleached kraft pulp mills are 25–30 kg COD/t of pulp for softwood. One mill producing eucalyptus pulp reported 17.3 COD/t pulp as a yearly average in 1997 and 21.7 COD/t pulp in 1998 after primary treatment only.

Nutrients originate mainly from the wood itself although biological effluent treatment may require the addition of nutrients if deficient. Studies at kraft pulp mills have shown that nitrogen discharges principally derive from the unbleached part of the process, whereas phosphorus discharges come from the bleach plant. The prospects of reducing nutrient discharges from the process are mainly dependent on the possibilities of further processing of the condensate and further delignifying the pulp in the closed part of the process. Table 4.5 shows specific figures for phosphorus and nitrogen discharges in kilogram per tonne of kraft pulp before treatment (OSPAR, 1994).

Currently, external treatment is done using sedimentation, and for pulp mill effluents secondary biological treatment is also used. Data in Table 4.6 show variations in total treatment effects of sedimentation and biological treatment of kraft pulp mill effluents as percent reductions.

In the recent plants, the reduction is in the upper part of the ranges. Aerated lagoon can be modified to incorporate sludge recycling. In that case, the treatment efficiency approaches that of an activated sludge plant. Alternatives to activated sludge exist, which are more compact and less expensive. The experience from such

Table 4.5 Discharges of Phosphorus and Nitrogen (kg/t) before Treatment

Nutrients	Unbleached	Bleached	Total from mills
Phosphorous (kg/ADt)	0.01–0.04	0.04–0.06	0.05–0.10
Nitrogen (kg/ADt)	0.2–0.4	<0.1	0.2–0.4

Based on data from OSPAR (1994).

Table 4.6 Reduction of Pollutants in Wastewater Treatment Plant at a Chemical Pulp Mill

	Reduction rate of	
Pollutants	Aerated lagoon	Activated sludge
BOD_5 (%)	40–85	85–98
COD (%)	30–60	40–70
AOX (%)	20–45	40–65
Phosphorus (%)	0–15	40–85
Nitrogen (%)	0	20–50

Based on data from Finnish BAT report (1997) and OSPAR (1994).

installations is more limited, but they are claimed to have equivalent reduction levels to activated sludge.

Data on current discharges to water expressed as loads based on available data from kraft pulp mills within the European Union are given in Table 4.7.

Emissions to Atmosphere

Figure 4.2 shows emissions to the atmosphere from a kraft pulp mill. Atmospheric emissions generate from

- Chip storage
- Digester
- Pulp washing
- Bleach plant
- Bleaching chemical preparation
- Chemical recovery
- Evaporation
- Bark furnace

Table 4.7 Discharges of Pollutants from a Kraft Pulp Mill

	Unbleached pulp	Bleached pulp
Flow (m^3/t)		
BOD_5 (kg/t)	40–85	85–98
COD (kg/t)	30–60	40–70
AOX (kg/t)	20–45	40–65
TSS (kg/t)	0.2–15	0.2–10
Total nitrogen (kg/t)	0–15	40–85
Total phosphorus (g/t)	0	20–50

Based on data from CEPI (1997), Finnish BAT Report (1996), and SEPA Report 4869 (1996).

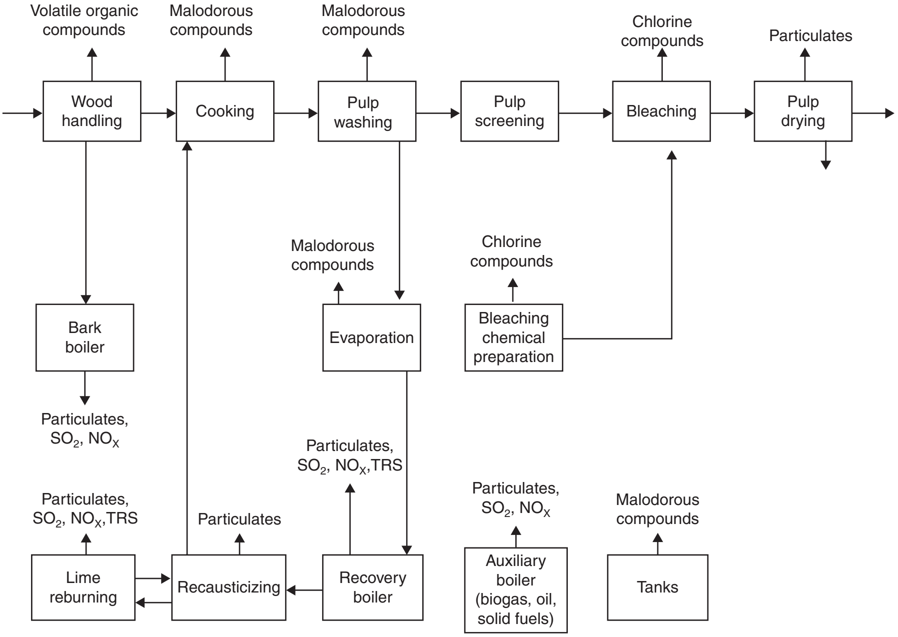

Figure 4.2 Emissions to air from kraft mills. Reproduced with permission from European Commission (2001).

- Recovery boiler
- White liquor preparation
- Limekiln
- Tanks
- Pulp drying (only for market pulp)

The emissions consist mainly of sulfur-containing compounds such as sulfur dioxide and malodorous reduced sulfur compounds such as methyl mercaptan, dimethyl sulfide, and hydrogen sulfide (Bordado and Gomes, 1997, 2003; Das and Jain, 2004; Hynninen, 1998; Pinkerton, 1993, 1998, 2000a, 2000b; Someshwar and Pinkerton, 1992; US EPA, 1973, 1986, 1993a, 1993b) (Table 4.8).

The latter compounds are commonly referred to as TRS. From furnaces nitrogen oxides are also emitted and furthermore small amounts of dust (solid particulates) as fly ash. From bleach plants and from bleaching chemical preparation, chlorine compounds may leak to the atmosphere. VOCs, mainly terpenes, are emitted to the atmosphere from wood chips stored in heaps outdoors the process. The VOC emission from chip piles varies among other things, with the time chips are stored, temperature and the wood species. Major sources of atmospheric emissions are discussed next.

The major source of air emissions in a kraft pulp mill is the recovery boiler. Emissions are mainly represented by sulfur dioxide. In addition, there are emissions of particulates (primarily sodium sulfate and sodium carbonate), nitrogen oxides, and

Table 4.8 Malodorous Compounds Formed and Released during Kraft Pulping

Malodorous compounds	Amount
Hydrogen sulfide	0.5–1.0 kg sulfur/t of pulp
Dimethylsulfide	1.0–2.0 kg sulfur/t of pulp
Methanol	6–13 kg/t of pulp
Ethanol	1–2 kg/t of pulp
Turpentine	4–15 kg/t of pulp
Guaiacol	1–2 kg/t of pulp
Acetone	0.1–0.2 kg/t of pulp

Based on Gavrilescu (2006) and Hynninen (1998).

malodorous compounds (hydrogen sulfide) (Adams et al., 1997; Borg et al., 1974; Pinkerton, 2000b; Reeve, 2002; Tran, 2007; Vakkilainen, 2000a, 2000b, 2005). The recovery boiler is fed with the evaporated black liquor. Approximately one-third of the dry substance in the evaporated liquor consists of inorganic chemicals and two-thirds is dissolved organic substance. After a conventional evaporation, the black liquor (strong liquor) has a dry solid (DS) content of about 65%. The aim of evaporation is to achieve a high DS content in the thick black liquor fed to the recovery boiler in order to generate more steam. By installing a further equipment, a DS content of more than 75–80% can be obtained. The sulfur emission from the boiler will typically be reduced by about 80% when the DS content is increased from 65–67% to 74–76% due to higher temperature in the recovery boiler and the more favorable incineration conditions. In some cases, emissions of sulfur have not reduced beyond DS of 72–73%. A drawback to the higher temperature is that emission of NO_x can increase. The recovery boiler is equipped with an electrostatic precipitator (ESP) in order to remove the large amount of particulates (mainly Na_2SO_4) from the flue gases. The dust is fed back into the furnace by mixing into the strong black liquor. Additionally, recovery boilers are often equipped with a scrubber in order to decrease the emission of SO_2.

Table 4.9 presents typical emissions to air from recovery boilers. The main principles and operating variables that affect the emissions from the recovery boiler are discussed next to explain the complexity of pollution prevention.

Table 4.9 Emissions to the Atmosphere from the Recovery Boiler and Limekiln

Pollutant	Units	Recovery boiler	Limekiln
Particulate matter	kg/ADt	0.2–0.45	0.03–0.05
TRS as S	kg/ADt	0.1–0.2	0.02–0.025
SO_2 as sulfur	kg/ADt	0.1–0.4	0.005–0.03
NO_x as NO_2	kg/ADt	0.7–1.1	0.1–0.2
Gas flow	m^3/ADt	7000–9000	1000

Based on Gavrilescu (2006) and Hynninen (1998).

In a conventional recovery boiler, there is an oxidizing zone in the upper part and a reducing zone in the lower part. The strong liquor is introduced through one or several nozzles into the reducing zone (Vakkilainen, 2000b). Combustion air is mostly supplied at three different levels as primary, secondary, and tertiary air (from the bottom up). A smelt consisting mainly of sodium sulfide (Na_2S) and sodium carbonate (Na_2CO_3) is formed at the bottom of the furnace. When sulfur is reduced to sulfide in the smelt, some hydrogen sulfide is also formed. Small amounts of hydrogen sulfide may leave with the flue gases if the air supply is not sufficient or if the mixing of air into the furnace is incomplete.

Temporary high emissions of hydrogen sulfide from the smelt may occur as a consequence of disturbances caused by deposits of dry substances on the furnace walls falling into the smelt. In the oxidizing part of the furnace, sulfur is oxidized to sulfur dioxide and sodium in the gas phase reacts with sulfur dioxide to form sodium sulfate. A higher DS content leads to a high temperature in the furnace and thus a lower emission of hydrogen sulfide and a higher emission of sodium. The higher sodium emission means that more sulfur is bound as sodium sulfate, and thus the emission of sulfur dioxide is decreased.

In order to decrease the SO_2 emissions from the recovery boiler, it is often equipped with a flue gas scrubber operating at pH 6–7. pH is controlled by adding sodium hydroxide (NaOH), weak liquor, or oxidized white liquor. A higher pH would remove hydrogen sulfide, but carbon dioxide would be absorbed, which would quickly neutralize the alkali. Surplus liquor from a scrubber is recycled to the process, normally to the white liquor preparation. The formation of NO_x in a recovery boiler is mainly influenced by the nitrogen content in the black liquor and excess O_2 during combustion. The NO_x formation per MJ input is generally low due to the relatively low oxygen concentration needed for an efficient recovery of chemicals, and the emission of NO_x normally varies between 1 and 2 kg/t of pulp. An increase in excess O_2 from 1.5% to 2.5% may increase NO_x by about 20%, and increased DS content from 65% to 75% may increase NO_x by up to 20%. The nitrogen content is higher in hardwood liquors than in softwood liquors, which can also result in about 10% higher NO_x. Reduced NO_x can normally be achieved by modifications to the air feed system and optimizing combustion conditions. Emissions are normally between 50 and 80 mg/MJ, but new recovery boilers can achieve levels down to about 40 mg/MJ or well under 1 kg NO_x per tonne.

Table 4.9 shows emissions to air from a limekiln. The major air emissions from the limekiln are sulfur dioxide, nitrogen oxides, reduced sulfur compounds (TRS), and particulate matters (Pöyry, 1992). The emissions from the limekiln in a kraft mill are mainly affected by solids retention time, gas contact area, the type of fuel, and temperature. Sulfur emissions from the limekiln are due to sulfur in the fuel and malodorous gases if such are burned. The role of sulfur entering the sulfur with lime mud is in this respect marginal. A limited amount of sulfur can be absorbed in the limekiln by gaseous Na, forming sodium sulfate. The main sulfur-absorbing compound is thus the Na_2CO_3 in the lime mud. When this capacity is exhausted, SO_2 is released. This effect is enhanced when malodorous noncondensable gases (NCGs) are incinerated in a kiln. Therefore, SO_2 emissions are usually a clear function of the amount of malodorous gas flow. To minimize the formation of SO_2, either the sulfur content in the fuel can be reduced or, if malodorous NCGs are to be burned in the limekiln, sulfur compounds can be scrubbed out of these gases prior to burning in the limekiln. A small internal NaOH scrubber for the malodorous gas flow (i.e., not for the total flue gas flow) will reduce H_2S almost completely while the methyl sulfides are reduced by about 50–70% and methyl mercaptane by less than 20%. Typical total sulfur emissions from limekilns are ten up to several hundred mg/m^3 if NCGs are burned and 10–30 mg/m^3 if they are not.

The TRS emissions from a limekiln consist mainly of hydrogen sulfide. Concentrations of H_2S are normally less than 50 mg/m^3, resulting in a total emission of less than 0.03 kg/t. H_2S formation in the limekiln depends on oxygen levels and the amount of Na_2S in the mud burned in the kiln. The presence of sufficient excess air can be ensured by a residual oxygen control system. The Na_2S content can be controlled by properly operated lime mud washing and filtering so that Na_2S is prevented from entering the limekiln. If Na_2S enters the cold drying and the heating section of the limekiln in the presence of CO_2 and water, H_2S is formed. With a proper capacity of the lime mud filter, a small amount of air is sucked through the lime mud cake and the residual Na_2S left on the surface of lime mud particles is then oxidized to sodium thiosulfate that does not cause any H_2S formation in the kiln. If H_2S problems arise, the reason in many cases is poor lime mud quality in terms of lime mud DS content (normally over 80%) and purity (low free alkali concentration is required). Technical options are improvement of green liquor clarification and the lime mud washing or replacing a part of the lime with makeup lime.

Particulate matter is made up of lime dust and sodium condensed out of the vapor phase. The emissions can be controlled internally by design and proper running of the kiln and externally by adding an ESP or a scrubber. An ESP is capable of reducing the concentration of particulates down to about 20–100 mg/m^3 and a water scrubber to about 200–600 mg/m^3. NO_x emissions are mainly correlated to burner design and for a particular burner, to nitrogen content of the fuel and combustion temperature. An increase in emissions would result from the use of fuel with a higher content of nitrogen. Both incineration of NCGs and the use of biogas and methanol as fuel increase NO_x formation.

There are also emissions from bark boilers. Bark burns autothermically at about 20% dryness. Before incineration the loose bark and wood sticks removed from the logs in the debarking drum are fed into a bark shredder and is finally pressed to a dryness of 38–45%. The consumption of energy in a press is about 5 kWh/t of bark having an initial dryness of about 35% and the increase in heat generation is about 2GJ/t 45% if the dryness increases from about 35% to 45%. At 45% dryness, bark represents a heat value of about 7–8 GJ/t and it can be used as a source of energy within the plant or sold as a by-product, for example, as pellets. At the plant it is normally used in an auxiliary boiler. If it is to be used as fuel within the process or sold as pellets, it must first be dried up to about 90% dryness. It can then, after being either gasified or pulverized, be used in the limekiln.

Bark is used as power plant fuel in pulp mills to a large extent. As bark contains only small amounts of sulfur, there will be only low sulfur dioxide emissions depending on if other sulfur-containing fuels are added. When bark is being burned together with fuels that contain sulfur (e.g., fossil fuels), the alkaline bark ash binds some of the sulfur and thus reduces the emissions.

In bark boilers, the emission of nitrogen oxides will also be lower than in the burning of other kinds of fuel due to the low combustion temperature. Emissions are typically 70–100 mg/MJ when only bark is fired, but at times when oil is used in the boiler, an increase to about 100–150 mg/MJ will be the case. Excessive oxygen increases NO_x formation, but lower excess oxygen levels increase CO and VOC. The total NO_x reduction achievable in a bark boiler is about 30–50% by making changes in combustion techniques and/or applying selective noncatalytic reduction (SNCR) process. Examples for the application of the SNCR process on bark boilers can be found in some Swedish mills. Given a heat production from bark of about 7 GJ/t of bark, the range of NO_x emissions is about 0.3–0.7 kg/t bark. The lower figure represents optimized combustion conditions and/or the use of SNCR where urea is used to reduce NO to nitrogen, carbon dioxide, and water. The NO_x emissions would then be about 40–60 mg/MJ or 100–200 mg/m^3 (normal temperature and pressure, dry gas).

Dust emissions are normally reduced to about 20–40 mg/Nm^3 (dry gas) at 11% O_2 when ESPs are used and about 200 mg/m^3 with cyclones. Emissions of gaseous sulfur are small at about 5–20 mg/MJ when burning bark. Probably some of the sulfur in the bark is removed with the ashes.

In integrated pulp and paper mills, the excess heat produced by the pulp mill is not quite enough to cover the energy consumption of the paper production. The additional demand for heat has to be produced in auxiliary steam boilers. Fossil fuel is used as the support fuel in bark and sludge boilers and as the main fuel in auxiliary boilers as well. The fuels used in the boilers are coal, fuel oil, natural gas, peat, wood waste, and fibrous sludge from effluent treatment. The emissions from power production are dependent on the fuel, the fuel mixture, and the impurities content. For instance, oil and coal contain sulfur but natural gas does not. Most of the boilers for solid fuels are circulating and fluidized boilers especially when difficult mixed fuels with varying properties are incinerated. These boilers offer the opportunity to use a wider range of fuels and generate lower emissions than grate boilers. The combustion efficiency is high due to the effective mixing of the materials and heat transfer between the solid material and the flue gas. NO_x emissions are relatively low due to the low combustion temperature (800–950°C). If the fuel contains sulfur, sulfur emissions can be prevented by the addition of lime to the bed. At temperatures below 900°C, sulfur reacts with lime or calcium in the bark and the sulfur dioxide emissions are reduced considerably.

Malodorous gases in kraft pulping are usually H_2S, methyl mercaptane, dimethyl sulfide, and dimethyl disulfide. Malodorous gases are sometimes referred to as TRS. The malodorous gas streams are generally divided into strong and weak gases. The latter normally refers to a concentration of less than 0.5 g of sulfur/m^3, while the more concentrated or strong gases are normally above 5 g/m^3. Concentrated gases come from the digester, evaporation plant, and condensate stripper. In total, they add up to about 25 m^3/t of pulp. The noncondensable gases from the cooking plant and the stripper gases from the steam stripping of foul condensates from the evaporation plant usually contain 1.0–2.5 kg sulfur/ADt (Finnish BAT Report, 1997) and are normally higher in case of hardwood pulping in comparison to softwood due to different lignin structure. Concentrated gases are collected and burned either in the limekiln, the recovery boiler, or in a separate burner. If a dedicated burner is used, a scrubber is normally added to control emission of the SO_2 formed. The heat energy can be used, but NO_x formation is high, up to 1 g/MJ of fuel. This level can be reduced by about 70% by optimizing combustion conditions.

The advantage of burning the malodorous gases in the limekiln is that no extra furnace is needed. In addition, the sulfur in the gas can be absorbed, which reduces the emission of sulfur dioxide. However, the sulfur content in malodorous gases can overload the absorption capacity in the limekiln. On average, 15% of the fuel used in a limekiln can be replaced by malodorous gas. However, the variation of the amount of energy of the gas may make it difficult to produce lime of good and uniform quality. Separating off methanol from the gases minimizes the problem with varying gas quality. The separated methanol can then be fed in liquid phase to the limekiln or to a dedicated burner for malodorous gases.

Diluted gases come from chip presteaming, screening, pulp washing, smelt dissolver, and ventilation of various tanks that contain black liquor etc. They add up in total to about 2000–3000 m^3/t of pulp with 0.2–0.5 kg sulfur/ADt (Finnish BAT Report, 1997). Diluted gases at some mills are collected and burned in the recovery boiler, in the limekiln, or scrubbed. Scrubbing is mainly effective on H_2S. Burning the weak gases in the recovery boiler may influence the operation of the boiler and would require modification of the boiler. At some mills both weak and strong malodorous gases are burned in the recovery boiler.

In cooking and evaporation, a part of the malodorous compounds are transferred to the condensates. In addition to reduced sulfur compounds, the condensates contain methanol and some other oxygen-consuming compounds. The foul condensates are collected and treated separately as described earlier. In bleached kraft pulp mills, using chlorine dioxide as bleaching chemical chlorine compounds from the bleach plant and the ClO_2 production are released to the atmosphere. Emissions of VOC from the process are reported to be about 0.4 kg/t of softwood kraft and less than 0.1 kg/t for hardwood kraft. There are also some emissions of VOCs from the chip heaps. As an example, VOC emissions from the chips are about 0.2–0.3 kg/m^3 of wood at kraft pulping.

Solid Waste Generation

Different types of solid waste are generated during kraft pulping (Gavrilescu, 2004). These are listed as follows:

- Inorganic sludge (dregs and lime mud) from the chemical recovery
- Bark and wood residues from wood handling
- Sludge from effluent treatment (inorganic material, fibers, and biological sludge)

Table 4.10 Generation of Wood Wastes in a Kraft Pulp Mill

Wood wastes	Quantity (kg/t of pulp)
Sawdust coming from slasher deck	10–30
Bark falling from debarking drum	100–300
Pins and fines from chip screening	0–100
Wood waste from wood yard	0–20
Total	160–450

Based on Gavrilescu (2004, 2006).

- Dust from boilers and furnaces
- Rejects (mainly sand) from the wood handling
- Ashes and miscellaneous material (such as building material)

Wood wastes generated in kraft pulp mill is shown in Table 4.10.

The most common way to use wood residues in the pulp mills is to burn it for heat (Huhtinen and Hotta, 2000). Solid residues from wood waste burning are ash and incompletely combusted carbon. Combustion of hogged fuel generates 10–25 kg ash per tonne of pulp (Koch, 1985). The ash content of the wood, bark, and wood wastes are listed in Table 4.11, and the emissions from combustion of hogged fuel are presented in Table 4.12 (Gavrilescu, 2005, 2006).

Many organic substances, which might be considered waste products, are burned for energy recovery. This normally includes bark and wood residues and could include water treatment sludge.

Dregs and lime mud are separated from the chemical recovery cycle in order to keep the amount of inert material and nonprocess chemicals in the cycle at an acceptable level and thus secure high reaction rates in the chemical recovery system. Bark and wood residues from wood handling is normally burned for energy recovery and should thus be considered as waste only if they cannot be burned and have to go to permanent landfilling. Wood ash from bark boilers contains nutrients taken from the forest with the wood raw material, and this ash can be suitable as a fertilizer as long as it is not contaminated by metals such as Hg, Cd, and Pb, although these come from the wood itself. A leaching of heavy metals from the recycled ashes spread to forest or agricultural land might be a drawback of these measures.

Table 4.11 Ash Content of Wood and Bark

Material	Ash content (%)
Wood	0.7–2.0
Bark	4–6
Wood wastes (as hogged fuel[a])	5–8

[a] Sand and dirt are included.
Based on Gavrilescu (2005, 2006).

Table 4.12 Emissions from Combustion of Hogged Fuel, Mass Percent[a]

Gases		Particulate matter
Nitrogen	65	Inorganic fly ash
Carbon dioxide	8	Fixed carbon
Oxygen	11	Traces of salts and metals
Water vapor	12	2–3% of total
	96–98% of total	
Carbon monooxide	0.1	
Unburned hydrocarbons	0.005	
Sulfur dioxide	0.01	
Oxides of nitrogen	0.005	

[a] No fossil fuels are used.

Based on Gavrilescu (2005, 2006).

Sludge from wastewater treatment is one of the main groups of potential waste. A large amount of sludge is generated in the primary treatment and in biological treatment with the activated sludge method. Aerated lagoons generate only small amounts of excess sludge, and the generation of sludge in anaerobic treatment is also moderate. Chemical flocculation produces a considerable amount of sludge. Biological and chemical sludge has poor dewatering properties.

The sludge is usually thickened before being dewatered in a filter press, screw press, or on a vacuum filter. Often, excess sludge from biological wastewater treatment is mixed with primary sludge and bark sludge before dewatering. Inorganic and/or organic chemicals are used to improve the dewatering of sludge by forming larger flocs. Mixed sludge can be dewatered to 25–35% dryness with filter presses and to 40–50% with a screw press using steam in the pretreatment stage. In sludge burning, the net energy production is about zero or negative if the dry solid content in the sludge is below 40% and if the sludge contains a high amount of inorganic material. To maintain good burning conditions, the use of auxiliary fuel is necessary unless the sludge is mixed with bark and other wood waste material. Burning reduces the volume of waste and the inorganic content remains as ash, which is normally transported to a landfill site. Sludge from chemical precipitation cannot be burned alone without the use of auxiliary fuel because of the high content of inorganic matter and water. The sludge is therefore often transported to a landfill site. Sludge from flocculation with only synthetic organic polyelectrolytes is suitable for incineration.

Other reports (CEPI, 97) describe little higher amounts of solid wastes as typically for kraft mills. There, unbleached kraft pulping is held to produce 20–60 kg DS organic waste/ADt (kraft) and 30–60 kg DS inorganic waste/ADt. For bleached kraft pulping, 30–60 kg organic wastes (dry basis) per tonne of pulp and 40–70 kg inorganic wastes (dry basis) per tonne of pulp are reported.

Green liquor sludge, dregs, and lime mud are often mixed. In total, the amount varies roughly between 10 and 60 kg/t of pulp with an average of about 30 kg/t (SEPA Report 4869, 1996). The composition in such a mixed waste varies as well. In Sweden, green liquor sludge is normally dried on drum filters with a precoat layer

Table 4.13 Generation of Pollutants during Kraft Pulping

Process steps	Pollutants
Wood processing	Bark, wood residues BOD, color, resin acids
Pulping	TRS (hydrogen sulfide, mercaptans), VOC, sodium salts, SO_2, nitrogen oxides BOD, color, resin acids
Pulp washing and screening, pulp thickening	TRS (hydrogen sulfide, mercaptans), VOC BOD, color, resin acids Knots, reject fibers
Bleaching	VOC Chlorinated organics, BOD, color, inorganic salts
Chemical recovery	Sodium salts and lime (fine particulates), SO_2, nitrogen oxides Dissolved sodium salts Lime mud, dregs
Wastewater treatment	VOC Sludge (primary, secondary, chemical)

Based on Gavrilescu (2005, 2006).

of lime mud given a DS of 30–70%. If centrifuges are used, the DS is about 8–20%. The sludge is normally landfilled.

According to SEPA 4869, for kraft pulp mills, the amounts of ashes, slags, particulate matter (e.g., from electrostatic precipitators) are between about 5 and 45 kg/t of pulp.

The amounts of wood yard waste to landfill vary between 1 and 20 kg/t of pulp. This waste mainly consists of bark, sand, and stones (SEPA 4869).

With aerated lagoons at kraft pulp mills, the amount of sludge is very small, usually less than 1 kg of DS/t of pulp. Biological treatment in activated sludge plant generates higher amounts of sludge.

Table 4.13 summarizes various types of pollutants generated during kraft pulping (Gavrilescu, 2005, 2006).

4.2 SULFITE PULPING

The main processes involved in sulfite pulping and the major sources of emissions (to water and air) are shown in Fig. 4.3. The central European pulp industry has made significant reductions in atmospheric and effluent emissions in the past 50 years (Knoblauch, 2004).

Emissions to Water

In the sulfite pulping, the wood required for manufacturing 1 tonne of bleached pulp is usually between 4.2 and 5.2 m^3 unbarked wood/ADt. The delignification is brought

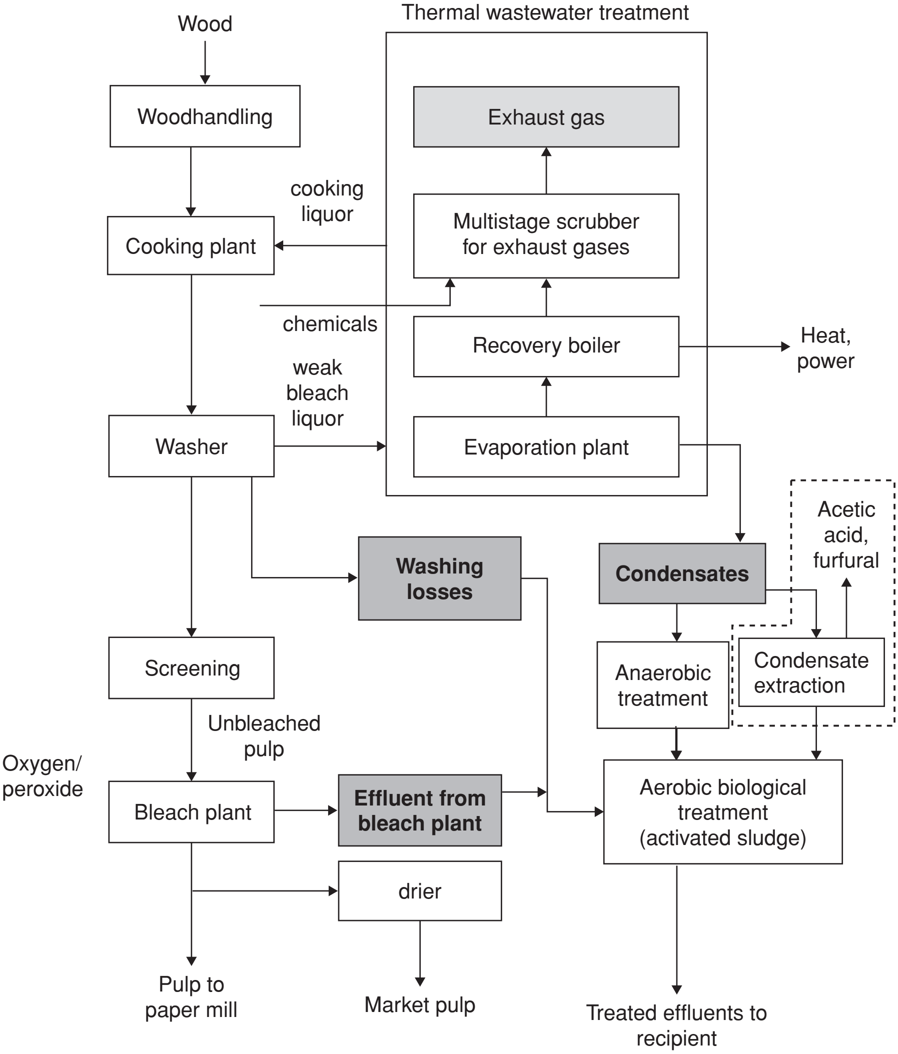

Figure 4.3 Emissions to water and air from sulfite pulping. Reproduced with permission from European Commission (2001).

down to a kappa number of about 14–22 for softwood and 10–20 for hardwood. The yield is somewhat higher than for kraft pulping (Smook, 1992). As a result, the amount of wood, mainly hemicelluloses, dissolved out in the open part of the process (after brown stock washing) is comparatively high in alkaline bleaching stages and can amount up to 40–50 kg COD/t. The specific wastewater volume of the bleach plant in better performing mills is in the range of 15–25 m^3/ADt. It is important to neutralize sulfite liquor before evaporation. Otherwise, acetic acid will be evaporated and turn up in the condensates instead of being led to the recovery boiler. The COD load in

Table 4.14 Emissions to Water before and after Biological Treatment in an Integrated Sulfite Pulp Mill Producing Dissolving Pulp

COD load before biological treatment	
Wood yard	≈1 kg/t
Bleaching (first and second stages)	≈15 kg/t
Evaporator condensates	≈30 kg/t
Total load	≈46 kg/t
Total flow	≈40 m^3/t
Emissions to water after biological treatment	
COD	4–5 kg/t
BOD5	Not detectable
TSS	0.4–0.5 kg/t
AOX	<0.01 kg/t
Total phosphorus	<0.1 kg/t
Total nitrogen	<0.2 kg/t

Based on data from European Commission (2001).

condensates is normally much higher at sulfite pulp mills compared to kraft mills as stripping is not a normal practice. The total load in condensates is up to 60–70 kg of COD/t. The differences between softwood and hardwood are quite small. Stripping and anaerobic treatment are possible options. Most of the contaminants are readily degraded in a biological treatment plant as in case of kraft pulping (Anonymous, 1998; Dowe, 1996).

In comparison to the kraft pulping, the data available for sulfite pulping are limited. Total emissions of organic substances (measured as COD) before treatment vary between 80 and 200 kg/t. Data indicate that the total effluents from modernized sulfite pulp mills are 50–100% higher than the one from modernized kraft pulp mills due to less closed processes. Discharges after treatment are very different within Europe, ranging, for example, from 10 up to 190 kg COD/ADt. Typical values for water consumption for magnesium bisulfite pulping are in the range of 40–100 m^3 water per ADt of pulp. Table 4.14 shows the pollution load in a sulfite pulp mill producing dissolving pulp for viscose fibers before and after treatment.

Emissions to the Atmosphere

Emission levels of sulfur from sulfite mills and the potential of further reductions are very much dependent on the mill. As there is difference between different sulfite processes, the values show higher variations than in kraft pulp mills. Also, they greatly depend on the collection and abatement systems that are used for treatment of gaseous emissions. Several devices and systems for collecting and purifying emissions to the atmosphere are found in sulfite pulp mills. These are following: cyclone for chip blowing; gases from the continuous pressure control relief of the digesters are led to combustion in the recovery boiler; collecting system for aerating gases from digesters, blow tanks, knot screens, washing filters, all weak and thick liquor tanks, and fiber filters. These gases are led to combustion in the recovery boiler; scrubbers for the absorption of sulfur dioxide in aerating gases from the bleach plant; noncondensable gases from the evaporation are led to combustion in the recovery boiler; absorption of SO_2 in the flue gases leaving the recovery boilers in the acid preparation plant (venturi scrubber system); collection system for ventilation gases from the boiler house's liquor and condensate tanks, weak liquor filter, and mix tank. The gases are led to combustion in the recovery boiler; dust separation from flue gases from the auxiliary boiler (burning bark, oil, or other fuels) with electrofilter (ESP) and wet scrubber; NO_x reduction in the bark boiler by injection of urea.

The major source of sulfur oxide emissions is the recovery boiler in a magnesium sulfite mill (McDonough, 2000). Magnesium oxide ash is collected from the flue gas in ESPs after the recovery boiler, and washed with water forming magnesium hydroxide. This liquid is used in venturi scrubbers to absorb SO_2 and SO_3 from the recovery boiler. The absorption system is made up with a number of scrubbers, normally three, four, or five. Emissions are about 4–6 kg SO_2 per tonne of pulp when three scrubbers are used and 2–3 kg/t when four are used. Each scrubber reduces the concentration by about 70%. There are also less concentrated SO_2 emissions from the bleach plant, the digesters, washing, and the auxiliary boilers.

Because of the higher temperature in the recovery boiler, emissions of NO_x from sulfite pulp mill recovery boilers are generally higher in comparison to kraft pulp mills (McDonough, 2000; Pinkerton, 2000b). NO_x emissions range normally from 1.5 to 3.0 kg/t of pulp. SO_2 emissions range from 0.5 to 3.0 kg/t of pulp.

Also, there are emissions to air from other combustion processes for steam and power generation. Different types of fuels may be used for steam generation. Generally, sulfite mills are operating a bark boiler, where bark, rejects, knots, fiber, and biosludge are incinerated as well.

In comparison to kraft pulping, emissions of malodorous gases in sulfite pulping are lesser (McDonough, 2000; Pinkerton, 2000b). However, emissions of furfural mercaptans and H_2S might cause odor, and emissions of gaseous sulfur may also cause annoyance. At some mills, emissions of malodorous gases are collected and burned in the recovery boiler. The reported ranges of total emissions to the atmosphere from European sulfite pulp mills are shown in Table 4.15.

Emissions of VOC from the process are about 0.2 kg/t of sulfite pulp. The chip heaps also contribute to emissions of VOC.

Table 4.15 Emissions from Atmosphere in Sulfite Pulp Mills

Emissions	Recovery boiler	Bark boiler	Total emissions from mills
Total gaseous sulfur (kg/ADt)	0.5–5	0.02–0.06	0.55–5
NO_x (kg/ADt)	1–3	0.1–1	1.2–4.2

Based on data from European Commission (2001).

Table 4.16 Generation of Waste during Production of Sulfite Pulp

Waste	Amount (kg/t)	Origin
Scrap (steel tapes, part of equipment, etc.)	2.8	Packaging of logs, maintenance of installations
Bark	90	Debarking plant
Sawdust	30–50	Wood handling
Rejects from coarse screening	23	Screening
Rejects from fine screening (chips, knots, bark, fibers, sand)	8	Screening (0.5–1% losses)
Sludge from pulp production	80	Mechanical and biological treatment of process water, recovery of chemicals
Mixed municipal waste	0.4	Operation of installations
Oil waste	0.03	Maintenance

Based on data from European Commission (2001).

Solid Waste Generation

Different types of wastes are generated in sulfite pulping, most of which can be utilized. The wastes generate from different stages of the production process such as debarking, chipping, screening, clarification of the cooking liquor, maintenance, as well as from treatment of raw and wastewater. The waste generated in production of sulfite pulp in a German mill is shown in Table 4.16.

In addition to this, the following types of waste have also to be considered: ash and cinder from energy extraction (combined burning of biofuel and fossil fuel); wood-room waste (sand etc.); ash and cinder from the recovery boilers; sand from fluidized bed boiler (if operated); in case of integrated pulp mills, residues from the paper mill. Wood waste as bark, chips, sawdust, knots, etc., is often burned on-site. Ashes from the recovery boiler and bark boilers are partly used for other purposes. Furthermore, sludge from clarification of the cooking liquors and base tanks is generated.

A German sulfite mill using surface water reported significant amount of sludge from raw water treatment (flocculation), amounting to 50 kg/ADt.

According to Pöyry (1997), the spans of waste from sulfite pulping to landfill in Europe are about 30–50 kg organic waste in DS/t of pulp and 30–60 kg inorganic waste in DS/t of pulp. Organic waste consists of wood residues, bark, pulping rejects, and wastewater sludge. If the organic waste is incinerated in dedicated incinerators, there is virtually no organic waste to be landfilled.

In an integrated sulfite pulp mill that is incinerating all organic residues on-site (bark, wood waste, sludge from biological treatment), the amount of waste is reported as 3.5 kg DS/ADt (100% DS). The ash from the incineration process can be utilized in different manners such as in cement industry.

4.3 MECHANICAL PULPING

With few exceptions, mechanical pulp mills are integrated with paper mills. This has both positive and negative effects on the environment. Emissions from mechanical pulp mills are lower than emissions from kraft pulp mills, mainly because of the high yield in mechanical pulp production (Salo, 1999).

Wastewater Emissions

Yield is higher in mechanical pulping as the losses occurring during the process, mainly in the form of dissolved ligneous substances, are low (Swedish Environmental Protection Agency, 1997). The use of wood is normally between 2.4 and 2.6 m^3/ADt for groundwood (GW), 2.3 and 2.8 m^3/ADt for thermomechanical pulp (TMP), and 2.8 and 3.0 m^3/ADt of chemithermomechanical pulp (CTMP) (CEPI, 1997).

In mechanical pulping processes, the water systems are usually quite closed in order to maintain high process temperatures (Smook, 1992). Freshwater is only used for sealing and cooling as surplus clarified waters from the paper machine are usually used to compensate for the water leaving the circuit with the pulp (5–10 m^3/t of pulp) and the rejects. For a TMP mill, sources of emissions to water are wood handling, cleaning, and bleaching (SEPA-Report 4713–2, 1997) (Fig. 4.4).

Most of the mechanical pulp mills are integrated mills (Biermann, 1996b; Gullichsen, 2000). Typical ranges of overall water consumption for GW, TMP, and CTMP processes are 5–15, 4–10, and 15–50 m^3/ADt of pulp, respectively. Figure 4.4 shows the sources of emissions to water and main substances of concern from a CTMP mill. Strict countercurrent water system is applied; that is, clean wash water is used for the last wash press and led toward the fiber flow. The highly polluted filtrate from the first press is sent to effluent treatment. The liquid stream after

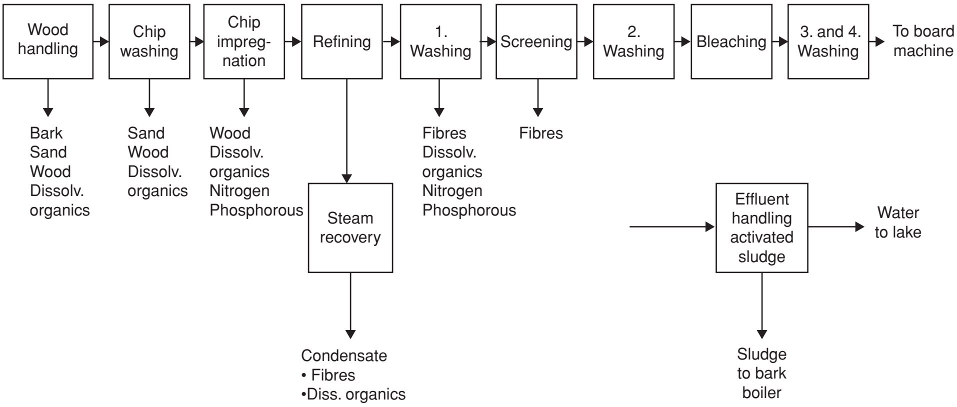

Figure 4.4 Emissions to water from a CTMP mill. Reproduced with permission from European Commission (2001).

separation of the fibers may be treated by flotation to take out solids from water before sending them to the wastewater treatment plant as well. Sealing and cooling waters are collected and used as process water. If the volume of the white-water tank is sufficient, a consumption of about 10 m^3 freshwater per tonne of pulp is required. If the properties of the final product require a low content of extractives (in case of board pulp or fluff pulp) or fines (in case of fluff pulp), some more freshwater may be needed. On the other hand, an internal treatment of the white water from the first washing stage by the use of a flocculation/flotation unit results in water consumption below 10 m^3/t. The flocculation/flotation unit removes extractives and fines and about 40–50% of the COD.

Emissions to water are dominated by oxygen-consuming organic substances that are lost in the water phase in the form of dissolved and dispersed organic substances. A yield of 92–97% means that 30–80 kg/t of the wood in form of solid and dissolved substances is lost during processing. The yield is dependent on the energy input and the temperature in the process and on the use of chemicals. Wood species, seasonal variations, and storage conditions of the wood also influence the amount of dissolved solids. During mechanical pulping, the stability of the cellulose and the lignin is not affected, but simple carbohydrates, hemicelluloses, lignins, extractives, proteins, and inorganic substances including nitrogen and phosphorus are dissolved and dispersed in the process water. With a decreasing yield and increasing temperature, the organic load of the water from pulping increases.

Typical load of pollutants and nutrients in water from the mechanical pulping of Norwegian spruce before external treatment for different pulps are shown in Table 4.17.

The releases of organic pollutants increase significantly if mechanical pulp is bleached in an alkaline peroxide step. This is due to the alkalinity during bleaching. The yield loss in connection with peroxide bleaching is 15–30 kg/t corresponding to an additional load of approximately 10–30 kg O_2/tonne measured as COD, respectively. The upper values of Table 4.17 are related to peroxide bleached mechanical pulps. Whereas in TMP mills, using only sodium dithionate as bleaching chemical, COD

Table 4.17 Typical Load of Pollutants and Nutrients in Water from the Mechanical Pulping of Norwegian Spruce before External Treatment

	Pulping process					
Parameters	GW	PGW	PGW-S	RMP	TMP	Bleached CTMP
Yield (%)	96–97	95–96	95–96	95–96	94–95	92–94 (91–93)
BOD5 (kg/t)	8.5–10	10–13	11–14	10–15	13–22	17–30 (25–50)
COD (kg/t)	20–30	30–50	45–55	40–60	50–80	60–100 (80–130)
Nitrogen (g/t)	80–100	90–110		90–110	100–130	110–140 (130–400)
Phosphorus (g/t)	20–25	20–30		20–30	30–40	35–45 (50–60)

Based on data from Finnish BAT Report (1997).

PGW, pressurized groundwood; PGW-S, superpressure groundwood pulp; RMP, refiner mechanical pulp.

levels of 2500–3000 mg O_2/L have been measured, referring to a water flow from the TMP mill of 3–4 m^3/t (paper machine not included). A GW mill has reported COD concentrations before treatment between 1700 and 2000 mg O_2/L.

The discharge of nitrogen in mechanical pulping originates from the wood and chelating agents—ethylenediamine tetraacetic acid (EDTA) and diethylenetriamine pentaacetic acid (DTPA) used in bleaching (Salo, 1999). A dosage of 2–3 kg EDTA per tonne of pulp results in an additional discharge of 150–220 g nitrogen per tonne of pulp. The discharge of phosphorus depends on the wood. Emissions of nutrients (nitrogen and phosphorous) are low but may have a negative impact due to eutrophication. About 20–30% of the bark is water-soluble of which 50–60% consists of phenolic substances and about 25% soluble carbohydrates. Depending on the storage of wood, carboxylic acids and alcohols might also be found in effluent from the debarking plant. Some compounds discharged from mills show toxic effects on aquatic organisms before treatment as, for example, some of the extractive components such as resin acids that may be leached from bark in the wood handling (Kostinen, 2000). The wastewater from debarking is usually treated together with other wastewater streams in external treatment plants.

Additives used for papermaking may cause a measurable part of the organic discharge after treatment because some substances are heavily degradable. Emissions of colored substances may affect the living species in the recipient negatively, because the water transparency is decreased (Bajpai, 2001). The releases after treatment from the mills depend mainly on the design and operation of the processes that cause the major part of discharges and the wastewater treatment plant applied. Table 4.18 shows the emissions achieved with activated sludge treatment at mechanical pulp mills.

The efficiency of biological wastewater treatment at mechanical pulp mills resembles that of chemical pulp mills. The COD reduction is however normally higher at levels between 70% and 90%. Moreover, at several plants tertiary treatment is employed, which polishes the effluent, thereby reducing discharges further. This is particularly true for pollutants associated with total suspended solids (TSS).

Table 4.18 Emissions Achieved with Activated Sludge Treatment at Mechanical Pulp Mills

	Pulping process	
Parameter	CTMP	TMP
Flow (m^3/t)	8–40	15–25
BOD5 (kg/t)	0.5–9	0.2–1.7
COD (kg/t)	12–30	2–8
Total phosphorus (g/t)	5–50	5–15
Total nitrogen (g/t)	200–500	60–160
TSS (kg/t)	0.1–12	0.5–1.5

Based on data from European Commission (2001).

Much higher values are reported elsewhere for mills employing less effective effluent treatment.

There are a few alternatives for CTMP plants for treating the wastewaters: the activated sludge treatment in one or two stages with or without a chemical treatment; internal treatment of the first stage white water plus activated sludge treatment for other effluents; evaporation and burning of the most contaminated wastewater and activated sludge treatment of the rest; a combination of anaerobic and aerobic treatment of wastewater. Today, the activated sludge treatment is the most common technique, and if properly designed, a BOD reduction of 98% and a COD reduction of 85% are easily reached. The reason why the anaerobic treatment is not used more commonly for CTMP mill effluents is that anaerobic systems are relatively sensitive to disturbances.

In Europe, there are an increasing number of paper mills that manufacture and use not only one single type of pulp but different types of pulps at one site. For example, a paper mill manufacturing mainly newsprint and supercalendered (SC) printing papers may use a combination of raw materials such as mechanical pulp (GW and TMP), deinked pulp from recycled papers, and a certain amount of purchased chemical pulp. In this type of mills, the water system is closely linked between the different processes. A German paper mill that manufactures newsprint and SC papers from 45,000 tonnes TMP/annum, 85,000 t/annum GW, 220,000 t/annum DIP, 45,000 purchased kraft pulp, and 93,000 pigments has reported organic pollutants before treatment as 14 kg COD/t, and 6.3 kg BOD5/t, respectively. After biological treatment in an activated sludge system, the following values have been measured: COD 3.4 kg/t, BOD5 0.1 kg/t, total water flow 12 –13 m^3/t, nitrogen 0.2–4.2 mg/L, phosphate 0.3–1.3 mg/L, AOX 0.11 mg/L (European Commission, 2001).

Emissions to the Atmosphere

Emissions to the air are modest in mechanical pulping. Production emissions of purchased electricity can be high (Nordic Council of Ministers, 1993). Atmospheric emissions from mechanical pulping are mainly linked to emissions of VOC. Sources of VOC emissions are evacuation of air from chests from woodchips washing and other chests and from sparkling washer, where steam released in mechanical pulping processes contaminated with volatile wood components is condensed. The concentrations of VOCs depend on the quality and freshness of the raw material and the techniques applied. The emitted substances include acetic acids, formic acids, ethanol, pinenes, and terpenes. Emissions of VOCs from a TMP mill before treatment is shown in Table 4.19.

There are different alternatives to reduce the VOC emission. Recovery of terpenes from those contaminated condensates that contain mainly terpenes or incineration of the exhaust gas in the on-site power plant or a separate furnace is available alternatives. In that case, about 1 kg VOC/t of pulp is emitted from the process. Some VOCs may be released from wastewater treatment, and unquantified emissions also occur from chip heaps.

Table 4.19 VOC Emission from TMP Mills before Treatment

Process stage		
Sparkling washer	Washing of woodchips	Evacuation of air from other chests
Total organic carbon: 6000 mg/m^3 (highest individual value: 9600 mg/m^3)	Total organic carbon: 300 mg/m^3	Total organic carbon: 150 mg/m^3
Pinenes 1: 13,000 mg/m^3	Pinenes 1: 500 mg/m^3	Pinenes 1: 50 mg/m^3

Based on data from European Commission (2001).

Figure 4.5 shows emissions to the atmosphere from a CTMP mill. The atmospheric emissions originate mainly from chip impregnation and steam recovery (VOCs) and the bark boilers where wood residuals are burned (particulates, SO_2, NO_x).

As in other pulp and paper mills, mechanical pulping generates emissions to the air that are not process-related but mainly related to energy generation by combustion of different types of fossil fuels or renewable wood residuals. The fossil fuels used are coal, bark, oil, and natural gas. In a typical integrated paper mill that uses mechanical pulp, high-pressure steam is generated in a power plant. The energy is partially transformed into electricity in a backpressure turbogenerator, and the rest is used in paper drying. The power plant burning solid fuels have ESPs for the removal of particulates from the flue gases. The emission of sulfur dioxide is limited by using selected fuels. Depending on the local conditions, there are paper mills using different amounts of energy from external supply.

For refiner mechanical pulps, the removed bark is usually burned in bark boilers. Together with the bark, parts of the rejects and sludge might be incinerated. Some mechanical pulp mills use no roundwood as raw material but wood chips from sawmills.

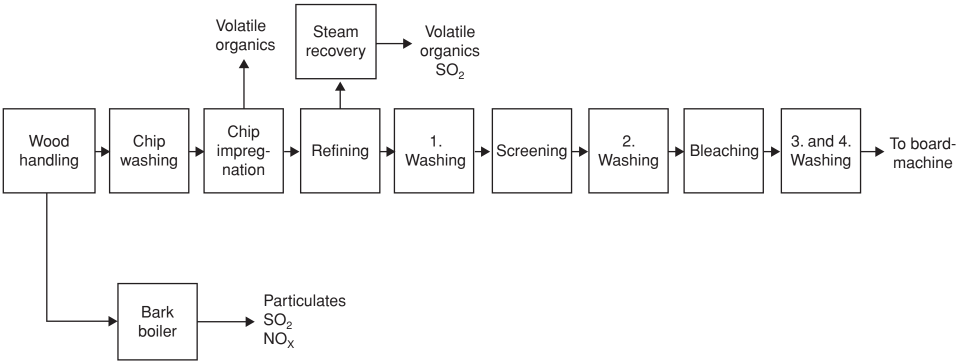

Figure 4.5 Emissions to air from a CTMP mill. Reproduced with permission from European Commission (2001).

Solid Waste Generation

The solid waste generated from the mechanical pulping processes consists of

Bark and wood residues from the debarking
Washing and screening of chips (about 1.5% reject)
Fiber rejects (primary sludge)
Ash from energy production
Excess sludge from external biological wastewater treatment

The wood-containing residues are usually burned in the bark boiler. Ashes are usually disposed of or used in the building material industry. The biggest waste fraction consists of different types of sludge, mainly fiber-containing primary sludge and excess sludge from biological wastewater treatment. The amount of waste for disposal can be reduced by increase of the dewatering performance of the sludge press. If the sludge has to be transported for further treatment, for example, incineration, it is reasonable to dry the sludge with excess heat from the process (e.g., hot air) up to 75% DS content. The options for further use depend on the quantities and qualities of the sludge produced. Primary sludge may be used as additional material in the brick industry or may be incinerated on- or off-site. For suitable solutions for further treatment of sludge and rejects, it is reasonable to hold different types of sludge separately.

Required emission levels from TMP mills are as follows (JRC, 1998):

Water
BOD 0.3–0.7 kg/ADt
COD 3–7 kg/ADt
AOX 0 kg/ADt
Nitrogen 0.04–0.1 kg/ADt
Phosphorus 0.004–0.01 kg/ADt

Air
SO_2 0.02–0.03 kg sulfur/ADt
TRS 0.1–0.3 kg sulfur/ADt
NO_x 0.2–0.3 kg/ADt

Waste
Nonhazardous waste to landfills 40–50 kg/ADt

4.4 RECYCLED FIBER PROCESSING

Using recycled fiber (RCF) as a raw material is considered to be more environment-friendly. The production process emissions are lower, and recycling reduces both the amount of waste paper sent to landfills and the wood harvesting demands. An often neglected characteristic is transportation emissions. Collecting waste paper and using small sites in its processing may lead to substantial transportation needs, assuming that waste paper is collected separately from other municipal waste. Taking this into account, using RCF can cause greater environmental impacts than the most modern chemical pulping technologies (Weaver et al., 1997). Another special characteristic of RCF processing is its dependency on the virgin fiber pulping, papermaking, printing, and packaging processes used: the chemicals that are used have an influence on recyclability of paper (Salo, 1999).

The environmental impact of recycled paper processing comprises basically emissions to water, solid waste generation, and atmospheric emissions mainly related to energy generation by combustion of fossil fuels in power plants (Ministry of the Environment, 1997; Salo, 1999). When abatement techniques are applied to reduce emissions, cross-media effects can occur.

Paper manufacturing in RCF-based paper mills can be subdivided into three parts: stock preparation, approach flow/paper machine, and upgrading of manufactured paper. Stock preparation and paper machine are connected closely with each other over the process water system. Table 4.20 presents emissions during stock preparation

Table 4.20 Emissions during Stock Preparation of Recycled Paper for Main Paper Grades

	Paper grades			
	Packaging paper	Newsprint	Lightweight coated/SC paper	Tissue paper and market pulp
Water				
Water flow	0–4 m^3/t paper	8–16 m^3/t paper TSS: usually below 200 mg/L	8–16 m^3/t paper TSS: usually below 200 mg/L	8–16 m^3/t paper TSS: usually below 200 mg/L
Emissions before biological wastewater treatment	TSS: usually below 200 mg/L	COD: 17–27 kg/t (1700–2700 mg/L)	COD: 17–27 kg/t (1700–2700 mg/L)	COD: 26–35 kg/t (2600–3500 mg/L)
	COD: 27–36 kg/t (6750–9000 mg/L) AOX: <4 g/t	AOX: <10 g/t	AOX: <10 g/t	AOX: <10 g/t
Waste				
Solid wastes (dry basis)	50–100 kg/t paper	20% losses	35% losses	500–600 kg/t paper
Organic content	70–80%	170–190 kg/t paper 35–45%	450–550 kg/t paper 45–55%	40–50%

Based on European Commission (2001).

Table 4.21 Emission Levels from Recycled Fiber-Based Paper Mills Manufacturing Testliner and Wellenstoff

Emissions	Value	Unit
CO_2, fossil	320–600	kg/t
CO_2, regenerative	0–15	kg/t
CO	n.a.	kg/t
NO_x	0.4–1.1	kg/t
SO_2	n.a.	kg/t
Dust	n.a.	kg/t
COD	0–2.2	kg/t
BOD5	0–0.2	kg/t
Suspended solids	0–0.5	kg/t
AOX	n.a.	kg/t
Total nitrogen	n.a.	kg/t
Total phosphorus	n.a.	kg/t
Evaporated water	1–2	m^3/t
Wastewater flow	0–11	m^3/t
Residues		
Waste to landfill	30–70 (at 100% DS)	kg/t

Based on FEFCO (1997).

of recycled papers for main paper grades being produced in Europe. The emission levels of whole paper mills for the main paper types produced from RCFs are shown in Table 4.21 (Testliner and Wellenstoff), Table 4.22 (newsprint), and Table 4.23 (tissue).

The recycled paper grades used for the production of Testliner and Wellenstoff consist 93% and 94%, respectively, of grades, according to category A of the European list of recycled paper grades, including mixed recycled paper grades, supermarket waste, as well as new and used corrugated case material. In total, about 50 kg residues are generated by the papermaking process per tonne net saleable paper (nsp). Related to the recycled paper input of 1.1 tonne/tonne nsp, 45 kg residues per tonne of processed recycled paper (= 4.5%) are treated by the mills. In the figures for the residues are included the ashes, the organic and inorganic sludges, and all the rejects going to landfills as well as the incinerated organic sludges and residues. On average, between 91% (Testliner) and 95% (Wellenstoff) of the residues are dumped on landfills. The weighted average amount of incinerated residues seems to be small—3% in Wellenstoff and 7% in Testliner production.

Mills equipped with boilers for the incineration of residue burn almost all their rejects with exception of pulper and high-density cleaner rejects. Between 0.9 and 3.6 kg of organic sludges per tonne net saleable product are reused in the production process of Testliner and Wellenstoff. About 87% natural gas is used in the production of Wellenstoff and 94% for Testliner production. All mills produce steam for the drying of the paper in the paper machine, but not all mills produce electricity by themselves. In some cases, electricity is purchased as grid power. The airborne emissions mainly depend on the type of fuel used. In combination with a well-adapted

Table 4.22 Emission Levels from Recycled Fiber-Based Paper Mills Manufacturing Mainly Newsprint

Emissions	Value (min/max)	Unit
CO_2, fossil		kg/t
CO_2, regenerative		kg/t
NO_x	0.72 (0.56–1.06)	kg/t
CO	0.14 (0.02–0.56)	kg/t
SO_2	0.54 (0.01–2.68)	kg/t
Dust	0.010 (0.003–0.05)	kg/t
COD	3.31 (2.47–4.45)	kg/t
BOD5	0.12 (0.03–0.28)	kg/t
Suspended solids	No data	kg/t
AOX	2 (1–3)	g/t
NH_4-N	20 (10–50)	g/t
Phosphate	5 (2–10)	g/t
Wastewater flow	10.56 (7.7–14.97)	m^3/t
Residues	(min/max)	
Bark	5.6 (0–28.6)	kg/t
Rejects, paper residues	100.2 (0–381.4)	kg/t
Ash, from waste incineration	90.8 (0–173.2)	kg/t
Waste, total	196.7 (91.8–410.7)	kg/t

Based on European Commission (2001).

Table 4.23 Emission Levels from the Manufacturing of Tissue Paper

Releases to surface water		
Effluent (m^3/ADt)	5–100	
COD (kg/ADt)	2–6	
BOD (kg/ADt)	1–2	
TSS (kg/ADt)	1–3	
AOX (kg/ADt)	5–15	
Total nitrogen (g/ADt)	5–100	
Total phosphorous (g/ADt)	1–30	
Solid waste		
Virgin fibers (kg/ADt)	10–40	
Recycled paper (kg/ADt)	400–1000	
Releases to air		
CO_2 (kg/ADt)	500–2000	Emission values depending on • the type of energy supply • the type of fuels used • process technology/technique • specific energy consumption
SO_2 (g/ADt)	50–10,000	
NO_x (g/ADt)	300–2000	

Based on European Commission (2001).

flue gas purification, the most significant ecological impact results from the fossil CO_2 emissions.

Water consumption for the production of Wellenstoff and Testliner ranges between 2 and 13 m^3/t nsp. When papers are produced with a closed water system, the lowest water consumption corresponds to the amount of water evaporated during paper drying. The weighted average figures of the water consumption are almost identical for both paper grades at about 6.5 m^3/t nsp. The average specific effluent ranges between 4.9 and 5.7 m^3/t nsp. Some mills also operate with a totally closed water system and zero effluent.

The waterborne emissions are reported as the substances leaving the mills with the effluent after a final wastewater treatment. The levels of suspended solids, COD, and BOD are low for the weighted average and approach zero for mills with a closed water system. The nitrogen and phosphorus content of the wastewater from RCF-based paper mills is very low. A controlled addition of nutrients to the biological wastewater treatment is necessary to provide nutrients for maintenance and growth of the microorganisms.

Tissue mills manufacture a big variety of products. Many tissue machines make frequent grade changes for different products, reducing somewhat efficiency of water, energy, and raw material use. Converting into finished product is often integrated with tissue production. Tissue mills need relatively high freshwater use on showers because the cleanliness of wires and felts is critical to the very lightweight sheet formation (down to 12 g/m^2).

Concerning fibrous raw material used, there are both tissue mills based on 100% virgin fibers and those using 100% RCFs. In between, there are all types of mixtures of fibers using 10%, 20%, and so on, up to 90% RCFs. The influence of raw materials on the whole environmental performance of a mill mainly related to the high sludge volumes generated during wash de-inking (removal of all fillers from recycled paper). The differences in emissions to water are not significant assuming proper effluent biological wastewater treatment. The environmental performance of the whole mill is influenced by other factors such as chemicals used, the type of fuel used and energy generation, and process layout.

Wastewater Emissions

Wastewater from a RCF-based paper mill is mainly generated during cleaning steps (JRC, 1998; Luttmer, 1996). It is common practice to withdraw wastewater at locations where the process water is mostly polluted. However, the location of wastewater generation varies from mills to mills. The process water is mainly contaminated during cleaning, de-inking, and fiber recovery. Therefore, wastewater from RCF-based paper mills consists of water from reject separation by screens and centrifugal cleaners; filtrates from washers, thickeners, and sludge handling; excess white water depending on the rate of recycling.

Wastewater from the European paper and board industry is to a great extent discharged directly to the surface water after primary and biological treatment at the

Table 4.24 Average Water Emission for Recycled Fiber-Based Mills after Primary Treatment and before Discharge to a Sewage Treatment Plant

Without de-inking		
BOD5	1900 mg/L	4.7 kg/t
COD	3800 mg/L (570–9000)	9.4 kg/t (1.2–24)
Kj-N	16 mg/L (10–40)	0.05 kg/t (0.02–0.1)
Discharge volume		5.5 (0.4–15.5) m^3/t
With de-inking		
BOD5	550 mg/L	10 kg/t
COD	1100 mg/L (440–1900)	20 kg/t (7–40)
Kj-N	20 mg/L (13–25)	0.35 kg/t (0.19–0.62)
Discharge volume		15 (9–39) m^3/t

Based on data from Luttmer (1996).
Kj-N, Kjeldahl nitrogen.

site or is discharged into a municipal sewage treatment plant after primary clarification for suspended solids removal. In Tables 4.24 and 4.25, average water emission data exclusively after primary treatment from RCF-based paper mills discharging into municipal wastewater treatment plant and those with on-site biological treatment are given.

Table 4.25 Average Water Emission for Recycled Fiber-Based Mills Discharging to Water Bodies after Primary and Biological Treatment at the Site

Without de-inking		
BOD5 before treatment	1800 mg/L	12.3 kg/t
BOD5 after treatment	10 mg/L (3.28)	0.06 kg/t (0.01–0.13)
COD before treatment	3200 mg/L	22 kg/t
COD after treatment	150 mg/L (60–270)	0.77 kg/t (0.29–1.12)
Kj-N	5.6 mg/L (3.13)	0.03 kg/t (0.01–0.04)
Total phosphorus	1.5 mg/L (0.5–1.8)	0.01 kg/t
TSS	25 mg/L (17–40)	0.13 kg/t (0.06–0.21)
Discharge volume		5.7 (3.1–11) m^3/t
With de-inking		
BOD5 before treatment	770 mg/L	8.3 kg/t
BOD5 after treatment	9.0 mg/L	0.09 kg/t
COD before treatment	1900 mg/L	21 kg/t
COD after treatment	290 mg/L	3.1 kg/t
Kj-N	7.8 mg/L	0.08 kg/t
Total phosphorus	n.a.	n.a.
TSS	n.a.	n.a.
Discharge volume		11 m^3/t

Based on data from Luttmer (1996).

COD emissions originate from both raw materials and additives. De-inking and bleaching processes release a substantial part of the COD from the recycled paper (Bajpai, 2006). De-inking processing results in higher COD emissions than emissions caused by processing without de-inking. In the latter case, much of the COD is retained in the product.

BOD5 emission data after biological treatment show no significant difference between recycled paper processing with and without de-inking. In properly working treatment plants, the concentration of BOD5 after treatment is below 20 mg/L, independent of the concentration of the inflow. After biological treatment, BOD5 emissions of 0.01–0.13 kg/t paper and board have been reported (European Commission, 2001).

Wastewater treatment plant effluents mostly contain low concentrations of nutrients in the form of nitrogen and phosphate. The presence of these compounds is mainly caused by the necessary addition of these nutrients for effective operation of the biological treatment plant that needs a nutrient supply in the range of BOD5/N/P 100:5:1. Organic-bound nitrogen compounds may also originate from some additives.

TSS data after treatment show only little variation. The upper level of the TSS ranges is caused by paper mill wastewater treatment plants that are not well operating. Because of the type of organics in paper mill wastewater, there is a relative tendency to build up bulking sludge in activated sludge treatment systems. Control measures to avoid and control this undesirable phenomenon are available.

Heavy metal concentrations in paper mill effluents are generally negligible. There is no significant increase in concentrations if secondary fibers are used. Occasional measurements of European de-inking processing mills have shown that some de-inking process mill effluents may contain elevated concentrations of copper and zinc. In that case, printing ink in recycled paper is considered to be the main source of heavy metals (Luttmer, 1996).

Sources of AOX are some additives (especially wet-strength agents), recycled paper based on chlorine-bleached pulp, and to some extent printing inks (Bajpai, 2006). AOX-containing compounds derived from recycled paper based on chlorine-bleached pulp have considerably decreased over the past years. AOX-reduced neutral wet-strength agents are also available and are an option for further reduction of AOX emissions. Occasional measurement in some European RCF-based paper mills (with and without de-inking) has shown that average AOX concentrations are in the range of 200 μg/L. Organic micropollutants as chlorophenols or polychlorinated biphenyls may be detectable in some recycled paper mill effluents in very low concentrations depending on the raw materials used (recycled paper, printing inks, and additives). In occasional measurements in recycled paper mills, chlorophenols up to 1 μg/L (0.1–0.7 μg/L) and polychlorinated biphenyls only in traces (values below the detection limit to 0.11 μg/L [maximum value]) have been observed (European Commission, 2001).

Salts, mainly sulfate and chloride, are introduced mainly through recycled paper and some additives as alum. Depending on the types of recycled paper used as raw material and the degree of closure of the water circuits, sulfate concentrations up to 1000 mg/L have been observed even if during processing no aluminum sulfate has been used.

Table 4.26 Achievable Dry Contents for Rejects/Sludge and Corresponding Energy Consumption for Different Fiber/Ash Contents

Rejects			Sludge		
Applied reject handling machines	Hydraulic reject press	Pneumatic reject press	Applied sludge handling machines	Wire press including prethickening	Screw press including prethickening
Achievable dry contents at			Achievable dry contents at		
<70% fiber content	Up to 65%	55–58%	<50% ash content	Up to 55%	Up to 65%
<30% fiber content	≈70%	60–63%	>50% ash content	Up to 60%	Up to 70%
Energy consumption (kWh/t)	15–20	8–12	Energy consumption (kWh/t)	10–15	18–20

Based on data from European Commission (2001).

Solid Waste Generation

Most of the impurities from the processed recycled paper end up as waste. The major waste materials are rejects, different types of sludge, and—in case of on-site incineration of residues—ashes. The major sources of solid waste in RCF-based paper mills are stock preparation, process water clarification, and wastewater treatment. Depending on used raw materials, process design and type of process, and wastewater treatment, different amounts and qualities of residues (rejects, sludge) are generated. The residues have to be handled and treated (thickened and dewatered) to generate a residue with a high DS content. Achievable dry contents for rejects and sludge are presented in Table 4.26.

The residues can be subdivided roughly in heavy and coarse rejects, light and fine rejects, and sludge. Depending on origin and nature, the sludge again may be subdivided into de-inking sludge, sludge from microflotation units from process water clarification, and sludge from wastewater treatment (primary sludge, excess sludge from biological treatment). The achievable DS contents after dewatering and thickening are 60–80% for coarse rejects, 50–65% for fine rejects, and about 60% for sludge.

Sludge from process water clarification is mainly generated at the fiber recovery in the white water circuits and the mechanical treatment unit of the wastewater treatment plant. The paper residue consists of mostly short fibers and fillers depending on the recycled paper being processed. In the board industry and for production of corrugated medium, it is often recycled to the process. For higher grade products, paper residue does not meet the quality requirements for recycling and is incinerated

Table 4.27 Composition of Sludge from Fiber Recovery and Chemical/Mechanical Treatment of Wastewater

Parameter	Values
DS content (%)	29.4–52.7
Volatile solids (% DS)	25.5–76.1
Lead (mg/kg DS)	10–210
Cadmium (mg/kg DS)	0.01–0.98
Chromium (mg/kg DS)	8.8–903
Copper (mg/kg DS)	19.9–195
Nickel (mg/kg DS)	10–31.3
Mercury (mg/kg DS)	0.1–0.89
Zinc (mg/kg DS)	34.2–1320

Based on data from Solid Waste Handbook (1996).

or dumped. If there is a previous de-inking process, the sludge may contain to a certain extent inks and pigment particles. Fiber recovery contributes to minimize the quantity of residues. The typical composition of paper residue from fiber recovery and mechanical treatment of wastewater is given in Table 4.27.

This residue contains mainly short fibers, coatings, fillers, ink particles, extractive substances, and de-inking additives. Ink particles are a potential source of heavy metals. The typical pollutant contents of de-inking residue have comparable pollutant loads as sludge from biological wastewater treatment plants with slightly higher values for some substances as copper and zinc. There are relatively significant variations in the pollutant content of the recycled paper and consequently in the de-inking sludge. De-inking sludge is normally dumped or incinerated. The ash can serve as a resource for building materials. Wastewater treatment sludge is generated at the biological units of the biological wastewater treatment plant and is either recycled to the product (corrugated medium and board) or thickened, dewatered, and then incinerated (on- or off-site) or dumped. In many countries, the dumping of waste with high organic content is discouraged by the governments and will be prohibited in the near future.

Emissions to the Atmosphere

Emissions to air from paper and board mills originate mainly from energy generation (steam and electricity) and not from the manufacturing process itself. Major pollutants in case of gas firing are CO_2 and NO_x; in case of oil or coal firing, CO_2, NO_x, SO_2, dust, and low concentrations of heavy metals. These emissions occur at the site of generation. Steam is normally generated at the paper mill in dedicated boilers, so the emissions occur at the site. In many cases, electricity is purchased from the grid, so the emissions occur at the power plant. The electricity/steam consumption ratio at paper mills enables the cogeneration of heat and power (CHP). Many paper mills apply CHP and then all emissions to air associated with the energy consumption occur at the site.

Only in some special cases, emissions (measured as organic carbon) from the drier section of the paper machine may occur. If so, they are caused by the use of additives (coating chemicals) or by not well-designed water circuits and wastewater treatment plants, respectively, but in most cases they are of negligible concern. Therefore, atmospheric emissions from paper mills are mainly related to energy generation.

The RCF processing and papermaking generate a number of wastes with a high organic content, for example, paper, rejects, de-inking sludge, and biosludge (JRC, 1998). This waste was formerly landfilled, but an increasing number of companies incinerate its rejects, and sludge in on-site incineration plants generating steam is used in production processes. The incineration is associated with emissions to air.

Local air problems might occur due to odor and coarse dust (Salo, 1999). Especially in the case of closing up the water circuits below a water consumption of about 4 m^3/t, odors caused by lower organic acids and H_2S may be perceived in the neighborhood of paper mills. But, also in paper mills with less water circuit closure, annoying odors may be found. They may be caused by too long retention times of process water in the water system (pipes, chests, etc.) or deposits of sludge causing the built-up of hydrogen sulfide. If so, they can be avoided by suitable process engineering measures. The wastewater treatment plant of RCF paper mills may also emit significant quantities of odor. If the wastewater treatment is well designed and controlled, annoying odors can be avoided.

The recycled paper is stored in recycled paper yards that are integrated in the paper mill. During the transport of the recycled paper to the pulper, dust might be generated especially when recycled paper is delivered as loose material in big containers or by bulk dumping. The control of this dust is rather a matter of industrial safety than of environmental protection.

Required emission levels from a de-inking pulp (DIP) mill are as follows (JRC, 1998):

Water

BOD 0.05–0.13 kg/ADt

COD 3.0–4.5 kg/ADt

AOX <0.005 kg/ADt

Nitrogen 0.02–0.06 kg/ADt

Phosphorus 0.005–0.01 kg/ADt

Air

SO_2 0.05–1.5 kg sulfur/ADt

TRS 0.01–0.05 kg sulfur/ADt

NO_x 0.6–1.5 kg/ADt

Waste

Nonhazardous waste to landfills 60–150 kg/ADt

4.5 PAPERMAKING

The main raw materials used in papermaking are either a combination of pulps or a single type of pulp. In stock preparation, pulp is refined, cleaned, and diluted to a very low consistency. Chemicals and fillers are added.

Wastewater Emissions

There are various sources of wastewater discharges from paper mills (Fig. 4.6). Pulp is cleaned before paper machine to remove the impurities. The rejects from the cleaners contain the impurities, for example, shives and sand and also some valuable fibers, suspended in water. These rejects are usually discharged to the effluent

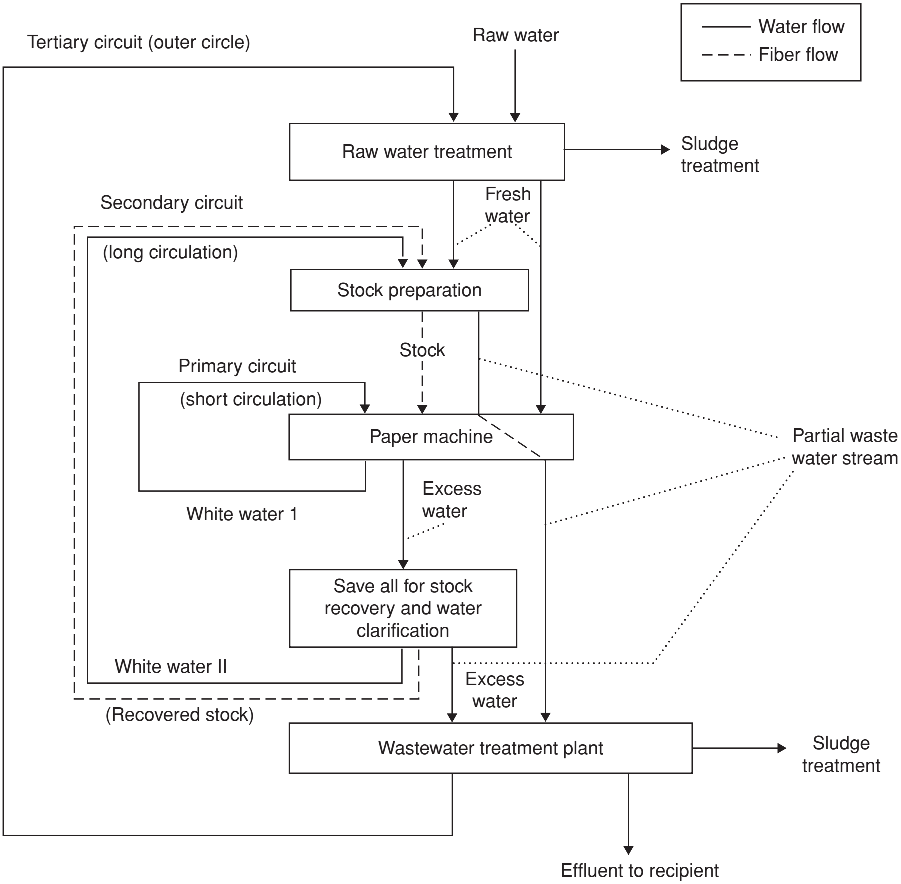

Figure 4.6 A simplified scheme of water and stock streams in a paper mill. Reproduced with permission from European Commission (2001).

treatment, but may also be discharged directly to the sludge dewatering (Ministry of the Environment, 1997; Salo, 1999).

The process water together with the chemical additives applied is drained off in the wire section of the paper machine, to the main part, and is then finally removed from the paper in the press section and the drying section. The white water also contains the spent shower water from the cleaning of wires and felts. The main part of the white water is recycled within the paper machine as dilution water and shower water. The excess of white water is discharged to the effluent or being used in stock preparation in integrated mills. This water usually passes through a fiber recovery unit before being discharged. The amount of discharged white water depends on the degree of closure of the water circuits. It contains the major part of the continuous discharges of suspended solids and dissolved organic substances, normally expressed as COD and BOD.

Temporary and accidental discharges are not directly connected to the process and occur occasionally. Examples of such discharges are overflows of white water or even pulp from tanks or other equipment with poor level control, spent wash water from cleaning of equipment, flushing water from flushing of floors, etc. Emissions to water or soil from storage and handling of potentially hazardous chemical additives should be prevented by appropriate design and operation of the facilities in such a way that potential pollutants cannot escape.

The spent cooling waters and sealing waters from the vacuum system and pumps usually do not contain suspended solids. These waters are often recycled to some extent. Clean cooling waters should be separated from the other effluents in order to minimize the load on treatment plants and to maintain their efficiency. The most common quality parameters used for final effluent discharges from paper mills include suspended solids, BOD (5 or 7), COD, total nitrogen and total phosphorus, AOX, and sometimes individual metals (Swedish Environmental Protection Agency, 1997). The data in Table 4.28 represent typical ranges for key

Table 4.28 Typical Wastewater Discharges from Paper Mills before and after Biological Wastewater Treatment

Paper type	Woodfree printing and writing	Paperboard	Tissue	Specialty paper
Before biological treatment				
TSS (kg/t)	12–25	2–8	2–30	20–100
COD (kg/t)	7–15	5–15	8–15	n.d.
BOD5 (kg/t)	4–8	3–7	5–7	n.d.
After biological treatment				
TSS (kg/t)	0.3–2.0	0.3–1.0	0.3–3.0	0.1–6.0
COD (kg/t)	1.5–4.0	1.2–3.0	1.2–6.0	1.5–8.0
BOD5 (kg/t)	0.4–0.8	0.3–0.6	0.3–2.0	0.3–6.0

Based on data from CTP (1996).

wastewater parameters in discharges from European paper mills manufacturing different grades.

The ranges reflect the differences in system closure, conditions of mills (size, age of equipment), applied internal measures to optimize water use, as well as the different efficiencies and process control of external wastewater treatment plants. In integrated mills, for example, RCF processing mills, the white water of the paper machine is integrated with the process water of the stock preparation. Therefore, it is sometimes hardly possible to distinguish emissions from stock preparation and paper machine in RCF processing mills.

The discharge of organic matter originates mainly from (1) organic matter carried over or included in the pulp; (2) organic matter dissolved from the pulp in the refining stages before the paper machine (this amount is generally higher for mechanical pulps than for chemical pulps); (3) organic chemicals applied as additives or auxiliaries in papermaking, which are not retained in the paper web. Usually, starch and their degradation products contribute significantly to the organic load. However, these substances are readily biodegradable. The significance of the contribution of chemical additives to the organic load of the paper mill depends on the amount and type of chemicals used. At least for some paper grades, the share of additives to the total organic load discharged to the recipient is significant as nowadays the water emissions of paper mills have become generally lower after efficient biological treatment. Generally, there is a lack of knowledge about the contribution of chemical additives to the total wastewater load. In an investigation of a few mills in Europe, the share of additives of the total COD load after biological treatment has been assessed. In the investigated example mills, they amount to about 26% for coated printing and writing paper, 20% for newsprint from RCF, 43% for hand towels from RCFs, and 35% for coated carton board from RCFs (Bobek et al., 1997).

AOX emissions from paper mills have decreased over the last years as chlorine bleaching is practically abandoned (Bajpai, 2005) and are in general orders of magnitudes lower than those from ECF pulp mills. Nowadays, sources of AOX (absorbable organic halogen compounds) are therefore mainly some additives (e.g., wet-strength agents and impurities as for example epichlorohydrin) and to less extent process water treated with chlorine containing disinfectants (if applied). Nitrogen and phosphorus compounds originate mainly from the necessary addition of these nutrients for effective operation of the biological treatment plant. Some chemical additives may also contain organic-bound nitrogen compounds. For example, optical brighteners may contain up to 30% organic-bound nitrogen (urea).

Solid Waste Generation

Various types of waste are generated in paper mills. Rejects are generated by cleaning of the pulp furnish before the paper machine head box. The rejects contain various impurities such as shives and sand and also some fibers. The DS content is usually around 1–25%. These rejects are normally led to the effluent treatment but may also be led directly to the sludge dewatering. Most of the solids will end up in the primary sludge from primary clarification. This is why the rejects are often not separately accounted for in the waste data.

Sludge from raw water and wastewater treatment represents one of the main groups of potential waste. Different types of sludge described as follows are produced.

- Sludge from chemical pretreatment of surface water to generate process water by means of chemical precipitation/flocculation. It is only generated in mills using surface water that needs this special treatment. In that case the amount of sludge can be significant.
- Sludge from primary clarification. It is generated at most mills. It consists primarily of fiber and fines and of inorganic material at mills using fillers.
- Excess sludge from biological treatment. It contains a high proportion of organic material. The generation of sludge in anaerobic treatment is moderate (about one-seventh compared to aerobic treatment).
- Sludge from chemical flocculation is generated at mills carrying out tertiary effluent treatment. This treatment produces a considerable amount of sludge. The amount of organic/inorganic material in the sludge varies from mills to mills depending on the dosage and type of flocculants used. Many mills that manufacture coated papers operate a separate treatment of the wastewater from coating operations. For this concentrated effluents, flocculation is a common practice resulting in sludge that has to be dewatered and further treated.

Table 4.29 shows some examples of the amount and types of rejects, sludge, and other waste fractions generated per tonne of produced paper. The quantities of solid waste generated in paper mills depend on the type of paper manufactured, the

Table 4.29 Amount of Solid Waste (t/annum) for Some Paper Grades

Paper grades	Solid waste, total	Bark	Rejects from screening/ cleaning	Sludges, total	Residues from incineration, total	Others, total	Specific waste (kg waste/tonne product)
Woodfree paper and board	29,761	0	0	27,972	1	1,788	33
Tissue from purchased chemical pulp	211	0	0	50	0	161	9
Specialty papers	161,945	407	639	76,506	26,842	57,551	168

Based on data from Solid Waste Handbook (1996).

raw materials used, and the techniques applied. It is difficult to find representative figures for the typical amount of solid waste for different types of paper mills that are sufficiently qualified, and that differentiate between different raw materials and paper grades. In different countries different waste fractions are reported.

Biological and chemical sludges have poor dewatering properties. The sludge is usually thickened before being dewatered in a belt press, filter press, screw press, or on a vacuum filter. Normally, they are mixed with primary sludge (or bark if available) before dewatering. Inorganic and/or organic chemicals are used to improve the dewatering of sludge by forming larger flocs. Mixed sludge can be dewatered to 25–35% dryness with belt presses, 35–40% with filter presses, and 40–60% with screw presses, using steam in the pretreatment stage. The achievable degree of water removal depends to a certain extent on the quantity of biological sludge mixed with primary sludge, the ash content, and the fiber content. In some paper mills, the sludge is also dried after dewatering.

In many European countries, the dumping of waste with high organic content is discouraged and will probably be prohibited in the near future. The EU Directive on landfill of waste will support this tendency in setting targets to cut the amount of biodegradable (municipal) waste sent to landfills. Consequently, alternative disposal routes and pretreatment options need to be developed for larger quantities of sludge. Many organic substances are burned for energy recovery. Burning reduces the volume of waste and the inorganic content remains as ash, which is normally transported to a landfill site. Ash is also used as raw materials for cement industry. Besides production-related rejects and sludge, ash and dust from power boilers form a group of waste, which is generated in some mills.

In addition, there are other types of waste listed as follows generated in smaller amounts, but that still may create problems as regards disposal.

- Chemicals including coating residues
- Plastics
- Scrap iron and other metals
- Spill oil
- Glass
- Packaging
- Building waste such as wood, concrete, and bricks
- Waste from laboratories
- Domestic waste
- Paper waste that cannot be utilized in the mill
- Wires and felts

Most of this material can be utilized when the single waste fractions are collected and stored separately.

Atmospheric Emissions

Air emissions from paper and board mills are mainly related to energy generation, that is, to various types of power plants and not to the papermaking process itself. Because atmospheric emission levels of paper mills are directly linked to energy consumption, energy saving will lead to a reduction in air emissions. For example, CHP consumes less energy than conventional separated generation of electricity and heat because the conversion efficiency of fuel use of CHP plants is significantly higher. For the amount of total primary energy used and the associated emissions, it is very significant whether the mill uses purchased electricity from the public grid or power generated on-site in a CHP. Furthermore, the emission levels depend on the type of fuels used and the implementation of emission control technologies for reduction of SO_2 and NO_x, particulates, and nonincinerated organic gaseous substances. Abatement techniques for air emissions are generally applicable to combustion processes of fossil fuels for generating power and steam.

Releases to air that are not related to energy generation are mainly VOCs. This emission is usually of minor importance and within generally acceptable limits. Situations where emissions of VOCs need to be controlled are related to a limited number of paper mills of different types. In the exhaust air of paper mills that utilize volatile organic additives in the production process, those substances are measured in low concentrations. Most volatile components of virgin pulps have been lost to atmosphere by the time that the pulp reaches the paper machine. However, in the drier section of the paper machine or after coating, the paper web is heated up to 100°C to evaporate the residual water.

Apart from the water vapor, volatile components from the fiber material and from chemical additives are released. Usually, no special abatement techniques for these emissions are applied in paper mills because the released loads are rather small. The results of an investigation of the exhaust air in seven paper mills in Europe are summarized in Table 4.30.

The concentrations of organic substances in the exhaust air of paper mills can usually be considered as low so that no abatement technique for air emissions is required. The measured concentration of total organic carbon varies significantly. Values between 2 and 135 mg/Nm^3 have been measured. A specific load between 0.05 and 0.5 kg orgC$_{total}$/t of paper was determined in the exhaust of the seven investigated mills (Öller, and Kappen, 1997). The emission of some single substances of concern in the exhaust air of coating machines as for example acrylonitrile (occur only when acrylonitrile butadiene binder systems are used) can be avoided or reduced by careful choice of coating color recipes. Coating color recipes that contain carcinogenic compounds should be avoided. Formaldehyde—concentrations between 0.1 and 4.8 mg/Nm^3 have been measured—is normally more difficult to prevent because it has different sources such as wet-strength agents, preservatives, and biocides.

Higher concentrations of VOCs are released in the following operations:

- Coating of paper with coating colors that contain organic solvents, although the basis of coating colors is exclusively aqueous (lower concentrations of

Table 4.30 Organic Substances Measured in the Exhaust Air of Paper Mills before Heat Exchanger

	Paper mills						
⟶	PM, woodfree paper, unsized	PM + CM, woodfree paper, coated	PM + CM, wood-containing, coated	CM, woodfree paper, double-coated	PM, woodfree, size press	PM, RCF paper, and board	PM, RCF paper
Total mass flow as orgC, total	0.7 kg/h	n.d.	n.d.	4.9 kg/h	1.6 kg/h	0.8 kg/h	2.4 kg/h
Mass concentration as mg orgC/Nm	2–17 mg/Nm^3	10–30 mg/Nm^3	48 mg/Nm^3 at predrier 24 mg/Nm^3 at postdrier	30–67 mg/Nm^3	2–77 mg/Nm^3	6–26 mg/Nm^3	3–8 mg/Nm^3
Remarks	98% from the drier section	Fluctuations; maybe partly caused by residual methane	90% from predrier; 10% postdrier	Emissions partly caused by residual methane	Main emissions (56%) from suction of wire and press section	70% from predrier	

PM, paper machine; CM, off-line coating machine; PM + CM, paper machine with in-line coating machine.
Based on data from Öller and Kappen (1997).

various volatile substances such as formaldehyde, alkyl-substituted aromatics, and lower alcohols can be measured in the exhaust of every coating machine).

- Preparation of papers with resins and production of specialty papers by using volatile additives.

VOCs that are released to the atmosphere are alcohols, formaldehyde contained in urea or melamine formaldehyde resins used as wet-strength agents, acetone and other ketones, phenols (only in special cases), solvents used for cleaning machine fabrics (usually a minor application), organic acids, and residual monomers of polymers.

In a few special cases, particulates from some finishing operations may raise concern. Emissions from sludge and residue incineration may also occur. However, on-site incineration of sludge and other residues is usually only carried out in integrated mills. In integrated mills, sludge may be incinerated together with bark in bark boilers or in recycled paper mills in dedicated incinerators together with other rejects.

In paper mills, odors may be found. They may be caused by too long retention times of process water in the water system (pipes, chests, etc.) or deposits of sludge causing the built-up of volatile organic acids, mainly acetic and propionic acids. These compounds may be formed by microbial action on organic substances (notably starches) under anaerobic conditions, which may be released at the wet end, during paper drying and during effluent treatment. To a small extent, hydrogen sulfide could also be generated under anaerobic conditions. If so, they can be avoided by suitable process engineering measures. The wastewater treatment plant may also emit significant quantities of odor. If the wastewater treatment is well designed and controlled, annoying odors can be avoided.

Required emission levels from a nonintegrated fine paper mill according to Pöyry (1998) are as follows:

Water

BOD 0.05–0.7 kg/ADt

COD 0.5–3.0 kg/ADt

AOX <0.005 kg/ADt

Nitrogen 0.1–0.2 kg/ADt

Phosphorus 0.01–0.02 kg/ADt

Air

SO_2 0.05–2.6 kg sulfur/ADt

TRS 0.1–0.3 kg sulfur/ADt

NO_x 0.9–3.0 kg/ADt

Waste

Nonhazardous waste to landfills 40–100 kg/ADt

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Chapter 5

Cleaner Production Measures in Pulp and Paper Processing

5.1 KRAFT PULPING

In recent years, the technological trends in pulp and paper industry, in general, have been directed toward developing and adopting cleaner production technologies/techniques for resource conservation and to reduce the pollution loads at source so as to make the paper industry environmentally friendly and sustainable. The environmental impacts of kraft pulp production mainly result from the chemicals used for both cooking and bleaching, such as sulfur, chlorine, chlorinated compounds, remaining organic and inorganic materials, lignin and undissolved fiber material, typically mixed up in the black liquor, and eventually Na and Mg salts, chelating agents and heavy metals such as manganese or iron. Thus, the major environmental problems of kraft pulp production are water consumption, wastewater loads, and gaseous emissions, including malodorous sulfur compounds and CO_2 (European Commission, 2001). In the last few years, the major cleaner production technological developments have been directed toward reducing pollution parameters specially color and adsorbable organic halides (AOX) through pulping and bleaching modifications, improved pulp washing, as well as end-of-pipe treatment methods. In air emissions, the major focus has been on reduction/elimination of noncondensable gases (NCGs) to reduce odor problem associated with kraft pulping process. With likelihood of ban on landfilling of solid wastes, options are being explored for its incineration or utilization.

The key production and control practices that will lead to pollution prevention and waste minimization in the kraft pulp mills are presented as follows (European Commission, 2001; Gavrilescu, 2005; Hitchens et al., 2001; Nilsson et al., 2007; RPDC, 2004; Suhr, 2000; Vasara et al., 2001; Woodman, 1993):

- Optimized wood handling
- Dry debarking
- Increased delignification before the bleach plant by extended or modified cooking

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Environmentally Friendly Production of Pulp and Paper, by Pratima Bajpai

- Highly efficient brown stock washing and closed-cycle brown stock screening
- Oxygen delignification
- Ozone bleaching
- Elemental chlorine-free (ECF) and totally chlorine-free (TCF) bleaching
- The use of oxygen and/or hydrogen peroxide in the alkaline extraction stage
- Removal of hexenuronic acids by acidic hydrolysis and hot dioxide stage
- Partial closure of the bleach plant
- Collection of spillages
- Improved pulp washing
- Stripping and reuse of concentrated, contaminated condensates
- Biological wastewater treatment
- Tertiary treatment of wastewater
- Increase in the dry solids (DS) content of black liquor
- Installation of scrubbers on the recovery boiler
- Collection and treatment of odorous NCGs for incineration in the recovery boiler
- Incineration of odorous gases in the limekiln
- Installation of low-NO_x technology in auxiliary boilers and the limekiln
- Selective noncatalytic reduction (SNCR) on bark boilers
- Over-fire air (OFA) technique on recovery boilers
- Installation of improved washing of lime mud in recausticizing
- Recycling/reuse of wastewater
- Solid waste management/utilization

Optimized Wood Handling

Wood is transported to the mills from the felling site by truck, rail, or barge, and may be received either as logs or chips depending on wood age. Logs are mainly delivered with the bark on it and have to be debarked before further processing. Chips are normally free of bark and can be used after screening and possibly washing. Some chemical pulp mills store wood chips in piles for 45 days or more during which time there is some degradation of resinous compounds (extractives) within the wood by oxidative and enzymatic mechanisms. The pile of wood chips can become quite warm during this maturation period. Storage for longer periods may reduce the amount of pulp obtainable from wood (yield) and pulp strength.

Debarked wood logs are reduced to chips in a chipper. Chip uniformity is extremely important for proper circulation and penetration of the pulping chemicals; hence, considerable attention is paid to operational control and maintenance of the chipper. Chips between 10 and 30 mm in length, and 2 and 5 mm in thickness, are generally considered acceptable for pulping. The chipped wood is passed over a vibrating screen that removes undersized particles (fines) and routes oversized chips for rechipping. Normally, fines are burned with bark as hogged fuel, although they may also be pulped separately in specialized "sawdust" digesters. In most mills, chips are segregated only according to chip length. Chip thickness screening has become important as mills realize the need to extend delignification and reduce bleach plant chemical demands. Both absolute chip thickness and thickness uniformity have a significant impact on delignification, because the kraft cooking liquor can only penetrate the chip to a certain thickness (Tikka et al., 1992). Thin chips are easier to cook to lower kappa numbers. Uncooked cores from overthick chips will lower the average kappa reduction of a cook and contribute to higher bleaching chemical demands. To improve thickness uniformity, many mills are now adopting screening equipment that separates chips according to thickness (Strakes and Bielgus, 1992). Oversized chips may be reprocessed in a crusher or rechipper. Sawdust and fines are normally burned in a power boiler but can also be cooked together with chips (if the digester has sufficient volume) or separately in a sawdust digester. Depending on the quality of chips from the chipper, the chips are often screened for thickness, as this is an important parameter in kraft pulping. The overall optimum can sometimes be reached by sacrificing some raw material to secure stable processing conditions, which, in turn, promote better pulp quality and less pollution. The material removed in the screening operation may be sold for other purposes or burned in a power boiler with heat recovery (US EPA, 1992).

Dry Debarking

The bark of the tree comprises about 10% of the weight of the tree trunk. Bark does not yield good papermaking material because it is resistant to pulping, contains a high percentage of extractives, and retains dirt. In most pulping processes, bark is removed from the logs before they undergo chipping. The most common debarking mechanism used for pulpwood is the debarking drum, which removes bark by tumbling the logs together in a large cylinder. Slots in the outside the drum allow the removed bark to fall through. The bark collected from these operations is usually fed to the hogged fuel boiler and used to generate process heat or steam. Wet debarkers rotate logs in a pool of water and remove bark by knocking the log against the side of a drum by using large volumes of water. The water used in this process is recycled, but a certain amount is lost as overflow to carry away the removed bark. In wet debarking, 3–10 m^3 of water per tonne of pulp is discharged. Organic compounds such as resin acids, fatty acids, and highly colored materials leach out of the bark and into this wastewater stream. This effluent stream is collected and routed to the wastewater treatment system, where the pollutants are normally removed quite effectively by the biological processes that take place there. Dry debarking methods such as dry drum debarkers eliminate the water stream and the pollutants associated with it. Dry debarkers already dominate the industry, and wet systems have been in the process of being phased out since the 1970s (Smook, 1992). Process water is used only for log washing and de-icing (in cold climates, water or steam is used for thawing of wood) and is recirculated effectively with minimum generation of wastewater and water pollutants. Dry debarking creates bark with a lower water content, which will result in a better energy balance for the mill. Less water is needed in the debarking, and the dissolved amount of organic substances is reduced (Finnish BAT Report, 1997; Pöyry, 1997; SEPA-Report 4712-4, 1997a).

Raw effluents from a debarking plant are toxic to aquatic life. Biological treatment has proved to be very efficient in eliminating toxicity. The dry debarking or one with low wastewater discharges can be applied at both new and existing mills. New mills almost exclusively and an increasing number of existing mills are using dry debarking.

With dry debarking, the wood handling wastewater volume is usually in the range of 0.5–2.5 m^3/ADt. Decrease in wastewater amount is obtained by increased internal water circulation. By changing from wet debarking to dry debarking, the wastewater amount would decrease often by 5–10 m^3/ADt. With dry debarking the total chemical oxygen demand (COD) loading can be reduced up to 10% (Salo, 1999). The higher bark dryness in the boiler feed improves the energy efficiency, meaning that emissions per the amount of produced energy will drop. Energy consumption in debarking may increase due to the operation of the debarking drum in dry debarking mode. On the other hand, substantial amount of energy may be gained if the bark is used as an auxiliary fuel at lower water content.

Where wet debarking is used, improved water recirculation coupled with grit and solid removal systems for water has been applied with success. Dry debarking usually requires fresh wood to obtain good debarking results. The costs of dry drum debarkers should not differ significantly from a wet system. Typical investment cost of a completely new dry debarking system is about €15 million for a capacity of 1500 ADt/day pulp.

The conversion of an existing wet debarking system to a dry debarking system costs €4–6 million. These costs include equipment and installation. Driving force for implementing this technique is that dry debarking decreases total suspended solids (TSS), biological oxygen demand (BOD), and COD load as well as organic compounds such as resin acids, fatty acids, leaching out of the bark and into this wastewater stream. Some of these substances are regarded as toxic to aquatic life. The measure also increases energy yield. Dry debarking is being used in several mills around the world.

Increased Delignification before the Bleach Plant by Extended or Modified Cooking

Extended delignification is done before the bleach plant to decrease the lignin content in the pulp entering the bleach plant to reduce the use of the bleaching chemicals (Bowen and Hsu, 1990). Reduction in the use of bleaching chemicals will reduce the amount of pollutants discharged while increasing the amount of organic substances going to the recovery boiler. In the recent years, new cooking methods have been developed that allow more selective delignification and provide mills with new pulping options. Mills can cook to lower kappa numbers, allowing less bleach chemical usage or permitting alternative bleaching methods. They can also maintain kappa numbers while improving yield and strength properties.

Continuous System

In the continuous system, modified continuous cooking (MCC), extended modified continuous cooking (EMCC), and isothermal cooking (ITC) represent the main alternatives (Andtbacka, 1991; Bowen and Hsu, 1990; Headley, 1996). The MCC process is based on two main principles. As compared with conventional cooking, it starts at a reduced concentration of effective alkali and ends at a higher concentration of effective alkali. The lignin concentration is reduced at the end of the cooking. This is accomplished by splitting the alkali charge into different insertion points and by ending the cooking in the countercurrent zone, where the liquor flows in an opposite direction to the chips. In a typical MCC digester, cooking is divided into two zones. The impregnation vessel has a 30-minute retention. The concurrent zone has a 60-minute retention, and the countercurrent zone has a 60-minute retention. The white liquor charge is split into three zones. Approximately 65% is added to the impregnation vessel, 15% to the transfer circulation line, and 20% to the countercurrent zone. Two benefits are gained by adding white liquor to the countercurrent zone. The initial hydroxide concentration is lowered. Some cooking is performed in the countercurrent zone, where the dissolved solids are lower.

EMCC is a further development in extended cooking. A fourth white liquor addition point is added to the high heat circulation, and the temperature in the high-heat zone is increased from approximately 290 to 300°F. The EMCC process further decreases the initial hydroxide concentration and increases the amount of cooking in the countercurrent zone.

Isothermal cooking (ITC) is developed by Kvaerner and expands on EMCC with an additional circulation loop and the fifth white liquor addition point (Engstrom and Hjort, 1996). The ITC circulation is a very high volume (2100 gal/b.d.st) and requires a special type of screen to handle the flow. The screens are equipped with backflushing valves that reduce blinding. The high circulation rates allow even more cooking in the countercurrent zone. As compared with EMCC, the initial hydroxide is reduced. The temperature in the digester is lower and nearly uniform throughout the digester. The amount of cooking in the countercurrent zone is increased. Existing digesters can be retrofitted to ITC provided an upflow exists in the digester. The downtime required is 10–14 days. The cost of a retrofit is approximately US$3 million. To date, several digesters in Europe and Japan have been converted to ITC. One retrofit has been installed in North America to a southern kraft mill.

Black liquor impregnation, also developed by Kvaerner, takes extraction liquor from the digester back to the impregnation vessel. This liquor has a relatively low hydroxide concentration and comparatively high hydrogen sulfide concentration. Black liquor impregnation is only applicable for new digester installations or when replacing the impregnation vessel due to corrosion or other problems. Existing impregnation vessels cannot be converted to black liquor impregnation unless operated well below design capacity. The retention time required is approximately 40 minutes compared with 30 minutes for a conventional impregnation vessel. The main benefit observed with black liquor impregnation is a 10% increase in tear.

Batch System

In the batch system, there are three processes: rapid displacement heating (RDH), SuperBatch, and EnerBatch (Barratt, 1990; Bowen and Hsu, 1990). In the RDH and SuperBatch processes, impregnation with black liquor is carried out to decrease the heat consumption and at the same time to increase the initial sulfide concentration and decrease the effective alkali charge. In the EnerBatch process, a pretreatment with white liquor followed by a pretreatment with black liquor is performed. All these displacement cooking processes show a substantial energy saving and an improved pulp quality. The lignin content is usually measured as the kappa number with a standardized method.

Conventional cooking has its limitations, regarding how low the kappa number can be brought, without deterioration of pulp quality (this kappa number is around 30–32 for softwood and 18–20 for hardwood). By the use of several cooking modifications, the kappa from the cooking of softwood can be reduced to a level of 18–22 for softwood and 14–16 for hardwood, while the yield and strength properties are still maintained. The kappa reduction depends besides others on the modified cooking technology applied and whether a retrofitted or new installation is used.

A number of continuous digesters have been retrofitted to ITC without having to sacrifice production. However, this possibility has to be evaluated in each individual case (this has to do with the dimensions of the pressure vessel in relation to the capacity). Some other continuous digesters have been rebuilt to MCC. To achieve this, white liquor is pumped into the digester at several points. With MCC and ITC, it is possible to cook the pulp to lower kappa number, without losses in quality (kappa number 20–24 for softwoods and 14–18 for hardwoods). In continuous cooking systems, the capacity of the plant would decrease with extended cooking and imply higher cost burden to the pulp mill. In batch cooking, extended delignification is carried out by means of displacement and black liquor recycling techniques. The process is possible to install as retrofit in conventional plants, if the digester capacity is large enough. In a new installation, the kappa number from the cooking may be kept at 15–16 for softwoods and at about 12 for hardwoods. In practice, the modifications of an existing batch cooking system are possible to carry out with additional batch digesters and additional investment costs, without losing the capacity of the cooking plant.

Currently, there are about 131 continuous and 40 batch digester systems with modified cooking worldwide, capable of producing about 125,000 and 30,000 ADt/day of pulp. Modified cooking capacity increased more than fivefold during the 1990s, but has tapered off in recent years. Figure 5.1 illustrates the acceptance of modified cooking in pulping for both batch and continuous digester systems. Table 5.1 shows the market share of the various systems offered, based on system capacity.

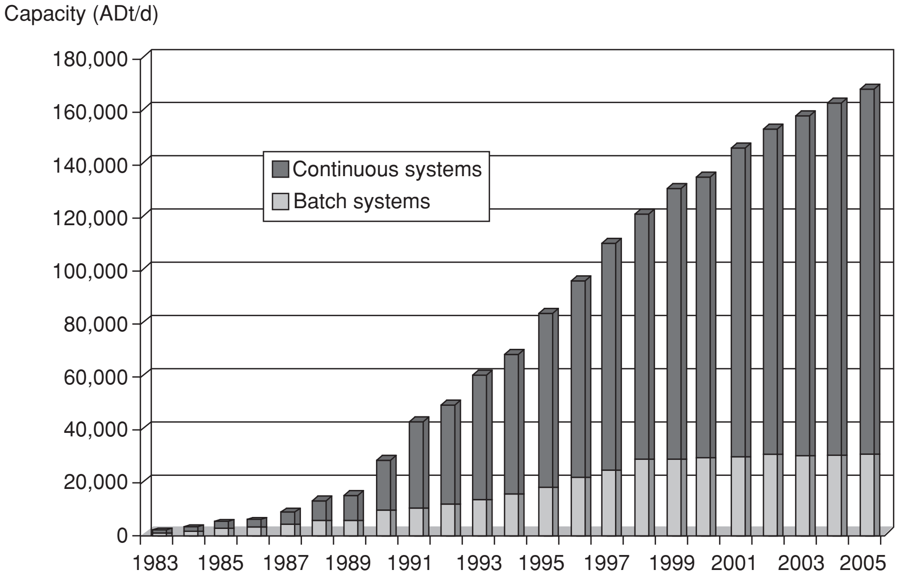

Figure 5.1 World's daily production capacity of pulp from modified cooking processes. Reproduced with permission from Beca AMEC (2004).

The main achieved environmental performance is lower lignin content resulting in reduced discharges from the bleach plant of not only organic substances but also nutrients. One kappa unit corresponds roughly to 0.15% lignin in the pulp. If the kappa number of pulp from cooking or oxygen delignification can be lowered by one unit, the COD released in the bleach plant would reduce by approximately 2 kg/ADt (COD from TCF bleaching can be as high as about 3 kg COD/kappa number). However, to get a figure of the total discharge from the bleach plant, one has to add the amount of

Table 5.1 World Market Share of Modified Cooking Processes

Compact cooking	12%
Low solids	34%
ITC	12%
MCC	19%
EMCC	4%
RDH	7%
SuperBatch	10%
Heat recovery	1%
Kobudomari	1%

Based on data from Beca AMEC (2004).

pollutants that has not been washed out in the closed part of the process. Extended cooking affects the following in the kraft process:

- The consumption of active alkali ($NaOH + Na_2S$) may slightly increase.
- The amount of dissolved substances going to the recovery system increases.
- Heat generation in the recovery boiler increases.
- The demand for bleaching chemicals decreases.
- There is a lower pollutant load in the wastewater from bleaching.
- In modified batch cooking, the energy consumption and blow steam amount decrease in the cooking, but the steam consumption in the evaporation of the black liquor may increase.

The impact of extended cooking on production is very site-specific. Kappa number reductions of 6–7 units for softwood and 4–5 units for hardwood have been accomplished without loss of strength properties.

Investment costs for modification of existing conventional cooking system for extended delignification are €4–5 million at the mill producing 1500 ADt/day (European Commission, 2001). To utilize BOD and COD reduction, the washing efficiency should be increased as well. This would cost €2–4 million more. However, with ITC there is no need to add more washing equipment if the retrofit is made at constant capacity. With continuous digester or when the recovery boiler is already operating with full capacity, the production loss can be 4–8%. In such cases, ways to accommodate for the increase in solids load are to be found as additional evaporation stages to increase the DS concentration in the black liquor, anthraquinone addition in pulping, or adding of incremental boiler capacity. Generally, the impact of extended cooking on production is very site-specific. If the chemical recovery system is a bottleneck at a mill, then introduction of extended delignification risks a loss in production due to the increased demand on that part of the system.

The reduction of emissions to water is the main reason to implement this technique. A beneficial effect is also a reduction of the consumption of expensive bleaching chemicals. This reduction should be compared to the possible loss of yield and increased wood consumption, in order to judge possible net cost savings case by case (Finnish BAT Report, 1997; Pöyry, 1997).

Highly Efficient Brown Stock Washing and Closed-Cycle Brown Stock Screening

The pulp coming from the digester contains both fibers and spent cooking liquor (black liquor). About half of the wood is dissolved in the digester. Consequently, the black liquor contains inorganic chemicals and a large amount of organic compounds and contributes to BOD, COD, color, and conductivity in the effluent. The black liquor is removed from the pulp in the subsequent washing stages and fed to the chemical recovery system, where cooking chemicals and energy are recovered (Bajpai, 2008).

The dissolved organic compounds together with the spent cooking chemicals are separated from the cellulose fibers in the brown stock washing stages. Modern systems normally recover at least 99% of the dissolved wood solids and pulping chemicals applied in the digester. In today's batch as well as continuous cooking fiber lines, washing already starts in the digester by displacing hot black liquor with cold wash liquor. Subsequent washing is carried out in various types of washing equipment, for example, pressure drum washers, compaction baffle filters (pressurized), drum displacement (DD) washer (multistage), displacement (twin-roll) wash presses, atmospheric diffusion washers, and pressure diffusion washers. Efficient washing reduces the carryover of black liquor with the pulp resulting in a decreased consumption of chemicals in oxygen delignification and bleaching and reduced discharges from the bleach plant.

In most mills in Europe, the water system in the brown stock screening plant is completely closed. With modern wood handling and cooking, less than 0.5% knots and shives are left in the pulp after cooking. The closing contributes to the reduction of organic compounds in the effluents, and they are then recovered and incinerated in the recovery boiler.

The closing of the washing and screening may require supplementation or replacement of existing equipment with new units to reach lower wash water consumption and to have better materials to resist corrosion. In a few existing mills, the capacity of the evaporation plant or the recovery boiler may need to be increased to cope with the improved closure of the washing and screening departments.

The closing contributes to the significant reduction of organic compounds in the effluents. They are then recovered and incinerated in the recovery boiler. Thus, the screening plant has no discharges to water. Energy consumption increases due to increased need for evaporation. The measure has been applied since 1980s with good experiences. In Finland, closed screening and brown stock washing are reality in almost all mills.

Investment costs for closed screening case are typically €4–6 million with new mills and €6–8 million at existing mills. Operating costs are €0.3–0.5 million/annum for a capacity of 1500 ADt/day (European Commission, 2001).

Today, it is possible to screen at higher pulp consistencies than before. Results are lower investment costs and lower consumption of electrical energy. The reduction of emissions to water is the main reason to implement the technique (Pöyry, 1997).

Oxygen Delignification

Oxygen delignification decreases the kappa number prior to chlorination, and therefore the effluent load (BOD, COD, color, 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 (Gullichsen, 2000; McDonough, 1996; Nelson, 1998; Pikka et al., 2000; Simons and AF-IPK, 1992; 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 color. The major areas of growth for oxygen delignification were initially 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 organic 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 economic, 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 taken on the reduction of environmental pollutants (Tatsuishi et al., 1987). In Japan, oxygen bleaching is used mainly to lower the bleaching costs. Figure 5.2 shows worldwide

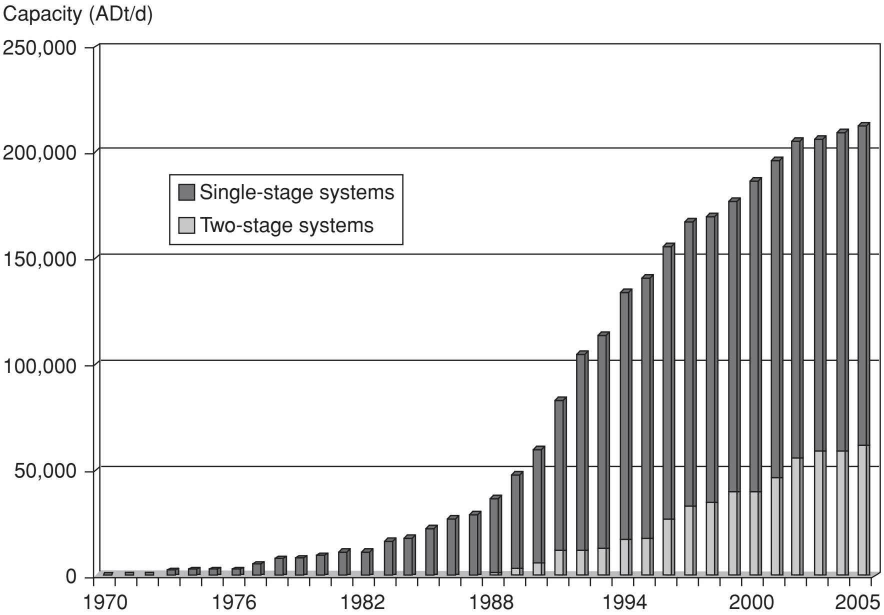

Figure 5.2 Worldwide production of oxygen-delignified pulp. Reproduced with permission from Beca AMEC (2004).

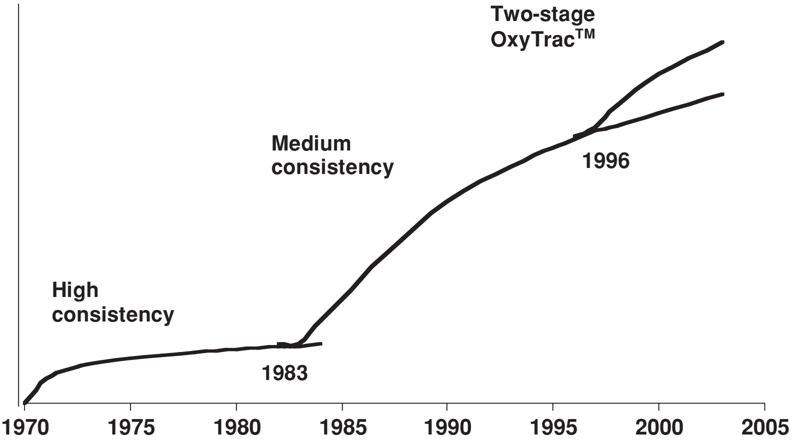

Figure 5.3 Evolution of oxygen delignification technology. Based on Lindstrom (2003).

production of oxygen-delignified pulp and Fig. 5.3 shows the evolution of oxygen delignification technology (Lindstrom, 2003).

Oxygen delignification involves reacting the pulp with oxygen under alkaline conditions and then washing to recover the dissolved lignin. The delignification reactor is pressurized and the temperature is elevated to about 100°C. The oxygen delignification takes place in one or two stages after the cooking and prior to the bleaching and can achieve a delignification efficiency of 40–60%. An efficiency over 40% normally requires two-stage installations. The waste liquor is sent countercurrently to the chemical recovery system. Figure 5.4 shows the basic process. Two types of systems are used commercially for oxygen delignification; these are generally

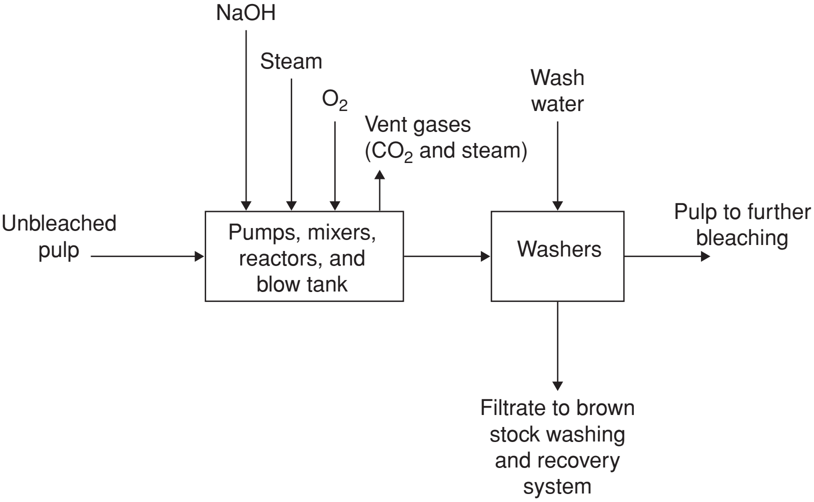

Figure 5.4 A flow sheet of oxygen delignification stage. Based on McDonough (1996).

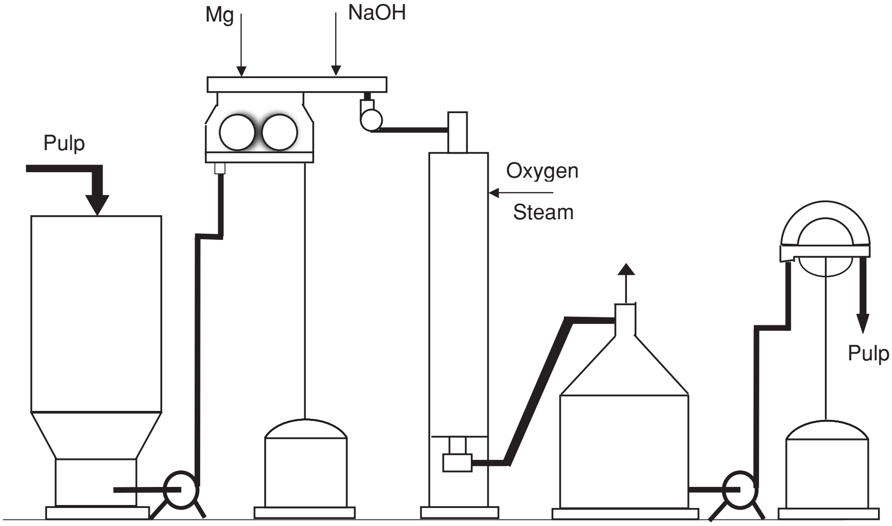

Figure 5.5 A high-consistency oxygen delignification process flow sheet (Reeve, 1996). Reproduced with permission from Pulp and Paper Technical Association of Canada.

characterized as high- and medium-consistency systems (Figs. 5.5 and 5.6). Figure 5.7 shows the flow sheet of a typical two-stage oxygen delignification installation.

Oxygen delignification is more selective than most extended delignification processes, but may require significant capital investment to implement (Gullichsen, 2000; Kiviaho, 1995; McDonough, 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

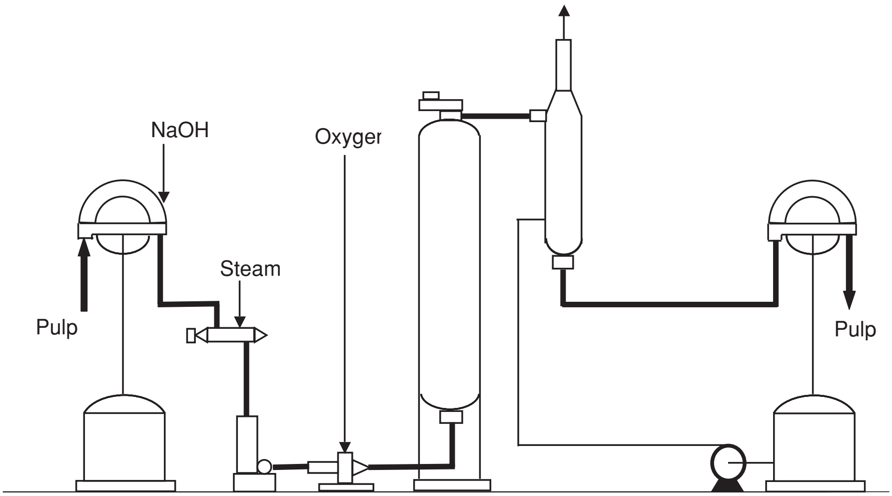

Figure 5.6 A medium-consistency oxygen delignification process flow sheet (Reeve, 1996). Reproduced with permission from Pulp and Paper Technical Association of Canada.

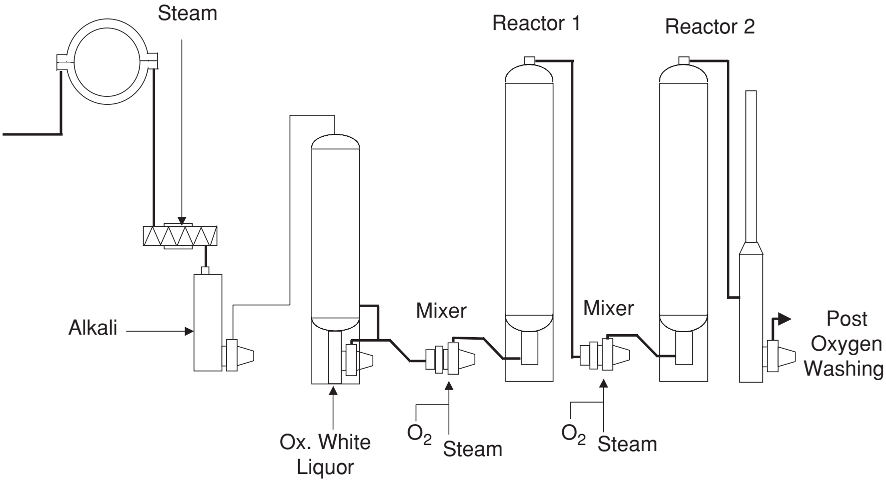

Figure 5.7 A flow sheet for a two-stage oxygen delignification installation (Kiviaho, 1995). Reproduced with permission from Miller Freeman Inc.

with the kraft chemical recovery system. This enables the recycling of oxygen-stage effluent to the recovery system by a 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 color. The decrease in color, 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. 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. Ozone, 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 fiber, nonwood, and other pulp types. 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. Because 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 a source of the alkali to maintain the sodium/sulfur balance in the chemical cycle (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 limekiln by 3–5%.

Oxygen delignification can be adopted in new and existing kraft mills but not in the same way and at the same costs. The installation of the oxygen delignification phase in the existing kraft mill may decrease the fiber line production, if there is not enough spare capacity in the whole recovery system. The additional evaporator steam requirements are from 0% to 4% for the high-consistency system and from 4% to 10% for medium-consistency system. The total additional solids load is about 70 kg/t for softwood and 45 kg/t for hardwood. The steam generation of the excess solids is about 1.5–2.5% less than the increasing of solids load because of a lower heating value of the black liquor from the oxygen stage.

The major benefits of oxygen delignification are decrease of the amount of chemicals in the final bleaching and total costs of bleaching chemicals and decrease of pollution load from the bleaching plant (COD and chlorinated organic compounds from final bleaching in the case of ECF bleaching). Modern mills are always designed for a combination of modified cooking and oxygen delignification, and for the effect on the environment (discharges of COD and AOX), both techniques have to be considered.

Table 5.2 presents kappa numbers currently achieved with different delignification technologies and gives a rough comparison of the effluent loads to be expected with and without extended delignification.

The reduction of kappa, organic substances, and the consumption of chemicals in oxygen delignification are strongly related to the efficiency of washing between stages. The mentioned environmental performance is not reached without efficient washing.

Table 5.2 Effect of Different Delignification Technologies on Kappa Number and Effluent COD

Delignification technologies →	Conventional cooking	Conventional cooking + oxygen delignification	Extended/ modified cooking	Extended cooking + oxygen delignification
Kappa number (hardwood)	14–22	13–15	14–16	8–10
Kappa number (softwood)	30–35	18–20	18–22	8–12
COD load (kg/t) (hardwood)	28–44	26–30	28–32	16–20
COD load (kg/t) (softwood)	60–70	36–40	36–44	16–24

Based on data from European Commission (2001).

The strength properties of oxygen-bleached pulp and conventionally bleached pulp are very similar although oxygen-bleached pulp has lower average viscosity. No significant differences are seen in the burst factor and the tear factor at given breaking length.

The investment cost of an oxygen delignification system is typically €35–40 million for 1500 ADt/day bleached pulp production. Its operating costs are €2.5–3.0 million/annum (European Commission, 2001). However, the oxygen delignification will decrease the chemical consumption in bleaching. The net effect is a cost saving, which depends on the wood species. At existing mills, additional DS loads to the recovery boiler have been reported up to 10% and more general it is at least 4–6% additionally, and 4–6% more capacity would be required in recausticizing and limekiln. Should this capacity not be readily available, it normally results to a corresponding loss in production capacity of the whole mill.

The reduction of emissions to water (effluent treatment plant and recipient) is the major reason to implement the method.

Ozone Bleaching

Ozone (O_3) is a powerful oxidizing agent for lignocellulosic material (Rice and Netzer, 1982). The high oxidizing potential of ozone makes it less selective toward lignin than chlorine and chlorine dioxide and therefore low charges of ozone must be used to prevent pulp strength loss. To achieve brightness comparative to chlorine and extraction stages, low lignin pulp from extended pulping or oxygen delignification must be used for ozone bleaching. A typical ozone stage is illustrated in Fig. 5.8. Ozone was introduced as a bleaching chemical on an industrial scale in the beginning

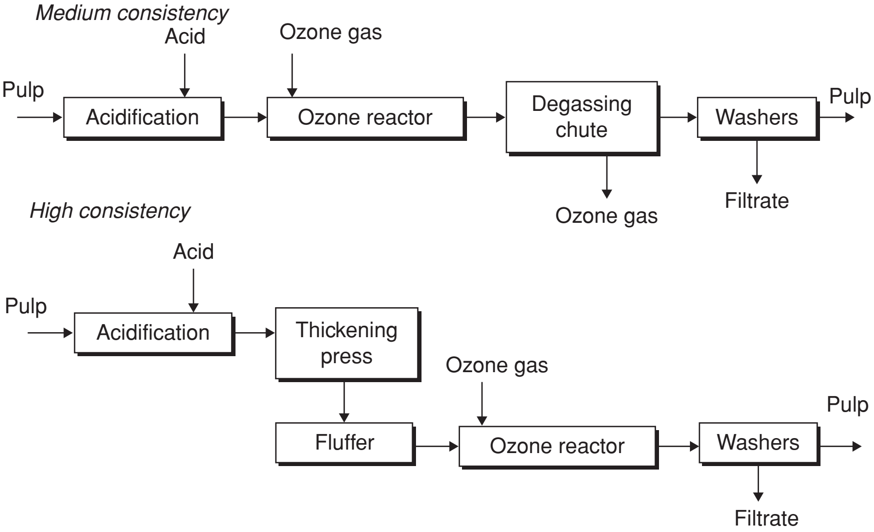

Figure 5.8 A typical ozone stage.

of 1990s. In 2005, it was being used in more than 30 mills in the world for the bleaching of chemical pulps (Bajpai, 2005). Ozone is found to efficiently delignify all types of chemical pulps. It is used at either medium or high pulp consistency in ECF and TCF bleaching sequences (Gullichsen, 2000; Lindstrom, 2003; Nelson, 1998; Pikka et al., 2000; van Lierop et al., 1996). 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 countercurrent 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 (Govers et al., 1995). The main reason underlying this evolution is the necessity to respond to growing environmental awareness, reflected in both regulatory constrains 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, and 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, that is, 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 more than 10,000 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 toward 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 (Bajpai, 2005; van Lierop et al., 1996). A highly selective ozone treatment remains elusive in spite of the substantial efforts directed toward elucidating the mechanisms of ozone and carbohydrate reactions and the conditions required to minimize these reactions.

Ozone has very high investment costs due to the high costs of ozone generators and auxiliary equipment for ozone generation (van Lierop et al., 1996). Because the ozone concentration will be only about 14–16% in oxygen, fairly large volumes of oxygen are required. Thus, the operating cost is rather high due to a relatively high cost of oxygen (needed for ozone generation) as well as to the high power consumption. A modern ozone generator may consume 10–15 kWh/kg ozone when feeding it with oxygen. The measure can be adopted in new and existing kraft mills. In ECF bleaching, replacement for chlorine dioxide further reduces the discharges of AOX ("ECF light"). In TCF bleaching, ozone is a common bleaching stage. In TCF mills, the use of ozone and other chlorine-free bleaching chemicals makes it possible to close up the filtrate streams from washing stages. A pressurized (PO) stage at the end of the bleaching sequence is another option to reduce the charge of chlorine dioxide. In TCF pulp mills, a PO stage is mostly used. Ozone with ECF bleaching plant normally results in pulp with the same papermaking properties. Investment costs of a 1500 ADt/day ozone bleaching system are €12–15 million. Corresponding operating costs are €1.8–2.1 million/annum. The reduction of emissions to water (AOX) is the main reason to apply this method.

ECF and TCF Bleaching

ECF bleaching is, by definition, a chlorine-free process in that no elemental (molecular) chlorine is used in the bleaching sequences. The focus on reduction in AOX and total organic chlorides in bleach effluents has promoted ECF and TCF bleaching processes (Govers et al., 1995; Moldenius, 1997; Moldenius and Lovblad, 1995; Pryke, 1997, 2003; Pryke et al., 1995). 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 in the paper industry beginning in the late 1980s. However, developments leading up to the various TCF technologies began much earlier in the twentieth 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's bleached chemical pulp market (AET, 2002a, 2007; Pryke, 2003). Demand for ECF increased dramatically over the last decade. In 2007, ECF commanded the highest worldwide market share at greater than 89%, totaling more than 88 million tonnes (Table 5.3). ECF market share continues to grow in all pulp-producing regions. This trend will continue as all new production planned in all producing regions will incorporate ECF bleaching.

In Scandinavia, ECF accounts for over 80% of bleached chemical pulp production. Conversely, TCF market share peaked in 1998, and has modestly declined over the past 10 years as a number of companies producing TCF on a campaign-basis have exited the market (Rodden, 2003). In addition, the only mill designed to produce exclusively TCF pulp was converted to ECF production. The company noted that (Botnia, 2007)

- ECF pulp is more suitable to their customer processes.
- ECF bleaching allows the mill to increase production capacity by 45,000 t/year.
- ECF bleaching allows higher pulp brightness without sacrificing pulp strength characteristics.

Table 5.3 World Bleached Chemical Pulp Production: 1990–2007

Year	ECF	TCF	Others
1990	4.4	0.2	64.0
1991	9.6	0.5	59.4
1992	17.2	1.4	53.1
1993	22.4	3.0	48.1
1994	29.2	4.7	42.1
1995	34.6	5.5	38.0
1996	38.0	5.3	36.3
1997	42.3	5.9	33.2
1998	45.9	5.8	30.5
1999	50.3	5.8	25.4
2000	56.0	6.0	21.2
2001	66.1	5.2	15.4
2002	67.7	6.1	15.3
2003	70.3	6.1	13.2
2004	72.0	6.1	11.5
2005	75.6	5.9	9.9
2006	79.7	5.5	8.3
2007	88.2	4.8	5.7

- The four-stage ECF bleaching sequence is simpler.
- Pulp strength properties are improved.
- ECF bleaching allows the mill to terminate cooking at a higher kappa number, thereby increasing pulp yield.
- Impact to the aquatic environment is unchanged.

Japan produces approximately 8.5 million tonnes of bleached chemical pulp and began converting production to ECF in 1996. During the period 2005–2007, over 2 million tonnes of pulp was converted to ECF, which represents 88% of Japanese bleached chemical pulp production. Continued growth is consistent with the commitment made by the major bleached pulp producers in Japan to eliminate chlorine, and convert to ECF. In North America, ECF production now represents 99% of bleached chemical pulp production. The transition to ECF was essentially completed in 2001 as the balance of US production came in compliance with the US Environmental Protection Agency's (EPA) Cluster Rule. The Cluster Rule is based, in part, on ECF as best available technology (BAT) for bleached paper grade kraft and soda mills. Total production in North America has recently declined by approximately 1 million tonnes over the period 2005–2007. In South America, ECF production continues to grow rapidly. More than 4.5 million tonnes of new ECF production was added in the region since 2005. In 2007, ECF represented over 90% of bleached chemical pulp production. Production of ECF pulp is also growing in the Southeast Asia region (AET, 2007). Significant ECF capacity was added in Indonesia and China in the period 2005–2007. In China where small mills are being shut down, new larger mills are coming on stream and utilizing ECF bleaching technology. China's ECF production increased from 1.1 million tonnes in 2005 to 2.6 million tonnes in 2007.

Recent studies comparing ECF and TCF have reiterated ECF's overwhelming product and yield advantages and ECF's environmental compatibility with aquatic ecosystems (AMEC and Beca AMEC, 2006). Over the next 5 years, bleached chemical pulp production is set to increase dramatically with significant expansions and new investments announced in Australia, Russia, Chile, Uruguay, Brazil, and Indonesia. More than 30 million tonnes of new production is planned or is on the drawing board. All of this new production is expected to be ECF. However, much of planned additional new capacity expected in 2010 and beyond has now been delayed due to the recent economic slowdown and the declining pulp and paper market worldwide. When the pulp and paper markets recover, ECF's market share will continue to grow due to its acknowledged environmental compatibility, cost-competitiveness, and high quality desired by producers and users alike.

Field studies and research 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 non-chlorine 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.

ECF Bleaching

ECF bleaching is done without the use of chlorine gas. In ECF, chlorine dioxide is usually the main bleaching agent. ECF bleaching is practiced on both conventional and reduced kappa pulps (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 the 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 (International Organization for Standardization) is 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 1 hour and a temperature of about 60°C. The alkaline stage is preferably pressurized, and oxygen and hydrogen peroxide are added to boost the delignification

Table 5.4 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

Based on data from Pikka et al. (2000).
[a] Kappa number 12.

in this stage to reduce subsequent chlorine dioxide consumption. The two final D stages normally have a retention time of 3 hours 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 oxygen and peroxide reinforced oxidative extraction EOP stage. The wash press in this position gives a higher degree of flexibility for filtrate circulations and reduction of effluent volumes. Table 5.4 shows typical mill data in the case of DEOPDED sequence with softwood kraft pulp of kappa number 12. Brightness versus consumption of active chlorine for pulps bleached in three, four, and five bleaching stages is presented in Table 5.5. In this example, the three-stage sequence can reach a brightness target of 88% ISO. The four-stage sequence can go up to 90% ISO and the five-stage sequence up to 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 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 5.6 shows brightness versus 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

Table 5.5 Brightness Development in Different Chlorine Dioxide Bleaching Sequences

Chemical consumption	Brightness (% ISO)		
(kg active Cl/ODt)	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).

Table 5.6 Brightness Development in a Sequence Replacing the First D Stage with a Z Stage

	Brightness (% ISO)	
kg active Cl/t	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

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

of peroxide use in a chlorine dioxide bleaching sequence is presented in Table 5.7. 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 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 hours at 90°C)

Table 5.7 The Effect of Peroxide Use in a Chlorine Dioxide Bleaching Sequence

	D(EOP)D(PO)		D(EOP)D(ED)
Chlorine dioxide consumption (kg active Cl/ ADMT)	Consumption in PO stage—3.0 kg P/ADMT Brightness % ISO	Consumption in PO stage—5.5 kg P/ADMT Brightness % ISO	Brightness % ISO
36	91.0	91.9	—
41	—	—	90.2
53	—	—	90.5
64	—	—	90.6

Based on data from Pikka et al. (2000).
Lab ITC^{TM}, O_2-delignified pulp; kappa number 12.0; viscosity 1017 dm^3/kg.
ADMT, air dry per metric tonne.

(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. In another mill, using ozone in the OA(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, 1997; Moldenius and Lovblad, 1995). 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., 1995). 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 (Axegård et al., 2003; European Commission, 2001; Haller, 1996). 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 fiber 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, bioaccumulative, 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 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, 2001). These regulations and guidelines ensure compliance with the International Stockholm Convention on Persistent Organic Pollutants, the so-called POPs treaty. 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 (AET, 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 EPA 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%.

Modified ECF Sequences

One promising trend today is the use of modified ECF sequences, that is, sequences that 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, that is, 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 5.8 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 the 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.

Table 5.8 (DZ) and (ZD) Treatments of an Unbleached Softwood Kraft Pulp[a]

Bleaching sequence	DEDED	(DZ)EDED	(ZD)EDED
ClO_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

Based on data from Chirat and Lachenal (1997).

[a] Kappa number 24.

AOX measured on the combined effluent.

The measure can be adopted in new and existing kraft mills. Conversion of existing mill to ECF mill has been possible but requires often considerable modifications in the fiber line and chlorine dioxide production: chlorine dioxide generators have to be upgraded to meet the increased demand of this bleaching chemical. Existing bleach plants have to be retrofitted with different chemical mixing etc. systems. Bleaching chemical cost will increase.

ECF bleaching eliminates 2,3,7,8-TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin) and 2,3,7,8-TCDF (2,3,7,8-tetrachlorodibenzofuran) to nondetectable levels. However, the complete elimination of dioxins in ECF-bleached effluents is a question of the kappa number and purity of ClO_2. With high kappa and impure ClO_2 (i.e., high concentration of Cl_2), the probability of forming dioxins increases. ECF bleaching eliminates the priority of chlorophenols proposed by the US EPA for regulation to nondetectable levels. It decreases chloroform formation and decreases AOX formation to a level of 0.2–1.0 kg/ADt prior to external effluent treatment. Usually, AOX levels less than 0.3 kg /ADt can easily be achieved by ECF bleaching.

Implementation of ECF has required the pulp and paper industry to increase the use of substituting bleaching chemicals that require considerable amounts of energy in manufacturing of chlorine dioxide, oxygen, and hydrogen peroxide. The production of ECF has been tested and practiced in full-scale pulp lines for several years. The investment costs of a 1500 ADt/day ECF bleaching system are €8–10 million at new mills and €3–5 million at existing mills. The operating costs are €10–12 million/annum. These costs are based on the assumption that an existing bleach plant can be used and the investment costs include then the necessary increase in chlorine dioxide production. The operating costs also contain, thus, the additional cost of using chlorine dioxide instead of elementary chlorine for bleaching.

The reduction of AOX emissions to water (effluent treatment plant and recipient) is the main reason to implement the method.

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.

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),

Table 5.9 Chemical Consumption in Bleaching of Softwood Kraft Pulp[a] in Q(OP)(ZQ)(PO) Sequence

Brightness (% ISO)	89.0
Diethylenetriaminepentaacetic acid	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

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

[a] Kappa number 11.

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 fiber lines that also bleach pulp with the use of chlorine chemicals. Typical chemical consumption (kg/ADt) in oxygen chemical bleaching of softwood kraft pulp (10 kappa number) to 88% ISO brightness is H_2O_2, 20; NaOH, 32; O_2, 6; O_3, 5; H_2SO_4, 20; and ethylenediamine tetraacetic acid (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 in bleaching of softwood kraft pulp (11 kappa number) to 89% ISO brightness in Q(OP)(ZQ)(PO) sequence is shown in Table 5.9. The chemical charges and process conditions will obviously vary depending on wood species, the degree of system closure, etc. The brightness development in TCF sequence depends on the proportions of various chemicals used. Table 5.10 compares the sequences

Table 5.10 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	—

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

[a] Kappa number 12.0.

Table 5.11 The Effect of Kappa Number after Ozone Delignification When Bleaching Softwood Kraft Pulp[a] in a Q(ZQ)(PO) Sequence

	Brightness after PO (% ISO)		
Kappa Number after Z	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

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

[a] Kappa number 12.0.

(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 the kappa number after ozone delignification when bleaching softwood kraft pulp of kappa number 12 in a Q(ZQ)(PO) sequence is shown in Table 5.11.

Today, TCF sequences are less selective than ECF and consequently have been unable to retain high-strength values at full brightness (Panchapakeshan 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 fiber strength (Ek et al., 1994; Moldenius, 1997; Moldenius and Lovblad, 1995). The lower strength has implications for paper machine productivity and virgin fiber requirements in recycled grades and recyclability. TCF production requires low lignin content of unbleached pulp and therefore has lower yield than today's ECF pulping and bleaching processes. Studies show that TCF bleaching of kappa number 8 pulp increases overall wood consumption up to 10% when compared to an ECF bleaching of kappa number 30 pulp (Steffes and Germgard, 1995). In a tour of Scandinavian mills, mill experience confirmed the yield loss. Wisaforest (Finland) claims it requires 6% more wood to make a tonne 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. 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 to US$190 million; operating costs increase US$20–75/t (Lancaster et al., 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 of 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 explain 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, peroxymonosulfuric 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 (Panchapakeshan and Hickman, 1997). 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 sulfite 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). 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.

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 (Panchapakeshan 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 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 cellulose is maintained through the bleaching process. Starting from the same kappa number levels, the bleaching yield in TCFz is generally lower by 0.5–1.0% compared with ECF bleaching processes (Panchapakeshan 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 is 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 (Panchapakeshan and Hickman, 1997). This must be confirmed by further experimental work. The behavior of TCF pulps toward heat- and light-induced degradation is different than that of ECF pulps (Panchapakeshan and Hickman, 1997). The higher proportion of carbonyl and carboxyl groups (photoreceptors) accounts 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 (Panchapakeshan 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 differ when changing from ECF to TCF pulps. This is due to the changes in the functional groups of TCF pulps (Panchapakeshan 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, the 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, woodfree 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. The first-pass retention is generally expected to increase for TCFZ pulps due to less refining, better fiber swelling ability, and, hence, the lowest production of fines. Due to the increased hydrophilicity of the pulp, problems may be encountered in the save-all, especially if the save-all is hydraulically limited (Panchapakeshan and Hickman, 1997). Optimizing furnish refining and adjusting drainage elements in the forming section will help improve the first-pass retention and also lower the amount of fines circulating in the white-water system. Decreasing the fine content helps improve the filtration rate in the save-all and also reduces the sweetener requirement. Increased swelling capacity of fiber 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 drier sections. This may require modifications to support the control sheet caliper. However, no significant changes should normally be required in the calender section.

The measure can be adopted in new and existing kraft mills. In existing mills, using the chelating stage, a new oxygen stage and washer are usually needed to convert the ECF bleaching sequence to TCF. If hydrogen peroxide or ozone stages are used, two new bleaching towers are used and reconstruction of bleaching filters. Ozone bleaching needs ozone generators and reactors. For peracetic acid, one bleaching tower is needed. In new greenfield mills, less modifications and investment costs are required but operating costs are likely to be the same order of magnitude. The investment costs of peroxide bleaching at new mills with a 1500 ADt/day production rate are €7–8 million; with existing pulp mills the costs are €2–5 million depending on the materials of the existing bleaching equipment. If the materials tolerate hydrogen peroxide, the costs are €2–3 million. Operating costs of peroxide bleaching are considerably higher, €18–21 million/annum, than of ECF bleaching due to the higher chemical costs. If both ozone and peroxide bleaching are applied, the investment costs are higher (European Commission, 2001).

Use of Oxygen and/or Hydrogen Peroxide in the Alkaline Extraction Stage

Addition of oxygen to the pulp in alkaline extraction is an efficient method for increasing the bleaching effect and decreasing the consumption of chlorine chemicals and, hence, the pollution load. Oxygen improves the dissolution of lignin. An oxygen-reinforced extraction stage is designated EO. When peroxide is added, it is designated EOP. Figure 5.9 shows the oxygen-reinforced extraction stage with H_2O_2 (EOP stage). The extraction process reinforced with atmospheric peroxide has gained notability due to its good effectiveness and low capital requirement for implementation. However, peroxide reinforcement can be more effective when pressurized in the so-called PHT-stage technology (Breed et al., 1995; Pereira et al., 1995). The most common types of alkaline extractions nowadays are those reinforced with oxygen and peroxide,

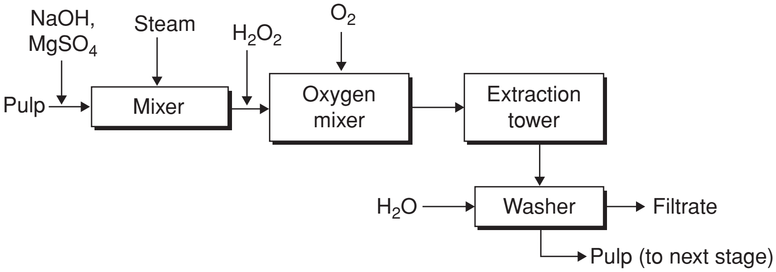

Figure 5.9 Oxygen-reinforced alkaline extraction (EOP) stage.

partially pressurized (EOP) or pressurized all the way, the so-called PO stage. The use of hydrogen peroxide in the extraction stage results in more reduction in chlorine chemicals and also decreases the color of mill effluent (Anderson, 1992). For a softwood kraft pulp (kappa factor 0.18), the use of oxygen and hydrogen peroxide in the extraction stage (EOP) results in reduction in kappa number after extraction from 3.5 to 2.5. Other advantages of alkaline extraction with oxidants include improvement of environmental parameters such as color, COD, BOD, and AOX (Smook, 1992). Significant reduction in effluent color is the greatest benefits of H_2O_2 addition in the extraction stage. It is common to use the alkaline extraction reinforced with oxygen (EO) or hydrogen peroxide (EP, PHT) or both (EOP, PO), to compensate for lower chlorine dioxide availability and also to make possible the bleaching in short sequences. Bleach plants that have a low availability of chlorine dioxide and require high peroxide dosages (0.8–1.0%) need more severe conditions for peroxide consumption. In these cases, pressurized peroxide stages such as PO or PHT are recommended because they allow the use of high temperatures. A very significant increase in brightness is achieved when peroxide is applied to the alkaline extraction for eucalyptus kraft pulp (Boman et al., 1995; Suss et al., 2000). Another positive effect is the peroxide effectiveness to bleach shives; even when they are not completely bleached, they are lighter and less visible (Anderson and Amini, 1996). H_2O_2 can also be used in the second alkaline extraction stage to counteract pulp darkening to reduce chlorine dioxide consumption.

A more powerful oxygen extraction stage is accomplished by raising the temperature in the stage, increasing the oxygen charge, pressurizing the preretention tube, and adding hydrogen peroxide. The most important factor is temperature. The use of pressurized peroxide stages (PO) makes possible to achieve a high final brightness in TCF bleaching (Anderson and Amini, 1996; Bajpai, 2005; Suss et al., 2000). In sequences with chlorine dioxide (ECF bleaching), a powerful peroxide stage will reduce the consumption of chlorine dioxide or even replace one chlorine dioxide stage. A hot, pressurized peroxide stage operates at temperatures above 100°C with a small amount of oxygen added. A prerequisite for successful peroxide bleaching is that the content of metal ions, for example, manganese, copper, and iron, is low. Several mills around the world are using the oxygen peroxide-reinforced extraction stage.

Removal of Hexenuronic Acids by Acidic Hydrolysis and Hot Dioxide Stage

This method is becoming a standard feature at bleaching plants using hardwoods. Hexenuronic acids (HexA) have attracted great attention recently because of their effect on bleaching operations (Jiang et al., 2000; Vuorinen et al., 1996, 1997). During kraft pulping, polysaccharides undergo some undesirable reactions and lead to the formation of HexA by the elimination of methanol from the 4-*O*-methylglucuronic acids, which are the side groups linked to the xylan backbone (Buchert et al., 1995). Hexenuronic acids are detrimental to kraft bleaching systems in the papermaking process; they reduce bleaching efficiency by consuming a disproportionate amount of bleaching chemicals. When the bleaching chemicals are being consumed in nonessential reactions, there is a decrease in the efficiency of the chemicals, as well as the cost efficiency of an operation (Bergnor and Dahlman, 1998; Chai et al., 2001; Vuorinen et al., 1996). Some studies have shown that the consumption of bleaching chemicals correlates with the amount of hexenuronic acid groups in hardwood kraft pulps. Approximately 35–55% of ECF bleaching chemical costs may be due to the presence of these acids. In addition, these groups are also a principal component impacting the retention of nonprocess elements, which can cause loss of efficiency and accelerate deposit buildup on process equipment (Laine et al., 1996). It also binds transition metal ions, intensifying the use of expensive complexing agents in hydrogen peroxide bleaching (Devenyns and Chauveheid, 1997). In addition, the presence of HexA not only increases the difficulty of reaching a high degree of brightness but also increases brightness reversion (Vuorinen et al., 1996). It has been also found that HexA groups contribute to the pulp kappa number and linearly correlate with kappa reduction, as these groups consume part of the potassium permanganate used in this determination (Chai et al., 2001; Li and Gellerstedt, 1997a, b). Because the kappa number is widely used for the evaluation of delignification efficiency in cooking and bleaching processes, the presence of hexenuronic acid affects the results of this analysis and thus gives erroneous information about the amount of residual lignin in the pulp (Tenkanen et al., 1999). These problems are more pronounced in the case of hardwood pulps because of their higher xylan content (Chai et al., 2001). Table 5.12 shows the undesirable effects of HexA in bleaching.

Low HexA pulps are likely to provide a cleaner production opportunity, likely to be cost-effective due to lesser consumption of bleach chemicals and pollution. HexA

Table 5.12 Undesirable Effects of HexA in Bleaching

Increased consumption of bleaching agents to reach target brightness and consequently increased contribution to AOX and calcium oxalate in effluent
May increase binding of transition metal ions, thus may increase the use of chelating agents (such as EDTA and diethylenetriaminepentaacetic acid) in H_2O_2 bleaching
Increased brightness reversion
May contribute to the formation and deposition of oxalates on bleaching equipment

can be degraded in acidic environment directly or indirectly by ozone, hot chlorine dioxide, and peracetic acid. Other ways of reducing hexenuronic acids is either by modifying the pulping conditions or through mild acid hydrolysis (Chakar *et al.*, 2000; Eiras and Colodette, 2003; Furtado et al., 2001; Jiang et al., 2000; Lindstrom and Larsson, 2003; Ragnar, 2003; Vuorinen et al., 1996). Eiras and Colodette (2003) also reported decrease in HexA content and improvement in brightness and brightness stability of the pulps by a hot D stage on the bleaching of oxygen-delignified kraft pulp. Bajpai et al. (2005) and Kumar et al. (2007) reported that hot acid pretreatment and substitution of the standard D_0 stage with the hot D stage in conventional ECF bleaching cause the reduction in HexA content, which helps in improving the brightness and other optical properties. It also helps in reducing the chlorine dioxide consumption and hence the generation of AOX. There are a number of hot acids or hot D stage in operation or coming into operation in BEKP mills.

Partial Closure of the Bleach Plant

Bleach plant closure, through filtrate recycle, to the recovery cycle, is becoming attractive in light of the stringent environmental regulations (Albert, 1995, 1997; Bajpai and Bajpai, 1999; Gleadow and Hastings, 1995; Gleadow et al., 1996; Johnson et al., 1996). Complete closure, however, is difficult with chlorine-based sequences because the resulting bleach liquor chloride level is a threat to the recovery boiler. Mills with oxygen delignification and a low chlorine dioxide charge may be able to close the bleach plant if chloride levels in the recovery cycle are monitored carefully. Fiber line and bleach plant process changes that reduce elemental chlorine demand, such as extended cooking, oxygen delignification, and high chlorine dioxide substitution, have been used for several years, but lower AOX limits, changing markets surrounding the use of chlorine chemicals, and the drive for bleach plant closure to reduce COD emissions have focused interest on TCF bleaching. The TCF bleach plant uses no chlorine-based bleaching chemicals, eliminating concerns about dioxins and furans and the more general measurement of chlorinated organic compounds. An added benefit of TCF processes is the high potential for complete reuse of bleach plant filtrates in the recovery cycle.

The Scandinavian approach focuses more on in-plant technologies, such as oxygen delignification, and less on out-plant treatment facilities. In this context, water cycle closure is progressively being implemented in both TCF and ECF bleach plants on both sides of the Atlantic. There are two basic approaches to closed-cycle mills that relate to the building of the bleaching effluent, namely integrated recovery and separate recovery, as shown in Fig. 5.10 (Johnson et al., 1996). Both ECF and TCF routes are being pursued in North America and elsewhere. In these two bleaching routes to closed cycle (ECF and TCF), the risks are taken in different ways. For the ECF route, the risk is in the process. On a small scale, the ECF route is feasible and the risks are minimized. However, it is not until full mill-scale operation that this becomes a viable reality and the risks of scaling, corrosion, and equipment suitability are solved. The risk of converting a TCF pulp mill to closed cycle is predominantly

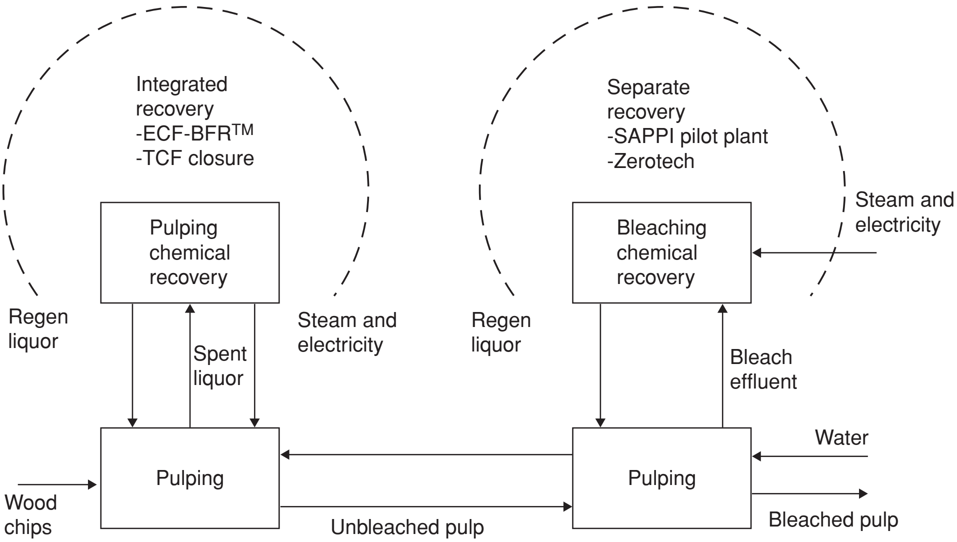

Figure 5.10 Closed-cycle approaches (Johnson et al., 1996). Reproduced with permission from Appita.

in product quality. The attainment of full brightness for TCF pulp, particularly softwood, has been difficult, and the added complexity of closed-cycle operation with the countercurrent filtrate streams needs careful evaluation. Also, there are major questions on chemical consumption.

The National Swedish Environmental Protection Board took a first step toward a closed kraft mill in oxygen bleaching along with other internal measures, 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 liquors 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 had been burned in the recovery furnace. 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.

A nonpolluting bleach plant by countercurrent washing and decolorizing and reusing the extraction stage effluent as wash water in the chlorination stage has been reported (Andersson, 1977; Lindberg and Lund, 1980). The entire effluent flow was treated by ion exchange resin, and condensate was stripped. The system reduced 90% of the effluent COD and color, 60% of the BOD, and significantly removed chlorinated phenols and guaiacols. The treatment system required half the energy cost needed for an aerated lagoon treatment. A full-scale installation for a 250 t/day kraft bleach plant has been in operation since 1973.

A closed-cycle concept was tested in mill-scale at the Canadian Pacific Forest Products Mill (previously Great Lakes Paper Co.) in Thunder Bay, Ontario, Canada, from 1977 to 1985. The process was proposed by Rapson and Reeve (Rapson and Reeve, 1973; Reeve et al., 1979, 1983, 1997). The key elements of the system include countercurrent washing in both the bleaching and pulping stages, closed screen room and wood yard, high chlorine dioxide substitution (70%), condensate stripping, and salt precipitation and separation. The sodium chloride obtained from the closed system was used to generate the chlorine and chlorine dioxide required for pulp bleaching. The cost of the closed cycle for a 1000 t/day DC-E_1-D-E_2-D bleach plant was US$13.8 million based on 1982 prices. Although the effluent-free objective was not achieved, this pioneering work resulted in the evaluation of many new concepts and served to illustrate the difficulties that must be overcome in achieving bleach plant closure. Based on EFM (effluent-free mill) demonstration experiences, Reeve reported several developments that would be needed to eliminate bleached kraft mill effluent (Reeve, 1984). Five of the developments relate directly to the successful recovery of bleach plant filtrates. First, chloride concentrations in the recovery process liquor cycles must be kept low, as these cause a number of problems including accelerated corrosion of evaporators and boiler tubes and recovery boiler operating difficulties. The experience at Thunder Bay demonstrated that the chloride loading to the recovery cycle must be significantly reduced, if successful filtrate recovery is to be achieved. Second, salt recovery must be accomplished with minimal evaporations. Third, the net flow of bleach filtrate to the recovery cycle must be low to minimize additional evaporation needs. This is important in making the recovery of filtrates economically viable. Fourth, bleach chemical consumption, due to higher levels of dissolved organic matter, must be minimized. Finally, minor wood components such as potassium, calcium, and pitch must be effectively removed from the system. Deposition of pitch and calcium on process equipment and in pipelines was a problem encountered during the EFM demonstration. Potassium adversely affects recovery boiler operation if allowed to accumulate in the system. Development of suitable methods to remove these impurities from the process would be required to minimize their impacts on mill operations.

Dorica et al. (1986) proposed a complete effluent recycling system based on ultrafiltration (UF) and reverse osmosis membrane techniques. The concept was based on E_1 effluent color removal by UF, chloride removal from UF 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 effluent were recycled. The chloride-rich diafiltration filtrate had a potential to be used for generation of sodium chlorate and chlorine dioxide, while 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, described earlier.

Effluent discharges in the kraft mills using TCF or ECF bleaching are generally less than 20 m^3/t, and AOX discharges in such mills are generally so low as to be of little environmental significance or interest (Anonymous, 1996). Several Brazilian mills are using oxygen/ozone in TCF bleaching processes, which are well known to have low effluent discharges but have not announced programs aiming at zero discharge. Champion International Corporation (Canton, NC) has invested heavily in, and is committed to, ECF technology. Champion International Corporation having

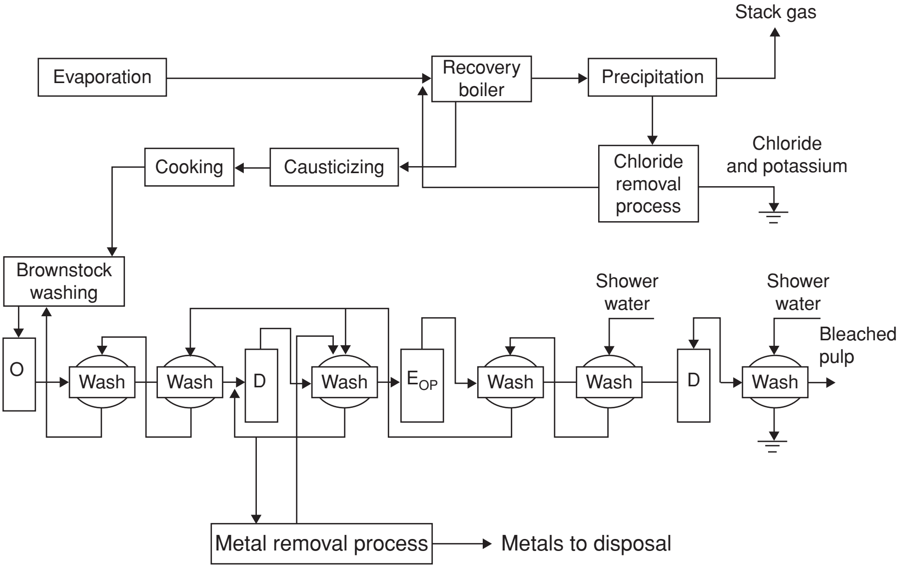

Figure 5.11 Overview of the Champion BFRTM process (Canovas and Maples, 1997). Reproduced with permission from Miller Freeman Inc.

nine bleached kraft mills in United States has developed a bleach filtrate recycle (BFR) process specifically to enable ECF mills to return bleach filtrates to the recovery cycle, which is the most significant challenge in enabling closed-cycle operation (Canovas and Maples, 1997; Maple et al., 1994). They consider the process to be technically feasible and have commercially demonstrated it with an initial installation in their Canton, NC, mill on the softwood fiber line. The BFR process encompasses a metal removal process to enable metal removal from the first D-stage filtrate, reuse of this filtrate for bleach plant washing, fiber line filtrate flow changes, water conservation measures, and a chloride recovery process for removing chloride and potassium from the recovery boiler precipitator dust (Fig. 5.11). The BFR process avoids chloride buildup through a combination of chloride removal, oxygen delignification, D_{100}, and E_{0P} processes. The problems with scale and loss of bleaching effectiveness due to metal buildup are not expected, due to the metal removal process.

A new bleach plant designed for TCF bleaching and extensive closure of the process water system was started up at the end of May 1995 in the SCA Graphic Sundsvall Kraft Mill at Ostrand in Central Sweden (Johnson et al., 1996). The design capacity is 1250 t/day. The mill of 1250 t/day design capacity was producing bleached hardwood pulp, mainly integrated with fine paper production in the adjacent Wifsta paper mill, and softwood kraft pulp for both fine paper at Wifsta and wood-containing printing papers (LWC and SC [supercalendered] papers) and tissue within the business group. The bleach plant has been designed for extreme closure of the water loops, and this involves better washing between the stages and a large buffer capacity of the liquor tanks, countercurrent washing in different ways, preferably a

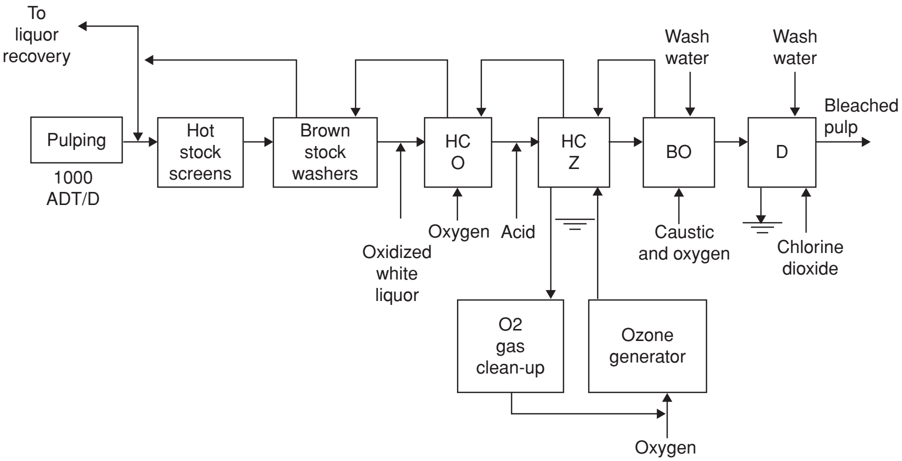

Figure 5.12 Union Camp Franklin fiber line (Johnson et al., 1996). Reproduced with permission from Appita.

somewhat modified jump-stage variant, and two spill systems for spent bleaching liquors of different degrees of cleanliness. The plant has been running more or less continuously at a very high degree of closure since August 1995. Serious scaling has been experienced. However, pulp properties have not been significantly influenced by the closure although certain targets in the bleach plant have had to be changed.

Union Camp Corporation (Franklin, VA) installed and started a high-consistency ozone bleaching line designated as C-free in September 1992 on the 900 t/day softwood bleach line. Both the O and Z stages are at high consistency and filtrates from 0, Z, and EO stages are sent back to the recovery via countercurrent washing with a bleed of part (2.1 m^3/t) of the Z stage to prevent scaling. The final D stage (7.3 m^3/t) is open to sewer. Figure 5.12 shows the Franklin fiber line. Union Camp has conducted several trials; the Z purge has been reduced or eliminated using following three strategies: (1) modification of the chemistry, (2) the use of additional processes, and (3) manipulation of internal filtrate flow configuration. Union Camp Technology has been licensed for installations at SCA (Ostrand), Sappi (Ngodwana), and Consolidated Papers at Wisconsin Rapids, WI (Johnson et al., 1996). Weyerhaeuser Paper Company has been upgrading the pulping and bleaching systems to improve environmental performance and to reduce costs. The company is supporting the demonstration 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.

In the Louisiana-Pacific (LP) Corporation at Samoa, California, a Swedish-style TCF pulp mill, the only bleach plant effluent discharged is from the chelation stage, amounting to only 6.76 m^3/t using the Q(EOP)PPP sequence of bleaching (Johnson et al., 1996). Mill trials of partial Q-stage filtrate recycle at LP have shown that, for peroxide-based TCF bleaching, low brown stock metal content is required to enable

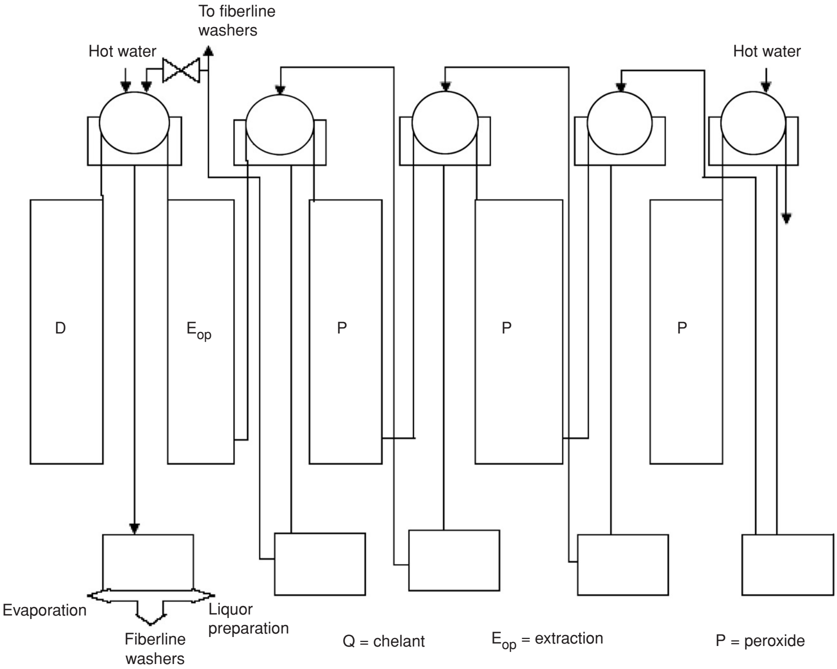

Figure 5.13 Louisiana–Pacific bleach plant filtrate recycle (Johnson et al., 1996). Reproduced with permission from Appita.

higher levels of filtrate recycle. LP successfully carried out a Lo-solids cooking trial in October 1995, which reduced brown stock manganese by 21% and the calcium by 23%. They believe that continuous operation of Lo-solids cooking will ensure optimal Q-stage filtrate recycle. Figure 5.13 shows filtrate recycle in the LP bleach plant.

Husum mill of MoDo paper AB, Sweden, tried with closed prebleaching for hardwood in 1993, and since then regularly produces hardwood pulp in a closed-loop fashion, marketed as MoDo balans (Anonymous, 1996). Bleach chemical used includes oxygen, ozone, and peroxide, and the sequence includes 3–5 kg ClO_2/t to decrease kappa number variations. Recycle of the ZP filtrates to brown stock results in increased chemical consumption during bleaching. Direct countercurrent filtrate recirculation is used in the bleach plant, with fresh caustic used in the Eo and P stages. 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 countercurrently, with no filtrate sent to sewer. The hardwood line averages 5 m^3/t effluents, on a monthly basis. With closed-cycle operation, there are scaling problems, which have resulted in reduced productivity. The scaling problems are addressed through intensive mechanical cleaning.

Technical and economic consequences of converting to low effluent pulp production for three hypothetical bleached kraft mills (an old mill, a modern mill, and a greenfield mill) were examined by Mannisto et al. (1995). Although liquid effluent-free production of bleached kraft mill was found to be technically possible, it was expensive. It was suggested that for the liquid effluent-free bleached kraft mill, the industry will need to focus its efforts on following key areas: (1) improving the quality of non-chlorine bleach sequences, (2) developing methods for removing and managing nonprocess elements (chloride, metals, nutrients), (3) minimizing increase in solid waste generation and air emissions, (4) managing the mill chemical balance, (5) managing upset conditions, and (6) developing design standards.

Nanofiltration and electrodialysis techniques have been shown to be technoeconomically feasible to purify the first extraction stage effluent and to recycle it as process water (dePinho et al., 1995). Zero discharge was accomplished in Selenga Pulp & Paper Company in Russia by employing activated sludge, chemical precipitation, and reaeration waste treatment methods (Kenny et al., 1995).

The Tembec Skookumchuck Kraft Pulp Mill, BC, Canada, has recycled 10–15% of Eop filtrate to the unbleached fiber line since 1996. Further steps toward system closure have involved evaluation of the effect of Eop filtrate recycling on corrosion of stainless and carbon steels, and optimization of the bleach plant scrubber, the heat exchanger, and spill control (Paleologou et al., 2004). No stainless steel corrosion and minimal carbon steel corrosion were observed. Five system closure scenarios were evaluated. The scenario selected involved recycling of all the Eop filtrate, removal of acid from the effluent of the chlorine dioxide generator, and the installation of a new effluent treatment plant (ETP). The impact of the following 14 projects was assessed, in most cases by computer modeling: improvements in brown stock washing control, improvements in bleach plant control, splitting of the second post-oxygen washer showers, application of Eop filtrate to the secondary D_0 washer showers, installation of a chloride removal system, pulp machine room water reduction, full Eop filtrate recycle to the post-oxygen washers, installation of an extra post-oxygen washer, evaporator condensate treatment for pulp machine room use, evaporator and recausticizer upgrades, installation of generator acid purification and acid evaporator systems, installation of sodium thiosulfate removal system, construction of a new effluent treatment facility, and decommissioning of the color clarifier. Six computer case studies were constructed with CADSIM software to evaluate the overall impact of the project. The proposed system is intended to reduce the impact of the mill's effluent flow into the Kootenay River. The proposed program involves a degree of risk as some technologies and strategies have not been proved on an industrial scale. The risk can be minimized by stepwise demonstration and implementation and continuous evaluation and validation.

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 such as Meadow Lake and Chetwynd. Evaporation is the only industrially proven technology. 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-bleached kraft pulp mills will have more difficulty achieving closure. Closed-cycle bleached kraft mill appears to be technically feasible. However, the challenge is to optimize process choice to give good economics.

Collection of Spillages

To minimize discharges of process effluents, chemical pulp mills need to carry out in-plant measures. Due to accidental discharges from chemical pulping, the external effluent treatment can be disturbed. Pulping liquor is lost from

Seals on brown stock washers
Pumps and valves in liquor service
Knotters and screens
Sewered evaporator boil-out solutions
Other intentional liquor diversions during maintenance, start-ups, and shutdowns

Liquor is also lost in spills, which result from process upsets, tank overflows, mechanical breakdowns, operator errors, and construction activities. The design of chemical pulp mills should be done around the following concepts:

- Collection of diverted or spilled liquor at the highest possible liquor solids concentration
- Return of collected liquor and fiber to the process at appropriate locations
- Curbing of isolated critical process areas (including tall oil and turpentine) to avoid concentrated or harmful streams entering the external effluent treatment or contaminating clean water sewers
- Conductivity or pH monitoring at strategic locations to detect losses and spills

Both the weak and the strong black liquors have special importance for efficient collection. These liquors cause unnecessary loading and disturb the external effluent treatment. The general concept for efficient recovery also requires to arrange the contaminated effluent sewers so that most of the spills, contaminated sealing waters, or floor washing in key areas—pulp cooking, washing and screening, used liquor storage and evaporation, and cooking liquor preparation—are collected in sumps and pumped either directly or via an intermediate tank into an appropriate liquor storage tank. The need of such recovery must be limited to areas where the mixed spill concentration is at least 2–3% dry dissolved solids. Floor washing and sealing water in these collection areas dilute the recoverable stream, so care must be taken not to dilute process liquors too much.

Hot condensates generated from pulp cooking and liquor evaporation should also be stored before their reuse in the pulp production. These condensates are divided according to their cleanliness to clean, semicontaminated, and contaminated fraction. The last-mentioned may find fewer uses because sufficient storage volume is sewered, causing some organic load and increase in total effluent temperature. Contaminated and semicontaminated condensate bleed-out is decreased simply by improved usage by replacing them with freshwater. One way is to feed them through steam stripping to remove reduced sulfur and volatile organic compounds (VOCs) and make them fairly clean hot water for a wider variety of process uses. Inside product areas, such as tall oil plant and turpentine recovery, care should be taken to avoid spills going to the external treatment. Soap and turpentine contain substances that may cause toxic effects in the biological treatment (European Commission, 2001).

A single-line kraft mill would need up to 5 collection sumps (equipped with conductivity-actuated recovery pumps), moderately complex mills would require up to 9, and complex mills up to 12 sumps. Training of staff can also be a very effective way of reducing discharges of harmful substances.

The effective spill control system is easier to install in a new installation rather than to retrofit in old mills. In existing mills, the solution to efficient process stream containment also lies in the key process equipment itself. Thus, building of spill containment should be done in connection with evaluation of other cost-effective improvements, especially in pulp washing and screening, evaporation, and liquor filtering (SEPA-Report 4713-2, 1997b).

It has been found that with good process management and properly designed spill containment, recovery and having 5–10% extra capacity in the evaporation plant, a reduction in effluent load of 3–8 kg COD/ADt can be achieved in comparison to mills with no or inefficient spill recovery and poor process stability. In total, spills can be less than 2 kg COD/ADt. Additionally, the risk of upsets in an external treatment plant is reduced, when accidental discharges with high organic and sometimes toxic load or continuously high or low pH of the incoming stream can be avoided. In order to handle the collected spills, 5–10% more evaporation capacity would be required. This would also consume 5–10% more steam and power. However, collection of spills means recovering of energy and chemicals when it is burned in the recovery boiler.

The investment cost of spill liquor handling systems is €0.8–1.5 million at a kraft mill producing 1500 ADt/day pulp mill. The operating costs of the system are estimated to be €100,000–400,000 million/annum, but can vary considerably between existing and new mills. With new mills, the operating costs are in the lower part of the range. The driving force for implementing this technique is reduction of discharges of BOD and COD.

Improved Pulp Washing

Washing of pulp not only has a significant role in influencing the process economy through recovery of chemicals used in cooking of raw materials and reduced bleaching costs but also minimizes the carryover of organic and inorganic substances along with pulp to the bleaching section and ultimately reduces the environmental impact associated with the discharge of toxic, chlorinated phenolic compounds.

In view of improving the washing process, new generations of pulp washing equipments have been introduced in the last decade, which have minimized water requirement, washing losses, and carryover of organic substances along with pulp to the bleach plant. Some of the examples are

- Pressure diffuser washer
- Horizontal belt washer
- Compact washer
- Drum displacer washer
- Screw press in combination with rotary drum washers

The major highlights/advantages of these modern pulp washing systems are summarized as follows:

Pressure diffusion washer

- An integral part of the continuous digester system.
- Also being used for post-oxygen delignification washing.
- Only washer that does not require knot separation and dilution ahead of the equipment. Eliminates air entrainment into the stock and the high operating temperature, give the pressure diffuser washer high displacement efficiency, resulting in better pulp washing.

Horizontal belt washer

- A very versatile pulp washer, which operates on dilution factors as low as 1.0.
- Extremely efficient for the washing of the slow draining agricultural residues.
- Belt washer accepts a feed consistency higher than that of the rotary vacuum drum filter, and the good pulp mat formation is ensured by a head box that evenly distributes the pulp suspension.
- A hood, which totally encloses the pulp mat, reduces the air circulation in the system.
- Consecutive displacement stages, without intermediate dilution, and overflow weir-type showers allow a single unit of this belt washer to perform better than a vacuum drum washing system.

Compact washer

- The compact washer can be either a pro-feed washer or a compaction baffle filter.
- Both these types use submerged displacement washing to increase washing capacity and efficiency.
- The pulp mat is pressed to a high consistency to remove black liquor with higher solids concentration.

Drum displacer washer

- The drum displacer washer incorporates all the washing stages on a single rotary drum.

- This unit allows four-stage washing to be done in one drum, and thus not more than one filtrate tank are needed.
- Less energy consumption (∼25%) compared to the conventional washing system.
- Less space requirement.

Screw press in combination with rotary drum washers

- Screw press installation prior to conventional drum washing helps tremendously in reducing the dilution factor as well as the carryover of the black liquor to the bleaching section.
- The extraction of black liquor also helps to reduce the foaming and increase the efficiency of drum washers.

Screening operation is also considered an integral part of pulp washing where knots, shives, and other impurities are removed. Thus, dewatering after screening has the function of the final washing stage, when its filtrate is used as wash liquor in previous stages (countercurrent washing). This is known as "closed screening" where specially designed equipment is provided to avoid the risk of foaming due to increased concentration of dissolved salt and organic substances in circulating liquor. The closed screening system is now a common practice employed by the mills in developed countries to reduce pollution. Majority of mills in India use vibratory knotters for the removal of uncooked material from the pulp, while almost all the mills worldwide have started using pressure knotters for this application. The use of vibratory knotters allows a lot of air getting mixed with the black liquor system, causing generation of foam, which reduces the pulp washing efficiency. The main benefit of a pressure knotter is that it can be directly connected to the other pressure screens, in case of a hot stock screening arrangement, and the possibility of air entrainment is totally eliminated, which is not possible with the vibratory knotters. The pressure screens are also capable of operating at a much higher consistency, that is, the range of 2–3.5%. This reduces a lot of pumping power and results in energy saving.

The measure can be adopted in new and existing kraft mills. In the existing mills, the modifications of a washing system may also be outweighed due to practical reasons by the complete set of new washing equipment. A closed washing system increases the importance of collection of temporary spills. The outgoing washing liquor contains both organic and inorganic substances. Washing waters withdrawn from the process are disposed through the external treatment. The washing loss after a conventional drum washing system could be about 5–8 kg COD/ADt, in comparison to 2–4 kg COD/ADt obtained in a modern washer system comprising a press washer. The remaining substances are adsorbed on or enclosed in fibers. In the latter system, the outgoing pulp consistency increases from roughly 10–15% to 25–35% and the water content decreases from 6–10 to 2–3 m^3/ADt (Josephson and Krishnagopalan, 1992; Pöyry, 1997).

Washing stages in series can reach up to 96–98% recovery efficiency of black liquor. When efficient washing takes place before an oxygen delignification stage, there will be reduction in the oxygen consumption. If there is an efficient washing system prior to the first bleaching stage, the carryover of organics to bleaching will drop, resulting in reduced AOX, BOD5, and COD discharge to the mill sewer. Washing losses were originally measured as the sodium sulfate content in the pulp. As this loss of makeup chemical has become less important, the washing loss is nowadays normally measured as COD.

The washing technology has been developed over the years and now solutions have been tested and proved on operation. Investment costs are typically €4–6 million for new mills and approximately €2–4 million for existing mills. No major additional operating costs are involved. The main reason to implement the method is the reduction of emissions to water.

Stripping and Reuse of Concentrated Contaminated Condensates

Contaminated (foul) condensates originate from the process vapors generated by digesters and the evaporation plant. In total, about 8–10 m^3/ADt of condensates are formed with a COD load of about 20–30 kg/ADt and 7–10 kg/ADt of BOD5. Normally, about 1 m^3/ADt is heavily contaminated (15–20 g COD/L), 4 m^3/ADt has medium contamination, and 4 m^3/ADt has low contamination. The COD is mainly methanol (5–10 kg/ADt) with some ethanol, a number of organic sulfurous compounds (1–2 kg/ ADt total reduced sulfur [TRS]), and inorganic nitrous compounds. Foul condensate also contains ketones, phenolics, fatty acids, and various dissolved gases. A large proportion of nitrogen discharged from a kraft pulp mill is contained in condensates. The foul condensates are normally treated in a steam stripper, often integrated in the evaporation plant, where the removal efficiency for most contaminant compounds is over 90%, depending on the pH. Stripping systems usually remove odorous gases (TRS) and COD at the same time. Stripped condensate COD concentration can be 1.0–1.5 g COD/L.

The contaminant-rich off-gases from the stripper are directly either led to incineration or fed to a methanol recovery column, where the concentration of methanol is increased. The vent gases are then condensed and cooled, producing a liquid, mainly consisting of methanol and having a water content of less than 20%. This methanol can be used as support fuel in a stand-alone NCG incinerator, in an NCG burner on the recovery boiler, or as fuel in the limekiln. The vent gases from the methanol recovery plant are then mixed with the other concentrated gases and led to incineration. About 7–9 m^3/ADt of weaker condensates (medium and low contamination) are formed with COD ranging from 0.5 to 2.0 g COD/L, containing a total of about 8–12 kg of COD/ADt. These moderately contaminated condensates can also be stripped in an integrated stripper and the vent gases fed to a methanol recovery plant. The total COD load before any reuse is thus reduced to about 5 kg/ADt, thus giving an overall reduction of about 50% compared to that achieved by only treating the most contaminated condensates. If the mill has no methanol recovery, the stripper off-gases are led to incineration in separate piping systems from the other concentrated gases. When burned, the organic and TRS compounds are converted to carbon dioxide (CO_2), sulfur dioxide (SO_2), and some sulfur trioxide (SO_3) by thermal oxidation. These oxidation products have a much lower odor intensity than TRS compounds. Cleaned condensates are free of inorganic metal ions and other ions, and it is possible to use them for washing in the bleach plant if bleaching filtrate recycle to chemical recovery is planned. This has been carried out in a limited number of predominantly TCF mills, where elimination of transition metal ions such as iron (Fe) and manganese (Mn) improves the efficiency of hydrogen peroxide bleaching. Condensates are often reused in brown stock washing, in the causticizing area (mud washing and dilution, mud filter showers), as TRS scrubbing liquor for limekilns or as white liquor makeup water. Consequently, in most mills, the majority of condensates is reused in closed parts of the process and, therefore, is not contributing to effluent flow. Other condensates are used in open mill areas, for example, the bleach plant, and end up in the effluent together with those condensates that are not reused but, instead, sewered directly (Sebbas, 1988; Zuncich et al., 1993).

Biological Wastewater Treatment

Biological treatment is carried out to remove the organic matter that is achieved by biological degradation. Pulp and paper mill effluents are mostly treated with aerobic methods. The commonly used aerobic treatment methods are aerated lagoon and activated sludge processes (Nesaratnam, 1998). In aerated lagoon, the reduction of pollutants is lesser.

Aerated Lagoon

An aerated lagoon or aerated basin is a holding and/or treatment pond provided with artificial aeration to promote the biological oxidation of wastewaters. It has a large volume; the residence times for the effluent is 3–20 days. The microorganisms grow in suspension in the bulk of liquid, reaching in the lagoon relatively low solids concentration, 100–300 mg/L. The growth of microbes requires oxygen, which is provided almost exclusively by mechanical aeration equipment. Surface turbine aerators are the most common aeration units, but in deep lagoons bottom aerators with self-induced or compressed air feed are also used. Aeration equipment also provides mixing required to keep solids in suspension and enhance microbial action. Aerated lagoons, due to the large area and volume, require earth basins and can be constructed with or without a settling zone. In the first case, the end of the lagoon is left without aeration and mixing, thus allowing solids to settle. In the latter case, this settling is carried out in a separate pond. The biological process does not involve recirculation of biomass from the end to the beginning of the basin. The settled sludge is seldom removed, once in 1–10 years.

The use of aerated lagoons has become less common for many reasons. These are mainly due to its low to moderate removal of effluent contaminants, the large land area and basin volume it requires, high energy requirement, and poor energy efficiency in aeration and mixing. In addition, effluent foam and smell problems are sometimes encountered. The settled sludge removal and disposal can also generate problems.

Treatment efficiencies vary widely depending on the type of effluent, design of the treatment plant, and operating conditions. Typical removal efficiencies are 40–85% for BOD5, 30–60% for COD, and 20–45% for AOX. There is no nitrogen removal, and the phosphorus removal is low in the range of 0–15%. The removal of solids is very case-specific and in some instances the outlet effluent contains more solids than the inlet stream. The incoming solids are adequately removed in a lagoon with a settling zone, but the microbial growth produces biosolids with poor settling characteristics. The discharge of solids is lower from high residence time lagoons and settling zones. In comparison to the activated sludge process, there can also be adverse effects, such as occasional heavy mist in humid and cold weather and odor from anaerobic or anoxic basin areas.

The lagoon process requires large land areas, which are not always available next or inside the mill area. The lagoon treatment produces less sludge than the activated sludge process, but the sludge is difficult to dewater efficiently. Thus, the sludge disposal by burning requires typically more dewatering chemicals and support fuel per dry weight than the sludge generated by the activated sludge process.

Aerated lagoons have been used for a long time in many pulp and paper mills for medium-level removal of effluent contaminants. Currently, many of the existing lagoons in the industry have been closed down or retrofitted into a high-efficiency activated sludge process or supplementary effluent treatment basins. The cost of this process is very dependent on where and how the aerated lagoon can be built. If it can be built by reclaiming a bay in the receiving waters and closing its open side with an earth dam, the cost is substantially lower than when the lagoon must be built on dry land. Thus, the investment costs vary a lot, being in the range of €16–20 million for a 1500 ADt/day kraft pulp mill. This cost also covers the primary treatment and sludge dewatering. The corresponding operating costs are €1.3–1.7 million/annum, comprising mostly of the cost of electrical power required for aeration and mixing in the lagoon.

Activated Sludge Process

Activated sludge process is an oxygen-dependent biological process that serves to convert soluble organic matter to solid biomass, that is, removable by gravity or filtration. It cleans up wastewaters in three stages:

- Stage I involves (anaerobic) equilibration.
- In stage II, activated sludge containing microorganisms is led into an aeration basin to speed up oxidation of organic matter and ammonia.
- In stage III, the sludge is allowed to settle and the treated wastewater is run off. Some sludge is removed and a portion is returned to the aeration basin.

The activated sludge plant consists of two main units, the aeration basin and the secondary clarifier (sedimentation basin). In the first stage, the aeration basin, the effluent is treated with a culture of microorganisms that is present in a high concentration. Activated sludge plants at kraft pulp mills have a retention time of about 15–48 hours with the higher values in recent installations. The sludge is separated from the water in the clarifier. The main part of the sludge is recycled to the aeration basin, which is necessary for keeping the high sludge concentration. A small part of the sludge, corresponding to the net growth, is removed from the system as the excess sludge. Oxygen and mixing are provided to the aeration basin by mechanical aeration equipment. Various types of aerators are in use, such as surface aerators, submerged turbine aerators, fine bubble aerators, and jet aerators. The three last mentioned types require compressed air from blowers or compressors. A large number of different process and plant designs exist for the activated sludge process. These alternatives may be different regarding design of the aeration basin, the clarifier, the aeration equipment, as well as the sludge recycling. One special process design is the pure oxygen-activated sludge, where pure oxygen or oxygen-enriched air is used instead of regular air.

The process can be applied in both existing and new kraft pulp mills. In the existing mills, some kind of water consumption reduction measures should preferably be carried out to reduce the investment costs. The activated sludge process is often used, when high or very high treatment efficiencies are required. In the latter case, however, a two-stage biological process is an optional choice. Activated sludge plants are used widely in the pulp and paper industry. As rough estimate, the activated sludge process is used in 60–75% of all the biological ETPs in this pulp and paper industry. This is also the most common process used in recently built plants. Advantages of the activated sludge process are the potential of high or very high treatment efficiencies, the possibilities to control the process (particularly the oxygen consumption), and the relatively low space demand. Disadvantages are the relatively high vulnerability to disturbances and consequently a risk of operational instability without any protective measures, such as an equalization basin, high production of biological waste sludge, and the high operating costs. Alternatives to activated sludge systems exist, which are more compact and less expensive. The experience from such installations is more limited, but they are claimed to have equivalent reduction levels to activated sludge systems.

Treatment efficiencies vary and depend on the effluent type, plant design, and operating conditions. Typical values are within the ranges of 85–98% BOD5 removal and of 60–85% COD removal. AOX reduction is in the range of 40–65%; phosphorus and nitrogen are reduced by 40–85% and 20–50%, respectively. The overall efficiency of TSS removal of primary and secondary treatment is about 85–90%. In the well-designed plants, the BOD5 can be reduced to about 20–40 mg/L and the amount of TSS to about the same level. Concentrations of phosphorous and nitrogen are to a high degree correlated to TSS as the amount of dissolved nutrients can be reduced to very low levels by running the plant properly. For COD, which is a measure of total load of organic substances, the concentration after treatment depends on the content of heavily degradable matter.

The ETP produces sludge that after dewatering can be burned, providing in some cases net positive heat value. The treated wastewater is clean enough for reuse in some points of the production process. The problem is that usually the wastewater treatment plant is located so far from the mill that recycling is not economical. Activated sludge plants have been used for many years in all types of kraft mills with good results. The investment costs of a completely new activated sludge treatment plant are approximately €19–24 million for a kraft pulp mill with 1500 ADt/day production, being at the lower end of the cost range for an unbleached kraft pulp mill. These costs also include the necessary primary treatment and sludge handling. The corresponding operating costs are €2.0–2.6 million/annum. The activated sludge process is preferably used, when high or very high treatment efficiencies are required.

Tertiary Treatment of Wastewater

In some cases, the effluent treatment is extended with a tertiary treatment, which is chemical precipitation in most cases. The dissolved organic substances are separated by precipitation and subsequent filtration or clarification. The chemicals used are usually aluminum (Al) salts, ferric (Fe^{3+}) salts, and lime (CaO). The chemical treatment gives a further reduction of some recalcitrant compounds such as high-molecular degradation products from lignin. A chemical floc (precipitation of organic and inorganic matter) is formed and this floc is then removed by sedimentation or flotation.

To optimize the flocculation, polyelectrolytes are used in the mixing phase. It is applicable to both new and existing mills. Tertiary treatment with chemical precipitation is mainly applied to reduce nutrient, especially phosphorus. When biological treatment is combined with chemical precipitation, phosphorus, nitrogen, COD, and AOX are reduced by 80–90%, 30–60%, 80–90%, and 80–90%, respectively (PARCOM, 1994).

The precipitation of organic material in the effluent with inorganic chemicals generates huge quantity of a slimy sludge, which is very difficult to dewater and dump as landfill. The chemical cost is substantial and the purification is selective; neutral substances cannot be captured as efficiently as dissociated ions.

The investment costs amount to €2.6 million for a kraft pulp mill with a capacity of 250,000 t/annum and €3.8 million for a mill with 500,000 t/annum capacity, respectively (European Commission, 2001). The investment costs of chemical precipitation include equalization tank, chemical dissolving equipment, chemical dosing equipment, precipitation and flocculation unit, and tertiary clarifier. Operating costs amount to about €50,000, being somewhat lower for the mill with less capacity. Usually, tertiary treatment of wastewater is only regarded as necessary when the nutrient concentrations in the effluent have to be lowered, that is, if the mill discharges to very sensitive recipients (PARCOM, 1994; SEPA-Report 4713-2, 1997b). Biological treatment and chemical precipitation of wastewater from the manufacturing of bleached kraft pulp are used on commercial scale in integrated kraft and chemithermomechanical pulp (CTMP) mills.

Increase in the Dry Solid Content of Black Liquor

The inorganic substances are reduced in the recovery boiler and separated as a smelt from the bottom. The organic substances are oxidized and generate heat. In a conventional recovery boiler, there is an oxidizing zone in the upper part and a reducing zone in the lower part. The strong black liquor is introduced through one or several liquor nozzles into the reducing zone. Combustion air is usually supplied at three different levels as primary, secondary, and tertiary air (from the bottom upward).

Emissions generated from the recovery boiler mainly consist of particulates, nitrogen oxides, and sulfur dioxide. The emission levels are kept low by optimizing the combustion parameters such as temperature, air supply, black liquor DS content, and the chemical balance. The objective of improved evaporation is to achieve as high content of DS as possible in the strong black liquor. The DS content in the strong black liquor is about 65% after a conventional evaporation. DS content up to 80% can be achieved by installing a superconcentrator. However, the achievable DS content depends on the wood species. A target for optimal DS content of thick liquor in a balanced mill could be 72–73% after evaporation but measured before the recovery boiler mixer.

This process can be applied in both new and existing kraft mills. A superconcentrator can also be implemented as a separate phase to existing evaporation plants. However, the maximum DS content is limited by the increase of the viscosity and scaling tendency of the strong black liquor. This depends on the wood species and temperature. In practice, with eucalyptus and some other hardwood species, it is difficult to achieve higher than 70% DS content. The sulfur emission from the recovery boiler is down to 5–50 mg S/Nm^3 or 0.1–0.3 kg S/ADt of pulp or sometimes almost down to zero because more sodium will vaporize and react with sulfur. The reduction of sulfur emissions by high DS content increases the emissions of particulates prior to flue gas cleaning. To compensate this, more efficient and expensive electrostatic precipitator (ESP) has to be installed. At high DS content of more than 80%, there is a substantial release of sulfur compounds from the last evaporator stage, which have to be collected and incinerated. Increasing DS content of black liquor tends to increase NO_x emissions from the recovery boiler if no countermeasure is taken.

This measure has been tested in several pulp mills in the world. In existing mills, the cost of improved evaporation and concentration of strong black liquor is tied to the target concentration. At existing mills with 1500 ADt/day kraft pulp production, the investment costs of increase in black liquor concentration from 63% upward are as follows:

Concentration from 63% to 70%, €1.7–2.0 million
Concentration from 63% to 75%, €3.5–4.0 million
Concentration from 63% to 80%, €8.0–9.0 million

The operating costs of the improvements are not significant because of the increase in energy economy (this being 1–7%) and gain in recovery boiler capacity.

The increase of DS into the recovery boiler may even result in some net savings. Kraft mills may face sulfur dioxide emission problem, and these emissions in the recovery boiler can be reduced by increasing the DS content of black liquor. Another case-by-case achievable result is the increase in the capacity of the recovery boiler (4–7%). Alternatively, flue gas scrubbers can be installed for the same purpose (Beca AMEC, 2004; Finnish BAT Report, 1997).

Installation of Scrubbers on the Recovery Boiler

The recovery boiler can be equipped with a flue gas scrubber to reduce the emissions of sulfur dioxide. A kraft recovery boiler scrubber of the wet type may include three process stages. Chloride is absorbed by cold water introduced in the flue gas inlet. The chloride efficiency is normally 60–70%. In the washing zone, SO2 and particulates are removed. Scrubbing takes places at a pH of 6–7. The pH value is controlled by addition of sodium hydroxide, weak liquor, or oxidized white liquor. SO2 reacts with the scrubbing liquor and Na2SO3, and also some Na2SO4 is formed. TRS in the form of H2S can be removed together with SO2. However, to remove hydrogen sulfide from the flue gases, a high pH of the scrubbing liquor would be required. At such a high pH, carbon dioxide would also be absorbed, which is unrealistic due to the relatively large amounts of carbon dioxide being formed in the combustion. Surplus liquor from the scrubber is recycled to the process, normally to the white liquor preparation.

Installation of a scrubber is preferably done at the same time as a new boiler is installed, although at much higher cost existing boilers can also be equipped with scrubbers. Recovery boilers burning high DS black liquor normally give rise to low sulfur emission, which makes the installation of scrubber less interesting.

The removal efficiency for SO2 is typically more than 90%. A scrubber on the recovery boiler can reduce the sulfur emissions from 0.5–2.0 kg/ADt down to 0.1–0.3 kg S/ADt or concentrations from 50–200 mg/Nm^3 down to 10–50 mg/Nm^3. Continuous SO2 measurement prior to and after the scrubber is needed to control the operation of the scrubber.

By introduction of freshwater in top of the scrubber, hot water can be produced (if there is a need). The water is normally clean enough to be used as wash water in the bleach plant. The scrubber needs alkali in the form of oxidized white liquor, weak liquor, or sodium hydroxide, which can increase the capacity demands of the recovery department.

Scrubbers on recovery boilers can be operated without problems. The equipment comes usually as a package from the supplier. The investment costs of a bleached kraft mill with a production capacity of 250,000 and 500,000 t/annum amount to €7.2 million and €10.4 million, respectively. They include scrubber, scrubber liquor pumps, circulation pumps, electrification, and instrumentation. Operating costs amount to €580,000 and €920,000 per annum, respectively. Scrubbers have been installed on numerous recovery boilers in the last decades (Pöyry, 1992; SEPA-Report 4713-2, 1997b).

Collection and Treatment of Odorous Non-condensable Gases for Incineration in the Recovery Boiler

Odorous gases containing reduced sulfur compounds (TRS) such as hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethylsulfide (CH_3SCH_3), and dimethyl disulfide (CH_3SSCH_3) are produced at various points in the kraft pulping process. The odorous NCGs are collected and treated in different ways depending on the TRS concentration, and volume of the source and the type of source. The sources containing little air or oxygen are collected in the concentrated NCG (CNCG) system. The other sources, containing more air and oxygen, are collected in the dilute NCG (DNCG) system. CNCGs are sometimes referred to as low-volume, high-concentration (LVHC) gases and DNCG as high-volume, low-concentration (HVLC) gases.

Control of TRS emissions can be divided to treatment of concentrated malodorous NCGs, which contain about 4 kg TRS/t (measured as S), and diluted or lean malodorous gases, which contain about 0.5 kg TRS/t (measured as S). The treatment of concentrated NCGs is normally carried out by collection of NCGs from the cooking and evaporation departments and their disposal by incineration. Several options are available.

The incineration of concentrated malodorous gases in the recovery boiler is one possible option. There are a few mills in the world burning strong malodorous gases in the recovery boiler. High-volume and low-concentration gases are formed in black and white liquor handling, pulp washing, and floor channels with black or white liquor residues. The actual composition varies greatly case by case.

The collection is carried out with gas pipelines and blowers for gas transfer. The collected lean malodorous gases can be incinerated as secondary or tertiary air of the recovery boiler. Depending on the volume of diluted NCGs and the lay out of the pulp mill, there can be several TRS destruction systems for different departments. An alternative for incineration is alkaline scrubber or oxidizing scrubber. The recovery boiler is able to destroy diluted malodorous gases. However, the recovery boiler is only one alternative for incineration of diluted gases. Normal amount of diluted NCGs at a 1000 t/day mill is about 50,000–100,000 m^3/h. The amount of the gases depends on the mill concept; with continuous cooking and diffuser washing the volumes are lower than with batch cooking and pressure washers.

The measure can be adopted in the existing and new kraft mills. In the existing pulp mills, it may be very difficult to retrofit a collection and treatment of diluted NCGs. This is due to the limitations of the lay out and long distances between sources of malodorous gases and the recovery boiler.

The investment costs of the weak malodorous gas collection and their disposal in the recovery boiler are €3.6–4.5 million for a kraft mill with 1500 ADt/day production. However, because much of the costs are for piping, the costs can be considerably higher at mills, which spread on a large area. The operating costs of the system are €0.3–0.5 million/annum. The more efficient reduction of TRS emissions of the kraft mill is the main reason to implement this technique (Beca AMEC, 2004; European Commission, 2001).

Incineration of Odorous Gases in the Limekiln

Control of odorous gas caused primarily by Total Reduced Sulphur (TRS) emissions can be divided to treatment of concentrated NCG and lean malodorous gases. The treatment of concentrated NCGs is usually done by collection and incineration of NCGs from cooking and evaporation departments. Incineration of concentrated NCG is conducted in the limekiln or in a separate NCG incinerator having SO_2 scrubber. The concentrated NCGs contain over 90% of all TRS compounds generated in the cooking of pulp.

High-concentrated and low-volume gases are produced in

- Turpentine recovery system
- Continuous digester flash steam condensers
- Foul condensate storage tanks
- Evaporator NCG relief and hotwells
- Batch cooking blow-heat recovery system instead of continuous digester flash steam condensates

The actual composition varies greatly from case by case. The major sources of lean malodorous gases are

- Washing and screening equipment of unbleached pulp
- Several tanks of pulp and washing liquor in the washing and screening
- Storage tanks of black liquor in the evaporation plant and storage tanks of white liquor in the recausticizing plant

The collection is carried out through gas pipelines, ejectors, and blowers for gas transfer. The collected lean malodorous gases can be incinerated as secondary air of limekiln or in a separate NCG incinerator, in a bark boiler or other auxiliary boiler or as secondary or tertiary air of the recovery boiler. Depending on the volume of diluted NCGs and the lay out of the pulp mill, there can be several TRS destruction systems for different departments.

The measures can be adopted in the existing and new kraft mills. In the existing pulp mills, it may be difficult to retrofit a collection and treatment of diluted NCGs. The TRS emissions of the kraft mill can be reduced by more than 90% by only collecting and burning the concentrated TRS compounds. The advantage of burning the malodorous gas in the limekiln is that no extra furnace is needed. Also, the sulfur in the gas can be absorbed in the lime, which decreases the emission of sulfur dioxide. However, only a limited amount of sulfur can be absorbed in the limekiln by gaseous sodium-forming sodium sulfate. The main sulfur-absorbing compound is sodium carbonate (Na_2CO_3) in the lime mud. When this capacity is exhausted, SO_2 is released. This effect is increased when malodorous NCGs are incinerated in a kiln. So, SO_2 emissions are usually a clear function of the amount of malodorous gas flow. To minimize the formation of SO_2, either the sulfur content in the fuel can be reduced or if malodorous NCGs are to be burned in the limekiln, sulfur compounds can be scrubbed out of these gases before burning in the limekiln.

TRS control can also decrease the malodorous constituents released in the wastewater treatment. An average 10–15% of the fuel used in a limekiln can be replaced by the heat value of the concentrated malodorous gases. However, the variation of the amount of energy of the gas may make it difficult to hold a lime of good and uniform quality. Condensation of methanol after the stripper column can reduce the problem with varying gas quality. However, it would require additional investment costs.

The measure is extensively used. Investment costs of collection and incineration of both strong and weak gases are typically €4–5 million at new mills and €5–8 million at existing mills with a capacity of 1500 ADt/day. There is no major increase in operating cost, if the heat value of recovered methanol can be utilized. Otherwise, an increase of €0.3–0.5 million/annum is expected. The reduction of TRS emissions of the kraft mill is a major reason to implement this technique (European Commission, 2001).

Installation of Low-NO$_x$ Technology in Auxiliary Boilers and the Limekiln

In the kraft mills, several types of fossil fuels (bark, coal, lignite, oil, or natural gas) can be used for supplemental steam production, typically coupled with turbines for electric power production. In burning of these fuels, environment-friendly incineration techniques are used to reduce particulate, SO_2, and NO_x emissions. Coal and lignite suit well to be burned as major or support fuel in fluidized-bed systems, which by careful operation control promote low-NO_x formation. In conventional oil or natural gas-fuelled boilers, the burners feeding the fuel–air mixture must apply designs that maintain low-NO_x burning conditions. Also, coal or peat is often burned as finely ground dust in conventional boilers, fed through burners that with proper designs provide low-NO_x burning. The primary burning air is brought through the burner in the fuel–air mix. Secondary and tertiary air is fed in separately to maintain an appropriate primary/secondary/tertiary air balance in the flame area to maintain low-NO_x combustion. Some air may still be fed, if necessary, above the main flame area to complete the fuel combustion. The reason of the multiphase air feed is to burn the fuel without excess air and actually even under reducing conditions, meaning that there is not enough oxygen to promote strong NO_x formation; the flame temperature is lower than in conventional burners, which further decreases NO_x formation. Part of the NO_x formed will reduce back to elementary nitrogen, for example, when a residual amount of the fuel is burned in the outer flame area or outside it.

Low-NO_x burners can be used both in the new and existing boilers. When powdered solid fuels are used, it is important that they are predried if they have high humidity to support fast and efficient burning. Also, it is required that the burning air is preheated to ensure quick ignition and complete burning. Generally, emissions vary with the fuel. In comparison to conventional burners with 250–500 mg/MJ NO_x emissions, the low-NO_x burners can reach 120–140 mg/MJ levels in stack emissions.

With online NO_x meters, emission monitoring can be carried out. Also, oxygen meters can help to determine that low-NO_x burning conditions are maintained. Low-NO_x burners have been applied successfully in the retrofit of existing boilers and construction of new ones. The investment costs are typically €0.5–0.8 million. No major increase in the operating costs is anticipated. Low-NO_x burners are mainly used to reduce NO_x emissions from auxiliary boilers (Finnish BAT Report, 1997; Pöyry, 1997; Rentz et al., 1996).

Selective Non-catalytic Reduction on Bark Boilers

Bark boilers give relatively low-NO_x emissions because of the low combustion temperature. When only bark is fired, emissions are typically 70–100 mg NO_x/MJ, and when oil is used in the bark boiler, NO_x increases to about 100–150 mg NO_x/MJ. NO_x formation is affected by excess oxygen and should be avoided. Too low excess oxygen increases the risk of emissions of CO and VOC. Primary NO is formed in furnaces either through reaction with nitrogen in air (thermal NO) or through oxidation of nitrogen in fuel (fuel NO). Formation of thermal NO increases with increasing temperature of the flame. A part of the NO is further oxidized to NO2. In the SNCR process, NO is reduced by urea to nitrogen, carbon dioxide, and water, according to the reaction $2NO + (NH_2)_2CO + 1/2O_2 \rightarrow 2N_2 + CO_2 + 2H_2O$. The reaction occurs at about 1000°C.

Equipment to inject urea or ammonia can be installed in both existing and new boilers. The optimal reaction conditions can be difficult to obtain in existing boilers, thus reducing the potential NO_x reduction to about 40%. The total NO_x reduction achievable in a bark boiler is about 30–50% by making change in the combustion techniques and/or by applying an SCNR process. The NO_x emissions would then amount to 40–60 mg/MJ equal to about 100–200 mg/Nm^3. Emissions of gaseous sulfur are low or about 10–20 mg/MJ when burning bark. Continuous NO_x measurement can be installed, and experience shows reliable results.

This technique is being used since the early 1990s. Good availability is normally reported, but a number of incidents have occurred where the injection of urea solution has caused damages inside the boiler. SNCR technique is difficult to control because of relatively fast changes of load might happen in bark boilers. This results in variations in NO_x reductions achieved by these techniques. The process can be a potential source of emission of N_2O or NH_3, but measurements demonstrate the risk to be marginal.

Full-scale trials with both urea and ammonia have been carried out in Sweden. The tests showed NO_x emission reductions of 10.30%, with one test up to 60%. The efficiency depends on many factors, for example, the boiler furnace configuration. In practice, this method also generates secondary ammonia emissions or ammonia slip. The injection of urea or ammonia into the boiler may damage the furnace and boiler tubes. For safety reasons, the Swedish Recovery Boiler Committee has advised against the installation of SNCR on recovery boilers.

The investment costs of adding SNCR to the bark boiler for a bleached kraft mill with a production capacity of 250,000 and 500,000 t/annum amount to €690,000 and €1.15 million, respectively. The investment costs include injection equipment, pipes, pumps, tanks, and rebuild/adoption of the boiler. The operating costs are mainly urea. About 1–2 kg urea is required for per kilogram NO_x removed.

NO_x has an acidifying potential and may increase eutrophication. In some sensitive lake areas in Europe, a further reduction of NO_x emissions by secondary measures as SNCR technique is therefore regarded as necessary. A fee on NO_x emissions in Sweden may also give an incentive for further NO_x reduction (SEPA-Report 4713-2, 1997b).

Over-Fire Air Technique on Recovery Boilers

The NO_x formation in the kraft recovery boiler is lower in comparison to other furnaces because it operates with a reducing atmosphere at the bottom. Modifications to the air feed system have been found effective with respect to NO_x reductions. Thermal NO_x by fixation of nitrogen in the combustion air can be reduced by limiting the amount of air in the combustion zone. A reduced NO_x formation can be achieved in a kraft recovery boiler through modifying the air feed system such as introducing a fourth air inlet in the upper part of the boiler. The reduction of NO_x emissions attributable to the use of this technique is variable, dependent on the boiler type and design and the method of OFA application, and will normally be 10–25%.

It is applicable to both existing and new mills. The achieved NO_x reduction seems to be different from recovery boilers to recovery boilers. Following experiences have been reported in some Swedish kraft pulp mills:

1. Installation and use of OFA technique on an existing recovery boiler and operation since 1990: 30% NO_x reduction achieved.
2. Installation of the OFA technique on an existing recovery boiler. The new air feed system is not any more used because of the increase of temperature in the overheater.
3. Installation of the OFA technique on an existing recovery boiler in 1995: 20% No_x reduction achieved and in operation since the beginning of 1997.
4. The first new recovery boiler with OFA technique in 1996.

The reduction of NO_x emissions with the use of this technique is variable. It depends on the boiler type and design and the method of OFA application. It has to be adapted to the specific conditions of recovery boilers. The application of this technique, which is widely used in other combustion processes, may result in increases in carbon monoxide and unburned carbon emissions if not well controlled. The investment costs of modifying the air introduction to the recovery for a bleached kraft mill with a production capacity of 250,000 and 500,000 t/annum amount to €1.7 million and €2.3 million, respectively. The investment costs include new air inlets to the recovery boiler, instrumentation, pipes, and fans. There is no change in operating costs.

NO_x has an acidifying potential and may increase eutrophication. In some sensitive lake areas, a further reduction of NO_x emissions by secondary measures is therefore regarded as necessary (SEPA-Report 4713-2, 1997b).

Installation of Improved Washing of Lime Mud in Recausticizing

Before the lime mud ($CaCO_3$) is sent to the kiln, it must be washed to remove residual sodium hydroxide (NaOH), sodium sulfide (Na_2S), and other sodium salts, and then dewatered. Improved lime mud washing can reduce the residual content of white liquor in the mud from 100 mg/L to 0–30 mg/L. The lime mud dryness in older mills is typically 60–65%, while modern mills using filters with a larger specific area and better dewatering capacity typically perform at 70–80% dryness. The more efficient filters reduce the concentration of Na_2S in the lime mud through both washing and oxidation. Sodium sulfide is oxidized to sodium thiosulfate ($Na_2S_2O_3$) by passing air through the mud mat on the filter. The lower concentration of Na_2S in the lime mud reduces the formation of hydrogen sulfide (H_2S) in the limekiln during the mud-drying process. Improved washing of lime mud has been practiced since the late 1980s in kraft pulp mills. Monitoring of residual NaOH is required to avoid plugging of the limekiln (SEPA-Report 4713-2, 1997b).

The main achieved environmental performance is possible reduction of H_2S (TRS) in the limekiln, which depends mainly on the availability of sodium in the lime and the sulfur content of all fuels fed to the limekiln. At the lowest sulfur input, a small reduction can be achieved, but with higher sulfur inputs, the effect can be nonexistent or detrimental. If washed to a very low sodium content, the emissions of TRS and also particulate emissions from the limekiln tend to increase. Improved washing of lime mud has been practiced over 10 years at pulp mills in Europe. Monitoring of residual sodium (NaOH) is required to avoid damming of the limekiln. Investment costs are typically €1.0–1.5 million. Driving force for implementing this technique is the reduction of H_2S (TRS) and odors from the flue gases of the limekiln (SEPA-Report 4713-2, 1997b).

Recycling/Reuse of Wastewater

In recent years, there have been considerable incentives to reduce the amount of water used by the pulp and paper industry, stemming from the need to reduce or eliminate the discharge of liquid effluents into the environment and regulations introduced to control the amount of suspended solids, oxygen-consuming wastes, and chemical toxic to marine life. The major advantages of wastewater recycling are

- Less water requirement depending on degree of back water recycling in the various mill operations
- Savings in energy
- Reduced wastewater discharge
- Simultaneous reduction in effluent treatment cost due to lower effluent discharges

The driving forces responsible for wastewater recycling in pulp and paper industry are the high cost of freshwater, inclination of the industry toward environment-friendly process, discharge norms laid down by regulatory authorities, community perception, and the high cost of secondary effluent treatment process.

Industry has several options with respect to minimizing the use of freshwater. These options can be spill control, process modification, water reuse, partial treatment and reuse, and full treatment and recycling.

Optimal water management involves developing an understanding of where detrimental substances are generated as well as which ones are critical to the process and how they impact on mill operation. Optimal solutions always require an integrated approach where product and process quality, novel treatment technologies, and economical factors are involved. Water conservation options also depend on the category and scale of operations.

The water consumption can be reduced to a great extent by making minor modifications in the process that may also involve recycling or reuse of process water in the system.

An effluent-free pulp mill is the dream of the environmentalists and of many engineers and scientists. Research toward this goal has been going on for more than three decades. Some of the simple water conservation measures in the pulp mill are

- Use of treated effluent for raw material washing
- Improving washing efficiency of pulp washers
- Use of paper machine back water in the pulp dilution in the unbleached tower
- Use of back water in centricleaning of pulp and vacuum pump sealing
- Recycling of bleach plant filtrate for pulp dilution in towers and vats and shower sprays in the preceding stage

Use of Bleaching Filtrates for Postprocess Dilution

Recycle of bleach plant filtrate from the last D stage to other acid stages and from the second alkaline stage to the first alkaline stage is practiced to reduce the effluent volume from the bleach plant. The concepts of jump stage and split flow countercurrent washing have been practiced in Scandinavian and North American mills for many years. Equipment parameters, metallurgy, and operating costs are the main considerations in choosing the degree of closure in an existing bleach plant. With bleach plant filtrate recycle, the water and heat consumption decreases while chemical consumption and corrosion increase. In a three-stage bleach plant shower, water usage can be reduced by 60–70% with fully countercurrent filtrate flow. An intermediate level of recycling can be chosen to suit the plant conditions by choosing a jump-stage configuration. The savings in water usage will obviously be lower. Effluent reduction and steam savings for a three-stage bleach plant with various closure options have been estimated to be 26.8% and 40.4%, respectively, by D-stage jump, 52.6% and 56.9%, respectively, by D/Eo-stage jump, and 70.7% and 80.7%, respectively, by following fully countercurrent configuration (Chandra, 1997). The assumptions for these estimates include a brown high-density consistency of 12%, a washer feed consistency of 1.5%, a dilution factor of 1.0, and a displacement ratio of 0.81. The consistencies of the CD, Eop, and D stages are assumed to be 10.5%, 9.5%, and 12%, respectively.

A closed-loop bleaching system developed by Swedish company MoDo uses oxygen in the first stage, and then hydrogen peroxide, ozone, and small amounts of chlorine dioxide are used in subsequent stages. Twelve washing stages are included, with clean water being added only at the final stage (Anonymous, 1997). The water is passed back through the pulp, not into the drains, and is then evaporated into steam. The MoDo Husum mill has a capacity of 690,000 t/year of bleached sulfate pulp. The Wisaforest pulp mill of UPM-Kymmene Corporation has started to use bleach plant filtrate for post-oxygen washing on fiber line 1 (Siltala and Winberg, 1999).

Recycle loops observed in market bleached kraft mills are described as follows:

- Blow gas condenser cooling water is used as a hot water source for bleach washing and machining showers (stock heating).
- Liquor evaporator condensates are utilized for brown stock washing.
- Chlorine dioxide plant cooling water is recycled to process freshwater supply.
- Chlorination effluents are used for unbleached stock dilution.
- Machine white water is utilized for the final bleach stage shower and dilution water.
- Machine white water is utilized for all dilution/shower water in stock preparation.
- Press effluents are reused for machine white-water makeup.
- Liquor evaporator condensates are utilized for boiler feed water makeup (clean condensates), causticizing mud washers, limekiln scrubbers, dreg washing, and wood yard requirements.

In addition, freshwater usage is to be eliminated in the following areas of the mills:

1. **Wood preparation:** All wood flumes utilize recycled waters. Wet debarking has typically been eliminated. Remaining water requirements are met with process wastewater.
2. **Washing:** Brown stock washing is typically accomplished entirely with wastewater from the evaporators and turpentine decanter underflow from pulping.
3. **Screening:** Stock screening is typically relocated immediately upstream of washing with screening dilution coming from weak black liquor. In the absence of this approach, stock screening typically retains its place in the process stream (after washing) with high levels of water recycle and water makeup from the Decker filtrate. Decker filtrate shower water is principally supplied from evaporator condensates.
4. **Cleaning/refining:** Stock preparation waters are met primarily with machine and/or press section white water.

5. Drying: Cooling water for drum bearing lubrication system, air conditioning, etc., is either recycled via an evaporative cooler or returned to freshwater reservoirs.
6. Liquor evaporation: Condenser cooling water is either recycled via an evaporative cooler or returned to freshwater reservoirs.
7. Causticizing: Water requirements for mud washing, dregs filter showers, and limekiln scrubbers are supplied by other subprocess waste streams. Cooling water is returned to freshwater reservoirs.

Increased Delignification before Bleaching/Modifying Pulping Process

The kappa number of the pulp going to the bleach plant can be reduced by using chemical additives, such as anthraquinone and polysulfides, or by using modified cooking techniques such as MCC and extended MCC, isothermal cooking (ITC™), black liquor impregnation, LoSolids™ cooking, and the use of oxygen delignification following low-kappa cooking (Chandra, 1997). This will result in lower quantities of pollutants going to the bleach filtrate, improving its suitability for recycling and reuse. It may also be easier with low-kappa pulp to use non-chlorine bleaching agents, such as ozone, peroxide, and peracids, to enable recycle of bleach effluents in the liquor cycle. These technologies have reduced the bleach plant effluent considerably.

A new strategy (change of pulping from soda to Organosolv process) of reduction of water consumption and effluent discharge was applied to the pulp and paper mill of Damuji at Cienfuegos, Cuba (Gonzalez et al., 2002). After a careful analysis of the water flows in the mill, and with the help of mathematical optimization through the use of the LINGO software, internal reuse of water was improved for each step of processes. As a result, freshwater consumption decreased by 88% and effluent discharge by 87%. Moreover, fiber recovery was better. Furthermore, on changing from soda to Organosolv pulping to reduce environmental impact, a good-quality paper could be obtained by using 35% of Organosolv pulp and 65% of recycled pulp. Economic analysis shows that the payback time would be 1 year.

Installation of Wash Presses at the End of Brown Stock

See section "Improved Pulp Washing."

Solid Waste Management/Utilization

The general trends in solid waste management/utilization practiced by paper industry internationally are (Monte et al., 2009):

- Landfill
- Incineration
- Land application

Landfill Application

Landfill has been the most common method till the recent past for disposal of sludge etc. (Gavrilescu, 2004; Monte et al., 2009). However, the major factors to be considered when planning for landfill site include

- Environmental suitability of area for landfill
- Geology of the area
- Environmental impact of runoff water from the site
- Impact on ground water
- Composition and volume of the sludge
- Transportation cost

The main disadvantages linked with the landfill are the possible risk of contamination of land and ground water due to which most of the developed countries are banning landfill in near future.

Incineration

The solid wastes rich in organics are incinerated mainly to reduce its volume and ultimate disposal in a feasible way, which is easier and cheaper to landfill. Sludge is mainly burned in fluidized-bed and grate boilers. Burning of sludge is also associated with several limitations such as high capital investment, need of auxiliary fuel due to high moisture content, and emissions of dioxin, NO_x, heavy metals, etc., in addition to other problems such as

- Storage
- Handling
- Low combustion efficiency
- Opaque stack gas
- Sticky ash formation

Briquetting

This is a technique of mass densification that has been successfully developed in India for preparing the binder less briquettes from raw material waste as well as using ETP sludge as binders for briquette making. The advantages of briquetting are

- Good substitute for conventional fuels.
- No sulfur and less ash content.
- Combustion is more uniform and sustained.
- Can be stored for extended periods.

Land Application (Composting)

Two factors, namely, continued decrease in availability of landfill space and increase in energy cost in incineration, have forced the pulp and paper mills internationally to look for the land application of the same as a low-cost disposal method. In composting process, microorganisms break down the organic matter of the sludge under aerobic conditions. It is suitable both for biosludge and for sludge from primary clarifier.

The following methods are practiced for composting of solid waste rich in organics:

- Windrow method (time 3 months)
- Aerated pile method (time 1.5 to 2 months)

The main advantages of composting are

- Increased water-holding capacity and permeability of soil
- Enhanced aggregation
- Reduced surface crusting
- Less capital investment

The compost prepared is used mainly for soil improvement, horticulture, and landscaping of landfill sites.

Sludge Dewaterability

The common feature of all the above-mentioned methods for improved management of biosludge generated in ETP is the requirement of sludge dewatering and needs to be dewatered to achieve high solid content as much as possible so as to facilitate subsequent handling and disposal. In a sludge suspension, water exists in the following forms:

- Free water (can be removed by simply gravity settling)
- Capillary water (can be removed mechanically by filtration and centrifugation)
- Bound and intercellular water (can be removed by drying)

Sludge thickening is usually obtained by sedimentation in a circular tank or clarifier. Mechanical dewatering employs equipments based on filtration, centrifugation, pressing, or combination of these. Presses usually operate at either low or high pressure. Depending on the type of press employed, the final solids content achieved is 25–45%. In recent years, the belt press is the most popular dewatering press used by pulp and paper industry. Chemical treatment by addition of polymers/flocculants is also practiced by some mills to improve the dewaterability of ETP sludge. With the combination of mechanical and chemical methods, the solid contents of the ETP sludge can be increased up to 25–30%.

5.2 SULFITE PULPING

Techniques available for prevention or reduction of emissions/waste both for new and existing installations are given as follows (European Commission, 2001; ICPDR, 2000; PNPPRC, 1993):

- Optimized wood handling
- Dry debarking
- Extended cooking to a low kappa
- Oxygen delignification
- Closed screening
- Efficient washing and process control
- Collection of spills
- TCF bleaching
- Partial closure of the bleach plant
- Pretreatment of wastewater from the oxygen stages in a UF plant followed by aerobic treatment of the total effluent
- Anaerobic pretreatment of the condensate followed by aerobic treatment of the total effluent
- Biological wastewater treatment
- Installation of electrostatic precipitator (ESP) and multistage scrubbers on the recovery boiler
- Reduction of odorous gases
- Emission-optimized recovery boiler by controlling the firing conditions

Because of the similarities between sulfite and kraft pulping, a number of measures for kraft pulping are applicable in most respects for sulfite pulping, too. This is considered to be the case concerning the techniques—optimized wood handling, dry debarking, closed screening, collection of almost all spillages, efficient washing, and process control, installation of low-NO_x technology in auxiliary boilers (bark, coal, oil), ESP for dust reduction in bark boilers, the use of sufficiently large buffer tanks for storage of concentrated or hot liquids from the process, aerobic biological treatment of the effluents, and tertiary treatment by use of chemical precipitation. So, these techniques are not described in this chapter.

There are differences between kraft and sulfite technologies concerning the techniques—extended modified cooking to a low kappa, oxygen delignification, TCF bleaching, partly closing the bleach plant combined with increased evaporation, stripping of most concentrated contaminated condensates and reuse of most condensates in the process, increase in the DS content of black liquor, installation of scrubbers on the recovery boiler, collection of weak gases for incineration in the recovery boiler, and ozone bleaching.

Some techniques of kraft pulping are not valid at all for sulfite pulp mills such as collection and incineration of odorous gases in the limekiln, installation of improved washing of lime mud in recausticizing, ECF bleaching technique, ESP for dust reduction in the limekiln, and incineration of odorous gases in a separate furnace including a scrubber.

Finally, there are a few additional techniques to be mentioned that are only applicable to sulfite pulp mills and are not valid for kraft mills. These are neutralizing of weak liquor before evaporation followed by reuse of most condensates in the process or anaerobic treatment, reduction of SO_2 emissions from the recovery boiler by installing ESPs, and multistage scrubbers.

Extended Cooking to Low-Kappa Pulp

In the manufacturing of conventional unbleached pulp, the lignin is extracted from the wood using a concentrated cooking liquor with magnesium sulfite and magnesium bisulfite as active constituents. In the cooking stage, the wood chips and liquors are charged into a batch digester where the cooking is carried out at elevated temperature and pressure. When a desired residual lignin content is reached, the contents are discharged into a blow tank and the cooking cycle is repeated. The batch digester plant consists of a series of batch pressure vessels, which are operated according to a certain cooking program. Cooking can also be carried out in a continuous digester, but this has been practiced with sulfite pulping much less than with kraft pulping. In the Magnefite process, the delignification of softwood can be brought down to a kappa number of 21–23 to maintain acceptable pulp strength properties. In acid sulfite cooking, common kappa numbers are between 14 and 22 for softwood and 10 and 20 for hardwood. The kappa number can be further decreased before bleaching by an oxygen stage. Two-stage sulfite cooking can bring the kappa number down to less than 10. Cooking can be extended further to produce a specialty pulp for dissolving uses but at the expense of yield. From the digesters, the pulp is blown to blow tanks. From these tanks, the pulp is then pumped to the wash room.

Oxygen Delignification/Bleaching

The difference between delignification and bleaching is that effluents from a bleaching stage cannot be recirculated into the chemical recovery system, whereas from delignification this is possible. Consequently, oxygen can be used as delignification and bleaching chemical in the same mill and increasingly used (Bajpai, 2005). However, there are a number of sulfite mills in Europe using this technique for further delignification, thereby reducing the kappa number by about 10 units. This is mainly because also without oxygen delignification only a short bleaching sequence is necessary to achieve full brightness of pulp. Furthermore, for oxygen delignification, a pressurized process is necessary and a base is needed to increase pH up to alkaline conditions. The chemical base used has to be compatible with the cooking chemicals; that is, for magnesium bisulfite, MgO has to be used. Only in that case, the organic material that is dissolved during oxygen delignification can be recovered and led to the chemical recovery system without major changes in the process. A few mills have applied this technique, thereby losing some points of brightness. It has however been shown to be possible to concentrate the effluent with UF and burn the concentrate in the bark boiler. Measured as COD, the reduction is about 50% of the discharges of organic substances from the oxygen stage. Finally, most sulfite pulp mills are producing TCF pulp.

TCF Bleaching

TCF bleaching is used since the beginning of the 1990s in the sulfite pulp mills in Europe. There is no sulfite pulp mill in Europe that uses chlorine as a bleaching agent. Most of the ECF pulp production is replaced by TCF bleaching. Existing bleach plants were converted by reorganizing and upgrading equipment. Bleaching sequences with chlorine application were converted stepwise to TCF sequences. First, molecular chlorine bleaching steps were dropped and ECF pulp was produced. Then, the processes were converted to TCF bleaching by further developing the process. The use of complexing agents in peroxide stages and the increase of consistency in the bleaching tower made it possible to manufacture high-quality TCF paper pulp. Further prerequisites for TCF bleaching such as extended and even cooking, high-efficient washing processes, and increase of evaporation capacities were implemented. Table 5.13 shows the process conditions of a typical TCF bleaching sequence.

The release of AOX is considerably reduced from formerly 4–8 kg AOX/ADt of chlorine-bleached pulp down to well below 0.1 kg/t. Releases of purgeable organochlorine compounds (POX) to air are reduced from about 20 mg POX/ADt down to zero. The TCF pulp produced does not contain AOX that might be released when it is repulped in paper mills. The demand of freshwater in the bleach plant could be reduced in TCF mills from about 25–35 m^3/ADt down to 10–15 m^3/ADt by increased closure of the water circuits, which results in lower hydraulic loads and in a few cases also in reduced organic loads. TCF bleaching leads to less emission of colored substances with wastewater, and the degradability of the wastewater in the biological treatment plant is enhanced (Nelson, 1998). Moreover, savings of energy

Table 5.13 Process Conditions of a Typical TCF Bleaching Sequence

Process conditions	O/EOP stage	Acid washing	EP/EOP stage(s)
Pulp consistency	10–14	3–5	14–40
Pressure	1–4 bar	–	1–2.5 bar
Temperature	65–75°C	50–70°C	65–80°C
Kappa number	21–24 → 11–13	–	3–5
Oxygen	5–15	–	0–7
Sodium hydroxide	15–25	–	5–15
Hydrogen peroxide	2–10	–	10–25
EDTA	–	0.5–1.5	–

are achieved by TCF bleaching. The steam demand in the bleach plant can be reduced significantly from 0.5–1.0 tonne of steam per tonne of pulp down to 0–0.2 tonne of steam per tonne of pulp. The power demand can be reduced by 20–30%.

The disadvantages are releases of complexing agents if they are applied in bleaching stages that discharge the washing liquids via wastewater treatment plants. But by optimizing the dosage of complexing agents, the amount can be reduced. It has been experienced that the sedimentability of the biosludge in the sedimentation tank can be deteriorated to a certain extent. In some mills, this effect does not occur. Because of possible risks, peroxide should be handled with care. Nowadays, for all qualities of TCF-bleached sulfite pulp, sufficient experience has been gained.

The investment cost of conversion to TCF bleaching and the upgradation of the existing bleach plant amounts to about €20–50 million for a sulfite pulp mill with a daily production capacity of 700 ADt/day. However, these figures depend to a certain extent on the pulp qualities to be achieved. On the other hand, the TCF conversion results in savings concerning operating costs (chemicals, energy). The savings depend on the price of chemicals and energy in the given country.

Partial Closure of the Bleach Plant

PWA Waldhof Manheim pulp and paper mill in Germany has been able to achieve closed cycle by using a single-stage bleaching process—hydrogen peroxide reinforced oxygen delignification with magnesium oxide (Nimmerfroh et al., 1995). The main features of this process are as follows: (1) dissolved organic compounds are returned to the recovery cycle, (2) magnesium oxide is recycled into the process and partly replaces the demand for makeup magnesium oxide, and (3) dissolved lignin and other organics are used to produce combustion energy. Peroxide-reinforced oxygen delignification with MgO offers the following advantages over caustic soda applications: (1) unburdening of the wastewater treatment as the dissolved organic compounds are returned to the recovery cycle, (2) generally lower COD load due to lesser release of hemicellulose, (3) lower COD load per decreased kappa unit, (4) lower costs of the alkali or no costs of the alkali at all, (5) higher pulp yield due to lower loss of hemicellulose, and (6) improved pulp strength as more hemicellulose is retained in the pulp. As a result of using a complete countercurrent 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. With this novel system, the mill was able to decrease significantly the effluent load from the bleaching plant in terms of COD.

Domsjo sulfite mill of MoDo in Sweden modified their sodium-based sulfite pulping and bleaching process to reduce the environmental impact and ultimately close the water cycle by TCF bleaching while maintaining high quality of the pulp (Johansson et al., 1996). The fresh spruce chips are cooked in the batch digesters. The old bleaching sequence C_DEpD 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

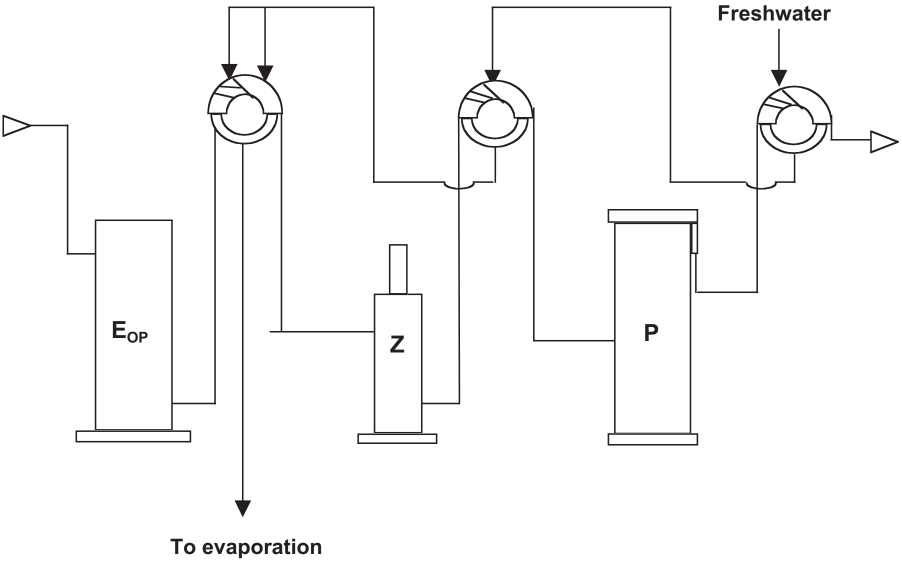

Figure 5.14 A closed-cycle treatment scheme of the Lenzing bleach plant (Krotscheck et al., 1995). Reproduced with permission from Miller Freeman Inc.

in a more even kappa number before the peroxide stage. Also, the wash liquor is deresinated to ensure low resin content both in the pulp and in the system. Bleaching with peroxide would only 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.

Since 1992, the whole production of dissolving pulp at Lenzing AG in Austria has been TCF with a bleaching sequence of $E_{OP}ZP$, following installation of the world's first ozone stage in the bleaching line of sulfite pulp. Most of the effluent from the bleach plant is completely recycled, and the mill has almost achieved the fully closed-cycle mode (Ricketts, 1994). The closed operation setup provides for the desired closure of the bleach plant by replacement of the freshwater used for showers and dilution at the extraction stage washer with ozone stage filtrate, as shown in Fig. 5.14 (Krotscheck et al., 1995).

Pretreatment of Wastewater from the Oxygen Stages in an Ultrafiltration Plant Followed by Aerobic Treatment of the Total Effluent

The wastewater from oxygen stages can be treated in a UF plant. The separated concentrate is burned in the boiler house and the permeate is treated in the external biological treatment plant.

Anaerobic Pretreatment of the Condensate Followed by Aerobic Treatment of the Total Effluent

In sulfite mills, condensates from evaporation of weak liquor contain relatively high concentrations of readily biodegradable organic substances. They can be treated very efficiently in a separate anaerobic treatment. Effluents from the bleach plant (filtrates), other wastewater streams from the mill as washing losses, rinsing waters, leakage, and spillage can then be treated together in an aerobic activated sludge system. All effluents containing particulate matters are first led to presedimentation tanks for mechanical purification and then to the activated sludge plant. Different leaching water (if existing), rainwater runoff, and cooling water may also be led to the activated sludge plant. Fiber sludge from the presedimentation tank and biosludge (surplus sludge) from the activated sludge plant are thickened in separate thickening tanks. Dewatering can take place using screw presses with a preconcentrator. The dewatered sludge is often mixed with bark and burned in the bark boiler. It can be installed in both existing and new mills.

Condensates from evaporation of weak liquor from sulfite mills contain relatively high concentrations of readily biodegradable organic substances. They can be efficiently treated in a separate anaerobic treatment. COD removal efficiencies amount to about 85%. The treatment efficiency for the aerobic treatment of the rest of the wastewaters from the mill achieves about 55–60% COD reduction. Depending on the process-integrated measures before the effluent treatment and the specific layout of delignification and bleaching stages, the final effluent loads of 25–30 kg COD/t can be achieved.

Anaerobic treatment of concentrated wastewater streams generates energy-containing biogas, which can be used as a fuel. Less excess sludge is generated. Aerobic biological treatment as a second stage consumes energy for pumps and aerators. Excess sludge has to be dewatered and further treated, for instance, in suitable bark boilers or fluidized-bed incinerators. This technique is operating in some mills. Several mills have applied this technique (Bajpai, 2000).

Biological Wastewater Treatment

In biological wastewater treatment, microorganisms use dissolved organic material in the water as a source of energy; the biodegradable matter is dissolved and the colloidal material in the water is transformed partly into a solid cell substance and partly into carbon dioxide and water. The biosludge is separated before the water is discharged. The microorganisms need nitrogen and phosphorus for proper growth. In pulp and paper mill effluents, the amount of nutrients is low compared with the amount of organic substances. So, it is necessary to add phosphorus and nitrogen to the wastewater to achieve efficient treatment. It is suggested to assess whether the initial nutrient supply in the wastewater is sufficient. Sometimes wastewater from bleached sulfite pulp mills contain enough phosphorus, and in integrated pulp and paper mills sometimes only very little of additional nitrogen is needed. So, overdosing of nutrients should be avoided by monitoring the concentration of the nutrients in the outlet. The temperature of the wastewater affects the functioning of the microorganisms. The temperature should not exceed 30–35°C in aerobic processes, and cooling can become necessary. The effluent temperature of sulfite pulp mills is normally between 29 and 35°C. Lignin, present in the effluent, is only partially degraded in biological treatment. The remaining lignin fractions give the treated water a brown color.

The process can be applied to both existing and new mills. The efficiency of the treatment varies, depending on the type of effluents treated. Aerobic biological treatment consumes energy. The consumption of electrical energy in activated sludge treatment is in the range of 1.2–2.0 kWh/kg of reduced BOD (aeration and pumping). The sludge generation in activated sludge treatment is in the range of 0.4–0.7 kg DS/kg BOD reduced (Finnish BAT Report, 1997). The fibrous sludge from the primary clarifier is generally incinerated as a substitute raw material in the brick industry. The excess biosludge is dewatered, washed with evaporator condensate, dewatered again, and finally incinerated in the recovery boiler together with thick liquor. In some sulfite pulp mills, the dewatered sludge is burned in the bark boiler.

Aerobic biological treatment such as activated sludge treatment for effluents from sulfite pulp mills has been successfully used for more than two decades. The total investment costs of the whole effluent treatment system including sludge dewatering are reported to amount to about €20 million (referring to an annual production of 45,000 tonnes of pulp and about 80,000 tonnes of fine paper). The costs imply a dimensioning according the maximum load. This results in higher costs but also higher security of the operation. Most of the sulfite pulp mills in the world have applied activated sludge treatment. However, the evaporator condensate is pretreated by anaerobic reactors that are followed by aerobic treatment (Pöyry, 1992).

Installation of ESP and Multistage Scrubbers on the Recovery Boiler

The recovery boiler is a significant source of SO_2 and particulate emissions; other source is the digester where liquor and gas are withdrawn at certain times during the process and the blow tank. The flows of the latter contain between 30 and 70% of the sulfur dioxide charged to the digester. They are usually recovered in tanks with different pressure levels both for economic and environmental reasons. SO_2 releases from washing and screening operations and from vents of the evaporators can be recovered by collecting the gases and introducing them in the recovery boiler as combustion air. The final sulfur dioxide emissions are closely related to the system of recovery of spent cooking liquor. The flue gas from incineration of the concentrated black liquor carries a considerable amount of SO_2 gas, which varies somewhat with sulfidity of the spent liquor from the particular sulfite process used. To control these emissions, proper design and operation of the furnace and auxiliary emission control devices (multistage scrubbers) can be applied. The magnesium bisulfite recovery process demands controlled oxidation conditions to reduce the formation of $MgSO_4$ and SO_3 and temperatures between 1250 and 1400°C to generate a clean ash with maximum reactivity in contact with water. The chemicals used in the cooking plant appear in the flue gas in the form of light MgO ash and the sulfur as SO_2. These two chemicals form fresh cooking liquor when brought together in a counterflow multistage scrubber.

The steps to regenerate the cooking liquor consist of a cleaning of the MgO ash by washing and slaking in water to form $Mg(OH)_2$. The SO_2 is scrubbed with this alkaline solution countercurrently and returning the SO_2-rich solution to the liquor preparation. The measures for SO_2 emission control can be considered as process-integrated technique because the liquids used in the scrubber and the washed off SO_2 are reused in the process. The technique is applicable to both existing and new mills. Factors that influence the possibility of further reduction of sulfur emission are the type of sulfite process—the type of cooking base and pH of cooking liquor—and to a certain extent the size of the mill.

Various types of scrubbers for the recovery of SO_2 are used in all sulfite mills applying recovery of chemicals from the cooking liquor. A small mill (Neusiedler AG) manufacturing bleached sulfite pulp from softwood (87% ISO) is operating a flue gas cleaning system consisting of an ESP and a counterflow three-stage scrubber.

A big Swedish magnesium-based mill (Nymölla) with an annual pulp capacity of 300,000 tonnes reported SO_2 emissions from the process in the range of 1.0–1.5 kg S/ADt. In the recovery system, absorption of SO_2 from flue gases from the recovery boiler takes place in five venturi scrubbers. A system for collection of various vent gases is installed. Vent gases from the cooking, washing, and evaporation departments are collected and introduced in the recovery boiler as combustion air.

Variations of the described SO_2 control systems are applied in all magnesium-based sulfite mills. However, different reduction efficiencies for SO_2 removal are reported. The recovery of SO_2 from incineration of spent liquor is inherent for the preparation of cooking liquor and carried out for both economic and environmental reasons. However, better performing systems are usually implemented for further reduction of the acidification potential of SO_2. Better performing systems are characterized by an additional scrubber stage for SO_2 absorption and collection systems for vent gases from the cooking, washing, and evaporation departments.

Reduction of Odorous Gases

See section "Emissions to the Atmosphere" in Chapter 4.

5.3 MECHANICAL AND CHEMIMECHANICAL PULPING

Techniques for prevention or reduction of emissions from mechanical and chemimechanical pulping are shown as follows (European Commission, 2001; Salo, 1999):

- Emission control from the wood yard
- Dry debarking

- Minimization of reject losses
- Minimization of disposal of rejects
- Efficient washing and process control
- Water recirculation in pulp and paper mills
- CTMP mill effluent treatment closing up the water circuits by the use of evaporation and burning the concentrates
- Installation of cogeneration of heat and power
- Heat recovery from refiners
- Abatement of VOC emissions from steam releases
- Emission-optimized incineration of solid waste and energy recovery
- Use of sufficiently large buffer tanks for storage of concentrated or hot liquids
- Biological wastewater treatment
- Tertiary wastewater treatment

No information is available on heat recovery from refiners and abatement of VOC emissions from steam releases.

Emission Control from the Wood Yard

Wood for mechanical pulping needs to be kept fresh so that it does not dry. Often, the wood logs are sprinkled with water to avoid drying out.

Dry Debarking

See Section 5.1

Minimization of Reject Losses

Methods available for separation of contaminants from the pulp are centricleaners and pressure screens equipped (with holes or slots). In centricleaners, particles heavier than fibers are separated, and in pressure screens, oversized material is separated. The rejects from centricleaners and pressure screens also contain a large amount of fiber material, which is recovered by adding several screens or centricleaners in series. With this type of arrangement, it is possible to save substantial amount of raw material and the suspended solids load to the effluent treatment is also reduced.

The screening process in mechanical pulping has another purpose than in chemical pulping, where the reject can be withdrawn from the fiber line. Basically, the idea is to separate the material and return it to the main fiber line after proper treatment. The reject treatment is mill-specific and many solutions are possible. The screening and cleaning systems are often based on cascading principles. Compared to the feed forward systems, these systems are less controllable. The pulp is cleaned and screened with pressure screens and centricleaners. Screening is carried out at a concentration of 1.3% or higher with holes having diameter of 1–2 mm or slots of 0.15–0.35 mm width. The operation at 3% accepts consistency, results in reduced shive content of 60% in some cases compared to conventional low-consistency screening. Centricleaners are often used as supplement to screens. The rejected material is different from the screening reject, being stiff particles with small specific surface. The main disadvantage with centricleaners is the low pulp consistency (0.5–0.7%). This corresponds to water volumes of 150–200 m^3/ADt, which is quite high. But most of this water can be recirculated and used for other purposes in the pulp mill.

The screened and cleaned rejects are usually refined in one to two stages between rotating refining plates before returning to the main fiber line. The initial breakup of the coarse fiber bundles in the refiner takes place in the breaker bar zone, where the oversized material is turned into single fibers. The fibers pass into a thin gap by the centrifugal forces and are intensively treated at high pulp consistency of 30–45%. The reject amount can be in the range of 20–30% and the energy consumption about 10–40% of the overall specific energy demand in the mechanical pulping. If efficient reject recovery and recycling are required, thermomechanical pulp (TMP) lines can be designed, for example, 20% reject refining calculated from the capacity of the fiber line. The final screening and cleaning rejects that cannot be returned to the fiber line are discharged from the process as solid wastes or incinerated in a boiler. An important issue is how the rejects from a screen are brought back to the main fiber line. In cascade coupling after separation, the rejects are recycled to a point ahead of the withdrawal (countercurrently). This produces a high volume of circulating waters, particularly in systems with high reject flows. The risk of high shive content in the accept flow is reduced with cascade coupling.

Addition of cleaning stages and reject refining can be applied in existing and new mills. This method results in reduction of fiber losses and decrease of waste generation by some percentage. Reject refining increases power consumption. The steam from a reject refiner is normally not recovered. On the other hand, rejects have already passed the very energy-intensive first refining stage so that, in total, energy will be saved when reducing the reject losses. Therefore, the net energy balance of this measure is positive. Residues from the process are decreased.

Investment costs of 700 ADt/day pulp capacity are typically €0.8–1.1 million and operating costs €0.3–0.5 million/annum. This measure is adopted to increase raw material and energy efficiency. Also, TSS load to the ETP that is usually recovered in the sedimentation tank is reduced (CEPI, 1997).

Minimization of Disposal of Rejects to Landfill

Rejects and sludge are dewatered before further treatment or final disposal. Dewatering is done by the use of wire presses or screw presses. Different types of equipment—belt presses (twin-wire presses), screw presses, and decanter centrifuges—are available. In most of the new installations, belt presses have been used, which produce high DS values, 40–50% with fiber sludge and 25–40% with mixed fiber/

biological/(chemical) sludge. Screw presses are used to increase the DS content after belt-press dewatering, when approximately 10% DS increase can be obtained. These presses can also be used for direct dewatering when higher DS content can be obtained compared to belt-press dewatering. After de-watering, the sludge and rejects can be incinerated for further reducing the amount of wastes from mechanical pulping to landfill disposal. Alternatives are incineration together with bark in bark boilers, separate sludge incineration. For co-combustion, particularly of rather low DS sludges, the fluidized-bed boiler is best for new installations. This can be run with 100% sludge, although the use of a support fuel is more common. The requirement of the support fuel depends on the DS and the ash content of the sludge. Generally, at least 35–40% DS is required for spontaneous combustion. Separate sludge incineration with moving-grate stoker equipment has also been successfully utilized.

The incineration in bark boilers has been used in a number of mills. The grate-type bark boilers can be converted to fluidized-bed ones, but huge investment is required. Separate incinerators are also used, but they consume lots of support fuel and standard sludge incinerators do not have a heat recovery part, which means that no steam or electrical power can be produced. As far as sludge dewatering is concerned, all types of presses have been used with good results. An increasing application of screw presses has been observed for some years due to an increasing interest in sludge incineration, requiring high DS values, but also involving additional investment costs.

Depending on the reject handling concept, the wastes from rejects can be reduced significantly. Usually, there are only ashes from incinerators that can be either landfilled or used for other purposes. With incineration in bark boilers, the energy content exceeding the evaporation of water in rejects can be recovered. In sludge dewatering, water emissions are increased through the dewatering of the sludge, which usually are led to the activated sludge system. They have to be considered when planning the effluent treatment. Energy generation is related to DS content of the dewatered sludge if the sludge is incinerated.

These processes have been used for several years in modern mills. Incineration in bark boilers is more common than in separate incinerators due to the poor heat economy of the latter alternative. Investment costs of a new sludge and reject incinerator are about €5–7 million and operating costs €0.5–0.6 million/annum, corresponding a pulp production of 700 ADt/day. Grate-fired boiler retrofit to a fluidized-bed boiler would cost approximately €10–15 million, and operating costs would be €0.3–0.4 million/annum.

This measure is adopted to reduce wastes to be disposed to landfill (Pöyry, 1992, 1997).

Efficient Washing and Process Control

This technique is pertinent for CTMP pulping. The washing process in CTMP pulping is comparable to washing in chemical pulping, but the efficiency requirements are generally less demanding. The objective is to separate the organic material dissolved in refining from fibers. The washing is often mill-specific, and many alternative solutions are possible for the type of washing equipment etc. In comparison to the chemical pulp, washing of CTMP is somewhat more difficult and it requires more capacity of the washing equipment. In practice, this means more surface area with drum washers of washing presses per tonne of pulp. The washing efficiency is usually 65–70% calculated from the recovered organic material. This typically corresponds to one washing stage, which can be carried out with drum washers, twin-wire presses, or screw presses. With improved washing, it is possible to increase the washing efficiency to 75–80% by installing more washing equipment in series. The washing equipment is usually the same as the equipment of the first washing stage.

It would be possible to concentrate the organic material in the same volume of effluents with improved washing and reduce the carryover to the paper or board machine. This may be an advantage if the effluents are further treated separately from the paper or board effluents, for example, in an anaerobic treatment. The improved washing is only used in a few integrated mills in the world.

Investment costs are typically €3–5 million at new mills and €2–3 million at existing pulp mills of 700 ADt/day (CEPI, 1997; Pöyry, 1997).

Water Recirculation in Pulp and Paper Mills

Water recirculation within the pulping process is very much dependent on the suitability of a specific water fraction for reuse and the contaminants that are allowed to accumulate in the process. There must be bleed-out points for sewering and disposal of contaminants at an effluent treatment in any case. In nonintegrated mills, normal water makeup is done with freshwater, and in integrated mills, paper machine white water covers most of the process water need. In the mechanical pulping process, the recycle streams are various filtrates, pressates, or similar from chip or pulp handling and cloudy or clear white water generated by fiber save-all equipment. These streams are fed to specific uses according to their availability and suitability. Many factors affect the degree of water recycling in the pulping. Considering the accumulation of undesirable compounds into the streams, these are generated by wood or chip pretreatment, refining, and bleaching and some is brought in integrated mills with the countercurrent flow of paper machine white water. In the process points where dissolved materials are formed, there must also be dilution to effectively carry away the undesirable compounds from the wood material or pulp. Otherwise, they are carried to the succeeding process stages with adverse effects. Additionally, in recycling and discharging of waters, a trade-off may be necessary to reach an economical balance. Discharging water from the pulping process by sewering more clear, instead of cloudy white water, provides better capture of fiber material in the pulp, but also retains more resinous compounds, which are not desired. The proper selection of water reuse is complicated by the color of process water, pH, dissolved and suspended solids content, including also residuals of used pulping chemicals that can cause unwanted chemical reactions or even increased pulping chemical consumption. Items forming the basis of water use reduction and recycling in pulping are use of countercurrent water flow principle, where feasible; improved fiber recovery by sewering clean instead of cloudy white water and in integrated mills by excess white-water input from the paper mill; rebalancing of tank volumes, especially white-water volumes for coping with process, fluctuations, start-ups and shutdowns; high-consistency thickening of pulp prior to feed to drying (or paper machine), which is effective both for nonintegrated and integrated mills, though for slightly different reasons; clear white-water usage in equipment cleaning showers and if acceptable, as flushing water.

In the papermaking process, freshwater is introduced mainly through the paper machine forming section and press-section showers, and then, it is fed upstream to various washing and diluting processes. Water loops are clearly separated by thickening steps and then stock is diluted with some freshwater to adjust consistency and to dilute the stock with clean water before it enters the approach system (Edelmann et al., 1997).

Enhanced water recirculation can be applied in new and existing mills. Assessment of the suitability of specific stream(s) for a specific reuse must be carried out to avoid adverse effect on the process itself and the product. Existing mills may need rebalancing their filtrate, white water, and pulp tank capacities, to keep freshwater makeup and effluent bleed-out to a minimum.

Because the water temperature in the pulping rises along the degree of water loop closure, in existing mills, problems may evolve in pulp bleaching and the performance of supporting equipment such as centrifugal pumps. So, energy balance evaluation is necessary. With efficient closure, in integrated mills, the countercurrent reuse of paper machine white water, the effluent discharge, and fiber losses to sewer are reduced. The degree of water reduction depends on the paper/board grade. Online monitoring of combined pulp mill effluent flow rate and laboratory monitoring of suspended and dissolved solids, pH, temperature, and organic content as BOD5 or COD are recommended. Also, online suspended solids or turbidity meter can be used. More dissolved or colloidal matter can be retained with pulp as a result of efficient water reuse in pulping. This must be compensated in the paper machine to avoid, for instance, an increase in machine breaks, changes in wet-end paper web retention, or sheet drainage.

Because most of the mechanical pulp mills are integrated with paper production, the measure to improve water reuse is typically linked to water use reduction in both pulping and papermaking.

The investment costs of an integrated mill, with 700 ADt/annum production and aiming at reduction of freshwater consumption from 20 to 10 m^3, are about €10–12 million. Reduction of effluent hydraulic and suspended solids load is the key component to promote the implementation. More concentrated wastewater can be treated more effectively and needs less investment and operating costs. Several modern mills apply efficient water recirculation around the world. There are also many old mills that have carried out the listed measures more selectively (CEPI, 1997; Edelmann et al., 1997).

Treatment of CTMP Mill Effluent

Wastewater from CTMP plants are treated using the following techniques:

- *Activated sludge treatment:* This method is found to be very effective. BOD reduction of 98% and COD reduction of 85% are easily achieved with this method. The disadvantage of this method is the fairly high concentrations of nutrients in the effluent. So, some CTMP plants complete the treatment with an additional chemical treatment.
- *Internal chemical treatment of white water plus activated sludge treatment of the rest:* In some CTMP plants, white water is treated with a chemical. This reduces COD by 40–50% and removes extractives and fines in a following flotation stage. A drawback of this method is the fairly high chemical costs.
- *Combination of an anaerobic and aerobic treatment of the wastewater:* This technique is used by only a few plants. Anaerobic treatment is very sensitive to disturbances, so it is not used more commonly.
- *Evaporation of the most contaminated wastewater and burning of the waste plus activated sludge treatment of the rest:* A new evaporator, the Zedivap evaporator, has been developed for evaporation of wastewater. This is an emerging technique. This technique is most suitable in such a case when the pulp capacity has to be increased and the biological treatment plant is becoming too small. The condensate from such an evaporation plant can be used in the CTMP plant as process water lowering the freshwater consumption considerably. Evaporation is also an alternative if tertiary treatment is regarded as necessary.
- *Evaporation of the whole effluents and incineration of the concentrates in a recovery boiler:* This results in zero discharge of liquid effluents. Several mills have been attempting to achieve complete closure by treating the effluent streams by different techniques. So far, only a few have succeeded in zero-effluent discharge: two Canadian bleached chemithermomechanical pulp (BCTMP) mills—Miller Western at Meadow Lake, Saskatchewan (Ricketts, 1994; Young, 1994a), and Louisiana-Pacific at Chetwynd, British Columbia (Young, 1994b). They have been designed for zero-effluent operation. The mills utilize different schemes for effluent treatment and reuse. The combined mill effluent is treated by conventional gravity filtration followed by mechanical vapor recompression (MVR), evaporation, and steam-driven concentration. After evaporation of the effluent, the distillate from the evaporation comes back to the distillate equalization pond, where bioactivity destroys the small fraction of low-molecular-weight volatile organics left in the water storage reservoir, where it is stored until it reenters the mill for reuse in the process. A portion (more than 60%) of the distillate goes directly back to the pulp mill as hot process water at 65°C. The total hot distillate flow to the pulp mill is used as wash water on the back end of the mill with full countercurrent flow through to the front end. The mill can run for 20 days from the clean water inventory

> in the water storage reservoir. This process has been in operation since February 1992. A net loss of water exists primarily because of evaporation from the ponds, plus a cooling tower and a heat recovery stack. Makeup water is brought in at an average rate of about 2 m^3/t pulp.

The Chetwynd mill has played a pioneering role in closed-mill technology on freeze crystallization, first coming online in June 1991 (Young, 1994b). Although it worked, it was not deemed sufficiently reliable due to some problems hampering the crystallization process, especially the formation of ice layers in the crystallizer tubes reducing heat transfer to zero and plugging the tubes. Therefore, in March 1993, the system was shut down and the crystallizer was converted to an MVR evaporator similar to the Miller Western Pulp Mill at Meadow Lake. The revised system came online in July 1993. The evaporation produces clear, hot product water for mill use. The condensed steam is sent to the distillate equalization pond for aeration and bacterial treatment. The pond has a capacity of 4 million gallons, with a retention time of 11 days. Water from the clean water pond is further clarified before returning to the mill. Natural evaporation from the distillate equalization pond is the primary source of the mill's water loss. Makeup water from the wells is about 1 m^3/t of pulp.

In fact, there are nine mills in Canada producing market high-yield pulps using mainly BCTMP from hardwoods and spruce. Their combined production is approximately 2.2 million t/year. The water usage is typically low, and two of the mills—Chetwynd, BC, and Meadow Lake, SK, Canada—are operated as zero-effluent (closed-cycle) mills. Most of the seven other BCTMP mills have very low water use compared to kraft or newsprint processes. The closed-cycle operations use large evaporators and polishing ponds to allow recycling of process waters (Paice, 2007). For the mills that discharge effluent, the effluent properties represent a challenge for biotreatment, especially the high concentrations of extractives and COD. A number of different methods have been used to generate effluent quality that meets regulations for BOD, suspended solids, and acute toxicity. These methods include activated sludge treatment, anaerobic treatment, and, more recently, biofilm-activated sludge.

Closing the CTMP plant is possible for both new and existing mills. Limitation is high capital cost of evaporation and possible recovery plant (as in Meadow Lake). The described concept was built for a greenfield mill and needs a lot of space, which existing mills often do not have. The solution will depend on local conditions and is often different for market CTMP mills compared to integrated CTMP manufacturing. When using evaporators, the bleaching of CTMP has to be modified. For instance, no sodium silicates can be used because of scaling. When using evaporators, the bleaching of CTMP has to be modified.

The water recycle system causes no losses in pulp production and has no negative impact on pulp quality. The system has operating costs competitive with conventional bleached CTMP water and secondary effluent treatment systems. After the optimization period, the effluent treatment operating costs at Meadow Lake are now below the cost of conventional secondary treatment. However, high investment costs of oversized evaporation and liberal sizing of the recovery plant and storage capacity for effluents (for 3 days) arose at the start-up phase. The attractiveness of the zero-liquid discharge approach is augmented by potential chemical and energy recovery that can be used to reduce cost of production and amortize capital costs. Marketing a zero-liquid discharge pulp to environmentally conscious consumers has certain advantages (Evans, 1991, 1992; Evans et al., 1993; Fromson and Wootton, 1993; Sweet et al., 1993; Ward et al., 1993).

Emission-Optimized Incineration of Solid Waste and Energy Recovery

Different type of solid wastes is generated in mechanical pulp mills, which must be disposed of. These wastes are bark, wood residues, pulp waste sludge, and screening rejects. The bark is readily used as fuel in the mill auxiliary boiler, but sludges have been landfilled. These sludge wastes can also be incinerated, but incineration is an expensive process. In incineration, it is necessary to apply environment-friendly techniques to minimize particulate, SO_2, and NO_x emissions. Because sludges represent waste that has often a lower heat value than true solid fuels, such as bark or wood, their incineration in a boiler designated solely for sludge is rare. In practice, mills that use bark, wood, peat, or coal as fuel for steam and power generation obtain cost-efficiency by burning the pulping and paper sludges in the same boiler with solid fuels of high heat value. This is also emphasized by the fact that sludges, unless at over 50% consistency and low in ash, would require, in any case, support fuel to dispose them properly by burning.

The environment-friendly technology most suitable for pulp sludge and reject incineration is the same than for wood, bark, and peat. However, certain specific features in preparation of sludge or burning can differ. The boilers are used to provide steam to be used directly as process steam for heating and drying, but in an increasing number of cases also for electric power production. However, when the boiler is small and its main purpose is to dispose sludge with a minimum amount of support fuel, the boiler cannot economically produce anything else but low-pressure steam for heating in the process or buildings. In the incineration of pulp and paper mill sludges, the environmental ends can be met by application of proper boiler and a series of fuel pretreatments. In paper and reject sludge incineration, both conventional and fluidized-bed boilers can be used. The fluidized-bed technology is more versatile with its better flexibility, higher efficiency, and low emissions. The heating value of bark from wet debarking or peat at 40–60% moisture is 4.5–10.5 MJ/kg. In contrast, the mechanically dewatered pulp sludges have a lower heat value, amounting to 2.5–6.0 MJ/kg due to their often higher moisture and ash content. The heat value of dry pulp waste can reach over 20 MJ/kg. The higher the humidity of the fuel, the lower the overall economy of the boiler and also more difficult is the operability unless efficient technology is applied. A fluidized-bed boiler is less sensitive to fuel humidity than a grate-fired boiler. Because some paper sludges often reach 20–30% ash content, and at worst with de-inking waste 60%, operational problems such as grate plugging due to ash are very likely in grate-fired boilers. High amounts of ash may also cause deterioration of fluidized-bed system efficiency, but in much lesser amount.

The major difference between grate firing and fluidized-bed technology is in the heat transfer method. In the fluidized-bed boilers, the main heat transfer method is by conduction, which by the aid of a fluidized sand bed inside the boiler, stabilizes the system's heat capacity and makes it less sensitive to fuel humidity and heating value fluctuations. In grate firing, the fuel particles are heated mainly by radiation. This makes the combustion temperature and burning time very important, and the system performance can easily drop when fuel humidity increases. Variations in sludge dryness at the grate-fired boiler entrance cause problems to maintain efficient burning because of temperature drops. The burning in a fluidized-bed boiler takes place at a lower temperature, typically in the 750–950°C range, than required in grate firing. This is beneficial in reduction of gaseous emissions. In addition, the heat transfer per unit area is a little higher with fluidized-bed systems. There are two main types of fluidized-bed systems: bubbling and circulating fluidized-bed boilers. In bubbling fluidized-bed boilers, the sand bed inside the boiler is fluidized and kept in the lower part of the boiler, except for a small part escaping the bed. This escaped fraction and possible semi-burned fuel is recovered in a cyclone and returned to the bed. In circulating fluidized-bed boilers, the sand bed extends up beyond the first heat exchange part, and then, the sand is separated from the flue gases in a large cyclone and returned to the bottom of the bed. On the efficiency point of view, both fluidized-bed technologies are good. However, if the fuel is high in coal content, the circulating bed type is better in preventing excessive concentration of heat, generated by coal burning in the bed.

The sludge heat value and the overall burning results can be improved by applying improved dewatering such as screw press. The aimed dryness target should be 45%, when ash content is below 30%, otherwise, higher and reaching, for instance, 65–70% at 50% ash content. When the amount of sludge is high, the proportionate amount of all the fuels over 30% shredding of sludge followed by palletizing or briquetting can be economical in increasing its bulk density sufficiently to render combustion easier. The sludge and other solid fuels can be fed alternately or in addition through a preheating treatment. Indirect drying utilizes low- or medium-pressure steam, generated at the mill, which at best could still be used elsewhere as lower pressure steam. The direct drying method uses the flue gases as a heat source.

The improvement of the overall combustion is case-specific. It can be achieved by adding efficient fuel pre-demoisturization for certain solid fuels, by mechanical dewatering of the combustion materials, or by drying them with heat. In general, when the fuel initial moisture has been in 45–50% range, a 10–15% improvement in heat economy has been recorded by increasing the dryness to 55–60%. Necessarily, the higher the fuel moisture entering the boiler, the higher is the flue gas flow.

The emissions from fluidized-bed boilers can better meet stringent demands than the grate-fired boilers. The fluidized-bed systems provide *in situ* SO_2 and NO_x emission control in addition to being simpler and more effective than the grate-fired ones. For SO_2 control, the boiler ash already contains some calcium that binds sulfur present in the fuel. Additional SO_2 reduction is obtained by lime injection to the boiler, by providing calcium/sulfur ratio in the range of 1–3. A high-calcium surplus provides up to 80–95% sulfur removal to boiler ash, being higher with circulating fluidized-bed boilers. Optimum sulfur capture takes place at about 850°C burning temperature. The drawback of lime injection is the increased ash amount.

In grate-fired boilers, there is no efficient internal means of controlling SO_2 emissions. External sulfur and SO_2 removal methods can also be applied. Wet or semiwet methods, which both apply alkaline washing liquid to bind sulfur, or dry methods are available. Dry methods are less efficient than enhanced control of fluidized-bed burning, lime injection into the boiler, or the external wet methods. The lower NO_x emission of fluidized-bed boilers is first of all because of lower burning temperature involved. Low-NO_x burners can obtain further decrease of NO_x. Some trade-off between SO_2 and NO_x reduction may be necessary because the NO_x emissions tend to rise; the higher is the calcium surplus in the boiler after lime injection. Additionally, the minimum NO_x formation in burning takes place at about 960°C, when the optimum SO_2 removal with lime injection is reached at lower temperatures. CO and hydrocarbon emissions are kept negligible by avoiding running the boiler at overload and maintaining oxygen excess in burning. The boiler particulate emissions are controlled efficiently by an ESP.

The implementation of fluidized-bed boilers for burning of wood residues or solids disposal can be applied both in existing and new mills. The controllability of the burning process and the allowance in terms of the solid fuel used and its quality variations are superior to that of grate-fired boilers. Improvements in grate-fired boilers coupled with upgrading of heat recovery and external flue gas cleaning can improve their economic and environmental performance, but not to the level of fluidized-bed systems. When major portion of the boiler fuel is sludge, the net heat economy is low. In mills where also other solid fuels are used for steam or electricity production, a better process efficiency is obtained by burning the sludge as minority fuel with them.

Emissions from modern fluidized-bed boilers burning pulping and reject sludge with support fuels can be efficiently controlled and optimized. Emission monitoring with online gaseous compound meters is increasing in popularity because of their improved reliability and lower cost as they become more common. Multipoint temperature and oxygen monitoring of the boiler are also beneficial. Reduction of wastes may increase the emissions to the atmosphere. Fluidized-bed boilers have been used with success for the last two decades and with the current designs have proved to possess many benefits over the grate-fired boilers. The modification of an existing bark boiler for sludge and reject incineration costs €0.5–0.7 million at a 700 ADt/day integrated mill, provided that the boiler has already extra capacity to burn these wastes.

The additional operating cost of the residue incineration is €250,000–350,000/annum (Finnish BAT Report, 1997; Paper and Timber, 1993; Pöyry, 1997). A separate sludge and reject boiler for a mill of the same size costs €5–7 million.

Use of Large Buffer Tanks for Storage of Concentrated or Hot Liquids from the Process

The use of large buffer tanks for storage of hot liquids in groundwood (GW) or TMP production is not pertinent in most cases because these pulps are produced almost solely in integrated mills. Much of the process water used in these pulping processes is received as excess white water from a paper or board machine. GW and TMP water consumption is low in comparison to papermaking, so there is commonly continuous bleed-out of excess contaminated water to the sewer. CTMP production has a slightly different situation because most of the mills are nonintegrated and produce market pulp. As with other mechanical pulping, different white-water grades are produced and recycled inside the pulping process. In integrated mills, the paper or board machine excess white water is fed as replenishment to the CTMP water system; in nonintegrated mills, freshwater is consumed. When bleaching is applied, water recycle by using bleaching filtrate, for instance, in chip impregnation improves water reuse. Excess contaminated water is sewered from chip wash and as excess white water or sometimes also from intermediate washing in pulp refining.

In CTMP pulping as opposed with chemical pulping, there are less chances of finding points of cost-effective overflow or spill recovery of process waters or reasons for very large water storage tanks. By the implementation, the typical countercurrent water flow principle to reach a low-freshwater consumption, the balance still needs to sewered. Nevertheless, the process tank capacities need to have sufficient volume to supply water during flow peaks, especially in pulp dilution and washing. These occur mainly when a pulping line is started up, during short-term fluctuations in the balance between pulp and paper production, or, for instance, when unbleached pulping is shut down but bleaching is still in operation.

The CTMP effluent is more contaminated than GW and TMP effluents due to chemical chip treatment. This calls for more careful tank-level management to minimize peak loads entering the external effluent treatment. The conversion of the electric energy in TMP and CTMP refining to energy in steam decreases the accumulation of heat to the water in the pulping system. In mills where steam is efficiently used for water heating or pulp or paper drying, the need for occasional steam blowout could be decreased. The evaluation and optimization of necessary tank volumes can be carried out both in existing and new mills. For existing mills, operating data from different production situations help in determining proper tank management procedures and need for tank volume increase. The environmental impacts are typically low, but the runnability of the external treatment plant is improved with decreased frequency of spill discharges. Level probes for key water chests are required especially for overflow control. By the improved mill closure, the control of contaminated and warm or hot streams into the sewers has become more pronounced.

The investment costs are very case-specific. When estimating a need of 2000 m^3 of extra water or stock volume and some additional tank, piping, electrification, and instrumentation, the additional investment costs are €100,000–250,000. The operating costs are low, comprising mainly of maintenance (CEPI, 1997).

Biological Treatment—Aerobic Methods

Two-stage activated sludge process is mostly used for the treatment of wastewater from mechanical pulp mills. In some mills, pure oxygen is used in the first stage, followed by a "normally" aerated second stage, whereas some mills use a high-load first stage, followed by a lower-load second aeration tank. Effluent from mechanical pulp mills can also be efficiently treated anaerobically because the COD concentrations in wastewater are often above 2000 mg COD/L. However, in most cases pulp and paper mill effluents are treated with aerobic methods, with the exception of CTMP or other concentrated effluent streams for which anaerobic treatment has sometimes been applied.

For the activated sludge process, a large number of different processes and plant designs exist. One special process design is the pure oxygen-activated sludge, where pure oxygen or oxygen-enriched air is used instead of regular air. Advantages of the activated sludge process are the potential of high or very high treatment efficiencies, the possibilities to control the process, particularly the oxygen consumption and the relatively low space demand. Disadvantages are the high production of biological waste sludge and the high operating costs. An equalization basin prior to the biological treatment can reduce disturbances and the risk of operational instability.

The process can be applied in both existing and new mechanical pulp and paper mills. In the existing mills, some kind of water consumption reduction measures should preferably be carried out to reduce the investment costs. The activated sludge process is often used, when high or very high treatment efficiencies are required. Activated sludge plants are used widely in the pulp and paper industry. As a rough estimate, the activated sludge process is used in 60–75% of all the biological ETPs in this industry. This is also the most common process used in recently built plants.

Treatment efficiencies are variable, depending on the effluent type, plant design, and operating conditions. Typical values are within the ranges of 90–98% of BOD removal (normally >95%) and 75–90% of COD removal. The overall efficiency of TSS removal of primary and secondary treatment is about 85–90%. The ETP produces sludge that after dewatering can be burned, providing in some cases net positive heat value. The treated wastewater is clean enough for reuse in some points of the production process. The problem is that usually the wastewater treatment plant is located so far from the mill that recycling is not economical.

Activated sludge plants have been used for many years in all types of and new mechanical pulp (and paper) mills with good results. The investment costs of a completely new activated sludge treatment plant are approximately €10–12 million for a new 700 ADt/day integrated mechanical pulp mill. These costs also include the necessary primary treatment and sludge handling. The corresponding operating costs are €0.9–1.2 million/annum (CEPI, 1997; Finnish BAT Report, 1997; SEPA Report 4713-2, 1997b).

Tertiary Treatment of Wastewater

Refer to Section 5.5.

5.4 RECYCLED PAPER PROCESSING

Techniques available for prevention or reduction of emissions/waste for new and existing recycled paper processing mills are presented as follows (European Commission, 2001; Salo, 1999; Suhr, 2000):

- Separation of less contaminated water from contaminated one and recycling
- Optimal water management (water loop arrangement) and water clarification
- Reduction of freshwater consumption by strict separation of water loops
- Closed water loop with in-line biological process water treatment
- Anaerobic techniques as the first stage of biological wastewater treatment
- Aerobic biological wastewater treatment
- Upgradation of stock preparation plants with reduced energy consumption and emissions
- Generation of clarified water for de-inking plants
- Cogeneration of heat and power
- Reject and sludge handling and processing
- Utilization and disposal of residue by environmentally sound techniques

Separation of Less Contaminated Water from Contaminated One and Recycling

The main principles for internal measures to reduce freshwater consumption and discharges from recycled paper mills are as follows:

1. Use of appropriate techniques to separate less contaminated water from contaminated process water. Measures to be considered are the separation and reuse of cooling water and the reuse of less contaminated sealing and process waters used in vacuum systems.
2. Reduction of freshwater consumption by recycling of white water in different positions depending on the water qualities required. Positions in the process of special interest when reducing freshwater consumption are dilution of fiber raw materials and fillers, dilution of process and product aids, the shower water system, the vacuum system, and sealing water for pumps and agitators.

3. Reduction of freshwater consumption by strict separation of water loops together with countercurrent flows.
4. Generation of clarified water from white water as a substitute for freshwater, usually made in the fiber recovery unit by use of bow-screens, polydisk filters, or dissolved air flotation (DAF).
5. Measures to handle the possible negative effects of the increased recycling of process water.
6. In some cases the further purification of clarified white water is applied. This purified water meets relatively high-quality requirements.

Ways of reducing freshwater consumption are separation of clean cooling waters from process effluents and their reuse for other purposes. For protection, a microscreen or other strainer is recommended to remove solids. Where cooling water fractions are sewered, it should be avoided to mix them to contaminated process water sewers to ensure wastewater treatment efficiency and reduce treatment costs. The most common equipment for vacuum generation, the liquid ring pump, consumes sealing and process water at a rate of about 1 L/min per installed kilowatt. The installed power for a vacuum system in a big newsprint machine may be as high as 3000 kW. This would result in a sealing and process water consumption of about 7 m^3/t for the newsprint machine. The sealing water will be contaminated with fibers, and the temperature will rise when it passes the liquid ring pump. The need for freshwater as sealing and process water of the liquid ring pumps can be reduced very much by recycling the water from the pumps through heat exchanger or cooling tower. Sometimes the process water for the ring pump must be clarified by use of a bow-screen before it enters the heat exchanger. It can also be necessary to control the pH value in a recirculation loop. Increase of the capacity of the process water storage may be needed to avoid unnecessary overflows of recycled water when there is a break or other imbalance situation in the processing of pulp. The increase of capacity usually implies installation of additional tanks, pipes, and pumps.

The separation and reuse of clean cooling waters and water from vacuum systems and sealing waters can be realized in existing and new mills. Separation and reuse of clean cooling waters from process effluents are relatively easy to carry out in new mills but difficult to implement in existing plants. However, cooling water separation and recycle after cooling are common. The same is valid for the recirculation of sealing waters. The measure has a significant effect on reduction of freshwater requirement and wastewater discharge. In existing mills freshwater use reduction of 10–15 m^3/ADt of cooling waters can be achieved. Separation of used cooling water from contaminated paper machine effluents can reduce the hydraulic loading to the external effluent treatment. By appropriate sealing water recirculation, it is possible to reduce the freshwater consumption for liquid ring pumps to less than 1 m^3/t. At the same time, it is possible to recover part of the energy if heat exchangers are used.

Separation and recycling of less contaminated water from contaminated are common practice in many mills in the world, but the degree of water recirculation varies. There are no important effects to environment. Some energy savings are possible.

Recycling of cooling and sealing waters requires typically additional investments in piping, pumping, and filtration of the water. The increase of the water storage capacity usually implies installation of additional tanks.

Freshwater reduction by recirculation of less contaminated water is a reasonable measure from an economic point of view. Discharge of less contaminated cooling and sealing water fractions together with contaminated process water are discouraged in many countries (CEPI, 1997; Pöyry, 1994).

Optimal Water Management and Water Clarification

Process water is reused in today's water loop systems. The main principle of the reuse of process water is the backward process water flow in the systems, countercurrent to the fiber flow. All paper mills use untreated, fiber-enriched white water from the paper machine for stock dilution in the mixing chest ahead of the paper machine or in the stock preparation. Part of the white water is clarified in save-alls using filtration, flotation, or sedimentation. The clarified water is then reused for the replacement of freshwater at the showers used for cleaning machine clothing. Excess clarified process water is discharged to the wastewater treatment plant. In some cases purified wastewater is partly reused as process water.

A minimized freshwater consumption in the production of Wellenstoff and Testliner in the range of 4–7 m^3 freshwater/tonne of paper produced is achievable. In Europe, a few mills are even operating with a totally closed water system. The freshwater consumption in these mills ranges from 1.0 to 1.5 m^3/t paper produced. This corresponds to the volume of the water, which is evaporated in the drier section of the paper machine. In many paper mills, freshwater is only used for the dilution of chemical additives and at locations of the paper machine where a highly, solid-free water quality is necessary. However, closing up the process water system offers both advantages and disadvantages. Enhanced water system closure leads to a considerable loading of the process water with colloidal and dissolved organic and inorganic compounds, which may cause serious problems in the production process if no control measures to avoid possible drawbacks are undertaken. Some of the benefits and drawbacks of water system closure are (Dutch Notes on BAT, 1996) as follows:

Benefits

- Reduced water consumption
- Reduced ground water withdrawal
- Reduced freshwater pretreatment
- Reduced wastewater discharge
- Production increase not hampered by end-of-pipe treatment
- Decreased fiber and filler losses
- Elevated process temperature, which results in improved dewatering of the paper web on the wire
- Reduced energy demand

Drawbacks

- Buildup of suspended solids
- Buildup of organic and inorganic substances
- More complicated processes
- Corrosion problems
- Increasing use of additives
- Clogging of equipment
- Product quality-related problems
- Scaling and slime forming
- Rise of temperature of the process water

In totally closed water systems, additional serious problems may occur, which need to be controlled. These are (1) significant decrease of the oxygen content of the process water approaching anaerobic conditions associated with a microbiological-induced reduction of sulfate to hydrogen sulfide and the formation of odorous low-molecular fatty acids; (2) intensified growth of microorganisms; (3) aggressive corrosion caused by high temperature and high contents of chlorides, sulfates, and organic acids; (4) significant emission of odorous organic compounds from the drier section of the paper machine to the surrounding of the paper mill; (5) impaired quality of the paper produced, affected by odorous compounds; (6) higher demand of slimicides.

Most of these problems occur at freshwater consumption levels below 4–7 m^3/t of paper. To control these problems, some mills manufacturing “brown papers” reopened their already closed water circuit and are now producing with a small volume of wastewater in the range of 2.5–5.0 m^3/t paper produced.

A few mills in Europe, because of local environmental requirements, applied new methods in the middle of the 1990s to control the demanding conditions of their closed process water loops. They installed in-line treatment plants to reduce the organic load of the process water. To control all problems described when closing up water systems and to fulfill paper quality requirements, a freshwater consumption of 4–7 m^3/t paper produced is often regarded as necessary. This corresponds to a specific wastewater volume of 2.5–5.5 m^3/t paper produced. The wastewater can be treated very efficiently in combined anaerobic/aerobic or aerobic treatment plants due to its suitable BOD5/COD ratio. In recycled fiber-based newsprint (de-inked grade), the lowest wastewater volumes reported are down to about 7 m^3/t and are normally in the range of 10–15 m^3/t.

For “brown” packaging paper, freshwater reduction to a level of 4–7 m^3/t paper produced can be realized both in existing and new mills. However, it seems that this level can be reached at low expense only in rather new or recently upgraded mills. In older mills still having a higher freshwater consumption, the reduction may cause corrosion problems, depending on the quality of materials used for machines and pipes. Additionally, existing wastewater treatment plants have to be optimized.

Water system closure generates less wastewater but with an increased level of organic contamination in the water circuits. As a result, the treatability of the wastewater can be improved. For Testliner and Wellenstoff, reducing freshwater consumption to a level of 4–7 m^3/t paper produced increases the COD of the process water on a concentration range that is suitable for an anaerobic wastewater treatment associated with the benefit of biogas generation. In de-inking plants, the degree of water system closure is limited due to the paper properties to be achieved. Wastewater flow down to about 10 m^3/t is achievable. The wastewater is usually treated by aerobic systems.

Monitoring devices are flow meters for freshwater feed on the paper machine and turbidity measurements for clear white water. Intensified process water reuse increases the temperature of the process water. Therefore, steam consumption for heating up the process water can be reduced. A freshwater consumption of 4–7 m^3/t paper produced reduces the risk of odorous emissions via the exhaust air of the paper machine. The applicability of anaerobic wastewater treatment methods results in a reduction of fossil fuel demand for papermaking.

The production of Wellenstoff and Testliner with a specific freshwater consumption of 4–7 m^3/t paper produced is common. Experiences show that this range of freshwater consumption does not result in negative effects on the runnability of paper machines and on paper quality. The experiences are good even in existing mills, and current paper machine design supports well their application. A number of full-scale plants manufacturing corrugating medium with good product qualities are operating.

Reducing freshwater consumption decreases the costs of freshwater purification and wastewater treatment. The measures applied depend on the specific conditions in paper mills. Closing up the water system is a prerequisite for efficient wastewater treatment. Driving forces for implementing measures to reduce freshwater consumption are saving freshwater costs (in some countries), saving costs of wastewater purification, saving costs of wastewater duties, and local environmental conditions.

In European countries numerous mills are operating, with freshwater consumption reduced to the described level (Dutch Notes on BAT, 1996; Göttsching et al., 1998; Mönnigmann and Schwarz, 1996).

Reduction of Freshwater Consumption by Separation of Water Loops

In the recycling of process water in integrated pulp and paper mills, the white-water flow from paper mills to pulp mills should be taken countercurrent to the product flow. In the case of an integrated pulp and paper mill, the pulp department, the bleaching department, and the paper mill have each its own white-water circulation, from which the excess water goes backward to the previous department where water quality is less demanding. The excess white water from the paper machine is used instead of freshwater in the bleaching department, and the excess water from the bleaching department is used instead of freshwater in the pulp mill. With this type of arrangement, substantial amounts of freshwater can be saved. Freshwater is mainly only needed as makeup into the paper machine system. However, in a tissue mill sometimes a lot of freshwater is required for efficient washing of machine felts.

It is of great importance to reduce the white water from going in the same direction as the product flow, that is, from the bleaching plant to the paper machine. This is done by subtracting as much water as possible from the fiber flow before it enters the bleaching system and again before it enters the paper machine system. In this way, the carryover of process disturbing compounds to relatively clean process water systems is reduced. The separation of the water loops is carried out with thickeners such as dewatering screws and wire presses or a washing stage, that is, a thickening step. The extra thickener leads to an improved separation of the "dirty" stock preparation and the "clean" paper machine and thus to significant reduction of organic substances that enter the paper machine loop. This process-integrated measure can be applied to both new and existing plants.

The main achieved environmental performance is reduction of freshwater consumption, possible reduction in the discharge load of COD, and no increase in concentration in the paper machine water loop, thus enhancing the runnability of the process. The reduction rate depends mainly on the situation before the improvements and the wastewater system applied afterward. Strict separation of water loops generates good opportunities for in-line treatment, in order to remove disturbing substances.

Measures for reduction of emissions to surface water are often closely related to reduction of freshwater. Water system closure does not reduce the pollution load but generates less wastewater with increased contamination levels. As a result, the efficiency of the wastewater treatment can be improved. Less wastewater has to be purified, and in general concentrated wastewater flows can be treated more effectively. By recirculation of process waters and increasing of storage capacity, the wastewater amounts can be reduced but not in the same extent as by collecting and separating of clean, warm cooling waters.

Advantages of reduced freshwater consumption and water loop closure are

1. Lower volumes to external effluent treatment; that is, the treatment plant can be built with smaller hydraulic capacities and lower investment costs. Contaminants are more concentrated in the effluent that often contributes to higher removal effectiveness.
2. Lower costs of raw water.
3. Lower losses of fibers and fillers.
4. Lower energy consumption.
5. Higher temperatures in the process water systems result in faster dewatering on the paper machine wire.

The need for freshwater in a modern recovered paper preparation plant can be reduced to approximately 1 m^3/t. Consequently, only about 10% of the total freshwater demand in a modern integrated newsprint mill based on recycled fibers ($\approx$10 m^3/t) is consumed in the recovered paper preparation plant. However, in a tissue mill sometimes a lot of freshwater is required for efficient paper machine felt washing. In recycled fiber-based mills without de-inking, no freshwater is needed in the stock preparation.

The separation of water loops by insertion of thickeners leads to considerable change in the composition of the paper machine water loop with respect to the levels of organic and inorganic substances. This will lead to a changed additive regime in the wet end that, in turn, will have its effect on the COD levels. In certain applications, the insertion of an extra water loop may drop the temperature in the paper machine loop, for example, when the paper machine loop is separated from the disperger and refiner that act as a heating device for process water.

The main principle, white water flowing backward in the system, countercurrent to the product, can only be applied in integrated pulp and paper/board mills. Recovered paper plants are, with very few exceptions, integrated with a paper mill. In stock preparation, the cleanness of the process water is less critical than of the white water of the paper machine. Therefore, the stock preparation utilizes to a very large extent excess clarified white water from the paper mill and internally clarified white water. But potential drawbacks of water system closure need to be controlled. Otherwise, the buildup of suspended solids as well as dissolved organic and inorganic substances in the white-water system may cause negative effects.

The costs of this measure depend on the number and nature of water circuit rearrangements necessary and the type of additional installation needed. The driving force for recycling process water is to decrease the wastewater load from integrated recycled fiber-based mills (CEPI, 1997; Pöyry, 1994; Senhorst et al., 1997).

Closed-Cycle Operation

Paperboard and roofing felt mills using recycled fiber as furnish are good candidates for zero-discharge operation because typically they do not have extensive treatment facilities already in place and their product quality standards are less demanding than for many other paper products. With closed-cycle operation, water leaves the process via drier evaporation, with wet solid wastes such as from the rejects handling system, and as moisture in the paper product. To achieve zero-discharge operation, less water must be added to the process on a continuous basis than that required to make up losses from the paper machine driers. To maintain the overall balance, zero-discharge mills have segregated rainwater, cooling water, and noncontact pump seal water. These streams are not part of the water balance, and the allowable freshwater makeup can be used for more critical applications. On an average, slightly over 1 m^3/t freshwater makeup to process is required to compensate for losses, mainly due to evaporation in the driers. This implies that larger production mills have a greater freshwater makeup requirement with zero-discharge operation. Some of the critical applications that must remain on freshwater, such as trim squirts and felt cleaning showers, are not directly related to production level, so it is easy for larger production mills to achieve zero discharge. Stuart and Lagace (1996) have reviewed typical process modifications required to implement zero-discharge operation at paperboard mills. The process equipment items used to achieve zero-discharge operation are not sophisticated and generally include primary treatment, adequate water storage, stainless steel metallurgy, and often a segregated cooling water system. Chemical programs must consistently achieve high first-pass retention of fines, clays, size, and colloidal contaminants such as pitch. Recycled water must replace freshwater for most applications, including gland water and paper machine shower water. In a typical effluent treatment installation for a closed-cycle paperboard mill, the loop is composed first of suspended solids removal by a primary clarifier, DAF unit, or screening equipment. Often, the sludge recovered in this treatment stage can be returned to the pulper to be incorporated into the board product. Clarified effluent is sent to a large storage tank, which is sized to hold the mill. Finally, recovered water is passed over sidehill screens to protect downstream equipment from clarifier upsets. Screened water is then used throughout the mill to replace freshwater. Most effluent treatment facilities at existing zero-discharge mills can be divided into three main categories:

1. Mills that invested in facilities able to remove suspended solids effectively and achieve lean white-water qualities under 200 mg/L suspended solids.
2. Mills that have small or nonexistent primary treatment facilities, whose TSSs in the recycled water are often above 1500 mg/L and can be as high as 5000 mg/L. Mills in this category typically have problems such as plugged showers.
3. Mills that have biological treatment facilities.

Several recycled paperboard mills have already implemented the closed white-water systems. Green Bay Packaging Inc. implemented a closed-cycle system in the 1970s using reverse osmosis as the method for purging inorganic matter. However, the mill is now operating in a closed-cycle mode without reverse osmosis or any other expensive technology (Young, 1994c). The mill has achieved system closure primarily by extensively replacing freshwater with process water and proper selection of chemical additives. The Haltown Paperboard Company mill has used a similar approach for mill system closure (Anonymous, 1993). In cases where high degrees of system closure were achieved, corrosion and bacterial growth in the paper machine area were observed. Several mills are attempting to achieve complete closure by treating the effluent stream biologically and reusing the treated effluent as the freshwater source.

Habets et al. (1997) have described a biological treatment concept that has been in operation in a German zero-discharge paper mill since September 1995. This mill is producing 400 t/day of corrugated medium and Testliner from water furnish and is being expanded to 1000 t/day. The biological treatment plant consists of an anaerobic and an aerobic stage. After the anaerobic process, where most of the COD is removed, the water is polished in an aerobic plant to remove residual BOD, sulfides, and precipitated $CaCO_3$. The methane gas produced is scrubbed to remove the H_2S and is used for steam generation in a boiler. The more detailed schematic of the plant (Fig. 5.15) shows the indirect cooling facility to bring the water temperature down from 55 to 35°C. A buffer/pre-acid tank is used for preconditioning the water with nutrients before feeding it into the upflow anaerobic sludge blanket (UASB) reactors of 720 and 1250 m^3 in volume, respectively. The aerobic polishing is done in two parallel carousel-type aeration tanks, each with a volume of 900 m^3. In this way, 28 t/day of incoming COD is reduced to 1.0 t/day of soluble COD and 1.0 t/day of solids. The sludge solids produced during the aerobic polishing are added to the stock preparation to be recovered in the product. The total investment for the in-line

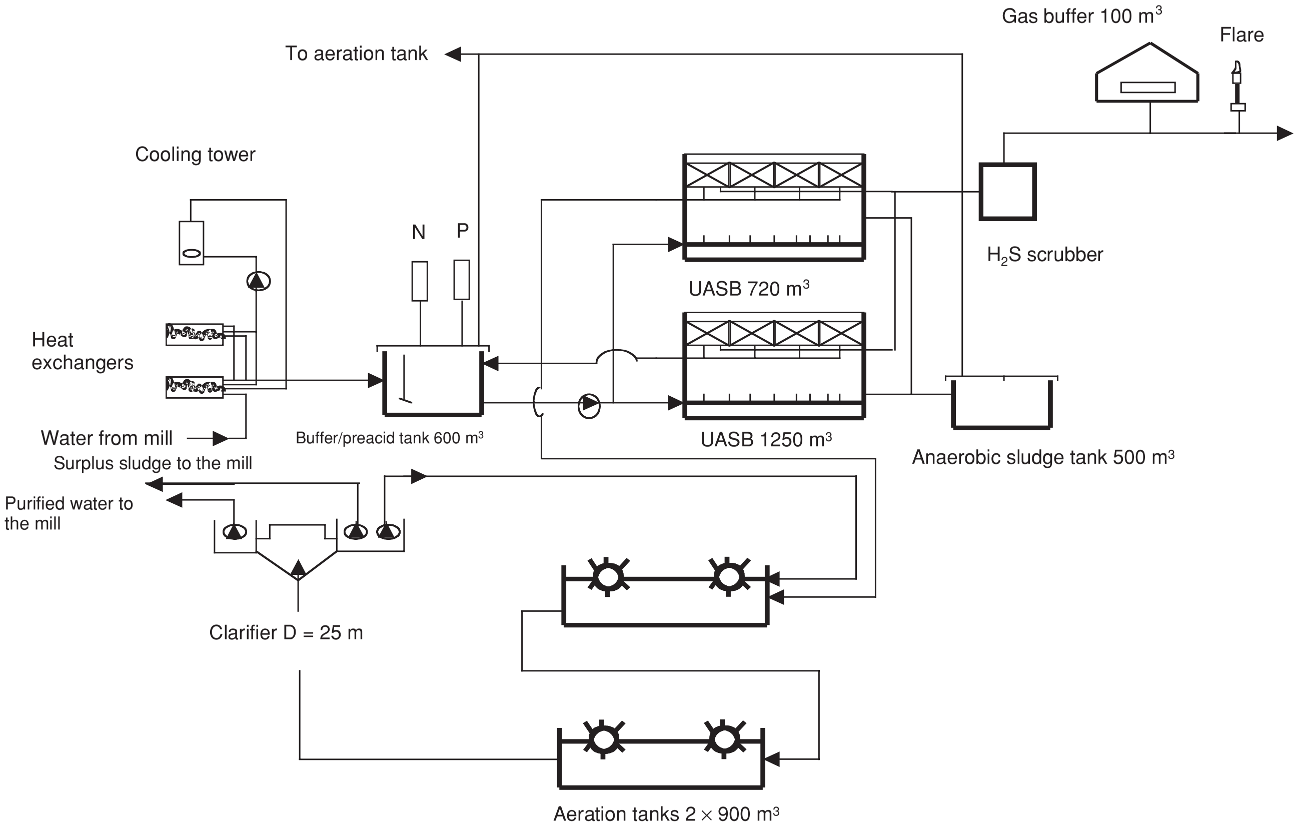

Figure 5.15 An in-line treatment plant (Habets et al., 1997). Reproduced with permission from PAPTAC, Canada.

biological plant was about 5% of the total investment for the new machine. Part of the in-line biological treatment plant was started up in September 1995 for treating the process water of the existing machine. The new machine was started in October 1996. Within a few weeks of the start, the process water quality had changed drastically. The levels of COD, sulfate, and calcium were reduced by 80, 60, and 80%, respectively. The pH of the process water increased from 6.5 to about 7.5, which allowed the use of papermaking chemicals that are more effective at higher pH levels. Volatile fatty acid levels in the product have been reduced to a much lower level than usually found in similar mills with an open circuit.

St-Laurent Paperboard Inc., a corrugated medium mill, situated at Matane, QC, Canada, has successfully undertaken and attained zero process effluent discharge (Rousseau and Doiron, 1996). The process effluent flow was steadily decreased from 6000 m^3/day to zero in October 1995. The mill now meets all present and future environmental regulations. Chemical dosages and injection points are being optimized. Although the chemical dosages have increased, the incremental costs are only a fraction of what it could cost to operate a secondary treatment plant. Furthermore, zero effluent has resulted in an old corrugated container yield increase from 85% to 92%, related to the higher overall retention of fines/clay into the paper. The reuse of process water has also resulted in energy savings of about 5%.

Based on two surveys conducted to characterize manufacturing conditions and water use practices at zero-discharge paperboard mills (Barton et al., 1995), the following conclusions were drawn:

1. Considerable white-water surge capacity is needed for zero-discharge operation, especially where white lined or colored grades are manufactured.
2. All but one of the mills visited by NCASI maintain zero discharge by providing either no external treatment or external treatment in the form of gravity clarification only. Only one of the mills used biological treatment.
3. Operational difficulties, which may be encountered due to closure of the mill water cycle, include (a) fogging in the machine area; (b) wet-end chemistry changes; (c) reduced felt efficiency; (d) reduced vacuum pump efficiency; (e) development of slime holes or other imperfections in the sheet; and (f) odor, either in the sheet or emanating from external treatment process.

Furthermore, accelerated corrosion rates associated with zero discharge dictate the need for stainless steel process equipment and piping. Zero-discharge implementation was shown to have a negative impact on the efficiency of a wet-end retention aid program (Lagace et al., 1997).

Strategies were developed to reduce freshwater consumption in a mill for de-inking old newspaper. Excess white water from a neighboring paper mill was reused. Impact on pulp quality and loss of fine fiber after closing circuits were determined through simulation (Savu et al., 2001). The de-inking mill comprises an alkaline and an acid loop in sequence with a daily capacity of 150 tonnes of de-inked pulp. Closure strategies were developed from either the original procedure or a completely open procedure. Distribution of fines, fibers, total dissolved solids, ashes, and some ions for each strategy in permanent use was determined by simulation. Varying degrees of closure, up to complete closure, were studied and strategies were evaluated for feasibility. Different options are suggested, but consideration must be given to possible increased consumption of chemical products, and feasibility of use. A reduction of 86% in freshwater consumption is achievable. Effluents are more concentrated.

The catalase enzyme produced during the metabolism of aerobic organisms catalyzes the breakdown of hydrogen peroxide was implicated in the early problems associated with hydrogen peroxide bleaching in the pulp and paper industry, particularly with de-inking processes (Lenon et al., 2000). Significant improvements have been introduced to control catalase production in de-inking plants, notably the increase of peroxide introduction, the thermal treatment of the pulp or process waters, and the addition of specific chemicals to deactivate or inhibit catalase. Specific treatments proved to be successful in controlling catalase generation include catalase deactivation with sodium azide, 3-amino-1,2,3-triazole, treatment with sodium hypochlorite, glutaraldehyde, increased rate of peroxide introduction, treatment with chlorine and hypochlorite, treatment with chlorine dioxide, treatment with biocides, treatment with peracetic acid, and thermal treatments. Centre Technique du Papier, France, has conducted a study over 2 years devoted to catalase-related problems in de-inking plants.

Durango-McKinley Paper, a 220,000 t/year producer of linerboard based in McKinley County, NM, USA, in the middle of the New Mexico desert, and serving the Los Angeles region, received a national environmental performance award from the US EPA in 2005 as a recognition of its environmentally friendly completely closed water cycle (Aukia, 2005). This mill lacks both the water resources necessary to sustain a standard mill process and the waterways to discharge water into—all the water used in the plant has to be treated and reused. In the closed system, process water is treated to avoid accumulation of impurities and chemicals. Water from various processes is fed to the reclamation process in separate streams according to the level of contamination. A pretreatment stage removes dirt, fiber, and other solids, which are recovered and sold for soil improvement. Further treatment stages comprise DAF, microfiltration, and reverse osmosis. Water lost by evaporation is replaced by water purchased from the nearby Tri-State power plant, from where the mill also obtains steam. For the manufacture of its linerboard, Durango-McKinley uses 100% recycled board and old corrugated containers supplied from various sources in New Mexico. The processes in the mill must be operated more carefully than in the case of an ordinary system, as the paper machine and the water treatment plant are interdependent of each other. As a result, the company strives to use as little additives as possible, employing a biocide program from Kemira. A pulsed biocide dosage is used to deal with variations in microbial contamination in the raw material.

Wastewater Treatment by Anaerobic Technique

The closure of water circuits in paper mills processing recycled paper causes high concentrations of dissolved organic substances in the process water. Therefore, before being released into receiving waters, the process waters have to be purified by biological treatment. With the combination of anaerobic and aerobic biological treatment, a significant reduction of the organic load of the wastewater can be achieved.

UASB reactor, contact reactor, fixed-bed reactor, and fluidized-bed reactor can be used as anaerobic reactors. The main purpose of the different reactor concepts is to ensure a high concentration of biomass within the reactors. This is achieved either by recycling washed-out biomass after settling in an external separator (contact reactor system) or by attaching the biomass to a supporting media within the reactor (fixed-bed reactor, fluidized-bed reactor, UASB reactor). The reactors can be operated as single units or as modular combined units. Reactor systems, which are operating with biomass supporting media, are especially suitable for high COD loads. Biogas, mainly a mixture of methane and carbon dioxide, which is produced by the anaerobic degradation of process water pollutants, can be used as an energy source after desulfurization. Compared to aerobic wastewater treatment, much less biomass is produced during the anaerobic degradation process. However, anaerobic-treated wastewater does not comply with requirements for the final COD and BOD concentration of the treated effluent. Therefore, anaerobic treatment is normally not used as a stand-alone treatment. The effluents of anaerobic systems are always posttreated by an aerobic biological stage.

For an economic application of anaerobic techniques as a first stage of biological wastewater treatment, the COD load of the process water should not be less than 2000 mg/L. Paper mills producing brown grades at a low level of freshwater consumption are easily reaching this level. Paper mills manufacturing de-inked grades can also reach this level before any treatment. Nevertheless, examples of anaerobic/aerobic wastewater treatment for de-inked grades are very few. The anaerobic degradation process could be disturbed by dissolved sulfate, when the concentration exceeds 1000 mg/L, because during the anaerobic process sulfate is transformed into hydrogen sulfide (H_2S), which is toxic to anaerobic microorganisms. Normally, a toxic level will not be reached.

When an anaerobic stage is added before aerobic treatment in an existing plant, the necessary capacity of aerobic treatment facilities can be reduced. In principle, there are no problems to expand an already existing aerobic treatment plant by an anaerobic pretreatment stage when the process water composition, the COD load, and the sulfate content are suitable for anaerobic treatment. The retrofitting of an anaerobic pretreatment stage is a convenient measure when the aerobic stage has reached its maximum capacity and is probably overloaded.

Combined anaerobic/aerobic wastewater treatment plants must first of all be regarded as end-of-pipe techniques. However, considering the efforts to control the application of chemical additives (e.g., cleaning agents, defoamers, and slimicides) to the papermaking system to protect the sensitive anaerobic microorganisms in the treatment plant, the biological treatment can also be (partly) regarded as a process-integrated environmental protection measure. Some paper mills are performing trials to recycle a part stream of the biologically treated process water back into the water circuit. The main problems they still have to face are the accumulation of chlorides, sulfates, and calcium in the process water, causing corrosion and calcium carbonate precipitation and scaling on pipes, wires, and felts. The precipitation of calcium carbonate is a complex problem, which needs further research work in the future.

Treatment efficiencies in anaerobic reactors depend on plant design and operating conditions. Typical efficiencies are within the range of 60–85% for COD removal and 85–95% for BOD removal. The total efficiency of combinations of anaerobic and aerobic techniques is in the range of 95–97% for COD removal and 99.0–99.8% for BOD removal. The organic load in the effluent is reduced to 0.5–1.5 kg COD/t paper produced and to 0.02–0.1 kg BOD/t paper produced, respectively. A 100% recycled fiber-based German paper mill (without de-inking) reported an improvement in treatment efficiency by use of combined anaerobic/aerobic treatment compared to a two-stage aerobic treatment. As yearly average values, the following values have been achieved.

In combined anaerobic/aerobic treatment plants, the energy demand related to 1-tonne COD removed (mainly used for pumping and aeration) is about 200–300 kWh, whereas in stand-alone and well-designed aerobic plants, the energy demand for 1-tonne COD removed amounts to 500–600 kWh. The volume of biogas produced during anaerobic degradation ranges from 400 to 600 m^3/t COD removed. The methane content varies in the range of 65–75%. Because the calorific value of methane is 35.7 MJ/m^3, the energy resulting from the thermal utilization of biogas in a cogeneration of heat and power (CHP) plant is in the range of 1900–2900 kWh/t COD removed, assuming an efficiency of the power plant of 75%. Energetic utilization of biogas not only covers the total energy demand of the anaerobic/aerobic treatment plant, a part of the produced energy ($\sim$70–80%) can be used for the paper production process.

The main parameter used to control the performance of anaerobic and aerobic wastewater treatment techniques is the COD, which is analyzed mostly on a daily basis. For anaerobic systems, the biogas production rate, continuously measured by a gas meter, is another important control parameter, as well as the continuous measurement of CO_2, CH_4, and H_2S contents of biogas.

Anaerobic pretreatment contributes to a significant reduction of the excess sludge production. Compared to stand-alone aerobic treatment of wastewater, in a combined anaerobic/aerobic treatment plant, the biomass production is reduced by 70–80%. External depositing of the sludge can be avoided by returning the excess sludge into the paper production process. However, returning excess sludge into the paper is only applicable in specific cases. The proportion of sludge on the raw material input is less than 1%. After desulfurization, the produced biogas can be used as fuel in in-mill power plants, substituting fossil fuels.

Combined anaerobic/aerobic treatment plants have been operated since 1990/91 (Bajpai, 2000). Compared to stand-alone aerobic treatment plants, they have proved themselves to be more stable systems with respect to changing COD loads and toxic or inhibiting substances in the process water. The availability of the plants is close to 100%. Suspended solids in concentrations above 200 mg/L could cause problems in anaerobic systems, especially in fixed-bed reactors. In some UASB reactors a slow disintegration of the biomass pellets was observed. In this case, the biomass can be replaced by new pellets from other UASB reactors to keep the reactor in effective operation. The anaerobic pretreatment considerably reduces the tendency for developing bulky sludge in the following aerobic stage. Excess sludge produced in the aerobic stage can be recycled to the paper production process without causing any problem.

The investment costs of combined anaerobic/aerobic wastewater treatment plants vary in a wide range depending on the specific COD load and the volume of wastewater. Assuming COD loads of 20–35 t/day, which correspond to an annual production of Wellenstoff and Testliner of 200,000–350,000 tonnes, the investment costs are in the range of €7–12 million. Taking into account the net energy savings by use of the produced biogas as fuel, the annual operating costs including chemicals and operating materials, waste disposal, staff, and maintenance are in the range of €0.6–1.0/t paper produced.

The most important reason to install combined anaerobic/aerobic systems for the biological treatment of process water was the improved stability with regard to fluctuations of COD loading compared to a stand-alone aerobic treatment plant. Another incentive was the production of biogas and its use as fuel in power plants. Energetic use of biogas not only covers the energy demand of the anaerobic/aerobic treatment plant, there is an energy surplus, which can be used in the production process. Finally, the considerably smaller volume of excess sludge produced is to be considered. By using combined anaerobic/aerobic techniques, instead of a one-stage or two-stage aerobic technique, the sludge production is reduced by 70–80%. This fact is of special interest for paper mills that do not have their own facilities for energetic utilization of excess sludge and do not recycle sludge into the production process, and therefore have to provide for expensive external disposal.

Numerous anaerobic plants are operated as the first stage of wastewater treatment in European paper mills producing Testliner and Wellenstoff (Göttsching et al., 1998; Hamm et al., 1991; Koepp-Bank, 1991).

Aerobic Biological Treatment

This technique has been used for the treatment of effluents from recycled paper mills for over three decades to remove oxygen-consuming organic substances and specific organic compounds. These substances are converted into biomass, carbon dioxide, and water by different variants of biological treatment systems. Low-load aerobic-activated sludge systems are widely used. The nutrient content in wastewater of recycled paper mills is generally low. So, to ensure efficient operation of the biological system, phosphorus- and nitrogen-controlled addition is necessary. To control eutrophication problems, overdosing of nutrients and unnecessary emissions of nutrients should be prevented. It is applicable to both new and existing mills. Removal efficiency is in the range of 95–99% for BOD5 and 75–90% for COD. Table 5.14 shows effluent properties by low-rate activated sludge treatment.

Removal efficiencies by use of combined anaerobic/aerobic biological treatment are usually slightly higher. The overall treatment efficiency is over 99% for BOD5 removal and over 95% for COD removal. But up to now, the application of anaerobic treatment is mainly limited to recovered paper mills without de-inking. In the Netherlands, the wastewater of three recycled fiber processing paper mills is treated

Table 5.14 Effluent Properties by Low-Rate Activated Sludge Treatment

BOD5 after treatment			COD after treatment			TSS		
mg/L	kg/t	Typical removal efficiency (%)	mg/L	kg/t	Typical removal efficiency (%)	mg/L	kg/t	Typical removal efficiency (%)
<20 (down to 5)	0.21	95–99	<230	2.3	80–85	<30	0.2	99

Based on data from Dutch Notes on BAT (1996).
Discharge volume $-11\ m^3/t$.

simultaneously by an anaerobic/aerobic treatment system. One of these mills is a de-inking plant. However, there are some promising trials on laboratory scale to apply combined anaerobic/aerobic biological treatment to de-inking plants, too. Recycling of a part of the water after biological treatment seems to be possible. At least one newsprint mill using 100% recovered paper as raw materials is using about 10% of the treated effluent (activated sludge and sand filter) in the paper mill without any problem.

Usually, the main effluent parameters are measured daily or at least a few times a week. Additional measurements to control the activated sludge system are necessary, for example, O_2 content, sludge volume index), water flow, and analyses of the biomass. During aerobic wastewater treatment, excess sludge is produced, which has to be thickened, dewatered, and further treated. A typical value for activated sludge plants is in the range of 0.6 kg excess sludge/kg BOD5 eliminated (as DS), generated during treatment. Thus, depending on the quality of recovered paper and on the process design, about 10 kg excess sludge from biological treatment per tonne of paper (on a dry basis) may be expected. For aeration of the active biomass (activated sludge) and for pumps, electrical energy is needed. The specific consumption of energy for degradation/elimination of 1 kg BOD5 amounts to 0.6–3 kWh/kg BOD5 eliminated. If the system is well designed, a value of less than 1 kWh/kg BOD5 eliminated can be achieved (Möbius, 1997). This value can also be used to compare expected operating costs of different wastewater systems.

Especially during the summer period, the wastewater treatment plant of recycled fiber paper mills may emit annoying odors. If the wastewater treatment is well designed and controlled, annoying odors can be avoided. Aerobic biological treatment for effluents from recovered paper mills has been successfully used for over 20 years (Bajpai, 2000). The phenomenon of bulking sludge has to be controlled.

Data on costs are only available for an integrated paper mill manufacturing paper based on mechanical pulp. The wastewater treatment system is comparable to the one applied for the treatment of effluent from recycled fiber processing. Therefore, the figures on costs can give a rough picture in which range the cost might be expected. The investment costs of a completely new activated sludge treatment plant are approximately €13.0–15.5 million for a new 1000 ADt/day integrated mechanical pulp and paper mill. These costs also include the necessary primary treatment and sludge handling. The corresponding operating costs are €1.2–1.5 million/annum.

Numerous aerobic wastewater treatment plants are operated in European paper mills producing paper based on de-inked recovered fibers (CEPI, 1997; Dutch Notes on BAT, 1996; Möbius, 1997).

Upgradation of Stock Preparation Plants with Reduced Electricity Consumption and Emissions

This applies mainly for recycled paper mills without de-inking, for example, paper mills producing case-making material (Testliner, Wellenstoff). However, the basic principles are applicable for all recycled paper processing mills. De-inking mills might have additional options in the de-inking process units.

There might be different goals for upgrading of stock preparation plant concepts. They depend on the priorities set by a given company such as better removal of smaller impurities and contaminants to improve product quality and efficiency of the paper machine, enhanced recovery of fibers from rejects, thus reducing the fiber losses, or energy savings. Another aim can be simplification of the stock preparation system, resulting in less energy consumption, less material losses, and less space needed. To simplify the stock preparation, especially for brown grades, the possibilities for removal of energy consuming dispersion and traditional cleaning stages are discussed. In contrast, extended process concepts with a higher number of process stages might be used to manufacture paper for special purposes or to meet the customer's needs (high-quality products).

The processing of recycled paper targets first of all the removal of nonfiber components, for example, plastics, metal, wood, sand, and the elimination of detrimental substances such as stickies, wax, or small pieces of undisintegrated paper (flakes) of wet-strength paper. The second goal of pulp processing is the treatment of the fibers themselves to control the quality of the paper to be produced. To achieve this aim, fibers can be fractionated into long-fiber and short-fiber fractions and further treated. For example, low-intensity refining improves the bonding ability of the recycled fibers, resulting in increased strength characteristics of the paper produced, and disperging improves the optical homogeneity of the paper.

For each specific treatment of recycled pulp, special machines are used in various ways. Thus, the screening and cleaning processes must operate in two to four stages to reduce the fiber losses in the final stage of each process. To realize an adequate runnability of the paper machine, it is also essential to operate additional cleaners and screens in the stock approach flow system. This prevents that deposits released from chest walls or from pipes enter the head box and the wet end of the paper machine. These deposits would lead to web breaks and downtime of the machine. A balance between cleanliness of stock, fiber losses, energy requirements, and costs has to be found and are to certain extent depending on the paper quality produced.

Rebuilds of stock preparation plants as well as of the stock approach flow system can be usually realized in existing mills. A "standard" stock preparation plant typically uses more machines than are required for this "minimized" stock preparation plant system. To adapt a "standard" system to a "minimized" concept, the shutdown of only a part of the equipment is necessary and probably some new pipes and pumps for the connection to the machine chest are required. The stock approach flow system has to be extended. Existing screens from the stock approach flow system or from the stock preparation plant are usually not sufficient, due to the limited capacity when screen baskets with a narrow slot width of 0.15 mm are installed. Therefore, investments of advanced pressurized screens for the approach flow system would be necessary.

The electricity demand for stock preparation and stock approach flow system is between 20% and 40% of the total power demand of a recycled paper processing mill without de-inking. Therefore, optimization of the stock preparation plant with respect to savings of electricity is worth considering. Reduced electricity consumption results in reduced airborne emissions, which depend further on the type of fossil fuel used.

Paper machines running with increased efficiency have lower electricity and steam demands per tonne of paper. The improved recycled fiber quality results in an improved paper quality. The rejects from different process stages can be collected separately and used for different purposes. For example, rejects containing high amounts of plastics can be incinerated for the benefit of considerable energy recovery, due to their high heat values. Rejects with high amounts of organic fiber material can be used for composting. The rejects of the high-density cleaner as well as of the pulper disposal system are usually disposed of by landfilling because of their high content of inorganic material (e.g., stones, sands, staples, and clips).

Worldwide, a large number of mills are producing Testliner with fractionation and dispersion. Sometimes refining is also included in the stock preparation plant. Nevertheless, no exactly identical systems appear to exist.

The principal driving force for implementing stock preparation plant concepts with a higher number of process stages is the high-quality requirements of the paper to be matched, which has to compete on the market with paper manufactured from virgin fiber. A further incentive is that paper machine runnability should be improved. The driving forces to implement stock preparation plant concepts with "minimized" process stages are lower investment and operation costs, mainly savings of electrical power as a result of the fewer machines required.

Several mills in Europe are equipped with a stock preparation system including fractionation and dispersion. However, the equipment installed and the number of process stages vary, and no exactly identical system appears to exist. Some mills also have implemented a DAF for process water treatment. The combination with washing has not been realized for Testliner production so far (Göttsching et al., 1998).

Generation of Clarified Water for De-inking Plants

Recycling of white water in recycled paper plant with de-inking is only possible if there is a system for clarification of white water. The systems for water clarification used are based on sedimentation, filtration (disk filter), and flotation. The best technique at the present time is DAF. Anionic trash and fine are agglomerated into physically treatable flocs by using additives. High-molecular, water-soluble polymers or inorganic electrolytes are used as flocculants. The generated agglomerates (flocs) are then floated off in the clarification basin. In DAF, the suspended solid material is attached to air bubbles. These bubbles transport the material to the surface of a circular or rectangular basin where it is scraped off and fed back to the stock preparation. The clarified white water is taken out from the bottom.

In a flotation system with a circular basin, the air bubbles are generated by mixing air into the circulation water at high pressure. When the pressure is reduced at the inlet of the basin, microscopic air bubbles are formed. The size of the bubbles is critical. Flocculation agents are usually added to the white water ahead of the flotation to improve separation. The advantage of flotation is that small-sized colloidal material can also be removed. This is a great advantage in the recovered paper plants with de-inking, where a large part of the solid material in the process water is colloid. In de-inking systems, flotation is today the only way to purify the process water for recycling. In a de-inking plant, the material is pumped to the sludge dewatering instead of being recycled in the process as in paper mills using virgin fibers. The flotation systems generally give very pure water, but the efficiency is dependent on several factors, which have to be monitored and controlled, for example, pH, volume flow, air bubble size, and consistency flow. However, at optimum conditions the efficiency is very high. Another advantage of flotation is that the saturation of air (oxygen) in the process water prevents the forming of anaerobic bacteria.

Upgrading of water clarification system is often combined with rearrangements of water loop systems. It can be adopted in new and existing recycled fiber mills. The advantage of DAF is that small-sized colloidal material can be removed. This is a great advantage in the recycled paper plants with de-inking, where large parts of the solid material in the process water are colloid. By use of DAF at the suitable position in the water loops, the degree of water loop closure can be continuously adjusted to the requirement of the process water quality, depending on the concentration of anionic trash, additives consumption, and product quality requirements.

Chemicals are needed as flocculants. Electricity is required mainly as pumping energy to saturate part of the untreated water, or a corresponding amount of clarified water, with air after raising the pressure to 7 bar. Floated sludge is generated, which has to be dewatered. DAF systems are mature concepts. All components can be combined on a modular basis for optimal results for different applications.

The driving force for upgrading the water clarification systems with DAF in de-inking plants is that it allows optimal water management and adjustment of water loop closure as required (CEPI, 1997; Pöyry, 1994; Schwarz, 1995).

Cogeneration of Heat and Power

Paper industry is a highly energy-intensive industry. Increased speed of paper machines, more sophisticated recycled paper processing systems, and technological development, in general, have resulted in higher consumption of electricity in paper mills, whereas the specific use of steam has remained virtually unchanged.

The energy losses from power generation and from heat production can be reduced by combined generation of both heat and power (CHP, also called cogeneration). Cogeneration plants raise the conversion efficiency of fuel use from around one-third in conventional power stations to about 80% (or more). Thus, for many paper mills, it is possible to increase the overall energy efficiency of the process by making use of the cogeneration, thus reducing fuel consumption and air emissions. The energy requirement and the heat/power ratio in the paper and board industry are very appropriate for the use of CHP. The characteristics of the processes as high and balanced electricity and heat needs, and regularity of operation over the year are also favorable.

Many paper mills have installed different kinds of cogeneration processes. For example, for boiler houses fired with gas, one or several gas turbines prior to the existing supplementary-fired steam generator can be installed to reach a higher output of electricity from the plant. If a steam turbine is already in operation, a gas turbine can be installed before the steam generator to generate a higher yield of power. There are different schemes for combined-cycle power plants on the market. Which system is applied depends mainly on the existing power plants already in operation and on local conditions. As an example, the more modern and most efficient combined-cycle gas/steam cogeneration is briefly described. This type is characterized by a very high efficiency and the ability to produce—for the same quantity of heat required in the paper mill—significantly more electricity than the previous steam plants. Where it is practicable, this system should be considered as preferable option.

As in normal gas turbine technology, air is drawn from the atmosphere and compressed. In the combustion chamber, fuel and air from the gas turbine compressor are mixed and combustion takes place. After combustion, the flue gas is expanded in a turbine, which drives a generator. In combined-cycle power plants, the thermal energy contained in the gas turbine exhaust gas is utilized in a heat recovery steam generator to produce steam that is used to generate additional electricity via a steam turbine. Plants for cogeneration of heat and power convert 80–93% of the energy input into 40–70% heat and 45–20% electricity depending on the specific need of the mills and the system applied. Conventional electricity generation converts somewhat less than 40% of the energy input into electricity. The rest of the energy input is lost.

Cogeneration is a well-known and developed technique. It can be applied to both new and existing mills, if the mill layout allows it. In existing plants, cogeneration can be implemented, for instance, by repowering existing steam backpressure units by transforming them into combined-cycle cogeneration plants. The relative small size of most tissue mills can make CHP less viable than for large mills.

Emissions per unit of generated heat or power drop significantly as a result of the increased thermal efficiency of CHP. Overall thermal efficiencies can reach 93%, thus reducing the carbon dioxide release rate by about 50% compared to conventional power generation combustion systems with an electrical efficiency of about 38%. In contrast, emissions to air on the site will increase.

In bigger cogeneration plants, NO_x and CO content of the exhaust gas is controlled continuously. Other mills may have periodic measurements of NO_x and CO.

In conjunction with the greenhouse effect, cogeneration power plants based on gas turbines in combined-cycle application are regarded as being an important option for the reduction of CO_2 because of their comparatively high thermal efficiency also for relatively small capacity units. The high electricity/heat ratio and the high efficiency of the conversion of fuels to power and heat reduce significantly the specific CO_2 emission per kWh produced compared to conventional power plants. The overall emissions for power generation decrease due to higher thermal efficiency.

Cogeneration of heat and power by using different schemes of combined cycles has been applied in a number of paper mills with good results. The achievable savings and the payback time depend mainly on the price of electricity and fuels within the respective countries. Investment costs and costs of depreciation and maintenance have to be considered. For the mills that have applied cogeneration of heat and power, this measure is a cost-effective measure (under the given energy prices). The specific investment for transforming existing steam backpressure units into combined-cycle cogeneration plants is in the range of €1000/kW.

It reduces significantly the consumption of fossil fuels, CO_2 emissions (greenhouse gas), and other air pollutant related with power generation by combustion of fossil fuels. Cogeneration of heat and power is often an economically viable measure and makes mills more independent from external electricity suppliers. If the whole cogeneration potential of a site is realized, in most cases the production of the plant will exceed the mill's electricity need. A certain amount of electricity generated at high efficiency will be available for the public grid, if the overall market conditions are favorable to it. It may contribute substantially to the commitments of the Kyoto protocol.

The use of combined heat and power generation is a well-known technique and is applied in numerous paper mills in Europe (Rentz et al., 1996).

Reject and Sludge Handling and Dewatering On-site

This technique applies for brown paper produced from recycled paper. However, dewatering is an environmental concern for all recycled fiber-based paper mills even though they will have different amounts and composition of rejects and sludge.

In recycled paper processing, the removal of impurities from the pulp slurry is one of the most important process steps. Impurities are removed by multistage cleaning and screening at various places of the stock preparation. In the production of Wellenstoff and Testliner, the material loss ranges between 4% and 8%, depending on the recycled paper grades processed, the stock preparation arrangement established, and on the paper quality to be produced. The rejects generated can be subdivided into heavyweight, coarse rejects and lightweight, fine rejects. Usually, these rejects have no material recycling potential and are disposed of by landfilling. Regardless of the reuse or final disposal, dewatering of the rejects is an essential stage of waste handling. All commonly applied methods for energy recovery and disposal benefit from a high DS content of the rejects. Today, the ragger as well as the rejects from pulper disposal systems is mostly not subject to any special dewatering. Due to their material composition, "draining off" results in a dry content of 60–80%. For dewatering heavy and coarse rejects produced by high-density cleaning and prescreening, screen spiral conveyors, vibrating screens, screw, and rake classifiers are used. DS contents of 60–80% are achievable. The dewatering of light and fine rejects from forward cleaning and fine screening using screens, endless wires, or vibrating screens is usually followed by a further dewatering by means of screw presses. The achievable DS content is in the range of 50–65%. The excess sludge generated in biological wastewater treatment plants in most European paper mills producing Wellenstoff and Testliner is reused in paper production. Related to the volume of recycled paper used, the volume of the reused sludge is less than 1% by dry weight. Such a small volume can be used as a raw material for paper production without affecting the runnability of the paper machine and the paper characteristics. In this case, dewatering facilities are not necessary. Various investigations have shown that the reuse of excess sludge from the biological wastewater treatment plant in paper production does not increase the concentration of detrimental contaminants in the paper produced, because the content of detrimental substances in the sludge itself is very low.

Reject dewatering facilities are common in new as well as in older paper mills. Retrofitting of more effective dewatering systems is possible. The resulting increases of the hydraulic load of the wastewater treatment plant have to be taken into account.

Depending on the types of rejects and the reject dewatering system, the water content of rejects can be reduced by 40–75%. In the case of reject disposal in landfill sites, the risk of generating leakage water is minimized. When co-firing rejects in power plants or in cement rotary kilns, the energy demand for the evaporation of water in rejects decreases. This contributes to a higher energy recovery rate.

Water emissions from reject dewatering facilities are controlled by flow meters. The water squeezed out is generally released in the process water system or to the wastewater treatment plant.

Reject dewatering results in an increased volume of water to be treated. Because dewatering is generally only performed by mechanical forces, the pollution of squeezed-out water is equal to that of the process water. When using screw presses, one has the possibility to heat the rejects by injecting steam, which affects the pollution of squeezed-out water. This must be considered especially in cases where the wastewater treatment plant has already approached its maximum capacity. Injecting steam has a cross-media effect on energy consumption and air emissions.

Reject dewatering processes have been used in paper mills for many years with good results in terms of the increased dryness of the reject and the availability of the machines concerned. To obtain a high dewatering efficiency, most new installations have screw presses in the past few years.

Investment costs of reject dewatering-–including a dewatering drum as a first stage and a screw press as a second stage-–to a DS content of 65% are about €200,000. Annual maintenance costs should not exceed €25,000. The costs correspond to an annual reject volume of 13,000 tonnes dry substance.

The driving force to implement reject dewatering processes is the reduction of waste volume to be disposed of by landfilling. Because co-firing of rejects for energy recovery, for example, in cement production, has become an alternative for disposal, such reject handling is given a high priority (Borschke et al., 1997; Göttsching et al., 1998; Krieger, 1998).

Utilization and Disposal of Residue by Environmentally Sound Techniques

The most important sources of solid waste in recycled fiber-based paper mills are stock preparation, process water clarification, and wastewater treatment. Two major types of processes have to be distinguished. In recycled paper processing paper mills without de-inking (e.g., Testliner, Wellenstoff, and paperboard) coarse impurities from the pulper disposal system, rejects from various screening and cleaning stages from the stock preparation plant, and sludge from wastewater treatment are the major waste fractions. The generated rejects amount to about 4–10%, related to the input of raw material. Rejects from the stock preparation plant of brown packaging papers without de-inking have only a limited recycling potential of material because they consist of an undefined mixture of nonpaper components that are removed from the recovered paper. Commonly, these rejects are dumped in landfill sites. However, due to their high heating value in the range of 22–24 MJ/kg dry substance because of the high proportion of plastics, rejects are suitable for energy recovery, replacing fossil fuels. Only for rejects from final cleaning and screening stages of the paper machine loop, there is a possibility of material recycling because they have a low content of plastics and other impurities. Therefore, in some mills this waste fraction is collected and dewatered separately and used as a cosubstrate for composting of biowaste. Especially, the current practice of composting varies significantly in different countries. Whereas in some countries composting of sludge from recycled fiber paper mills is encouraged, there are others (e.g., Germany) who discourage or ban the composting of waste from paper production. Recycled fiber paper mills with de-inking additionally produce high amounts of de-inking sludge and often sludge from process water clarification. The generated rejects and sludge amount to about 15–40%, related to the input of raw material. In de-inking pulp (DIP) plants the de-inking sludge, containing mainly short fibers, coatings, fillers, and ink particles, is the crucial waste fraction to be handled. Commonly, most of the sludge is still dumped in landfill sites. In a few countries land spreading in agriculture or composting is practiced, whereas in other countries this option is discouraged or banned. In bigger DIP plants, de-inking sludge together with the sludge from wastewater treatment can be incinerated. There are different options for the energetic utilization of rejects and sludge containing organic material (e.g., plastics, fibers, and fines). These are incineration in an in-mill reject incineration plant, co-firing in an in-mill coal-fired power plant, and co-firing in the cement industry. Rejects can be used as a substitute fuel in the cement industry replacing fossil fuels. Wastes that are fed through the main burner will be decomposed in the primary burning zone at temperatures up to 2000°C. Inorganic components will be bound in the cement clinker. Waste fed to a secondary burner, preheater, or precalciner will be burned at lower temperatures, which is not always enough to oxidize the organic material completely. The rejects are normally fed at the secondary firing stage at the entrance of the rotary kiln. Feeding rejects and sludge of paper mills in the secondary burner runs a certain risk that emissions of unwanted hydrocarbons (VOC, dioxins) occur. In this combustion zone, temperature rises only slowly, which might cause plastics to smoulder. Therefore, operators of cement kilns have to make sure that the use of rejects from paper mills as substitutes for fossil fuels does not result in increased emissions of VOC or halogenated organic substances. Analyses and control of the composition of the residues to be burned and the resulting emissions to air can avoid this risk. The suitability of waste fractions from paper mills as substitutes for fossil fuels in the cement industry has to be decided case by case. When incinerating the rejects from recycled paper processing mills, the chlorine content of the fly ash can be a limiting factor for the further usage of the ash in case of cement factory. To obtain a high surface and good ignition behavior, a pretreatment of the rejects is necessary. This comprises mainly primary crushing, screening, and secondary crushing. Shredding and screening can be combined, for example, with a magnetic separator and an air separation, to recover ferrous metals and to remove impurities that could damage the postcrushing aggregates. Usually, the pretreatment of rejects is not performed in the paper mills.

So far, no reject utilization options mentioned previously can be regarded as BAT in general. Reject utilization techniques differ from paper mills to paper mills, mostly depending on local conditions. Because in the near future landfilling as today's predominant disposal option will only be permitted for inertisized waste or for waste with a low content of organic compounds, the development of reject utilization techniques represents a challenge for the paper industry. Recovery operations are considered as preferred waste treatment options. Possibilities to reduce the amount of waste to be landfilled should be identified and ensured that they happen, where feasible.

Incineration combined with power and steam generation is regarded as an environmentally sound solution. Different technical options for incineration of residues with energy recovery are realized in European paper mills. These are combustion of rejects from recycled fiber mills without de-inking in reject incineration plants; co-incineration of rejects from recycled fiber mills without de-inking in coal-fired power plants including flue gas treatment; incineration of rejects and sludges from DIP plants combined with power and steam generation. The last technique is more widely used today in European paper mills and is considered as BAT, where feasible.

Incineration of residues (rejects and sludge) combined with power and steam generation can be applied in most new and existing mills. However, the applicability depends on the type and capacity of the boiler in each case. For instance, small mills cannot apply this technology. They have often only very simple oil or gas boilers with limited capacity or technical feasibility to burn solid materials. The higher chlorine content of the rejects needs special attention (corrosion, waste gas treatment). When applied, fluidized-bed boilers are generally more appropriate and can be retrofitted with less additional costs than grate-fired boilers. On the operating point of view, the fluidized-bed boilers have many benefits, among others lower sensitivity to fuel quality or quantity variations and in most cases lower emissions, over the grate-fired units.

The main achievement is the reduction of the amount of material to be landfilled by about 80–90%. Additionally, a change in quality is achieved; that is, the organic materials are nearly completely eliminated. For the final disposal or use of the ashes, there are different options depending on the ash qualities achieved. In some cases ash will be landfilled, others use them in building industry or other add-value purposes.

Energy recovery may be a secondary target to apply this technique. After dewatering there is a slight positive energy balance in the range of 4–5 MJ/t, referred to incineration of dewatered sludge (at 58% DS). However, for some paper mills applying wash de-inking sludge incineration results in a net consumption of energy. This is typically due to high ash content and thus lowered energy value of sludge.

Emissions to air are released from the incinerator and have to be treated. In contrast, potential emissions from the landfill gases are reduced. Normally, the purification of waste gas from incinerators generates a certain amount of waste that has to be disposed of. In case of wet waste gas treatment, wastewater is generated.

The incineration of sludge combined with power and steam generation is used in many modern mills. However, the incineration of *rejects* is much more difficult and involves potential emission and corrosion problems. The possibilities in practice are dependent on the capacity and type of the boiler. Technology can be applied in a limited extent in smaller paper mills.

The devolatilized chlorine from fluidized-bed combustion will, besides as HCl, also be as potassium chloride (KCl) and sodium chloride (NaCl). These substances are known to condense on the tube surface with a tendency to increase the possibility for molten phase corrosion. This type of corrosion can be encountered in superheaters when the steam temperatures are above 500°C.

Investment costs of a new sludge and reject incinerator are about €7–9 million and operating costs €0.7–0.9 million/annum corresponding a pulp production of 700 ADt/day. The area required for landfilling can be significantly reduced by incineration of residues depending on the organic content of the materials to be burned. In many countries, the landfilling of waste with high organic content is discouraged.

Some DIP plants in Europe for newsprint and tissue have installed fluidized-bed incineration systems (CEPI, 1998; Finnish BAT Report, 1997).

5.5 PAPERMAKING

Techniques available for prevention or reduction of emissions/waste for new and existing paper mills are presented as follows (European Commission, 2001; Salo, 1999):

- Water management and reducing water usage for different grades of paper
- Control of potential disadvantage of closing up the water systems
- In-line treatment of white water by use of membrane filtration
- Reduction of fiber and filler losses
- Recovery and recycling of coating color-containing effluent

- Recovery of pigments
- Separate pretreatment of coating wastewater
- Measure to reduce frequency and effects of accidental discharges
- Measurement and automation
- Equalization basin and primary wastewater treatment
- Aerobic biological treatment
- Chemical precipitation
- Substitution of potentially harmful substances
- Pretreatment of sludge
- Options for waste treatment
- Installation of low-NO_x technology in auxiliary boilers
- Use of combined heat and power generation
- Optimization of dewatering in the press section of the paper machine
- Energy savings through energy-efficient technologies
- Measures for external noise control

Water Management and Reducing Water Usage for Different Grades of Paper

Basic water reduction solutions comprise:

- Efficient separation of cooling waters from process water and their recooling with cooling towers for reuse. About 10–15% fresh makeup water is required for reuse stream. For protection, a microscreen or other strainer is recommended to remove solids. Where cooling water fractions are sewered, they are not led to contaminated process water sewers.
- In integrated mills, the water circulation in the paper machine is kept separate from pulping sections and excess white water from the paper machine is fed in countercurrent mode to the pulping department.
- The shower water system is usually the biggest consumer of freshwater in the paper machine system. Shower water consumption is usually in the range of 4–15 m^3/t, assuming a total water consumption of about 20–30 m^3/t of paper. To reduce the freshwater consumption to reasonable levels, most of the freshwater must be replaced by clarified white water. Efficient fiber recovery with associated clear (or superclear) white-water production to replace freshwater in paper machine showers is applied for this purpose. Thus, shower water system with significantly reduced freshwater demand can be achieved. However, normally it is not recommendable to use save-all filtrates for the press-section showers because otherwise precipitation of colloidal material from the clarified white water on the felt may occur. This may lead to clogging of the felt. Up to now, high-pressure felt showers require freshwater. In case an

operator still wants to use filtrate, it has to be carefully investigated how to treat the water that at least the colloidal material is getting away.

- Recycling loop for part of the vacuum pump sealing water with cooling and solids removal.
- Management of all raw material flows through the paper mill in considering them as a unit of fibers, chemicals, and water that interfere with each other. All input of chemicals, for instance, is controlled and investigated how they influence water quality and wet-end chemistry (controlled system input).
- Design and maintenance of piping and storage chests in such a way that excess water volumes can be stored and the water quality is not deteriorated.
- Training and motivation of the staff is crucial to achieve and maintain low water consumption.

Depending on the starting point, the characteristics of the mill and the product quality, with these arrangements the freshwater consumption of an uncoated paper or board machine could reach 5–12 m^3/ADt and a coated printing paper machine 7–15 m^3/ADt. Reducing water consumption aiming toward the further reduction of effluents requires additional implementation of a physicochemical, biological, or mechanical means or their combination to treat the water for recycle. The amount of many accumulated inorganic and organic substances is an important restriction to achieve this goal because these impurities have to be kept at low levels to prevent problems in machine operation and fulfill paper or board quality requirements.

Water reduction measures can be carried out both in existing and new mills. However, the separation of pulp and paper water loops in integrated mills or a high degree of water system closure is more expensive in older mills because the major rebuild of piping and major modifications to the machine wet end are likely when aiming to further closure. In existing machines these modifications are beyond a point difficult to reach without major rebuild or expansion of the process. With new machines the reduced water consumption can be applied somewhat more easily. Another problem to be addressed in existing mills is the suitability of materials to withstand accumulation of corrosive substances, such as chlorides, and elevated or increased water temperature. In general, water loops are the most difficult to close, the more differentiated the products are and the more often the type of paper produced is changed. Smaller mills with only one paper machine usually face more production changes during the year (or day) than bigger mills manufacturing bulk grades. The individual configuration of plants has to be considered.

The achievements depend mainly on the preceding situation of the mill. In existing mills, freshwater use reduction of 10–15 m^3/ADt of cooling waters and a reduction of 5–8 m^3/ADt of process water can often be obtained without the implementation of any special in-mill treatment, but the degree of closure depends very much on the product. With low-brightness boards, lower effluent volumes can be more easily achieved than with liquid-packaging boards or printing and writing papers.

Consumption of freshwater depends mainly on paper grade, amount of showers, and the amount of fiber containing waters used for the paper machine showers, mill conditions, and gathering of water usage information. Lightweight paper products generally require somewhat more water per tonne of end product.

Typical monitoring devices include flow meters for paper machine freshwater feed, shower water feed, and major white-water streams. Suspended solids or turbidity measurements for clear white water are emphasized especially, if it is used for paper machine showers.

In paper mills with low water consumption, contaminants are more concentrated in the effluent, which often contribute to higher removal efficiencies. To a certain extent, losses of raw material and energy might be reduced. Lower water volumes usually also mean lower heat load to the recipient.

The measures described are implemented in many paper mills. The experiences are also good in existing mills, and current paper machine design supports well their application. Clear or superclear white water from the save-all is increasingly used in paper machine showers. If the white-water solids content or the particle size rises beyond the shower nozzle capacity, the nozzles would plug. The water distribution to such showers should go through a protective in-line strainer and equipped with an automatic purge, to protect against the effects of save-all upsets and in addition in avoidance of white-water replacement with freshwater. Also, shower cleaning equipment, with internal brush or other purging equipment, can help avoiding problems. However, in existing mills low water consumption as the result of a combination of different measures usually needs many years of development and improvements in the process.

No general information on cost structures for water loop closure is available because each single plant is an individual case in this respect. The expenses depend mainly on the technical characteristics of the mill and the local conditions. The costs of these measures depend on the number and nature of water circuit rearrangements necessary and the type of additional installation needed.

A bunch of possible measures to reduce freshwater consumption is called for in mills where freshwater availability is restricted or it is a paid commodity. The improvements have often a net positive effect because of possible savings achieved by lower costs of raw water, lower losses of fibers and fillers, sometimes lower energy consumption, and lower volumes of wastewater to be treated. Both increases of production capacity and limited hydraulic capacity of the existing ETP are also reasons to apply these measures (CEPI, 1998).

Control of Potential Disadvantage of Closing Up the Water Systems

Increased recycling of process water in paper and board machines causes an increase in the concentration of colloidal and dissolved organic and inorganic constituents in these streams. This can have an adverse effect on the runnability of the machine, the quality of end product, and even the production costs due to increased use of chemicals. These potential negative effects need to be controlled. The enhanced recycling of process water in paper mills can have adverse effects on the runnability of the machine, the quality of end product. These harmful effects need to be controlled when paper mills are aiming at low water consumption (CEPI, 1998). The advantages and disadvantages of increased closure of water circuits in paper mills are listed as follows:

Advantages

- Improved retention of soluble material in the paper web
- Reduced energy requirement for heating and pumping
- Better dewatering properties of the wire that leads to energy savings in the drier section
- Less investment costs of reduced equipment
- Saving raw materials due to lower losses
- Higher reduction efficiencies of wastewater treatment
- Reducing total releases to water bodies

Disadvantages

- Higher concentrations of dissolved and colloidal materials in water circuits
- Risk of slime production leading to deposits and web breaks
- Risk of lower product quality, for example, concerning brightness, strength, softness, and porosity
- Increased consumption of process aids
- Risk of corrosion (higher concentration of chlorides)
- Higher risk of blocking of pipes, shower nozzles, wire, and felts
- Problems of hygiene control for tissue, food contact, and medical applications

The pulp and the water carrying it contain dissolved and colloidal organic compounds called “anionic trash.” At higher concentrations these organic substances affect the retention and formation of the paper web and increase plugging of machine press felts and cause sticking of the paper web on machine rolls. When producing papers from mechanical pulp, the problems are more prominent because most of the compounds of the wood are still present in the pulp and are partly dissolved in the process water. In the production of food-packaging materials, the product must be free of harmful soluble matter. The temperature rise at the paper or board machine also needs to be controlled so that limits of operating temperature, 45–55°C at the wet end, are not exceeded. On the other hand, on the paper machine wire section, a hot pulp suspension is advantageous because the viscosity of water is decreased with increasing temperature, resulting in improved dewatering.

The requirements in controlling the effects of closed-up water circuits are as follows:

1. The paper or board machine white-water system does not receive water from integrated pulping departments or from parallel machines. The separation of water loops is usually carried out with thickeners. The optimum design of water loops is also crucial.

2. The recycled cooling or sealing water and clean white water feed to machine showers are treated with an appropriate strainer to protect against plugging or wear of machine equipment.
3. Sealing water recycles are cooled sufficiently by heat exchanging equipment or clean makeup water. Especially, vacuum pump performance limits allowable sealing water temperature.
4. The composition (e.g., presence of colloidal substances), hardness, pH, and temperature of recycled waters fed to a specific use are compatible with the equipment or the process streams there. It is beneficial to determine the water quality that is really needed.
5. The pulps should be efficiently washed prior to feed to the paper mill to reduce the content of dissolved or colloidal substances.
6. The selection of the paper chemicals and the machine aids has to be reassessed when closed-loop principles are applied, because some chemicals behave very differently in the changed chemical environment.

The measures can be applied both at new mills and at existing mills. However, existing mills usually need many years to implement most of these improvements. The required level of measures varies for individual cases: the machine type, the product(s), and the degree of closure are the key parameters. The requirements are the lowest in production of unbleached packaging grades and get strict for high-quality grades, such as fine papers.

Elevated dissolved or colloidal matter concentrations due to increased process water recycle tend to retain more of these substances in the end product. Limits to this are set by the product quality and the acceptable consumption of papermaking chemicals. Also, in sealing and cooling water applications, the stream temperature and dissolved and particulate solids concentrations set limits and must be attacked by cleaning equipment and/or sufficient bleed-out. For sealing, the current technology also offers mechanical seals that do not need water.

The measures are considered to be an integral part of the measure described previously. They support these measures to achieve and maintain low freshwater consumption without significant adverse effects.

At the points where the effluent is discharged out from the paper machine, monitoring with flow meter is practical. Online suspended solids or turbidity measurements are important peak indicators. At least in the external treatment plant, the temperature shall be monitored.

Control of paper machine water and recycle quality calls for improved control and monitoring of the pulping process as well. In some cases the need of paper chemicals and paper machine aid chemicals will increase. The type of the used chemicals must be reassessed to maximize the suitability for a certain paper grade.

The risk of scaling caused by calcium compounds, slime, and pitch problems is pronounced and must be counterattacked with appropriate mix of water fractions, pH control, increased dosage of machine aids, or appropriate purge of calcium out of the system. If the machine can be operated at more than 50°C, the growth of microorganisms and their activity in the water system are lower. But anaerobic activity may still occur at more than 50°C (thermophilic bacteria), generating odor in sulfur- and carbohydrate-rich environment that needs to be controlled.

The optimization required by the implementation of these control measures is usually carried out in steps over a long period in existing mills. The success in applying this technology depends on the wet-end chemistry case by case. Some mills have been attacking the control problem just by using more chemicals. The selection of proper chemicals and additives and their combination is a fairly sophisticated procedure and often poorly understood, but necessary to obtain maximum runnability and low cost and environmental impact. Economical paper production in numerous partially closed-cycle mills has been successfully implemented even for high-speed paper machines. Through the use of enhanced recycle water purification, certain problems can be solved and machine control with chemicals can be relieved, but other problems have sometimes evolved.

The expenses depend mainly on the condition of the mill. The costs of the measures depend on the number and nature of rearrangements necessary and the type of additional installation needed. No data on single costs are available.

Internal Treatment of White Water by Use of Membrane Filtration and Recycling of Treated Process Water

Solids and colloidal material less than 1 μm size are not well removed by conventional filtration. So, small bacteria and colloids escape the filter media. However, this is only true for unflocculated solids and colloids. They can also be transformed into 100–1000 μm flocs by flocculation and easily filtered off. But the addition of flocculants may have the drawback that undesirable salts are introduced in the water system (modern organic/synthetic flocculants do not introduce a significant salt burden). Membrane technologies, depending on the applicable membrane cut-off size (corresponding to the approximate "molecular weight" of organic compounds removed) and filtering pressure, can theoretically remove almost 100% of the organic material, without introducing undesirable compounds in the water circuits.

There are different membrane processes according to the differences in pore size:

- Microfiltration, which operates at below 1 bar pressure and uses membranes with 0.1–0.2 μm pore size, could be used where 1–5 mg/L of very fine solids is acceptable after treatment.
- UF operates at 1–2 bar pressure difference, and it is regarded a possible solution for 100% removal of residual solids and colloids and high-molecular-weight organics from water or effluent streams of pulp and paper mills. There are few full-scale applications for white-water treatment with UF technology in Europe.

- Nanofiltration or reverse osmosis use pressures reaching 15–25 bar, but so far these methods have not been seriously considered for full-scale use in pulp and paper industry.

Any type of membrane filtration cannot handle sudden peaks of suspended solids. If the suspended solids are only homogenous (even), a police filter is needed to avoid sudden peaks. Key issues affecting the selection of a membrane technology, if considered for paper mills, are as follows:

- Input stream, its composition, and hydraulic load, including peak operating conditions.
- Clean water quantity and quality required and the applicability of treatment output in varying operating conditions for intended end uses and effect on pulp or paper quality.
- High-pressure filtration methods produce cleaner water, but consume more electricity and must be sized larger or equipped with more efficient pretreatment or countermeasures to protect against plugging.
- Maintenance requirements (symmetric or asymmetric membrane structure, washing with acids or alkaline, spare capacity, automated or continuous cleaning). Symmetric membranes have higher tendency to plug. Plugging can be avoided by maintaining highly turbulent conditions close to the membrane wall, but this requires somewhat more energy.
- Final treatment and disposal of the concentrate or sludge, which in most cases is waste. Liquid waste may be concentrated enough to cause toxic effects at an external effluent treatment, or it may require further concentration or absorption into a solid fuel for disposal by incineration. Some inorganic salts in the concentrate are corrosive, which must be taken into account in selection of equipment and piping materials.

When considering this aspect, UF can be used as a kidney to handle disturbing matter in the white water and close the water system further. For in-line white-water treatment, the kidneys might consist of a disk filter, bow-screens, and the UF system. The prefiltered white water is piped to the UFs system feed tank and pumped the UF unit. The number of filters in operation regulates the clean UF permeate capacity. The pressure difference is kept as low as possible, for instance, to 0.7–0.8 bar. The quality of the UF filtrate is sufficient for use, for example, shower water, sealing water, and for dilution of paper machine chemicals. The concentrate from the filters can be piped to the main effluent treatment.

Membrane filtration has been applied in a few mills in the world to remove suspended solids, bacteria, colloids, anionic trash, and high-molecular organic compounds from partial water streams of paper or board mills. The treatment of excess white water for reuse with UF membrane filtration is usually only applied in special cases.

For higher concentrated process water in paper mills as those from production of “brown paper” from recycled fiber, the application of biological in-line treatment of process water followed by sand filtration is a feasible option. There are also combined systems under development, so-called membrane bioreactors. In special applications, such as coating chemical recovery from paper machine coating effluents, UF membrane technology is already a tested technology and several applications exist. In general terms, paper machine water loop closure with self-contained removal of dissolved organic or inorganic constituents is a technique that still undergoes some development work. It is not as well established as, for example, biological treatment.

The removal efficiency of UF membranes for organic compounds is case-specific, the target levels being set by the allowable contaminant levels in the paper machine system and specific uses of recycled water. Besides partly removal of organic compounds, other membrane filters with smaller pore sizes (as nanofiltration or reverse osmosis) can also reduce inorganic material, but the system size and the pressure/energy required increase exponentially when the removal rate for low- molecular-weight organic compounds or salts is increased. UF in white-water application usually means the treatment of clear filtrate and/or parts of the cloudy filtrate from the disk filter. The UF membranes remove, in practice, 100% of TSS, 99% of bacteria, 100% of turbidity (all colloidal material is removed), and 45–70% of anionicity. Dissolved COD is lowered by about 10–20%. That means, UF still allows parts of the organic substances (e.g., all low-molecular-weight organics) and soluble inorganic matter to pass through. First of all, UF of white water gives better quality of recirculated water that can be used for low- and high-pressure shower water in the wire section, dilution water for chemicals, press section lubrication water, or other washing and cleaning purposes. There are not yet experiences whether the permeate could also be used for felt cleaning.

A possible reduction of water consumption can indirectly lead to a decrease of the discharged nutrients load (nitrogen and phosphorus) because the total nitrogen and phosphorus releases are governed by the minimum concentration that is required for the growth of biomass in wastewater treatment plants. The concentrate from membrane filtration (3–5% of feed) is led to biological treatment or is to be disposed of by incineration. The latter would require a concentration step before combustion, which calls for the control of volatile organics, when it is performed with evaporation. The incineration of the concentrate in an auxiliary boiler mixed with normal fuels may be possible depending on the type, capacity, and fuel feeding system of the boiler.

In a full-scale UF application in Finland, the concentrate is further treated in the biological treatment plant. In that case no reduction of the total pollutant load to the recipient is achieved. However, investigations for how to use permeate for other purposes (e.g., high-pressure showers) to replace freshwater and whether to treat the concentrate separately (may be by combining UF with other techniques) are still carried on.

UF requires electricity in the range of 2.6 kWh/m^3 treated white water for pumps to overcome the pressure difference. There are no data available to compare environmental performance of common activated sludge systems with the system using UF and biological treatment of the concentrates in an integrated manner. For membrane filtration, the solution to how to treat the liquid or solid wastes is crucial.

Membrane treatment processes used specifically for paper or board machine white water have been tested in full-scale in a few mills in Europe.

The practical limitations of membrane filters are usually set by the membrane material itself, which is sensitive to plugging, unless the units are equipped with pretreatment for solids removal or in-built systems that provide cleaning or maintain strong turbulence close to the membrane surface. Regular washing of filters with acids or alkaline solutions (NaOH, detergents, and tensides) is required, generating small amounts of liquid waste. When the flux of permeate goes down, the membranes must also be changed from time to time (the lifetime of a membrane is about 15 months).

For membrane filtration of white water, the capital costs would be about €0.3/m^3 corresponding to 5000 m^3/day treated white water. Service and maintenance costs (membrane change and working hours) are in the range of €0.05/m^3, energy costs about €0.07/m^3, and washing chemicals €0.02/m^3. The total operational costs are in the range of €0.14/m^3.

This technique may be applied first in mills that face strict requirement for discharge because either they are situated on a sensitive recipient or they intend a significant increase of capacity. In the latter case, authorities in some countries require that the effluent load should not increase with capacity. Usually, the pioneers that achieve much lower emission by use of new technologies use the "green mill concept" as part of their marketing philosophy. These techniques may also be applied in cases where availability of water is scarce.

UF of white water may also reduce downtime of the paper machine caused by required washing off substances concentrated in the recycled clear filtrate (Bentley, 1999; Teppler et al., 1996).

Reduction of Fiber and Filler Losses

Efficient fiber recovery within the paper or board production is very important because in virgin fiber processing typically over 98% of the pulp fed through the paper or board machine stock preparation is acceptable for the end product. The chemical or mechanical pulp fractions used should already prior to the machine stock preparation warrant this high pulp quality. In the paper and board machines, the waste management involves mostly with screening in stock preparation, wet-end save-alls, and wet- and dry-end broke handling.

Partly related to fiber management, the measures are also taken to reach reduced water usage and closure of water loops. By improvement of water loop closure in most cases, reduced discharge of organics out from the mill is also obtained. Rejects from the screening of paper or board machine stock preparation should be returned in integrated mills to the pulping department, where reprocessing is done and the good stock will finally end up back in the machine and in the end product. An efficient screening prior to the machine consists of cascading pressurized screens and several cyclone stages.

Fiber and filler recovery in paper and board machines has significance in terms of reduction of suspended solids. When the pulp discharges from the machine head box to the wire and starts forming the paper web, a fair amount of fibers and fillers is not retained for the first time but discharged to collection pits, under the machine. The short-circuit water is recycled untreated. The rest of this water is passed through a save-all unit, typically a drum or disk filter or a DAF unit, to separate solids from the water stream. These solids are then collected into a chest and recycled back to the paper machine feed. The clarified water, called white water, is typically collected as clean and cloudy fractions and recycled for appropriate uses in the paper machine: pulp dilution in the machine stock preparation, broke dilution, paper machine showers. In integrated mills the excess white water is best used in the pulping process or, if acceptable, in the parallel paper or board machines, but in nonintegrated mills it is sewered.

For paper machine fiber and filler recovery with a save-all unit, for most cases the disk filter is an efficient solution to attain high recovery. Especially, a precoat-type unit, which utilizes a small amount of paper machine pulp feed on the filter surface to improve filtering efficiency and solids recovery, is often used at modern mills. The filter works in batch mode, but the solids removal and the regeneration by applying the precoat take only a short period. The disk filter allows efficient fractionation of white water to clean and cloudy parts; in closed-cycle mills even a superclean fraction may be separated for specific uses. The superclear filtrate from a disk filter could have 10–20 mg/L suspended solids and clear filtrate 20–50 mg/L solids, in comparison to well over 50 mg/L of conventional filters. Clear filtrate can be used in many machine wet-end shower applications and cut freshwater usage. The cloudy filtrate and the rest of clean portion can be used in pulp dilution preceding the paper machine, in so-called short circuit, or in machine broke dilution and in integrated mills in the pulping process. Thus, depending on the situation before implementing improvement measures, even 10–20 kg/ADt more pulp (and additionally fillers, when applicable) is returned to the machine feed instead of being sewered in excess white water.

In the paper machine and even preceding it, other methods to cut fiber and filler losses are also available: tuning of the pulp refining and screening just ahead of the feed to the paper machine to maintain proper balance of different types of fibers in pulp. Heavy refining increases the amount of short fiber that in turn may be removed as reject in screening. In integrated mills, certain fraction of rejects from the screening may be recycled to the pulping department: efficient control of paper machine head box to produce an even paper web across the machine width; sufficient use of paper chemicals and machine aid chemicals together with modern control system to reach improved fiber retention on the wire and good paper web formation. However, overdosing should be avoided.

The broke and white-water storage capacity has also an effect in solids management and water conservation. The chest sizes should allow machine flow at least 2–3 hours to be stored in broke chests to recover these fractions that are high in fiber content. This reduces the frequency and length of sudden peak fiber or hydraulic discharges to the mill sewer. In paper machines producing coated grades, the broke collected after the coater should be mixed with fresh pulp and wet-end broke in such proportion that the amount of fine solid matter in the paper machine wet end keeps in control.

Metso Paper has developed an innovative filler recovery concept to help producers of coated paper and board resolve this problem (http://www.metsopaper.com). The new technology eliminates the need to send coating and filler pigments for disposal at landfills after being used only once. The new solution utilizes OptiThick^{TM} GapWasher technology developed for the twin-wire forming sections of paper machines, and is a key component in Metso's new filler recovery plant concept. Using this technology, paper mills can cut the flow of solid waste to landfill sites and increase their reuse of filler pigments, which offers considerable potential for savings. The concept was developed for paper machines equipped with several coating stations and producing a heavily coated end product. These machines have high levels of pigment in their stock preparation and water management systems, resulting in a high solid waste load. The accepts in the OptiThick GapWasher system comprise only a few percent by weight of particles larger than 45 μm in diameter, as measured by wet sieving. In some cases, pigment particles under 45 μm in diameter, contained in centricleaner rejects, for example, are acceptable for replacing new filler. Studies have shown, however, that more than 90% of the acceptable fraction of the latter rejects consists of particles smaller than 32 μm. For particles larger than 45 μm, further cleaning of the accept flow is still needed before it is returned to the paper machine approach system. After separation in the GapWasher, the rejects fraction, which now comprises mostly low-quality fiber, other wood-originated particles, and coarse pigment fraction, is in concentrated form. Its lower ash content and the lack of any viable reuse method mean that this fraction is dried and used as a fuel.

In typical GapWasher applications, the concentrated web is the accept and the filtrate is the reject. In pigment recovery, the case is exactly opposite. Because the feed pulp consists mainly of fine and coarse pigment particles, low-quality fibers, and some impurities, the aim is to separate the fine pigment particles and water into the filtrate and leave the coarse pigment, low-quality fibers, and impurities between the wires. After separation, the pigment in the filtrate can be reused as fillers. Full-scale GapWasher use has produced excellent rejects cleaning efficiency to date. Feeding 50–100 t/day (on dry basis) of rejects into an OptiThick GapWasher system has yielded a recovery rate of about 80%. Feed consistency has been 4–8% and ash content about 70–85%. The recovered 80% portion of the pulp comprises some 80–90% ash. Measurements typically show that more than 95% of the sample mass consists of particles under 45 μm.

The Wiggins Teape Group Ltd. has patented a fiber and filler recovery system, whereby the recovered material from the effluents is reused in paper production (US Patent 5478441). The first step is the screening and/or cleaning of the paper mill waste sludge from the mechanical primary clarifier to remove large contaminants. This is done at relatively low DS content within the range of 2–6% by weight. It is accomplished using a high-density cyclone cleaner to remove the large dense contaminants followed by the further treatment of the accept by means of a high-consistency rotating screen to remove lightweight contaminants. The rejects from both the cyclone cleaner and the rotating screen are then further treated by means of a pressurized vibrating tailing screen. Accepts from this are recycled back to an earlier process, while the rejects are discharged to landfill. The second step is the thickening and heating of the resulting sludge. Thickening of the sludge is accomplished using a series of screw thickeners followed by one or more screw presses, effectively to raise the consistency from about 4% to 30% by weight. The thickened sludge is then passed through a plug screw to produce a seal and thereby a closed system. From the plug screw the fiber/sludge is fed to a fluffer, which transforms the compressed fiber sludge into crumbs before it passes into the heating chamber. Heating is conveniently made by the injection of superheated steam to a temperature of 125°C. The bleach addition is made at the point between the thickeners and the plug screw. Once the fiber/sludge mixture has emerged from the disperser and has been diluted, typically with white water, it is suitable for use in a conventional papermaking stock, normally when combined with additional papermaking fiber, which can be fresh virgin pulp or a different broke. Additional filler may be added, if necessary, although filler is present in the sludge and in various types of broke. This additional papermaking fiber can be mixed with the sludge prior to the screening and/or cleaning step or to a dispersion step, and/or the sludge can be treated on its own before being mixed with the additional papermaking fiber.

Stora Enso Uetersen mill is using Trenntechnik, a filler recovery system connected to the effluent treatment (Pelikan et al., 1997; Templer, 1993). The effluents of two paper machines and one coating machine are collected for recovering the filler and reusing it in the paper machine. This is also the pretreatment method for the effluents before these waters are led to the municipal wastewater treatment plant. The first phase is to separate the large particles, such as pieces of paper and bigger coating particles from the wastewater with a drum screen. After that there is a sand trap before the wastewater is routed to the Fourdrinier wire, with which the pigments are separated from the filtrate. Then, the pigment-containing filtrate is channeled to the sedimentation and flotation phase, from where the sludge is pumped to the vibration screens. The last separation phase of the pigment recovery process is done with centrifugal cleaners. The excess of the sedimentation and flotation phase is pumped through the condensing tower to the municipal wastewater treatment plant. The rejects of the process are utilized in cement/brick work. The fibers of the reject may be chosen for utilization in the mill's own paper production or for other purposes.

The listed improvements can be applied in both existing and new mills. However, in older mills the paper machine areas are more limited for rebuilds due to space or layout problems.

The total solids losses from a paper machine, from rejects from paper machine stock preparation, excess sewered white water, paper machine press sections, and pulp tank overflows are found in the range of 10–100 kg DS/ADt. Better performing mills reach 10–20 kg/ADt (i.e., 1–2% loss) for many paper grades. Some existing liner and fluting or specialty paper lines exceed 50 kg DS/ADt. When carried out in an existing mill producing 1000 ADt/day of printing grades, a recovery of 10–20 kg/ADt of solids means that this solids load is not passed to the primary effluent treatment and to effluent sludge disposal.

The reduction in solids discharge reduces only slightly the organic load measured as COD or BOD5. However, higher COD and BOD5 capture is obtained for effluents from production of paper grades containing high-yield pulps.

White water and broke chest level monitoring is important. Paper mill effluent sewer equipped with flow indication and turgidity meters helps to register surges in solids discharge. Due to lower suspended solids discharge, the external effluent treatment operation is improved. Less sludge from primary treatment is produced. Fibers and fillers are used for the product and must not be handled as waste. When fibers and fillers are recovered to a higher extent, it has also to be considered that raw material and energy that were necessary to produce this material are saved.

These measures are implemented in many paper mills without any problem. Generally, there are two means to be considered: good unit processes and more accurate process control and monitoring of unit operations by means of automation.

Improved stock recovery is usually economically beneficial because of better raw material efficiency and less waste to be disposed of. Reduced solids load to the external treatment and minimization of discharges of suspended solids to the recipient might also be a motivation to implement the described measures for fiber recovery or spill prevention (CEPI, 1998).

Recovery and Recycling of Coating Color-Containing Effluent

ECC International has applied the technique of forced evaporation to the recovery of diluted coating colors, which have been studied using laboratory and pilot-scale tests. The research system included a screening system, a stirred storage tank, a heat exchanger, and a forced circulation design evaporator unit. In a typical experiment, the waste color was screened, and then it was placed in the stirred tank and recirculated through the evaporator via the heat exchanger. The evaporator was operated at 5–10 kPa and 50–70°C. The apparatus ran continually until the desired solids were achieved. The recovered colors could then be blended with fresh color and used for their original duty with no significant decrease in performance (Skuse et al., 1999). The capital cost of the mill-scale equipment is said to be relatively low, and because only very low-grade heat is needed, a lot of the energy requirement of the process may be readily available in the paper mill. The process produces very clean water as a by-product, leaves no wastes requiring treatment, and can raise the solids level of the split color to above 60%. In addition, the majority of the soluble components of the color, such as thickeners, optical brightening agents, and dispersants, are also recovered (Phipps et al., 1998). In the laboratory and pilot-scale test at the ECC International Technicentre, the coating performance of the recovered colors was the same as that of the fresh material. The evaporation process had no effect on the efficiency of the optical brightening agents used. Some changes in the viscosity of the recovered colors were observed, but once they were blended with fresh color for the coating work, no significant differences in viscosity or runnability were encountered (Phipps et al., 1998). This method was not studied further in this study. One important reason for that was the fact that the method has not been tested on mill scale. The other reason was that there was no compelling need to raise the solid content of the recovered material when it is used as a filler in this case.

UF has become one of the main methods for recycling of pigment and chemicals with retention of their functional value (Mahmood, 2006; Nygard et al., 1998; Roitto, 2007; Siivonen and Genduso, 2003; Singh et al., 1999; Tizon et al., 2005). Cellier, Activity of ABB France, in cooperation will PALL Corporation, has developed a UF system based on the cross-flow filtration technology with ceramic membranes for liquid/solid separation specially for the paper industry and is designed for the treatment of effluents (mainly rinsing water) resulting from the coating process (coating color kitchen and associated equipment) (Tempesta, 2007). It uses Membralox® ceramic elements, which are asymmetric multichannel membranes consisting of a porous alumina support and a filtering layer (alumina or zirconia). The ceramic membranes are fitted with a 316-L stainless steel housing (module). They are resistant to chemical attacks, extreme pH and temperature values, and are compatible with organic solvents. The standard UF range is 20–100 nm. ABB UF systems are composed of several Membralox modules in series and/or in parallel according to the required filtration area. Each system can be extended by adding new modules. The feeding is continuous and the working tank operates at a constant level. The feed stream moves parallel to the membrane filtration surface, and purified liquid passes through the membrane. The separation is driven by the pressure difference from one side of the membrane to the other—referred to as transmembrane pressure. Cross-flow filtration streams are divided into three parts: (1) feed that enters the filtration channels, (2) permeate, a solution that passes through the membrane pores (clear water), and (3) retentate (or concentrate), the solution retained by the membrane (raw materials). With the turbulence created by the cross-flow velocity, particles are continually swept away to avoid the clogging up of the membrane surface. The retentate is the result of the concentration of the original feed stream. It flows through the channel and is recycled back into the feed stream.

The UF stage enables to recycle rinsing water by decreasing the COD value and lower the load of the wastewater treatment plant as well as the relating operating and energy costs. The UF unit also helps to minimize the perturbations in the wastewater treatment plant, such as highly variable effluent flow and concentration rates, COD peaks due, for instance, to a paper break. Recovered permeate or “clear water” can be used as rinsing or process water in the paper mill. According to the application, solid matters contained in the concentrate slurry can be added as a component to the coating color or precoat directly at the mixing stage. The system has been implemented at Cascades Blendecques S.A., France; Cartiera di Sarego (Burgo Group spa), Italy; Thai Paper Co., Ltd., Thailand; Advance Agro Public Co., Ltd., Thailand; Suzano de Papele e Celulose S/A, Brazil.

Metso Paper has also developed a UF process called OptiCycle C for treatment of coating effluent and recovery of coating color solids. The core of the OptiCycle C process is the OptiFilter CR, which consists of flat polymer membranes in a cell construction. Feed flow is kept turbulent through the use of rotors between the cells, which maintains high filtering capacity and promotes longer membrane operating life. OptiCycle process comprises the collection and screening of the coating color-containing effluent. The system consists of one or several OptiFilter CR filters, piping, tanks, and dosing systems for the concentrate and permeate, as well as the membrane

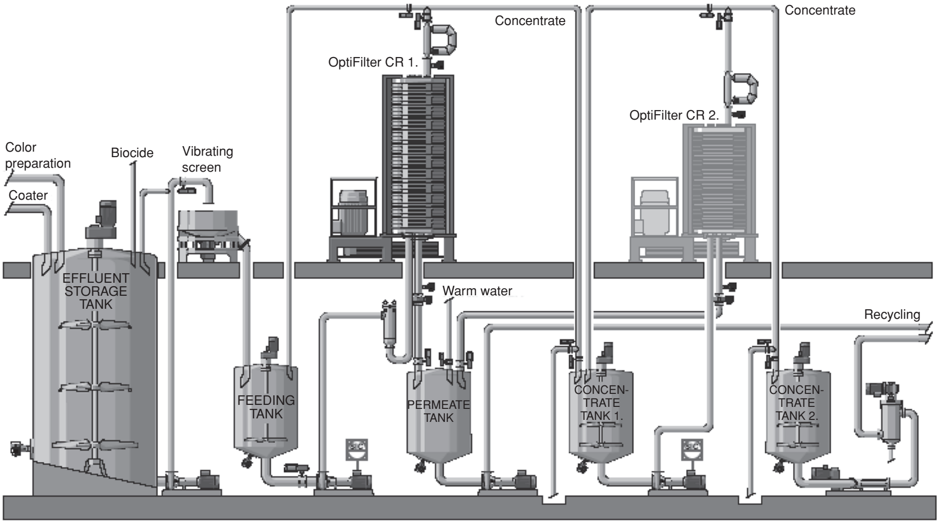

Figure 5.16 A two-stage OptiCycle C process flow scheme (courtesy Metso Paper).

detergent system (Fig. 5.16). The concentrate DS content and the pressure difference over the membranes are measured and automatically controlled to maintain optimal performance in continuous operation. The concentrate is recycled in the fresh coating color. The permeate can be reused, for example, in coating preparation as washing water, or as dilution water for starch. The concentration process can be divided into two stages if required. The first-stage UF concentrate is pumped to the second-stage filter via an intermediate tank, and the final concentrate of high solids is collected in a storage tank. This process connection results in considerably higher DS content of the concentrate. The second-stage filter can be used alongside the first-stage filter if needed. Metso's two-stage UF plant allows pigments and chemicals to be recovered from coating effluent with solid contents up to 50% (Roitto, 2005).

OptiCycle C process has been implemented at Tullis Russell, first in the UK (Anonymous, 2003), to improve the economics of coating by eliminating the loss of coating color and the subsequent disposal costs. It also reduces mill water consumption and its effluent load. The other mills employing OptiCycle C are Stora Enso Oulu—supplied by Valmet Raisio (Kraatari and Ryyppo, 1999), M-Real Husum, Sweden (Ryyppö, 2006).

A small UF unit can handle 2000 L/h effluent in 2% of solids. This kind of system is feasible for a mill using 10–50 t/day coating color. Investments amount to about €0.2–0.3 million for this size. Remarkable savings (costs of landfill, saving of expensive coating color) can be achieved by recycling coating chemicals. In some cases, the value of recovered chemicals and reduced costs of dumping can give a payback time from about 1 to 2 years. Another example was reported as follows: the investment a process that is capable to handle 200–400 m^3/day coating effluent costs about €0.5–1.5 million. Typical running costs are €0.1 million/annum.

These techniques are required to cut the mill suspended solids discharges and improve the operability of the external effluent treatment. The key factor for implementation of UF is reducing the costs of dumping and savings in raw materials of costly coating colors. Therefore, it is crucial for the applicability of this technique that the recovered coating colors can be reused. Several plants all over the world are using this technology (Nygard et al., 1998; Roitto and Alho, 1997).

Recovery of Pigments for Use in Papermaking

Ahlstrom, which is now a part of Metso, has developed a technology called FilRec for pigment recovery. FilRec is the system in which the pigments of the hydrocyclone system reject are recovered for use as a raw material in the paper production. The ash content of this reject can be as high as 80–85%. The reject of the hydrocyclone system includes a combination of fibers, fillers, pigments, latex, and other additives originating from coating, which are unable to be reused directly, primarily because of their particle shape and size (Koepenick, 1997). This process has four stages. The feed flow of FilRec is typically the reject of the final stage of the short-circulation hydrocyclone. First, the fractionation splits the feed flow into coarse and fine fractions with a screen, which has a slot size of 200 μm. The coarse fraction consists of stiff fibers and coarse solids, while the fine fractions contain mainly pigment flakes, fillers, and water. Second, the filler recovery stage classifies the solids according to particle size with an Ahlcleaner RB 77 Eliminator. The accept includes fine filler as particle size mainly below 10 μm, which is returned to paper production as recovered filler. Pigment flakes and coarse fillers are concentrated to 20–50% solid content and directed to the mineral dispersion stage. During dispersion, the pigment flakes and coarse fillers are subjected to turbulent shear forces. These forces, together with a crushing effect, break down the coarse particles. The pigment flakes and coarse filler particles are circulated in the dispersion loop, on average three to six times, until they are small enough to be accepted as fillers. However, a small outlet flow from the dispersion loop is taken with the coarse fraction from the screen to be classified in the reject stage of the Ahlcleaner RB 77. From this stage, reusable fibers and fine fillers are returned to the paper production. Recovery of fillers by FilRec is said to have no effect on paper machine runnability or paper quality (Koepenick, 1997).

In Caledonian Paper in Irvine, UK, the effluent treatment process with the recovery system of pigments was started in 1995 (Frette, 1995). The mill produced 200,000 t/annum of LWC paper. The recovery process separates paper clay from latex. The paper clay is returned to the coated broke line and the latex is sent to the fluidized-bed boiler, where it is burned with bark and fibrous material from the final stage of effluent treatment and thus produces steam for the mill. The boiler consumes the solid waste of the mill and decreases the need for solids disposal in a landfill; only ash is removed from the mill. A total of 10,000 m^3/day of liquid effluents are generated, containing 13–15 t/day of suspended solids. About half of the effluents, in which there is a low suspended solids contents, for example, the clear filtrate from the paper machine, are sent directly to the local sewage pumping station for disposal straight out to sea. So the solids-bearing effluent is processed in the new ETP. At first, the mixture of water, china clay, and latex is piped to a series of settling tanks for chemical pretreatment and then into a lamella clarifier. Here, it is mechanically separated and the clay is precipitated out of the solution onto a series of sloping metal plates before being recovered from the bottom of the lamella. The advantages of the recovery process for Caledonian Paper are the savings in the consumption of china clay (~1800 t/annum) and the costs of transferring solid waste to the landfill (Frette, 1995).

Separate Pretreatment of Coating Wastewaters

The discharges of coating color can be divided into two main types of wastewaters:

1. Undiluted surplus coating color (~50–70% DS) from coating kitchen and coater station. In case of product changes and during breaks, the system has to be washed (disperger, chests, pumps, piping, and coater station). Furthermore, sometimes not all of the coating colors can be completely used and the rest is washed as well. The concentrated discharge can be collected in tanks or mobile containers for solid waste disposal.
2. Diluted coating components from washing water from tanks etc. The DS content of dilute effluent is typically 2–4%. If they are discharged to the treatment plant, sudden high organic loads have to be handled in the treatment plant (COD values >10,000–100,000 mg/L). The diluted spills are collected in tanks and pretreated before discharge to the external wastewater treatment plant. If wastewaters are not treated before biological treatment, they can have adverse effects on the wastewater treatment plant, causing difficulties in primary clarification and in biological phases. A typical pretreatment arrangement is as follows.

The wastewaters are collected into an equalization basin. The wastewaters are screened with a step screen and pumped to a chemical precipitation. The chemicals are added in a rapid mixing unit. Aluminum sulfate and polyaluminum chlorides are used as precipitation chemicals. Polyelectrolyte is used as a flocculation aid chemical and it is dosed into the flocculation tanks. The flocculated wastewater flows into a lamella clarifier where the suspended solids settle on the bottom of the clarifier, and the clear overflow is discharged to the wastewater channel for further treatment. Sludge from the bottom of the clarifier is collected to a sludge tank, and from there it is pumped to a centrifuge for dewatering. The dewatered sludge at the concentration of about 30–40% is transported to a landfill. At one mill, however, the precipitated coating colors are dewatered by centrifugation and reused as coating color for precoat. This option needs a lot of development work.

The pretreatment of coating wastewaters can be applied at both new and existing mills. However, in existing mills the arrangements for wastewater collection and rerouting may be more complicated and more expensive. New installation will probably prefer UF of coating wastewater because usually they offer a relatively short payback time.

The main achievements are operational benefits especially in the wastewater treatment plant. TSS loads to the wastewater treatment plant are reduced, and also accidental spills (sudden SS loads) to the treatment plant can be minimized. The upsets of the primary clarifier can be reduced because there are less sudden disturbances in settling of TSS or increase in the torque of the clarifier drive mechanism. The risk of clarifier overloading is also reduced. The upsets of biological system are reduced because the inert matter (e.g., pigment particles) in coating effluent is not carried over and accumulated to the active biomass of the biological treatment process. Thus, the environmental load is reduced. The clear filtrate from the coating color effluent treatment can be reused elsewhere in the paper mill, for instance, for dilution of coated or uncoated broke. However, wastewater streams are only controlled and concentrated but waste remains.

The separation of coating chemicals from the biological wastewater treatment may have a positive effect of the further treatment of the biological sludge. It is easier to burn the sludge of the mill's main wastewater treatment plant because a pretreatment for coating wastewaters reduces the ash content of the main sludge streams. However, compared with UF of coating colors, waste is still produced because the experience to recycle the precipitated coating colors is still very limited. Flocculation results in a certain increase of salts in the effluent.

The process has been used many years in paper mills across the Europe. However, some difficulties have been detected from the dewatering of the sludge produced. If the dewatering device is not chosen properly, there may be wear problems.

The investment for the separate coating wastewater treatment by means of flocculation is about €1.2–1.4 million for a production of about 1000 ADt/day. The annual operating costs are €75,000–150,000/annum, excluding landfill costs. Because the value of the chemicals is lost when they are landfilled, there is no possibility for payback.

The driving force to adopt this measure is the difficulties in the external wastewater treatment plant if this pretreatment is not applied. The high TSS of coating wastewater can upset the operation of primary clarifier and biological process and result in sludge incineration problems (CEPI, 1998).

Measures to Reduce the Frequency and Effects of Accidental Discharges

In a paper machine, the objective is to maintain long nonstop runs of the paper web through the machine to obtain the end product. Variations in the machine performance or pulp quality during operation are likely and up to a limit are kept under control but at worst lead to paper breaks and lost production. In addition, the machines need maintenance, much of which cannot be done when the machine is in operation, thus calling for more short stops and start-ups. If the machine produces a variety of paper grades, the thing is still further complicated with stops required to change from one grade to another. The accidental discharges normally occur due to paper machine operational upsets, scheduled maintenance shutdowns, and start-ups and poor management of white-water tanks or machine broke chests in the wet-end or dry-end broke chests or off-machine coating.

By improved paper machine automation, the online monitoring of the paper sheet and machine parameters becomes fast and more accurate. The pulp discharge from the head box, the speed of machine rolls, by variable speed drives, and the amount of steam used for drying can be better balanced and optimized according to the needs. As a result, paper quality is improved, and when the controls are properly built and connected to affect each other, the number of machine breaks also decreases. On the other hand, in production of high-quality grades, the refining and screening operations must meet higher standards because less quality variations are allowed in the paper web.

The most important item keeping the accident discharges to a minimum is the proper sizing of the white water and broke chests. As a rule of thumb, the broke chests should have enough volume to store at least 3 hours worth of pulp at the rated production. Otherwise, there is an increased probability that significant water and solids discharge to the sewer occur. The white-water storage capacity must match this broke storage so that no freshwater is required during sheet breaks or when the broke is returned to the machine. In paper machines producing coated grades, the return of the broke collected from on- or off-machine coaters must be controlled carefully. This is because the proportion of coated broke must be below a case-specific limit to make a proper mix of fresh pulp and different brokes and thus to avoid problems in the paper machine wet-end. The coated broke storage volume must meet this demand. The control of white-water tank level according to broke inventory, pulp inventory, and production plan must be exercised to prevent spillage. In mills that change paper grades frequently the tank control is more difficult, because the inventories are often kept low in order to minimize losses from cleanups at grade changes. For this reason also, the machine feed characteristics must be controlled more carefully so that the amount of broke stays low. In mills with many paper machines such losses may be reduced, if another machine can use this material.

To protect the wastewater treatment plant, and simultaneously the environment, the implementation of an equalization basin (retention basin) could be considered. In the case of accidental spills, the wastewater can be conveyed to this basin. From there it can be discharged to the wastewater treatment plant in a controlled manner. Measures to avoid accidental discharges from handling and storage of chemicals are the following:

- Design and operation of facilities in such a way that dangerous substances cannot escape.
- Quick and reliable detection of leakage from all parts of the facility that comes into contact with dangerous substances. Escape prevention of leaks and appropriate disposal. When not double-walled and provided with a leak indicator, the facilities should be equipped with a collection system/device of

a tight and durable design. Collection chambers may not have any discharge openings.

- Operating instructions including monitoring, maintenance, and alarm plans are drawn up and observed.
- The wastewater treatment is the most crucial point for accidental discharges. A well performing treatment plant and a good communication between employees of the production units and of the wastewater treatment unit are a prerequisite. In the case of an accidental spill, the latter can take adequate measures to protect the treatment plant.

Control of accidental discharges is of primary importance in the paper machine and can be applied in existing and new mills. However, problems may arise in existing old mills if they do not have enough space to expand water or pulp storage. These measures reduce the frequency of hydraulic or solids peak discharges from the paper machine.

Online monitoring of sewered effluent flow rate and laboratory monitoring of suspended and dissolved solids, pH, temperature, and organic content as BOD5 or COD of the sewered and occasionally some recycle streams are recommended. Also, online suspended solids or turbidity meter can be used.

The development of an efficient white water and pulp chest management results in improvements of production economy and reducing the number of accident discharges.

The increased level of automation has been proved effective in increasing the control of accidental discharges although the main reason for its implementation is usually improved machine runnability and, in most cases, increased capacity. Static and currently dynamic modeling has brought improved understanding at many mills for advance control of machine operations.

Investment costs of one additional white-water tower of 3000 m^3 and one uncoated broke tower of 2000 m^3 would be about €1.0–1.2 million. If a second broke tower for coated broke is required, it would cost with necessary auxiliary equipment, piping, and electrification about €0.4–0.5 million. These investments correspond to a paper production of 1000 ADt/day.

First, these measures are to prevent upsetting discharges from the paper machine entering the mill sewer and keeping the load to the external effluent treatment more stable. Second, the process automation coupled with sophisticated white water, pulp, and broke inventory improves the machine runnability.

Measurement and Automation

Unstability in stock preparation and wet-end area causes web breaks and thus disturbances in water systems. So, for effective papermaking, accurate process control and online measurements are important. The major areas where measurement and automation increase both quality and productivity and environmental performance are discussed as follows:

- *Save-all operation:* Suspended solids or turbidity measurements are important peak indicators when target is to use filtrate as much as possible for shower waters. Unnecessary fiber losses are thus avoided and the load on wastewater treatment is diminished. Feed consistency measurement and control facilitate the optimization of filter operation.
- *Blending:* In thick stock proportioning and blending, variations in consistency and pulp quality (e.g., freeness, fiber length, and ash content) are stabilized to avoid quality variations at the paper machine.
- *Refining:* The refining control strategy requires accurate flow and consistency measurements at minimum. For optimum refining control result, pulp quality measurements such as freeness/drainage and fiber length measurements are needed.
- *Wet-end management:* The information on head box and white-water total solids and filler consistency levels provides an early indication of potential problems in wet-end chemistry. Automatic retention aid control where the target is to retain uniform amount of fines and fillers in the paper web is based on online fiber and filler consistency measurement in short circulation. The use of white-water consistency control has drastically increased the stability of wet-end operations and reduced the number of wet-end breaks. In addition to the consistency variation in short circulation, variations in the incoming dissolved and colloidal material are a major source of problems in paper machine runnability and optimization. Cationic demand is measured from the white water and is used to control the detrimental substances. While retention control acts by controlling flocculation, charge control stabilizes by controlling coagulation.

The above-mentioned measurements and controls can be applied at both small and large mills. Biggest benefits are obtained when high-quality end products are produced. It is difficult to quantify the environmental benefits achieved because they depend on the characteristic of the installation, the degree of productivity before improvement, the paper grade(s) manufactured, etc. Water management is facilitated, and the pollution load to the wastewater treatment as well as the loss of material (waste) is reduced.

The increase of productivity and decrease of breaks or losses by use of better process control and automation have only positive effects on the environment. Less disturbances in water systems, less energy consumption, and less waste are the result of these measures. Measurement and automation have been applied in many existing mills to increase efficiency without problems and are the natural part and further developed at new mills.

From economic point of view, the goal is to enhance papermaking profitability. Eliminating one 7-minute break a week means results in 0.5% more uptime, which in a 300 t/day mill yields 1.5 t/day more production. If the net cost of lost production is US$500/t, the savings due to better stability would be over US$260,000/year. In addition, the energy that is wasted during the break, for example, in drying cylinders and pumping, is saved. High and uniform retention also means savings in the wastewater treatment plant. The wastewater treatment plant need not be overdimensioned for peaks, when a more uniform wastewater load is reached with a more uniform retention control. Against this savings, the investment and operating costs of the equipment have to be taken into account. The payback time for measurements and control when implemented is typically less than 1 year. After appropriate training, the mill operators can operate the unit. The mill's electrical and instrumentation people can do the necessary maintenance work when needed.

Measurement and automation are primarily applied for economic reasons and to achieve higher paper quality. It results in time-savings in paper production (e.g., allows faster grade changes, faster start-ups, and faster recovery after sheet break), lower production costs (e.g., by furnish component optimization, effective usage of additives, and decreased energy consumption), and maximized paper quality (e.g., through less cross-direction (CD)/machine direction (MD) variation, optimized dewatering, and formation).

Optimized dewatering for a given machine is obtained by a proper stock preparation and wet-end management (e.g., refiner control and control of chemicals). It is furthermore easier to manufacture a wider range of paper grades (Nokelainen and Piirainen, 1995; Nokelainen et al., 1997).

Installation of an Equalization Basin and Primary Treatment of Wastewater

This measure is not considered as a stand-alone technique for most paper mills, but as a pretreatment. Pretreatment is usually carried out before biological treatment to facilitate and improve the treatment process. In some special cases where the organic load is too low for efficient biological treatment, it may be the only wastewater treatment.

The following methods are considered the most important ones:

- Coarse screening is carried out to remove larger objects and sand, which may cause damage to the subsequent equipment.
- Equalization and spill collection may be required for effluents with large variations as regards flow and content of pollutants. Such variations may disturb the function of the subsequent treatment processes, particularly biological processes. A value of 4 hours retention time in the equalization basin can be taken as an indication for appropriate design. However, the appropriate retention time of the equalization tank depends on fluctuation of water quality.
- Primary or mechanical treatment by means of gravity forces is carried out for the removal of suspended solids such as fibers, bark particles, and inorganic particles (fillers, lime particles, etc.). A certain minimum size of the particles is required. The finer particles will settle too slowly for practical use or not settle at all. Sedimentation is the first type of treatment to be applied at a pulp and

> paper mill, and/or a pretreatment ahead of, for instance, a biological process. Flotation can also be used for primary clarification. Some smaller mills use primary treatment by means of filtration as the only wastewater treatment. The particles, settling to the bottom of the primary clarifier, form a sludge, which has to be removed. This is achieved by pumping, in circular clarifiers in combination with bottom scraping. The sludge is normally low in DS content, approximately 1–2%, and has to be dewatered before final disposal. In some mills the sludge from the primary clarifier is reused in the production process, which provides the sludge properties to be suitable.

The process can be applied at both existing and new paper mills. Some kind of water consumption reduction measures should preferably be carried out to reduce the hydraulic load and thus investment costs of the clarifiers.

The result of the primary treatment depends on the effluent properties, but also on the degree of internal fiber recovery in the pulp or paper mill. For suspended solids (TSS), the removal rate may be within 60–90%. For settleable solids, the removal will normally be higher, approximately 90–95%. TSS values after the primary sedimentation may be in the range of 30–200 mg/m^3.

The ETP produces sludge, which after dewatering has to be further treated. There are many different options for further treatment of this sludge, which are to a certain extent site-specific. One option is incineration providing in some cases net positive heat value. Gravity-type primary clarifiers have been used for many years in all types of paper and board mills with good results.

Investment cost of primary treatment for a new 1000 ADt/day integrated paper mill, comprising pumping, primary clarifier, sludge dewatering, and chemical dosing systems, is €3.5–4.5 million. The operating costs depend very much on the required chemical consumption (if so), being €0.4–0.6 million/annum. Primary treatment is used to reduce TSS load to the recipient or biological treatment.

Secondary Treatment—Aerobic Methods

For secondary treatment, the basic alternatives are between the use of aerobic and anaerobic/aerobic biological systems. However, anaerobic treatment is restricted to wastewater that contains high loads of biodegradable organic substance to allow methanization. It is therefore mainly applied at recycled fiber processing mills, especially in paper mills manufacturing corrugating medium or board. There are a wide variety of designs of aerobic treatment of paper mill effluents. Activated sludge systems, aerobic submerged biofilters, trickling filters as one or more step application or in combinations with each other, sequencing batch reactors, rotating biological contactors, are in usage.

The main technologies for external biological treatment of paper mill wastewater are

Activated sludge treatment (single and two-stage)

Activated sludge with carrier material

Two-stage anaerobic + activated sludge treatment
Two-stage installations with a high sludge loading step
Multistage biological treatment followed by filtration/biofiltration/UF
Multistage biological treatment and treatment processes using ozone
Low-capacity trickling filters
High-capacity trickling filters + activated sludge treatment

It is a good general principle to provide some hydraulic buffering to protect the treatment plant from large variations in flow or organic load that may otherwise cause periods of poor plant performance. Buffering also allows for plant size to be optimized for the average flow rate. Biological treatment can also be combined with advanced treatment as ozone treatment or membrane filtration if more stringent requirements have to be achieved. In Germany, there are two systems that combine biological treatment with ozonation and UF for further reducing the COD load to the recipient.

The process can be applied at both existing and new paper mills. In some special cases where the organic load is too low for efficient biological treatment, virgin fiber mills may only apply primary treatment to meet the required standards.

For biological treatment of papermaking effluents, the following pollution load reduction efficiencies can usually be easily achieved:

- Activated sludge: 85–96% for BOD5; 75–90% for COD. These removal efficiencies are achieved by low-load activated sludge systems with a food/mass ratio between 0.1 and 0.2 kg BOD/kg TSS per day. In a few applications also for high-load plants, good removal efficiencies are reported.
- Trickling filter: 60–70% for BOD5; 50–60% for COD.
- Moving bed biofilm reactors/suspended carrier reactors: more than 85–95% BOD5; 80–90% COD.
- Submerged biofilter: 60–80% for BOD5; 50–60% for COD.

It should be noted that the removal efficiencies depend to a certain extent on the incoming concentration of pollutants. Concentrations of organic substances in the wastewater, on the other hand, are governed by raw materials used, paper grades produced, specific water consumption, and applied process-integrated measures. Wastewater from paper mills after treatment can reach values between 50 and 150 mg COD/L. BOD5 levels below 25 mg BOD5/L are normally achievable and can reach values down to 5 mg/L. The COD/BOD ratio of filtered samples of paper mill wastewater after biological treatment is usually between 4 and 7 or 8 (up to 10). The load discharged to the recipient depends mainly on the paper grade manufactured, the product properties to be achieved, the water flow per tonne of product, the chemical additives applied, and the design and operation of wastewater treatment. Proper design and maintenance of the treatment plant are a prerequisite for good-performing biological systems.

Usually COD, BOD5, TSS, nitrogen and phosphorus, and AOX are controlled. Additional measurements to control the biological system are also recommended, for instance, O_2 content, sludge volume index, water flow, and from time to time microscopic examination of the activated sludge. The latter is gaining increasing importance.

During aerobic wastewater treatment, excess sludge is produced, which has to be thickened, dewatered, and further treated. A typical value for low-load activated sludge plants is in the range of 0.3–0.4 kg excess sludge/kg BOD5 eliminated (as DS), generated during treatment. Sometimes slightly higher values are also observed. The treatment of lower BOD concentration in submerged biofilters generates less excess sludge: about 0.2 kg excess sludge/kg BOD5 eliminated (as DS). High-load plants have a higher specific excess sludge generation. For aeration of the active biomass (activated sludge) and for pumps, electrical energy is needed.

The specific energy consumption for degradation/elimination of 1 kg BOD5 amounts to 0.3–3 kWh. It depends mainly on the specific amount of oxygen needed for degradation of organic substances and the designed load of the activated sludge system. High-load activated sludge systems require about 0.3–0.5 kg O_2/kg BOD5 eliminated. Low-load systems need 1.5–2.0 kg O_2/kg BOD5 eliminated. Consequently, high-load activated sludge treatment consumes about 0.5 kWh/kg BOD5 eliminated, and low-load activated sludge consumes about 1.5–2.0 kWh/kg BOD5 eliminated. If the low-load system is well designed, a value of less than1 kWh/kg BOD5 eliminated can be achieved (Möbius, 1997). This value can also be used to compare expected operating costs of different wastewater systems. Mineral nutrients are usually added to the biological treatment plant to keep the balance carbon/phosphorus/nitrogen, which is of crucial importance for the growth of active biomass. Usually, phosphorus is added as phosphorus acid and nitrogen in form of urea. Part of the added nutrients normally will be released together with the treated effluent. When the system is well optimized, nutrient discharge of 1 mg total phosphorus/L and below 10 mg inorganic nitrogen/L is achievable. Especially during the summer period, the wastewater treatment plant of paper mills may emit annoying odors. If the wastewater treatment is well designed and controlled, annoying odors can be avoided.

Aerobic biological treatment for effluents from paper mills has been successfully used for over 20 years. The tendency of sludge bulking in activated sludge treatment needs to be controlled by appropriate measures. It generally appears when there is a disturbance in the system caused, for example, by variations in pollution load, variations in dissolved oxygen in the activated sludge basin, lack or excess of nitrogen and phosphorus, or variation in the amount of recycling sludge fed back to the aeration basin.

Sludge bulking is usually temporary. A stepwise approach may give insight in the origin of sludge bulking. This approach may include, for instance, control on the design of the treatment plant, microscopic examination of the activated sludge, and monitoring of the incoming wastewater. In general, monitoring is necessary to get insight in possible causes for problems. In some cases, it appeared that lower carboxylic acids, such as acetic acids, were the main cause for prevalent growth of filamentous bacteria that are responsible for sludge bulking. Filamentous bacteria can also appear when sulfur is present in the effluents. For less critical paper or board grades (e.g., Testliner or paperboard), the reuse of (parts of) treated effluent from biological wastewater treatment, usually after additional treatment by flotation or sand filtration, is also an option.

Some examples of treatment systems in French paper mills are presented as follows:

- Activated sludge for a printing paper mill (200 t/day paper production): €2 million
- Activated sludge for a printing paper mill (300 t/day paper production): €3 million
- Biofiltration for a specialty paper mill (130 t/day paper production): €1.5 million
- Activated sludge for a printing paper mill (260 t/day paper production corresponding to 2.5 t COD/day): €2 million
- Activated sludge for a corrugated paper mill (100 t/day paper production): €1.5 million

The investment costs is presented as follows: activated sludge treatment, €300–600/kg COD/day; biofiltration, €500/kg COD/day. The range of investment costs depends above all on the quantity of polluting load per day to be treated.

Numerous aerobic wastewater treatment plants are operated in paper mills (Möbius, 1997).

Chemical Precipitation of Wastewater from Paper Mills

Chemical precipitation could be a complement to biological treatment either before or after. In some cases, chemical precipitation as complete secondary treatment for untreated wastewater from paper mills can be an option to reduce emission to water. Chemical precipitation involves the addition of chemicals to alter the physical state of dissolved and suspended solids and facilitate their removal by sedimentation or flotation.

Different substances have been used as precipitants. The most common ones are aluminum salts, ferric chloride, ferric sulfate, ferrous sulfate, or lime. To optimize the flocculation, polyelectrolytes are used in the mixing phase. Suspended and colloidal matters are separated by precipitation and subsequent filtration or clarification including the removal of nitrogen and phosphorus. By chemical precipitation, it is possible to obtain a clear effluent, substantially free from matter in suspension or in a colloidal state. This treatment is applied as stand-alone treatment or in combination with biological treatment. The latter is applied when lower emissions of organic substances (measured as COD and/or BOD) are supposed to achieve. Chemical precipitation has a role to play in particular when nitrogen, phosphorus, and TSS are of concern while biological treatment when oxygen depletion is the problem and not eutrophication. It is applicable to both new and existing mills. It is especially applied at smaller mills.

Chemical precipitation as complete secondary treatment of untreated wastewater from paper mills is mainly applied to reduce nutrients, especially phosphorus, TSS, and part of the organic matter (particulate and colloidal compounds). Sometimes chemical precipitation is also applied in combination with biological treatment.

Reduction rates of about 97–99% for TSS and 70% for COD referred to the raw effluent (before any treatment, i.e., before the primary clarifier) are achieved. The COD reduction is mainly due to reduction of TSS. The soluble part of COD (and BOD) is only slightly reduced ($\sim$10%). The reduction of the soluble compounds of COD and BOD can be achieved by biological treatment. The COD/BOD ratio in the range of 3 after chemical precipitation shows that a substantial part of the removed COD is consisting of less biodegradable, and therefore potentially more harmful matter. It also shows that these effluents are appropriate for further biological treatment.

The precipitation of TSS, nutrients, and to less extent organic material with inorganic chemicals results in a great quantity of sludge that is difficult to dewater and often dumped to landfill. The amount of generated sludge is in the range of 3–6 kg/m^3 including 60–80% water (after presses or centrifuges the dry substance is about 20–40%). The chemical cost is substantial and the purification is selective; neutral substances cannot be captured as efficiently as dissociated ions or colloidal and particulate matter. The use of precipitants results in an increase of salts (chlorides or sulfates) in the effluent. The use of metal salts is normally between 200 and 400 g/m^3. The treatment consumes some energy for pumps and drives. No specific problems are known that are linked to the application to this technique.

The investment costs of physicochemical treatment amount to €1 million for a printing paper mill with a capacity of 100 t/day. The investment costs of chemical precipitation include equalization tank, chemical dissolving equipment, chemical dosing equipment, precipitation and flocculation unit, and clarifier. For operating costs, no data were available.

Usually, chemical precipitation of wastewater from nonintegrated paper mills is applied when the nutrients, TSS, and nonsoluble parts of the organic matter in the effluent have to be removed.

Substitution of Potentially Harmful Substances by Use of Less Harmful Alternatives

In paper industry, water is the medium where most of the released substances may end up because usually the additives are added to the aqueous fiber filler suspension and are then either retained in the paper or come to the white water. Air is of less importance and soil may be affected via waste disposal (composting, use of paper sludge in agriculture, landfilling). The expected discharge of additives to the water is directly related to the retention of the chemicals to the paper product, the degradability of the substances, and the retention in the wastewater treatment plant. The higher the retention, the lower the discharge to the effluent and the lower the potential environmental effect of the applied additives. In the case of product aids, a maximum degree of retention is desirable from an economic (loss of additives) and ecological point of view. Because product aids are designed to give paper a particular characteristic, for reasons of costs and efficiency they generally have a relatively high level of retention to the cellulose fibers. Process aids are usually less retained because they produce their effect in the water circuits of the paper mills. A large proportion is discharged with wastewater.

Furthermore, it should be noted that broke is normally repulped so that some of the additives are returned to the water circuit. Knowledge about the retention of additives is therefore important. The degradability of a substance, on the other hand, is the crucial point to avoid the risk of accumulation of a given substance in environment and organisms, respectively. Some water authorities use both the retention factors and the biodegradability of substances to assess and minimize the contribution of additives to the COD load after treatment.

Besides a general approach for reduction of releases of chemical additives to water, there might exist some candidates for substitution/replacement from an environmental point of view. This might be especially the case when chemicals are considered as hazardous and there are less hazardous substitutes achieving the same purpose available. Biodegradable, nontoxic, and non-bioaccumulating chemicals should be favored whenever possible. Chemicals suspected to pose a risk to humans or environment should be avoided, for example, those with ozone-depleting effects, suspected endocrine disruptors, and CMR substances (carcinogenic, mutagenic, and reprotoxic). Organically hydrocarbons as benzene (carcinogenic), toluene (toxic), and xylene (toxic) originating from solvents and detergents that might be used for cleaning of wires, felts, and machines should be replaced by solvents that show less toxic effects. Alternatives (e.g., esters) that are to some extent biodegradable are also available.

Some substances—mainly process aids—are neither retained nor biologically degraded (substance A). In this case the applied additives end up completely in the recipient. Some substances—mainly process aids—are partially retained and partially eliminated in the wastewater treatment plant (substance B), and some others are again retained to nearly 100% and do not even reach the treatment plant. It can be assumed that most of the product aid additives are both partially retained and to a certain extent eliminated in the wastewater treatment plant. Process aids have a low retention to cellulose fibers and can therefore be expected to end up in the wastewater.

Reduction of harmful additives in paper processing will result in less impact on water and waste compartments. It can also be beneficial from the perspective of life-cycle management. By using environmentally sound product aids, harmful substances can be prevented from ending up in the product that in turn might be used as raw material in recycled fiber processing.

Some water authorities set requirements to minimize the contribution of additives to the COD load after treatment. Requirements on reduction of releases of biocides can also be found. Biodegradable, nontoxic, and non-bioaccumulating chemicals should generally be favored whenever possible. Chemicals suspected to pose a risk to humans or environment should be avoided, especially those with ozone-depleting effects, suspected endocrine disruptors, and CMR substances (Bobek et al., 1997; Braunsperger, 1996; EurEco, 1997).

Pretreatment of Sludge (Dewatering) before Final Disposal or Incineration

In ETPs large amounts of sludge are generated in the primary treatment, biological activated sludge plants, and chemical flocculation plants, including coating color treatment. Aerated lagoons, as well as anaerobic plants, typically generate sludge in lesser amounts. The sludge handling includes the following main stages:

- Reuse of fiber sludge from primary treatment. This is practiced in many cases.
- Thickening and dewatering of fiber/biological/(chemical) sludge.
- Final disposal of dewatered sludge.

Reuse of fiber sludge is practiced in cases where this is suitable with regard to product requirements etc. Internal fiber recovery, however, often leads to low fiber discharges and poor sludge properties, in which cases reuse of the sludge is not feasible. Biological and chemical sludges have very poor dewatering properties, and normally they have to be mixed with fiber sludge for acceptable dewatering conditions. So, in the presence of biological/chemical sludges, at least a part of the fiber sludge should be dewatered, rather than reused. Also, a far-reaching internal fiber recovery will mean increased difficulties in dewatering biological/chemical sludges.

The dewatering aims at removing water from the sludge as far as possible to facilitate the final disposal. Different types of mechanical equipment are available for this operation. Biological and chemical sludges should normally be thickened prior to the dewatering. This means an increase of DS content from about 1–2% to 3–4% or higher. The thickening is usually performed in a gravity thickener, which is basically a settling basin with low load. Prior to dewatering, the sludge must normally be conditioned with chemicals. Usually, a polyelectrolyte is enough. This refers particularly to sludge mixtures with biological and/or chemical sludge.

Dewatering equipment includes belt presses (twin-wire presses), screw presses, decanter centrifuges, and chamber filter presses. Most new installations during the last two decades have been belt presses, which have a reliable function and produce fairly high DS values, 40–50% with fiber sludge and 25–40% with mixed fiber/biological/(chemical) sludge. However, recent trend is to use screw presses. Screw presses can be used to increase the DS content after belt-press dewatering; approximately 10% DS increase can be obtained. It can also be used for direct dewatering; higher DS content can be obtained compared to belt-press dewatering.

An increasing application of screw presses has been observed for some years, due to an increasing interest in sludge incineration, requiring high DS values. Decanter centrifuges are at present mostly used for sludges with very poor dewatering properties, such as pure chemical sludge or biological sludge (if it is dewatered separately). They produce lower DS contents than the belt and screw presses. Rotary precoat filters can also be used for this application achieving higher DS contents.

The resulting filtrate has very low content of suspended solids, normally below 10 mg/L (superclear filtrate). Dewatering methods for all sludges are available. They are capable of dewatering to such DS contents that are necessary for final disposal.

The measure can be adopted in existing and new mills. Nowadays, it is impossible to run a mill without dewatering because the disposal of large amounts of thin sludge faces problems. The sludge dewatering can reduce the sludge volumes up to 20 times. The environmental achievements are seen at the disposal place. The reduced pollution of ground water is one of the effects.

The sludge produced at the ETP after dewatering can be burned, providing in some cases net positive heat value.

Many types of dewatering equipment, ranging from low-efficiency drum filters to high-efficiency screw presses, have been used in all types of paper and board mills. The current heavy-duty belt filter press and screw press designs used for high sludge dryness target have proved efficient in most cases. Continuous rotary precoat drum filters are also operated in paper industry resulting in 40–50% DS together with high-quality filtrate (10 mg SS/L). This is achieved by more rotational speed for thinner-shaved cake. However, the higher the proportion of biosludge in the mixture to be dewatered and the higher the dryness target, the more sensitive the overall system has become to qualitative and quantitative variations in the system feed or to other operation setup parameters.

Investment costs of sludge dewatering in a 1500 ADt/day newsprint mill are as follows:

Wire press €1.5–1.8 million
Screw press €1.7–2.0 million
Centrifuge €0.7–0.9 million

The operating costs, assuming dewatering of both primary and biological sludge, are €0.3–0.6 million/annum. The cost is dependent on the sludge composition and demand of flocculation chemicals.

More suitable DS content for transportation and final disposal is the driving forces to implement this technique (Finnish BAT Report, 1997; Pöyry, 1997; SEPA-Report 4713-2, 1997b).

Options for Waste Treatment

Residues and wastes are generated in the production of paper and board. The waste fractions in paper mills are fiber and paper sludge; for mills using recovered fibers—rejects from paper and cardboard recycling and de-inking sludges from paper recycling; for integrated mills with virgin pulp production—bark, dregs, and green liquor sludge (from black liquor treatment), waste from the preparation of water for industrial use, sludges from wastewater treatment plants, waste not otherwise specified.

The waste fractions are separated and merged in different ways, depending on the options for reuse/recycling and further treatment and disposal. Figures for single waste fractions are scarcely available. Often, only data on sludge and rejects or sometimes only sludge are reported. Therefore, in the following the paper mill, residues are discussed as one material flow.

The most important specific residues are rejects from stock preparation, fiber and paper sludge, and sludge from water treatment. They are generated at both virgin and recycled fiber mills. However, at virgin fiber mills the quantities produced are smaller, usually less than 50 kg/t, whereas in mills using recycled fiber (e.g., tissue mills) the quantities are very much larger, for instance, up to 1000 kg DS/t of tissue. The composition and amount of the solid waste depend on the paper grade produced, the raw materials used, the process techniques applied, and the paper properties to be achieved. Waste management consists of waste prevention, reuse, material recycling, composting, energy recovery, and final disposal. There is no standard solution for the waste handling in paper mills.

The residues of paper mills—except the ashes from power plants or boiler houses and from on-site incinerators—are characterized by a relatively high amount of organic material. Nevertheless, landfill is still widely used for waste disposal in many European countries. At the same time, in many Member States, the dumping of waste with high organic content is discouraged by governments and will probably be prohibited in the near future. The EU Directive on landfill of waste will support this tendency in setting targets to cut the amount of biodegradable (municipal) waste sent to landfills. Consequently, alternative recovery operations as material recycling and incineration with energy recovery will play an important role in the future. This treatment options are discussed in the following as techniques to consider in determination of BAT. Recovery operations—where the residues are put to some further use whereby some or all of the constituents (including energy) are reused or recovered—are considered as preferred waste treatment options, where feasible. BAT is to identify these possibilities and to ensure that they happen. Some important technical aspects are highlighted, and the benefits, concerns, or limitations of different treatment options are discussed.

The main treatment options for material recycling and the factors governing the treatment option choice show that several factors govern the option chosen by a given mill. The main factors might be local infrastructure, costs, and competition, with residues from other industries. The latter is especially relevant for the utilization of paper sludge in cement and brick industry. Concerning transport, the principle of proximity reduces environmental impact and costs. In some countries, composting of paper sludge or land spreading in agriculture is practiced. For this alternative, the control of the potential pollutants is of crucial importance. However, sludge from paper mills usually does not contain more pollutants than sludge from municipal treatment works, and restricted application can have some positive effects on the soil ($CaCO_3$ as a neutralizing agent of acidic soils, moisture retention by fibers and fines on dry soils, low nitrogen content). The possible benefits vary according to the soil type. The periods of land spreading are restricted to some months of the year. It is therefore necessary to build ensure sufficient storage capacity for the sludge. The feasibility of land spreading is strongly dependent on the acceptance to apply sludge to agricultural land. In some places this practice is encouraged as an economically beneficial disposal route, whereas in other places there is a concern about land spreading of paper sludge. The major concerns are possible contamination of soils with low concentrations of heavy metals and organic micropollutants, local opposition because of nuisance problems or image problems for agricultural products from land-spreading areas. For composting, the quality demand of the compost is most important to get a marketable product. Composts made from organic waste mixed with different quantities of recovered paper and residues of the paper industry fulfill these requirements such as the degree of maturity or suitability for plant growth. Furthermore, parameters such as salt and organic substance content and the process-specific leachate emission are positively influenced. The concentration of harmful substances, especially those of heavy metals, must be considered as a limiting factor.

Another option for treatment of sludge from paper mills is the utilization in the cement and brick industry (to improve porosity) or other building material. In the cement industry, both the material and the energy content of the paper residues can be recovered. For the use in cement industry, sludge from primary clarifiers (or mixed with excess sludge from biological treatment) that contain fibers and fines and inorganic compounds (e.g., fillers, and coating pigments) is especially suitable. The sludge ($\sim$50% moisture content) is dried with waste heat from the predrier of the cement kiln so that no additional thermal energy is needed to reduce the moisture of the sludge down to 10–15%. Thus, when burning the dried sludge in the cement rotary kiln, the calorific value of the organic substances is used and the ash from incineration of the sludge (mainly) remains in the product (cement). The inorganic substance of the ash of the incinerated sludge is also a compound of the cement clinker. If cement (or brick) manufacturing industries are local to the mill (short transport distance) and are able to use the sludge, it is a viable option.

Residues and sludges contain organic substances that can be burned on- or off-site in dedicated incinerators with energy recovery (for on-site incineration in nonintegrated mills the amount of sludge to be burned is usually not sufficient). Incinerators with energy recovery can be divided into monoincineration and coincineration. In monoincinerators—usually fluidized beds, multiple hearth furnace, or kilns at a temperature range of 850–950°C—exclusively waste from paper industry is burned. These installations achieve the legal requirements for waste incineration when air emission abatement is applied and are considered as BAT. The ashes can be landfilled or further used in building industry. Coincineration of paper industry residues is practiced in cement kilns, coal power plants, municipal waste incinerators, blast furnaces (iron and steel industry), and foundries. For this option, residues with a high calorific value are especially suitable to replace fossil fuel (e.g., coal and fuel oil). The paper mill residues are usually mixed with other fuels burned in these installations. Before incineration, they have to be dewatered and sometimes also dried (e.g., for cement and iron and steel industry). As a rule of thumb, it can be said the more similar the characteristics of the residues to be burned to the normal fuel the easier the coincineration. Homogeneity of secondary fuel and uniform and constant composition of the residues are also important. The control of these parameters makes paper industry waste more interesting for combustion installations.

The effect of coincineration of paper mill residues and sludge on air emissions depends on the composition of the burned material. Coincineration of fiber and paper sludge—especially those with high alkali content—in coal or lignite fire power plants either has no effect on air emissions or leads to a slight reduction of pollutants. Emissions of SO_2, HCl, and hydrofluoric acid are reduced by coincineration of sludge with high alkali content (de-inking sludge, fiber sludge containing coating pigments, and fillers). The content of heavy metals in fiber and paper sludge is also low compared to coal and lignite. Rejects from stock preparation of recycled paper mills manufacturing corrugating material have higher chlorine content (1–3% mass). First experiences in a full-scale plant in Germany showed however that coincineration of rejects in lignite-fired power plants is feasible. No increase of dioxins has been measured. Incinerators sometimes face the considerable obstacle of local objections. In integrated pulp and paper mills, a major portion of the sludge is usually incinerated together with bark in bark boilers. Integrated recovered paper mills may have installed an on-site incinerator. In those mills, ashes and residues from air emission control, for example, dust from ESP or gypsum from SO_2 removal (if applied), have also to be handled as a waste fraction (Guillet, 1997; Hamm, 1996; IPTS, 1997; Wünschmann, 1995a,b).

Installation of Low-NO_x Technology in Auxiliary Boilers (Oil, Gas, and Coal)

In the paper mills, a variety of fossil fuels may be used for supplemental steam production. By burning of these fuels, environmentally sound incineration techniques are called for to minimize particulate, SO_2, and also NO_x emissions. Low-NO_x technology applied to burning of solid fuels and pulp and paper mill wastes with fluidized-bed boilers has already been discussed. Coal and lignite suit well to be burned as main or support fuel in fluidized-bed systems, which by careful operation control promotes low-NO_x formation. In conventional oil or natural gas-fueled boilers, the burners feeding the fuel–air mixture must apply designs that maintain low-NO_x burning conditions. Also, coal or peat is often burned as finely ground dust in conventional boilers, fed through burners that with proper designs provide low-NO_x burning.

The primary burning air is brought through the burner in the fuel–air mix. Secondary and tertiary air is fed in separately to maintain an appropriate primary/secondary/tertiary air balance in the flame area to maintain low-NO_x combustion. Some air may still be fed, if necessary, above the main flame area to complete the fuel combustion. The purpose of the multiphase air feed is to burn the fuel without excess air and actually even under reducing conditions, meaning that

- There is not enough oxygen to promote strong NO_x formation. The flame temperature is lower than in conventional burners, which further decreases NO_x formation.
- Part of the NO_x formed will reduce back to elementary nitrogen, for instance, when a residual amount of the fuel is burned in the outer flame area or outside it.

Low-NO_x burners and multiphase air feed can be used both in existing and new boilers. When powdered solid fuels, such as coal or peat, are used, it is important that if they have high humidity they are predried to support fast and efficient burning. Additionally, they require that the burning air is preheated to ensure quick ignition and complete burning.

In comparison to conventional burners with 250–500 mg/MJ NO_x emissions, the low-NO_x burners can reach considerable lower levels in stack emissions.

Emission monitoring with online NO_x meters can be carried out. Also, oxygen meters can help to determine that low-NO_x burning conditions are maintained. For accurate measurements, in-field sampling and laboratory analysis are required. Low-NO_x burners have been applied in the retrofit of existing boilers and construction of new ones. Investment costs are typically €0.6–0.9 million for 1000 ADt/day paper production. Operating costs increase with €0.1–0.2 million/annum.

Air emissions from nonintegrated paper mills are mainly related to steam boilers and power plants. These plants are generally standard boilers and do not differ from any other power plants. It is assumed that they are regulated like any other plants of the same capacity. Low-NO_x burners are mainly used to reduce NO_x emissions from auxiliary boilers (Finnish BAT Report, 1997; Ministry of Education, 1994; Pöyry, 1997).

Use of Combined Heat and Power Generation

Refer to Section 5.4.

Optimization of Dewatering in the Press Section of the Paper Machine (Wide Nip Press)

A paper machine constitutes a huge dewatering process. It comprises, in principle, the three major parts: the wire section for sheet formation and first dewatering by gravity and vacuum/suction, the press section for further dewatering of the wet web by mechanical forces, the drier section for drying the web to the final dryness by evaporation on steam-heated cylinders. After the press section, normally the web dryness is 45–50%; that is, about 1 kg water/kg furnish is left. To evaporate these last "water drops," a lot of evaporation energy and a long drier section are needed.

In a paper machine, most of the energy is needed for paper drying (steam 572 kWh/t). Electrical energy is needed for roll and cylinder drives (electrical 100 kWh/t) and to create vacuum (electrical 67 kWh/t). The higher the dryness of the paper web after the press section, the lower is the thermal energy required for the final paper drying. By 1% increase of the dryness of the paper web entering the drier section, approximately 4% heat (in terms of low-pressure steam of ~2 bar) can be saved. Therefore, measures have to be taken in the paper machine to maximize the dry content by wet pressing.

In a conventional roll press nip, the nip pressure has reached its high limit and cannot be further increased to improve dewatering in the press section. By substituting conventional short nip presses with wide nip press(es), so-called shoe press(es), a higher pressure impulse than in a conventional roll press is achieved, resulting in an intensified dewatering of the wet web and higher dryness of the paper web after the press section. The shoe is loaded against a counter roll with hydraulics. The press concept leads to a significant extension of the pressing zone and contact time in the nip compared to conventional roll presses. High after-press dryness gives drying energy savings and a good runnability in the drier section because of the good wet strength of the web.

The shoe press can be applied both in new and existing paper machines with most paper grades (apart from tissue), provided that sufficient space is available in the press section and that the building construction permits the higher weights of a shoe press. The foundations must be suitable for the greater weight of the machinery associated with the shoe press concept. The maximum load of the hall crane has in some cases to be increased due to the heavier shoe press rolls. Because of the large additional investment costs, the economic advantage is doubtful in the case of smaller paper machines, say with a trimmed width of less than 2.5 m. With bulk-sensitive grades, basically woodfree grades, low-load (600 kN/m) long shoe (250 mm) is advantageous. With wood-containing grades, higher load (800 kN/m) and shorter shoe (180 mm) can be used. The shoe press has been developed even for high-speed machines (today up to 2000 m/min).

The effects on the environment are related to savings of thermal energy for paper drying. Dryness increases between 5% and 15% points are reported after the installation of a shoe press in existing paper machines for packaging paper and board (Göttsching et al., 1998). Of course, this increase depends significantly on the previous performance of the rebuilt press section and the selected new shoe press concept. In one case, the rebuild of the press section resulted in a dryness increase of 6% after the installation of one shoe press. The specific steam demand for paper drying was reduced from 2.13 to 1.76 tonnes of steam per tonne of paper, which is equivalent to an 18% thermal energy saving. The reduction in air emissions due to energy production depends strongly on the type of fossil fuel used. In the paper mill concerned, 46,000 tonnes of steam (equivalent to 5.1 M m^3 natural gas and an avoided CO_2 emission of 8900 tonnes) has been saved annually. In a press with shoe nips, the press section length, number of components and fabrics, as well as the service life of the fabrics will also stay constant with increased production. The shoe nip is a soft nip. There are less service needs, less fabric consumption and waste from it, less vibration and noise. This means that the emissions per tonne of paper are lower. The shoe press is a tool for increasing the machine speed while maintaining good runnability. High efficiency saves raw materials and energy and ensures higher machine uptime with less waste. High after-press dryness means lower energy need and thereby less emissions in energy production. In paper machines with limited drying capacity, every 1% reduction in sheet moisture can be translated into a 4–5% productivity increase. If the drying capacity of the paper machine is not limited, an equivalent steam consumption decrease in the drier section can be achieved. Drier section steam savings up to 170 kWh/t can be reached.

However, for a given paper density, the dryness improvement is furnish-dependent. With woodfree paper grades, the after-press dryness is about

3–5 percentage points higher when applying the shoe press. With wood-containing paper grades, the corresponding figure is about 4–7 percentage points. The difference is even bigger, up to 12 percentage points, at high machine speeds, because with a long nip dwell time of shoe nip, the dryness will stay at a high level when increasing the machine speed. With wood-containing grades, the whole shoe press load capacity can be utilized, because the best paper properties can be achieved with a high-pressure level in the nip. When replacing a roll press with a shoe press in a paper machine, the typical total saving in drier energy is 20–30%.

Replacement of the conventional roll nips with shoe nips will not significantly increase the electricity requirements. The shoe press has a higher specific electricity consumption but fewer nips producing a drier sheet, which compensates for each other. Reduced thermal energy consumption can be transformed into avoided air emissions by a calculation based on the specific emission figures of steam generation. However, it has to be taken into account that the reduction in the volume of airborne emissions is affected by the type of fossil fuel used in the power plant. The increased dryness after shoe pressing results in an increase of the apparent density and internal bond strength of the finally dried sheet. The relationship is almost linear. Higher strength of the paper web generally improves the runnability of the paper machine due to less web breaks. The result is a higher paper machine efficiency. For example, after shoe press rebuilt, if the number of unplanned web breaks is reduced by two per day (durability of each 20 minutes), the daily paper machine production capacity will increase by almost 3%. If the production capacity of a paper machine is limited because of its drying capacity, the reduced steam demand for drying after installation of a shoe press makes it possible to increase the speed of the paper machine. In those cases, production can be increased by up to 20% for the same amount of steam as was used before the application of a shoe press. If steam is produced in a cogeneration power plant, the lower steam demand for drying results, however, in a reduced production of electricity. Therefore, more power has to be purchased as grid power. If the paper machine is speed limited due to its drives, the installation of a shoe press contributes to thermal energy savings, and increased paper machine production capacity because of less web breaks and increased paper machine time efficiency.

One example of a press rebuild is Nordland Papier in Germany. In the compact three-nip press section of this copy paper machine, the last roll press nip was replaced with a shoe press nip. After the rebuild, dryness after the press section was about 3–4 percentage points higher. At the same time, the production speed was increased from 850 to 1200 m/min, the increase in production being 30%. To reach this dryness improvement, a linear load of 500–600 kN/m was applied on the shoe press. Later production broke down all records and this rebuild machine became the most efficient fine paper line in the world. Saving in the specific steam demand for paper drying was 30%. Similar results have been achieved in several equivalent rebuilds around the world during the past years. Meanwhile, numerous installations exist all over the world.

The investment costs of a shoe press in a paper machine of 5 m untrimmed width total about €10 million (including the whole installation). The operation cost including felts, roll covers, roll grinding, and drive energy for a shoe press is roughly identical with the cost of a conventional press. The savings of steam for paper drying are in a range between €10 and €15/t steam resulting in a specific steam consumption of 2 tonnes of steam per tonne of paper and savings between €20 and €30/t paper. In press rebuilds, the typical repayment period of the investment is about 2.5 years, if there are no other limits in speed increase.

The driving forces for implementing a shoe press are manifold. Besides improved strength characteristics, cost savings can be obtained due to a reduced steam demand for paper drying at constant paper production, or alternatively the production capacity can be increased at identical operation costs. Better dryness gives energy savings. The press section concept can be simplified. The shoe press has been a key component for further machine speed increase. In a modern high-speed paper machine, the required drier section length is 35% less due one shoe press nip in the press section. Better dewatering effects enhance product quality (higher uniformity of the paper).

There are several rebuilds and new high-speed machines around the world using the shoe press component. Since 1997 all new high-speed paper machines include shoe presses. For example, at the beginning of 1998, one new LWC machine in Finland and an SC paper machine in Canada started with a shoe press in the third press nip position. Half a year after the start-ups, both of these were the fastest LWC and SC paper machines in the world with a production speed of over 1600 m/min. A fine paper machine with two shoe nips started in USA in summer 1998. In the area of Testliner and Wellenstoff, in Germany, the following installations are known (in alphabetical order): Papierfabrik Adolf Jass/Fulda, Papierfabrik Klingele/Weener, Papierfabrik Schoellershammer/Düren, Papier- und Kartonfabrik Varel/Varel, SCA Packaging Industriepapier/Aschaffenburg, Stone Europa Carton Aktiengesellschaft Papier- und Kartonfabrik Hoya/Hoya, Zülpich Papier/Zülpich (Göttsching et al., 1998).

Energy Savings through Energy-Efficient Technologies

There are opportunities for energy saving in many stages within the manufacturing process. Usually these measures are linked with investments to replace, rebuild, or upgrade process equipment. However, these measures are mostly not just applied for energy saving. They attract special interest because they increase, at the same time, production efficiency, improve product quality, and reduce overall costs. It is therefore essential that energy saving techniques become incorporated into all aspects and levels of papermaking. The connection between energy matters and processes (synergistic effects) has to be kept in mind when discussing energy-efficient techniques. Most of them can lead to process advantages and enhanced productivity. Some energy-efficient technologies are presented in Table 5.15.

To summarize the possibilities for energy savings, the areas offering most direct opportunity for energy saving are refining, pressing, and drying. However, once the "good housekeeping" changes have been made, drying is also the most capital-intensive process to modify. Those offering smaller savings but also synergistic

Table 5.15 Energy-Efficient Technology

High-consistency slushing
Best practice refining
High-consistency forming
Twin-wire forming
Optimized vacuum systems
Variable-speed drive system
High-efficiency electric motors
Well sizing of electric motors
Hot presses
Extended nip presses
Cross-direction moisture profile correction with infrared heaters
Exhaust air humidity control
Exhaust air heat recovery
Condensate recovery
Direct gas-fired ventilation air
Increasing size press solids

Based on data from European Commission (2001).

advantages are slushing, forming, and size pressing. Besides the selection of technologies, the manner of operation (energy-efficient practice) and the energy management in the mill is an important issue. Equipment is often not used at its optimum energy efficiency, and with better management further savings can be achieved. The pinch method for optimization of thermal integration of paper mills can be a beneficial tool to move toward energetically optimized processes.

In some countries, information on energy balances of paper mills is poorly available. Different reporting schemes, if any, for energy consumption are used. Energy demand also depends on the product quality (especially in tissue mills) and partly on local conditions. Therefore, it is difficult to present energy consumption values associated with the use of energy-efficient technologies.

The technique described later should be taken as only one example for possible energy savings through energy-efficient technologies. Heat exchangers recover the energy in the exhaust air from the drier section of the paper machine that is—together with refining—the most important stage in any energy consumption consideration.

Energy Savings through Heat Recovery Systems

The purpose of the heat recovery system is to lower the mill's consumption of primary energy by utilizing waste energy from the process in an economically profitable way. Nearly all the heat energy consumed in a paper mill is used for paper drying, easily making the drier section the biggest energy consumer in a paper machine. Roughly 80% of the energy needed in the drier section is brought as primary steam to the drier cylinders, the rest coming as drying and leakage air and with the paper web. Nearly all energy leaving the drier section is exhausted with the exhaust air. About 50% of this energy, that is, something about 620 kWh/t of paper, can be recovered by an efficient heat recovery system (at winter conditions). Typical applications are using either air-to-air heat exchangers or air-to-water heat exchangers, both of plate design (some applications also use scrubbers). The former is mainly used for heating hood supply air and machine room ventilation air. The most common application for the latter is the heating of circulation water and process water, respectively. These heat exchangers are part of heat recovery towers.

It can be applied both at new and existing plants if processes produce exhaust air flows with high energy content and if there is a need for heating energy for different purposes. Heat exchangers for heating hood supply air are always applicable. Whether heat recovery for heating of circulation water (for heating of the machine hall) or process water can be applied depends on the specific characteristics of production and climatic conditions. Because of the interaction between system units, optimized heat recovery system can only be achieved by analyzing the entire heat recovery system.

This measure saves considerable amounts of primary steam, which correspondingly means a lower environmental impact from steam generation. The achievements depend besides others on the climatic conditions.

Preventive maintenance contributes to avoiding unnecessary and expensive shutdowns. Energy saving measures are preferably based on accurate energy balances of the whole mill including energy flow diagrams and alternative process options. There is a strong link between water and energy systems.

Different types of heat recovery systems are available depending on the supplier of machinery. The optimum heat recovery system for the specific requirements of each paper mill has to be designed individually for each application. Usually, the heat exchangers are equipped with washing devices to maintain clear surface and to avoid clogging.

Heat recovery systems usually have short payback times. It is not always economical to recover as much heat as possible. The specific situation needs to be always analyzed. The solution will depend on the relative energy price per kWh for fuel, steam, and electricity. Driving force for implementing this technique is saving of energy, reducing droplets, and mist formation.

Measures for Noise Reduction

The industrial noise sources are of the two types—internal noise source and external noise source. The number of internal noise sources is big in papermaking. A possible measure for internal noise control is the installations of a new closed hood with higher sound insulation. For external noise control, examples of measures are the installation of absorptive silencers and/or pipe resonators to reduce noise levels from exhaust air fans and vacuum pumps, silencers and sound insulation hoods for the fans on the building roof.

Noise reduction measures should preferably concentrate on the major sources, especially to all openings in the roofs and walls. The major external noise sources of a paper mill are process ventilation (continuous), machine room ventilation (continuous), vacuum pump exhaust (continuous), and steam exhaust (only occasional). Additionally, a variety of other noise sources are present especially in old mills, where sound insulation of machinery has not been properly performed. In the planning and operation of installations, measures necessary for noise prevention must already be taken into account during the planning phase. When implementing noise reduction measures, the following technical aspects should be considered:

- Obtaining information at an early stage about noise emissions of machinery, installations, and parts thereof
- Use of low-noise machines and processes
- Reducing noise generation and transmission
- Reducing sound emission, for example, use of sound absorbers
- Maintaining of machinery and soundproofing equipment

The starting point for noise abatement is the authorities' requirements depending on the mill location (distance to the neighborhood, recreational or industrial area, etc.) and the requirements in the given country. The immission (reference) points can be located at the mill border and/or in several locations in the residential area. The target values in the residential areas must usually be always fulfilled when new machinery is being delivered. However, also existing noise sources must more and more frequently be attenuated, because the requirements are becoming stricter. Noise cancellation is relatively expensive in most cases. Therefore, layout aspects and the design of noise abatement measures are very important at an early stage of a project. When existing noise sources have to be attenuated, the costs of silencers and sound insulation enclosures can become high. It is important to reduce the noise at the source. This is, however, not always possible. In those cases sound insulation enclosures for noisy equipment or silencers might be needed. When silencers are dimensioned, the nature of the noise source must be known.

External noise attenuation measures can be applied in both existing and new mills. It is mainly the procedure to determine the current and targeted noise levels that make the difference. In cases of existing machines, the attenuation procedure starts with noise measurements at the immission (reference) points in the residential area. Measurements will continue in the mill to find the most critical noise sources. Silencer dimensioning is an interaction of measurements and calculations. In new installations, the sound power levels are based on the machine deliverer's sound power level data. Calculations of predicted noise levels in immission points are made using computer programs for noise propagation, for example, according to VDI 2714, including the contribution of all relevant noise sources. Limitations of space might lead to somewhat different layout solutions for existing mills.

Silencers may increase the pressure loss of exhaust air that leads to a slight increase of power consumption (kWh/ADt) from fans. But the additional power consumption is not significant.

Silencers have been successfully used in many mills in the world. Maintenance consisting of regularly cleaning and changing of absorption material (when needed) is required where the exhaust air contains moisture and particles.

It is very difficult to give accurate figures on cost of sound attenuation because the costs depend on the size of the mill, the paper grade produced, the speed of the paper machine, etc. Total sound attenuation costs (external and internal) of a papermaking line are estimated of being in the range of 0.5% of the investment costs of the machinery, or even higher depending on the target noise levels. External sound attenuation costs of a paper machine are in the order €0.2–0.4 million depending on the target level and the delivery scope. When the sound pressure level target is decreased from 85 dB(A) to 75 dB(A), the costs are doubled.

From the health point of view, noise can stand for one of the most serious of all environmental problems. A large number of people in the EU territory are exposed to injurious noise. Official requirements in different countries, together with EU directives, have led to increased demands for noise prevention at the machine design stage. But they have also set noise standards for existing equipment and external noise control.

Depending on the type of area affected by noise impact from paper mills, for example, in Germany, the following noise levels have to be achieved to avoid harmful noise impact in the neighborhood. However, the variation range of external noise level targets in different EU member countries is big. The explanations for the great variations are the distance of the mill to residential area, differences in population density, traffic density, environmental targets, etc.

Different types, design, and amounts of silencers are used in most European mills. General measures for noise attenuation are implemented in numerous plants in Europe.

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Chapter 6

Recent Developments in Cleaner Production

This section discusses technologies that (1) are under development and may, if proved technically and economically attractive, also result in the reduction of emissions or energy and resource savings and (2) have been used for some time and are technically proved but whose economies vary depending on local cost conditions and are, therefore, used in some countries but not in others.

6.1 USE OF COOKING CATALYST

The driving force of present pulping technologies is to remove as much lignin as possible so that less chemicals are required during bleaching (Quinde, 1994). This approach will permit to lower the amount of chlorine or increase its substitution for ClO_2 to bleach pulp at equivalent quality standards. Alternatives to achieve this goal can be extended delignification, oxygen delignification, increased chlorine dioxide substitution, peroxide-reinforced oxidative extraction, optimization of the C-stage parameters, enzymatic pretreatments, and/or non-chlorine bleaching sequences.

At present, available pulping technologies such as modified continuous cooking, extended modified continuous cooking, rapid displacement heating, and SuperBatch are able to delignify beyond the kappa number of 30–32; however, because they require extensive retrofitting or digester replacements, their usefulness is limited if capital expenditure is a constraint. An ideal alternative process to achieve extended delignification should be one with less extensive and/or expensive modifications. Nowadays, applications of anthraquinone (AQ) as a pulping additive have become a simple and practical approach to overcome the above concerns. Other chemicals such as polysulfides and surfactants are also becoming strong candidates to be considered as pulping additives during kraft pulping (Bajpai et al., 2005a; Borchardt et al., 1997). Digester modifications and pulping additives do not work antagonistically but are complementary.

Environmentally Friendly Production of Pulp and Paper, by Pratima Bajpai

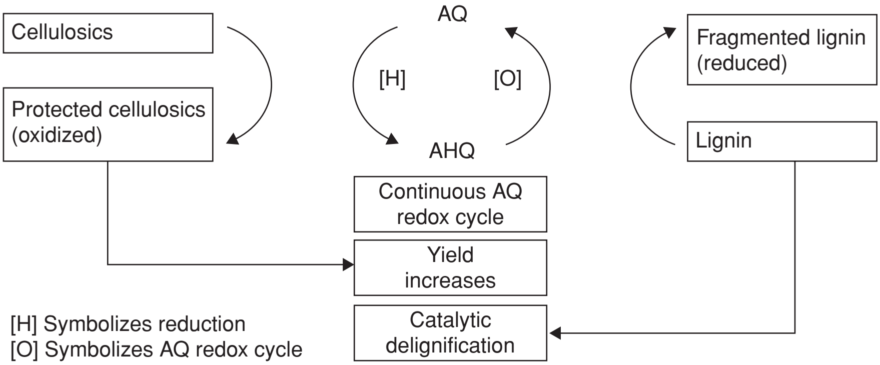

Figure 6.1 An AQ catalytic cycle.

Anthraquinone

AQ and a few closely related compounds can act as redox (reduction–oxidation) catalysts for alkaline pulping (Fig. 6.1). Very small amounts of AQ are enough. The addition of 0.5–1.0 kg AQ/t wood to a standard kraft cook results in a reduction of kappa number of 4–6 while increasing pulp yield by 1–2%, at constant pulp strength (McDonough and Herro, 1997). The yield can vary significantly with wood species and cooking conditions. Since AQ increases the pulping reaction rate, white liquor requirements can typically be reduced by 8–10%. This can eliminate or reduce black liquor shipments, increase washing efficiencies, and reduce consumption of makeup chemicals. If a mill suffers from total reduced sulfur (TRS) emission problems, AQ can reduce the amount of sodium sulfide (Na_2S) required because AQ and Na_2S compete with each other to prevent carbohydrate dissolution. A bleached pulp mill may choose to take the benefit of the lower kappa number that resulted from extended delignification by reducing the bleaching chemical demand.

It is generally accepted that AQ reacts with the reducing end group of cellulose, thus stabilizing the carbohydrate against alkaline peeling and producing the reduced form of AQ, anthrahydroquinone, which reacts with the quinone methide of the lignin polymer (Dimmel, 1995; Fullerton and Wright, 1984). Two major effects occur simultaneously: delignification is accelerated by more efficient reduction reactions, and pulp yield is enhanced by better stabilization of cellulose end groups. AQ is used in many kraft mills around the world (Ahluwalia et al., 1992; Goyal, 1997; Laubach, 1998; Quinde et al., 2004).

Polysulfide

Polysulfide is another additive that is able to selectively oxidize the active end group of the carbohydrate polymer, minimizing alkaline peeling and increasing pulp yield (Jiang, 1993; Katz, 1993; Pekkala, 1982, 1986). Polysulfide pulping is a variant of kraft pulping in which half or more of the sodium sulfide of kraft white liquor is first oxidized. This orange liquor has the ability to preferentially oxidize end groups of hemicelluloses, making them more stable to alkaline attack and resulting in higher yields of pulp from wood. Laboratory studies have shown that the addition of polysulfide to modified cooking makes it possible to produce a fully bleached pulp from softwood brown stock in the kappa range of 15–18 with final yield and strength properties comparable to those from conventional kraft brown stock at the kappa number of about 30 (Jiang, 1995). However, the use of polysulfide has achieved limited commercial acceptance due to the instability of the polysulfide ion at normal kraft cooking temperatures, thus requiring extended impregnation time at low temperature and a slow heating rate to cooking temperature. Kraft polysulfide pulps have different papermaking characteristics due to the retention of hemicelluloses, and may be undesirable in some paper grades.

Mead Corporation has patented MOXY polysulfide process. It is being used in few mills. The pulp yield is generally about 1–3% higher (from wood) than that of kraft pulp at the same kappa number. The Pulp and Paper Research Institute of Canada (Paprican) has also developed a polysulfide generation system that has been used in one Canadian mill up to July 2003.

Both AQ and polysulfide are expensive to produce, and the yield gains are small. In a kraft mill, such yield gains are often difficult to measure due to process variability, and in some cases the economics are marginal. Therefore, neither technology has been extensively used.

Surfactants

The first patent on the use of nonionic surfactants as additives on pulping dates since 1975 (Parker and Lundsted, 1975). Anionic surfactant carries no charge, and its hydrophilic portion contains several polar ether linkages derived from the polymerization of ethylene oxide and/or propylene oxide with the hydrophobe. According to Chen (1990, 1994), the surfactants help the penetration of the cooking liquor by wetting and emulsifying the wood extractives. However, the wetting effect on the chip surface and improved penetration of the liquor into the interstices of the chip should also be considered. This action will allow to have a more efficient and faster delignification with the resulting effects of lowering the kappa numbers and/or reducing the rejects (yield increase).

Surfactants as surface-active chemicals are effective at very low concentrations. Usually, they are applied at 0.025–0.06% based on oven dry (o.d.) wood. The dosage will depend on the degree of delignification, and the target kappa number must be based on the capacity of reject processing equipment in the mill. Additional benefits of surfactants are their ability to keep both lignin and wood extractives in solution in the black liquor. The later benefit was already envisioned by Mutton (1958) who stated that application of surfactants would help the deresination in the hot alkaline extraction stage. Full utilization of aspen in western Canada has been slow to develop because of problems associated with excessive pitch and subsequently poor-quality pulp. Due to the low ratio of saponifiables-to-unsaponifiables in its extractive composition, attempts have been made to favorably alter this ratio during pulping. A common operation when pulping hardwoods (they lack resin acids) is the addition of “tall oil,” which is composed mainly of sodium salts of resin and fatty acids. This acid fraction is able to aid in the dissolution and emulsification of the neutral unsaponifiables present during pulping. Even though this is a very common practice, not all mills have quoted effective results. Some mills reports favorable results on addition of tall oil at a rate of 1.5–2.5% of o.d. wood. In the case of softwoods (presence of resin acids), even though they contain higher amount of total extractives, they have fewer problems related to pitch than hardwoods. This phenomenon can be explained because of the emulsifying action of the resin acids (Quinde, 1994).

Combination of AQ/Surfactant

There has been growing interest in combining AQ and surfactant-based digester for gaining additional benefits. The surfactant, when used in conjunction with AQ, improves AQ selectivity by transporting the AQ to more reaction sites. This can result in a 20% AQ reduction while maintaining the same AQ benefits. The ability to reduce the total quantity of AQ in the system results in reduced downstream problems such as evaporator and economizer fouling and residual AQ in the crude tall oil. As mills continue to run their systems beyond designed capacity, the need for a digester additive program will increase. Digester additives can provide an alternative to expensive capital expenditures and allow the mill more operational flexibility as illustrated in Fig. 6.2.

Combination of AQ–Polysulfide

It has been proved that the combination of AQ and polysulfide gives more yield gains than the sum of respective yield increase. This augmentation is called the

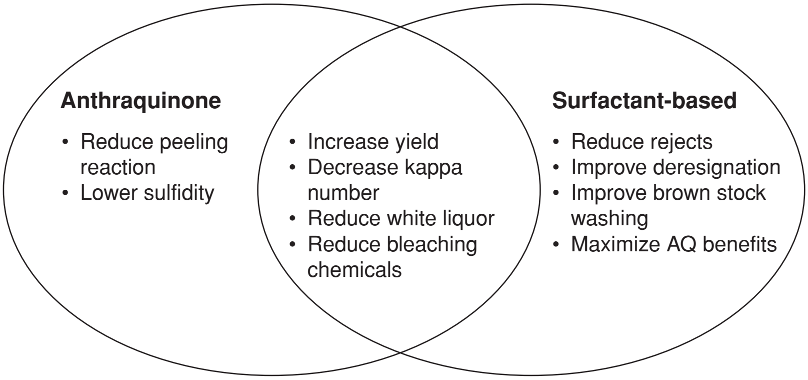

Figure 6.2 Benefits of AQ and surfactant-based digester additives.

synergistic yield, increasing effect of polysulfide and AQ (Jiang, 1993; Malkov, 1990; Yamaguchi, 1983). This synergistic effect decreases at low kappa number. Strategies for implementing AQ and AQ–polysulfide-extended digester delignification are site-specific.

6.2 ORGANO SOLVENT PULPING

Pulping processes under development are based on organic solvents (Baeza et al., 1991; Muurinen, 2000; Young and Akhtar, 1998). For some of these processes, it can be expected that the gaseous emissions of sulfur dioxide and odorous gases are reduced because of the use of sulfur-free technology. All new pulping processes intend to achieve a closed mill by direct recovery of the solvent after the cooking step by distillation and combustion of the dissolved wood components or its alternative use as chemical feedstock for different products. The principal aims of Organosolv pulping are reduced environmental impact and improved economy of the pulping process. Table 6.1 compares Organosolv pulping processes with modified kraft pulping (Ministry of Food, Agriculture and Forestry, 1997; Young and Akhtar, 1998).

The Organosolv pulping processes can be classified into organic acid-based, alcohol/water-based, and mixed processes, which use inorganic and organic pulping chemicals. None of the proposed Organosolv processes have been implemented successfully on a mill scale. A full-scale Organocell plant in Kehlheim, Germany, had to be shut down due to insolvable problems. The Repap Enterprises Alcell mill at

Table 6.1 Organosolv versus Kraft Pulping Process

Pulping process	Raw materials	Cooking chemicals	Cooking process parameters	Kappa before bleaching
ALCELL	Northern hardwood	Denatured ethanol/water mixture	190–200°C	N/A
ASAM	Softwood	Sodium sulfite (alkaline)	175–185°C	13–20
	Hardwood	Anthraquinone	11–14 bar	
	Annual plants	Methanol		
FORMACELL	Softwood	Acetic acid	160–180°C	2–10
	Hardwood	Formic acid		
	Annual plants			
MILOX	Hardwood	Formic acid	60–80/	30–35
	Annual plants	Hydrogen peroxide	90–110°C	
Modified kraft	Softwood	Sodium hydroxide	155–175°C	10–20
	Hardwood	Sodium sulfide	8 bar	
	Annual plants			

Based on data from Young and Akhtar (1998).

Newcastle, NB, Canada, had a similar fate. It is too early to make a conclusive judgment on the alternatives, but it is clear that Organosolv pulping is not AMT (accepted modern technology). Information on the environmental impact of the Organosolv pulping processes is scarce and is mainly derived from pilot-scale trials. Whether the advantage can be achieved in full-scale plants is to a certain extent doubtful or at least not proved.

6.3 BLACK LIQUOR GASIFICATION

Gasification is a promising technique for pulp mills for the generation of surplus of electrical energy but yet to achieve widespread acceptance (Bajpai, 2008a). Production of a combustible gas from various fuels—coal, wood residues, and black liquor—is possible through different gasification technologies. The principle of the gasification of black liquor is to pyrolyze concentrated black liquor into an inorganic phase and a gas phase through reactions with oxygen (air) at high temperatures.

Gasification may become part of integrated gasification and combined-cycle (IGCC) operation, or lead to pulp mills becoming biorefineries (Katofsky et al., 2003). Figure 6.3 shows a simplified schematic for the black liquor IGCC.

In the gasifier, the organic matter in black liquor is partially oxidized with an oxidizing agent to form syngas, while leaving behind a condensed phase. The syngas is cleaned to remove particulates and tars and to absorb inorganic species (i.e., alkali vapor species, SO_2, and H_2S), and this is done to prevent damage to the gas turbine and to reduce pollutant emissions. The clean syngas is burned in gas turbines coupled with generators to produce electricity, and gas turbines are inherently more efficient than the steam turbines of recovery boilers due to their high overall air/fuel ratios

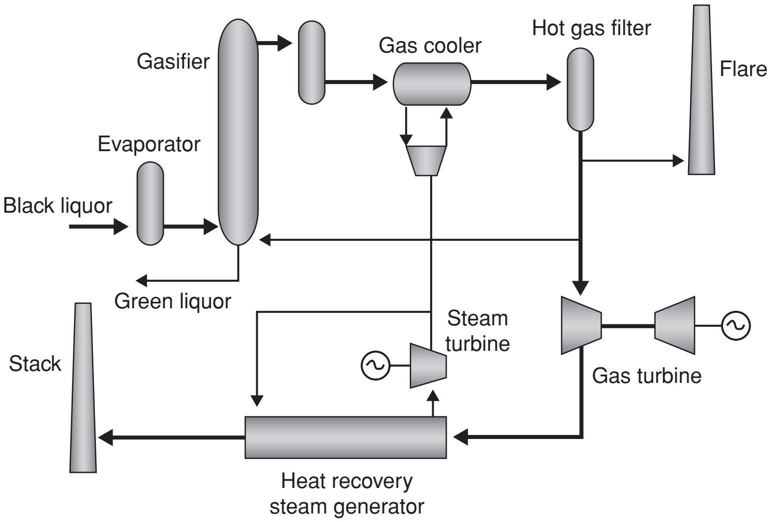

Figure 6.3 Integrated gasification and combined cycle. Based on Sricharoenchaikul (2001).

(Nilsson et al., 1995). The hot exhaust gas is then passed through a heat exchanger (typically, a waste-heat boiler) to produce high-pressure steam for a steam turbine and/or process steam. The condensed phase (smelt) continuously leaves the bottom of the gasifier and must be processed further in the lime cycle to recover pulping chemicals.

In recovery boilers, essentially all of the alkali species and sulfur species leave in the smelt (mostly as Na_2S and Na_2CO_3), but in gasifiers, there is a natural partitioning of sulfur to the gas phase (primarily H_2S) and alkali species to the condensed phase after the black liquor is gasified. Because of this inherent separation, it is possible to implement alternative pulping chemistries that would yield higher amounts of pulp per unit of wood consumed (Katofsky, 2003; Larsen et al., 1998). Gasification at low temperatures thermodynamically favors a higher sodium/sulfur split than gasification at high temperatures, which results in higher amounts of sulfur gases at low temperatures. Because a large amount of the black liquor sulfur species leaves the low-temperature process as H_2S, H_2S may be recovered via absorption to facilitate alternative pulping chemistries.

The partitioning of sodium and sulfur in black liquor gasification requires a higher capacity for the lime cycle compared to the current technology. The sodium/sulfur split results in a higher amount of Na_2CO_3 in the green liquor because less sulfur is available in the smelt to form Na_2S. For each mole of sulfur that goes into the gas phase, one more mole of Na_2CO_3 is formed in the condensed phase (Katofsky et al., 2003). The increase in Na_2CO_3 results in higher causticization loads, increases in limekiln capacity, and increases in fossil fuel consumption to run the limekiln. This leads to higher raw material and operating costs, which must be reduced in order to make the gasification process economically favorable.

Black liquor gasification may be performed either at low temperatures or at high temperatures, based on whether the process is conducted above or below the melting temperature range (650–800°C) of the spent pulping chemicals (Sricharoenchaikul, 2001). In low-temperature gasification, the alkali salts in the condensed phase remain as solid products while molten salts are produced in high-temperature gasification. Low-temperature gasification is advantageous over high-temperature gasification because gasification at low temperatures yields improved sodium and sulfur separation. Additionally, low-temperature gasification requires fewer constraints for materials of construction because of the solid product. However, the syngas of low-temperature gasification may contain larger amounts of tars, which can contaminate gas cleanup operations in addition to contaminating gas turbines upstream of the gasifier. These contamination problems can result in a loss of fuel product from the gasifier (Sricharoenchaikul, 2001).

Gasification Processes

The different gasification processes for kraft black liquor recovery can roughly be categorized into low- and high-temperature processes. Low-temperature processes work below 715°C and the inorganic salts are removed as dry solids (DS).

High-temperature processes operate above 900°C and an inorganic salt smelt is obtained. Trials to develop a commercially feasible process for black liquor gasification have been performed by several companies, and the history of black liquor gasification development is well described by Whitty and Baxter (2001) and Whitty and Verrill (2004). However, only two technologies are currently being commercially pursued: the Manufacturing and Technology Conversion International (MTCI) (low temperature) (Durai-Swamy et al., 1991; Mansour et al., 1992, 1993, 1997; Rockvam, 2001; Whitty and Verrill, 2004) and Chemrec (high temperature) (Brown and Landälv, 2001; Kignell, 1989; Stigsson, 1998; Whitty and Nilsson, 2001; Whitty and Verrill, 2004) technologies.

MTCI has two projects running today, both in mills with an Na_2CO_3 semi-chemical cooking process. The first project is for Georgia Pacific Corporation's Big Island mill in Virginia. This system is a full-scale gasifier, designed to process 200 tonnes DS/day and is fully integrated with the mill. The second project is for the Norampac Trenton mill, Ontario, Canada, which had no chemical recovery before the steam reformer commission began in 2003 (Middleton, 2006; Newport et al., 2004; Vakkilainen et al., 2008). This gasifier has a processing rate of 115 tonnes DS/day.

Chemrec is working on both an atmospheric version and a pressurized version of a high-temperature downflow entrained flow reactor. The atmospheric versions mainly considered as a booster to give additional black liquor processing capacity. The pressurized version is more advanced and would replace a recovery boiler or function as a booster. A pressurized system has been built within the Swedish National BLG program (2004–2006) in Piteå, Sweden. It is a development plant built for 20 tonnes DS/day. The system includes the processes of gasification and quenching, gas cooling, and gas cleaning. The produced gas has been determined to contain about 41% H_2, 31% CO_2, 25% CO, 2% CH_4, and 1.4% H_2S (Lindblom, 2006). The aim of the program is a verified process that will be ready for scale up (15 times) as well as an optimized integration of the process with the pulping cycle. Figure 6.4 shows the CHEMREC DP-1 plant.

The CHEMREC BLGCC system has several advantages over recovery boilers; the most significant being dramatically improved electricity yield. The CHEMREC BLGMF system combines black liquor gasification with a chemical synthesis plant for production of green automotive fuels such as methanol or DME (dimethyl ether). The new combined pulp and chemical production facility requires additional energy to compensate the pulp mill for the withdrawal of the new green automotive fuels. The efficiency of the CHEMREC BLGMF system for generating the new green automotive fuels is very high, and the cost of these fuels from a full-scale unit is competitive with petroleum-based alternatives. The CHEMREC BLGH_2 system utilizes the syngas from the black liquor gasifier as feedstock for novel green hydrogen production.

The investment cost for a full-scale pressurized black liquor gasification process (PBLG) unit is estimated to be slightly higher than for a new conventional recovery boiler (Warnqvist et al., 2000). However, pressurized black liquor gasification with an integrated combined-cycle (BLGCC) has the potential to double the amount of net electrical energy for a kraft pulp mill compared to a modern recovery boiler

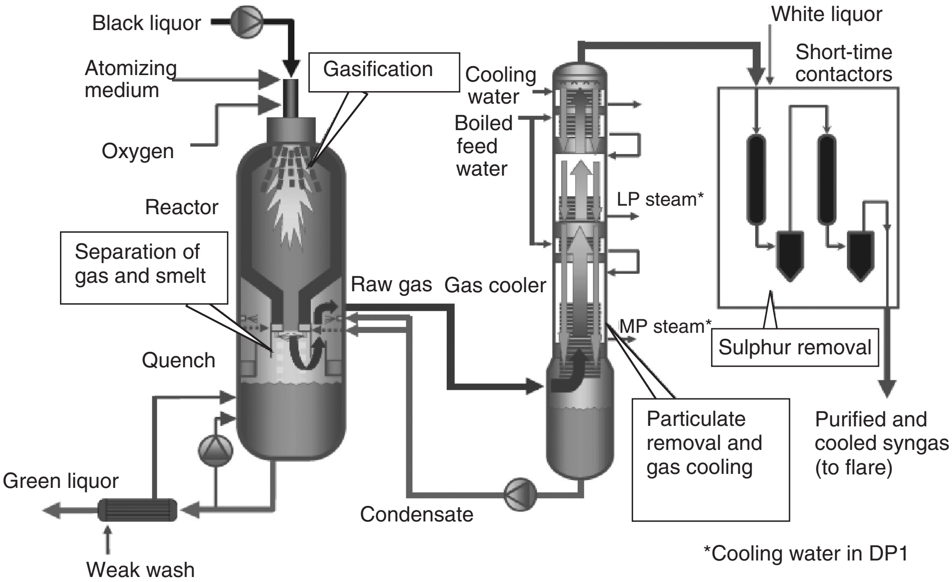

Figure 6.4 The CHEMREC DP-1 plant.

Source: http://www.chemrec.se/admin/UploadFile.aspx?path=/UserUploadFiles/2005%20DP-1%20brochure.pdf. Reproduced with permission.

with a steam turbine (Axegård, 1999). For more closed systems with less need of steam, this increase in electrical energy will be even higher. Another advantage with the PBLG process is the increased control of the fate of sulfur and sodium in the process that can be used to improve the pulp yield and the quality for the mill. This control is very important for the green liquor quality and is quite limited with a conventional recovery boiler. A disadvantage with gasification is that it will increase the causticizing load. However, BLG has a lower requirement for makeup salt cake compared to the recovery boiler. Even though the PBLG process might have a lot of advantages compared to the recovery boiler, there are still a number of uncertainties for this technology.

Black liquor gasification is still a developing technology. Only small (100–350 tonnes DS/day) commercial atmospheric units have been built. Similar size pressurized demonstration units do not yet exist. It will take some time before reliable large units are available. Black liquor gasification can produce more electricity (Vakkilainen et al., 2008). Current commercial atmospheric processes are not as energy-efficient as the kraft recovery boiler process (Grace and Timmer, 1995; Mckeough, 2003). The black liquor gasifier needs to operate under pressure to have an electricity advantage.

Even though there are significant gains to be made, there still remain many unresolved issues (Katofsky et al., 2003; Tucker, 2002): finding materials that survive in a gasifier, mitigating increased causticizing load, how to start up and shut down, tar destruction, alkali removal, and achieving high reliability. The full impact of the black liquor gasification on recovery cycle chemistry needs to be carefully studied with commercial units. The first large demonstration units will cost two to three times more than a conventional recovery boiler. Although this will improve with time, price will hinder the progress of black liquor gasification. A small BLG with a commercial gas turbine size of 70 MWe requires a mill size of over 500,000 ADt/annum. Commercial gasifiers probably need to be over 250 MWe in size. It is therefore expected that full-size black liquor gasifiers will be built in new greenfield mills, and not as replacement units of old recovery boilers.

6.4 REMOVAL OF CHELATING AGENTS

The chelating agents, ethylenediamine tetraacetic acid (EDTA) and diethylenetriamine pentaacetic acid (DTPA), are applied because of good sequestering properties, that is, their ability to suppress the activity of dissolved transition metal ions without precipitation. These metal ions are able to catalyze the decomposition of hydrogen peroxide into radicals. Totally chlorine-free (TCF) bleaching is currently only possible by treating the pulp with EDTA or DTPA before the hydrogen peroxide stage. Increased concentrations of chelant are therefore found in effluents generated from the production of TCF pulps. In effluent analyses of a TCF mill producing market kraft pulp, 25–40% of the charged chelant has been identified. This corresponds to chelant contents of 10–15 mg/L in the effluent at a charge of 2 kg/ADt. Although chelants are nontoxic to mammals at environmental concentrations, there is some concern about their potential to remobilize heavy toxic metals out of sediments and their low biodegradability.

EDTA is resistant to aerobic biodegradation in the activated sludge plant operated under “normal” conditions (pH 7). Furthermore, EDTA does not adsorb onto sludge so that it passes through treatment plants without notable degradation. Virtapohja and Alén (1997) investigated the biodegradation of EDTA in a full-scale activated sludge plant under mild alkaline conditions (pH 8–9). An average EDTA reduction of about 50% (compared to about 10% at pH 7) was obtained. pH adjustment to 8–9 with calcium oxide (dosage about 90 mg CaO/L) did not interfere with the normal operation of the activated sludge plant. The biodegradation of EDTA in activated sludge plants under alkaline condition looks promising. The treatability of EDTA-containing bleach plant effluents in activated sludge plants under mild alkaline conditions has been confirmed by investigations both in the laboratory (van Ginkel et al., 1997, 1999) and in full-scale activated sludge plants.

Biodegradation of EDTA increases the release of nitrogen. Enhanced degradation of EDTA in activated sludge plants is therefore of clear benefit, not only for environmental reasons, but also as a means to increase the level of the nutrient nitrogen, which is usually deficient in effluents from pulp mills.

Another technical option to reduce the consumption and discharge of Q used before the peroxide stages in TCF mills is the use of kidneys. Kemira NetFloc system has been demonstrated to be a very efficient tool to remove problematic substances such as extractives and metals from pulp and paper filtrates. In the NetFloc system

(Rampotas et al., 1996), the pH is increased and carbonate is dosed for precipitation. Metals bound to EDTA (or DTPA) are released and precipitated. A high-molecular-weight polyethylene oxide (PEO) for flocculation is added to the selected filtrate. In the actual application, a water solution of the PEO is made in a polymer preparation unit and the PEO solution is dosed into a filtrate pipe. The flocculation reaction between PEO and extractives is fast, and it is completed before the filtrate leaves the pipe. It has recently been discovered that the PEO–resin flocs collect any undissolved substances in the filtrate. This means that precipitated metal salts (e.g., hydroxides and sulfates) will end up in the resin sludge. The final operation includes separation of resin sludge from the filtrate, which is usually done by mechanical means, for example, a flotation unit. The treated filtrate with the recovered Q is reused in the process, and the resin sludge may be either pumped to the green liquor sludge filter or burned in the bark boiler directly or after dewatering in a press.

By reducing the amount of metals entering the bleach plant, a smaller charge of chelating agents is needed prior to the peroxide stage. Additionally, the recovery of Q itself reduces the consumption needed. Expected reduction rates are over 80% for calcium, manganese, and iron. The recovery of Q results in a lower charge of fresh Q. Thus, lower levels of metal complexes will be found in the effluent (Kari and Giger, 1996).

6.5 ENERGY-EFFICIENT THERMOMECHANICAL PULPING PROCESSES

The thermomechanical pulping (TMP) process is a heavy energy user. It consumes large amounts of electrical energy in the range of 1600–3200 kWh/ADt. The process shows a great flexibility in many respects, and it is not likely that the industry would switch the existing TMP processes to pressurized groundwood (apart from some cases), which consumes less power (about 600–1200 kWh/ADt less) than TMP production for the same grades. Therefore, a lot of development work has been focusing on reduction of the power consumption in the TMP process. There have been promising pilot trials such as the Finnish Pulp and Paper Research Institute (KCL) multistage process, which indicate that significant power reductions of about 10–15% (200–450 kWh/t) are possible by changing the refining strategy. This claim cannot be fully verified at present stage. However, since the mid-1990s, there are also a few mill-scale applications of new energy-efficient TMP processes such as RTS, Thermopulp®. These processes consume substantially less energy than "normal" TMP processes.

The RTS technology developed by Andritz combines conditions of a low residence time (R) at a temperature (T) exceeding the glass transition temperature of lignin and elevated disk speed (S). Residence time as used in this process refers to the time when the pulp is at high pressure and temperature, not the time when the pulp is retained in the plates of the refiner. The objective of the RTS conditions, according to Andritz, is to thermally shock the wood fiber while in chip form, subjecting it to higher temperatures for a shorter period and thus making it more receptive to initial defiberization during the primary refining operation. RTS also differs from a standard TMP process in that the rotational speed of the primary refiner is much higher.

Andritz points out that the concept of reduced energy consumption by increasing the disk speed of refining has been established using single-disk and double-disk refiners in both pilot plant and mill applications. The speed increase for this process typically comes from installation of a speed increaser between the refiner motor and the refiner. Andritz says that RTS is designed to avoid the shortcomings of the TMP process that produces stronger fibers but darkens the pulp. By exposing fibers to high temperatures while still in chip form, the heating occurs primarily through the lumina cavities, which means that the cellulose wall layers are heated first, while the middle lamella of the fiber has the least exposure to heat. The low retention time at elevated temperature minimizes thermal darkening reactions of the color bodies associated with the middle lamella lignin. The result is a brighter and more easily bleached pulp. As for strength, most fractured fibers that are produced by a conventional TMP process occur during primary refining. Because RTS softens chips by increasing fiber wall temperature prior to primary refining, fiber cutting is reduced, and fiber development is improved. Thus, RTS can reduce or eliminate the requirement for kraft pulp in some paper grades. Also, RTS operation at high refiner disk speed reduces the residence time between refiner plates and increases specific refining power. This produces an improved pulp "fingerprint," which establishes potential pulp quality.

High-speed refining, according to Andritz, is the key to improved operator efficiency. By subjecting thermally softened chips to higher refiner speeds for extremely short periods, high-speed refining can elevate pulp quality while using 10–25% less electrical power. RTS system can produce equivalent pulp strength at lower energy. Conversely, RTS will produce pulp with dramatic increases in tear and bonding strength at specific energy levels comparable to conventional TMP.

In the mid-1990s, several lines of the Thermopulp process went into operation both in Europe and in North America. The first RTS installation was at Perlen Papier AG, Switzerland, in 1996. Both systems can be considered as available techniques but would normally only be installed at new mills or when existing equipment is replaced. The first full-scale experience suggests that an energy reduction in the order of 15% compared to conventional TMP is possible using this system. Specific energy consumption of the first commercial RTS operation is 1.85 MWh/t at a freeness level of 94. In the Thermopulp process, the first refining stage is performed at a relatively low temperature. The pressure and temperature are raised before the second stage refining, which is performed at very high pressure and temperature (up to 700 kPa and 170°C). Energy savings of 10–20% have been reported. Specific energy consumption in mill scale at a North American mill is 1.75 MWh/t at a freeness of 160. It can be expected that the new technology will only be implemented gradually due to remaining lifetime of present equipment and plants (Johansson et al., 1998; SEPA-Report 4712-4, 1997).

6.6 RECOVERY OF BOILER ASH AND CARBON DIOXIDE GAS TO PRODUCE RECYCLED MINERAL FILLERS

This process utilizes ash and carbon dioxide to produce a type of recycled mineral filler precipitated calcium carbonate (RMF PCC) for use in paper. Ash results from the combustion of de-inking residue, and carbon dioxide is generated during combustion. This process derives from the chemistry used to produce pure precipitated calcium carbonate (PCC), a commonly used mineral in papermaking. PCC is more pure. The main advantage to the papermaker, however, is that the chemical process of their production allows individual PCC particles to assume a variety of shapes and sizes (morphologies). Careful selection of size and shape can maximize PCC functionality over a wide range of papermaking applications. These advantages are also imparted to the paper when RMF PCC is used as the filler. The process to produce a recycled mineral filler PCC (RMF PCC) can be described by the following equation:

Materials	Boiler ash +	$Ca(OH)_2$ +	CO_2 =>	Ash/$CaCO_3$ +	H_2O
Quantities	5–50 g	37–70 g (fresh lime)		22–43 g (recycled mineral filler)	100 g

The ash resulting from the combustion of paper mill residuals or de-inking sludge contains mainly compounds rich in calcium, silicon, and aluminum. These result from the minerals contained in the waste, mainly calcium carbonate and kaolin clay. It has been discovered that the calcium aluminosilicate minerals in boiler ashes are suitable for nucleation and growth of PCC. It has also been discovered that these ashes can replace up to one-half the lime (CaO) that is used to produce calcium hydroxide slurry. Individual particles of RMF PCC are composites of PCC and boiler ash. The reaction is controlled, so that PCC of a particular morphology precipitates on and covers the surface of an ash "core." The process has been patented and is supplied by Speciality Minerals Inc, one of the leading suppliers of PCC to the European paper industry.

One of the German paper mills (Haindl Schongau) has conducted pilot test to adapt the existing plant for production of pure PCC to the production of recycled mineral filler PCC. Development work on the use of PCC for coating is also underway. The process reduces significantly the amount of solid waste to be deposited from de-inking plants. Utilization of boiler ash as a raw material in the production of PCC reduces consumption of fossil fuels for production of CaO from limestone quarry ($CaCO_3$) by up to 50%, and thus reduces emissions of CO_2 by a corresponding amount. If paper mills that generate large quantities of de-inking residuals reduce the amount of solid waste from the de-inking process by incineration, CO_2 is emitted to air, and ash must still be disposed. A process to produce RMF PCC can partly or completely consume ash and CO_2 generated at these mills. This is in addition to reductions at the limestone quarry in both fossil fuel consumption and CO_2 emissions.

In countries where the cost of landfill is high and rising, the option of handing over de-inking ash as a raw material for production of PCC is appealing because it is beneficial for both economic and environmental reasons. However, the brightness of recycled mineral filler PCC, based on a realistic mixture of one-third ash and two-thirds of pure PCC, is 90% and thus lower than pure PCC (96%). It might also raise abrasivity. On the other hand, RMF PCC has better opacity properties than pure PCC. The economics of recycled mineral filler PCC depend very much on the quality of the recovered paper from which the de-inking residue is produced (high amounts of calcium carbonate fillers are beneficial). The higher the calcium contents in the recovered paper, the better for the operation of this process. A prerequisite for the implementation of recycled mineral filler PCC is the presence of a boiler combustion of de-inking residue. Normally, the plant producing pure PCC is adapted for recycled mineral filler PCC production. Step by step, lime is replaced by de-inking ash (Roberts, 1998).

6.7 IMPULSE TECHNOLOGY FOR DEWATERING OF PAPER

This technology has the potential for energy saving. It may provide opportunities to achieve high solids content after the impulse unit and thus saving heat energy for subsequent drying. The paper web reaches a dryness of about 40% in an ordinary press section. In extended nip presses, the web may reach dryness levels of about 50%. From impulse drying, some reports have stated dryness levels of 55–65% before the drying section, which gives a possibility to decrease the heat consumption. Higher dryness level means that less water has to be evaporated in the drying section by means of steam, and the drying section could be made smaller (shorter). The technology is also expected to provide a smooth paper surface with a high mechanical integrity and a sheet that retains a high bending stiffness. This combination of properties is of great value both in packaging materials and in printing papers.

Impulse technology tries to combine pressing and drying into a single compact process. The wet paper web is exposed to an intense impulse of heat energy under pressure between a press element and a heated element in a paper machine. This induces a sudden increase of the surface temperature of the paper to considerably higher temperatures than employed in traditional technology.

When the paper web gets into contact with the hot surface, generated steam starts to displace water in the paper web. The hot side of the web will be compressed due to thermal softening and may be subject to chemical modification. The web enters a second impulse stage immediately after the first unit. In the second stage, which acts from the reverse side, water is displaced in the reverse direction. The two impulse steps must be adequately balanced to produce a symmetrical sheet.

Some different concepts have been investigated and tried under various names such as hot pressing or pressure drying. The development work is still at an early stage. Many obstacles have been experienced in the development work, and the technology has not yet resulted in full-scale implementation. It should be realized that this technology has been investigated and developed since the beginning of the 1970s without any final breakthrough.

By increasing the dryness of the paper sheet from 50% to 51%, there will be about 35 kg less water per tonne of paper to evaporate. Thus, the impulse drying technology has the potential of reducing the amount of water to evaporate by 175–350 kg/t of paper. This would simply save the amount of steam consumption by 175–350 kg/t or about 0.44–0.9 GJ/t of paper (assuming 2.5 MJ/kg steam), corresponding to about 10–25% of present steam consumption in papermaking. However, when calculating the energy saving, the energy needed for the impulse drying itself has be taken into account. While for impulse drying high temperatures are needed, steam cannot be utilized. On the other hand, paper mills normally have excess amount of steam available, which is also a less expensive energy. Thus, the need for high-value energy, such as electricity, decreases the possible benefits for environment and the potential for profitability (SEPA Report 4712-4, 1997; Talja et al., 1998).

6.8 CONDEBELT PROCESS

The Condebelt process is based on the condensing belt principle, and it is a very promising method, offering several advantages over conventional cylinder drying (Fig. 6.5). In the Condebelt drying concept, a wet web (sheet of paper) is carried between two steel bands, one hot band and one cold band, and subjected to high pressure (maximum 10 bar) and temperature (maximum 180°C). Heat is transferred from the hot band to the sheet, and moisture evaporates and traverses through two wire screens to the cold band, where it condenses. The condensate is carried away by the thickest of the two wire screens. The sheet is dried in absence of air. In contrast with conventional pressing technologies and impulse drying, the pressure is maintained for several seconds, resulting in good paper qualities. Drying rates are 5–15 times as high as in conventional drying. Condensing belt drying can dry paper from 44% (exit conventional pressing section) to 94%. The technical life of paper machines is approximately 20 years and investment costs are extremely high.

At the moment, it is best suited to board grades, but it has also a considerable potential with paper grades. In this process, drying shrinkage of the web is eliminated, and even stiff fibers can effectively be plasticized and bonded to each other. Compared to cylinder drying, this results in improved strength properties, especially in the cross-machine direction. Condebelt drying improves significantly strength (20–60%), surface smoothness, dimensional stability, and resistance against humidity. In Condebelt drying, with recycled fibers, it is possible to achieve the same strength values as with virgin fibers in conventional drying.

This drying process offers opportunities for lowering the grammage of board, reducing the weight of corrugated boxes, increasing the use of recycled furnishes and high-yield pulps. The disintegration of condensing belt-dried board needs slightly more energy than cylinder-dried board. However, the recyclability of the board is

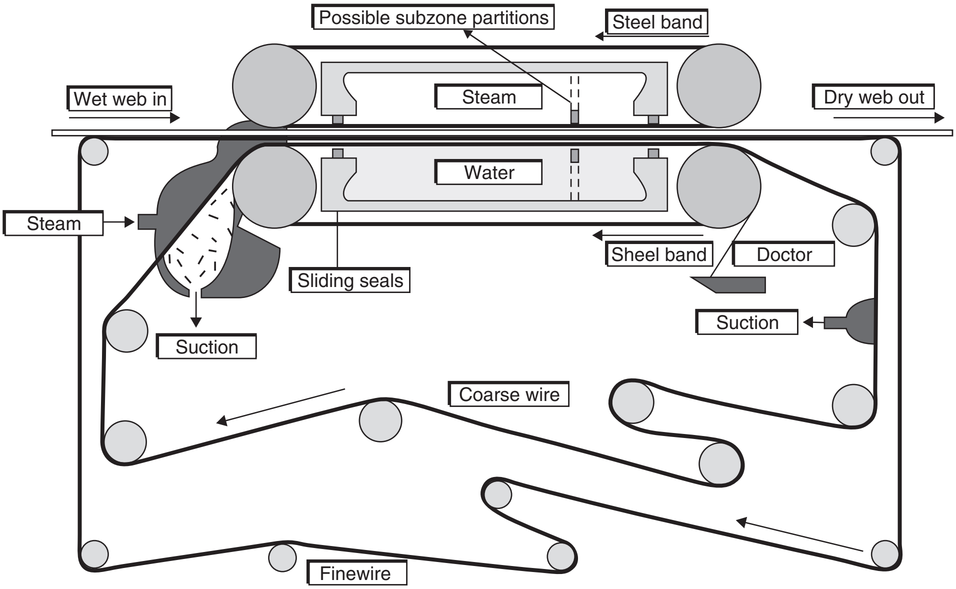

Figure 6.5 A schematic diagram of the Condebelt drying process (high Z-pressure-type). Reproduced with permission from European Commission (2001).

good, especially when the remade web is dried using the condensing belt process. The deterioration of board properties after multiple recycling and condensing belt drying is quite moderate. This shows that condensing belt drying can form part of an ecologically sustainable paper cycle.

Presently, there are few Condebelt drying processes in commercial operation. The use of this new drying technology does not result in significant direct energy savings. However, the strength improvements give the potential for savings through reduced basic weight. That means, more square meters from the same amount of fibers can be manufactured without losing product quality. Furthermore, because of the improved paper sheet properties with Condebelt drying, it seems to be possible to use lower grade fiber material or high-yield pulp (e.g., 10% less wood per tonne of liner). Higher strength and better protection against adverse moisture effects can have the effect that surface sizing could often be dispensed with, although normally they would be used. Although the specific consumption of electric energy and primary steam roughly equals that of traditional drying, there are greater opportunities to save heat energy. This is because almost all of the evaporated water and its latent heat can be recovered from the cooling water at a fairly high temperature (normally about 80°C). This energy can also be used in other parts of the process using heat pumping. The environmental benefits are potential savings of raw material (fibers, sizing agents) and a somewhat higher potential for energy recovery (Ojala, 1999; Retulainen, 2003).

6.9 INTERNAL HEAT PUMPS

There are many applications for heat pumps in the pulp and paper industry, but the investment costs are quite high, which have hindered the use of this kind of equipment. Also, the environmental problems that are associated with the conventional working media have made the use of heat pumps even more difficult even if the thermodynamics of the heat pump is very advantageous. As an example the discharged moist air may hold a temperature of 105°C with a dew point of 61°C. In such a case, a heat pump may produce heat corresponding to 750 kWh/t or 2.7 GJ/t by means of only one-third or 250 kWh/t of power to the compressor motors. This is based on a coefficient of performance of 3, which is quite normal.

The potential of this technology is large, but the number of actual installations in the pulp and paper industry is small due to the investment cost as well as the mentioned difficulties with suitable working media. Because this is conventional technology, a breakthrough requires the discovery or development of a new suitable media, and also more cost-effective equipment, especially on the compressor side (SEPA-Report 4713-2, 1997).

6.10 TOTAL SITE INTEGRATION TOOLS

The technological development in the papermaking process has been realized through step-by-step actions because of the complexity of the process. It can be illustrated by an example on the use of water. Increased recycling of water will lead to a different process chemistry, lower utilization of secondary heat, different water management practices, new reject streams, changes in the operation of effluent treatment, increased consumption of electricity, and reduced consumption of heat. On the other hand, energy consumption is also affected by the production speed of the machine and by unit operation development of the paper machine. The technological choices will have effects on the energy balance of mill site. It can be concluded that intelligent process solution in the future will try to combine the whole energy system—water, fiber, and chemicals—to create a good integration of the mill.

The main issue is how to come up with process and mill concepts capable to reduce emissions to air and water and at the same time to reduce the formation of solid waste and energy. The requirements for the new process are better paper quality and runnability, and better process management. This calls for more knowledge on the behavior of the processes. Also, the changes to the process caused by adoption of new techniques have to be identified so that compatible process technology can be developed. Consequently, it is clear that new optimization tools can support the development of future papermaking processes. Some computer-based tools contain information on contaminant concentrations in the different parts of the processes; behavior models for the contaminants; process parameters for separation and treatment methods; methods to optimize water treatment concepts with respect to contaminant concentrations and behavior; identification of heat sinks and sources; methods to optimize the use of heat through careful process integration; information on the emissions from the new mill concept to air and recipient and formation of solid wastes; detailed process design based on the choices made; and methods to analyze and to develop the operational runnability of the process (Edelmann, 1999).

6.11 WASTEWATER TREATMENT FOR WATER RECOVERY AND REUSE

The emerging techniques of wastewater treatment for water recovery and reuse in pulp and papermaking are given as follows (Bajpai, 2008b):

- Advanced oxidation treatment technologies
- Fungal/enzymatic treatment
- Sequential anaerobic/aerobic bioprocesses
- Membrane processes
  - Microfiltration (MF)
  - Ultrafiltration (UF)
  - Nanofiltration (NF)
  - Reverse osmosis (RO)
- Membrane bioreactor (MBR)
- Other techniques
  - Combination of biological and chemical processes
  - Aerobic cyclic softening (AZE) process
  - Ozone treatment in combination with other processes

Advanced Oxidation Treatment Technologies

Biological processes are commonly used to treat wastewater in pulp and paper industries, but some limitations are associated with these methods, such as the large area required for the aerobic process, the difficulty in controlling the population of microorganisms, and the rigorous control of pH, temperature, and nutrients. Also, the presence of toxic or recalcitrant compounds is harmful to biological degradation (Bajpai and Bajpai, 1996). Nowadays, advanced oxidation processes (AOPs) are used for oxidizing the recalcitrant materials in the wastewaters due to the high oxidative power of the $OH^{\bullet}$ radical (Hirvonen et al., 1996) associated with AOPs. AOPs are defined as near-ambient temperature and pressure water treatment processes that are based on the generation of hydroxyl radicals ($OH^{\bullet}$) to initiate oxidative destruction of organics. The hydroxyl radical is a powerful, nonselective chemical oxidant, which reacts typically a million to a billion times faster than ozone and hydrogen peroxide, resulting in greatly reduced treatment costs and system size.

The goal of any AOP design is to generate and use the hydroxyl free radical ($OH^{\bullet}$) as strong oxidant to destroy compound that cannot be oxidized by conventional oxidants. AOPs are characterized by production of $OH^{\bullet}$ radicals and selectivity of attack, which is a useful attribute for an oxidant. The versatility of AOP is also

Table 6.2 Advanced Oxidation Processes

H_2O_2/UV/Fe^{2+} (photo-assisted Fenton)
H_2O_2/Fe^{2+} (Fenton)
Ozone/UV (also applicable in the gas phase)
Ozone/H_2O_2 (peroxone)
Ozone/UV/H_2O_2
Ozone/TiO_2/electron-beam irradiation
Ozone/TiO_2 /H_2O_2
Ozone + electron-beam irradiation
Ozone/ultrasonics
H_2O_2/UV

enhanced by the fact that they offer different possible ways for producing $OH^\bullet$ radicals. A list of the different possibilities offered by AOP is shown in Table 6.2.

Hydroxyl radicals can be created in reactions involving, for example,

- Ozone (O_3)
- Hydrogen peroxide (H_2O_2)
- Ozone + hydrogen peroxide
- Photooxidation
  - Ultraviolet (UV) + ozone + H_2O_2
  - UV + H_2O_2
- Photocatalysis
  - UV + TiO_2
- Electron beam irradiation
- Sonolysis

AOPs offer the potential for a complete destruction of hazardous organic compounds in process wastewater without generating secondary pollution. Conventional treatment processes such as air stripping, carbon adsorption, and membrane separation merely transfer pollutants from one medium to another resulting in the requirement of further treatments or disposal. AOPs are best suited for destroying toxic organic solutes in solutions with low suspended solids and low concentration of organic contaminants. AOPs can be used as stand-alone treatment processes, or as post- or pretreatment steps to conventional processes as part of an integrated treatment system.

In a study, the bleaching effluent from a waste paper pulp mill was treated with the solar photo-Fenton process in a laboratory-scale reactor (Xu et al., 2007). The treatment involved a constant intensity of irradiation with a solar simulator of 250 W xenon lamps at different pH and temperatures as well as initial concentration of hydrogen peroxide and iron. Total organic carbon (TOC) removal of over 90% was observed at optimum conditions, particularly at high temperature. The large-scale application of the process has strong potential for the efficient removal of organics from the effluent. This can be realized with the use of economical irradiation source of light and the high temperature of the original effluent.

The photocatalytic treatment of wastewaters from board paper industries with the photo-Fenton reagent or semiconductor TiO_2 resulted in a considerable decrease of the organic pollutant load (Amat et al., 2005). This could be achieved using solar light and has been scaled up to a pilot plant. The best performance was obtained for wastewaters from higher degree of circuit closure, when chemical oxygen demand (COD) values were quite high. In fact, closure of the circuits results in an accumulation of reluctant phenolic pollutants, while starch derivatives are continuously degraded by microorganisms in the circuits; as phenolic compounds are more easily degraded by photocatalytic means, these methods are suitable for closed circuits. These results show a satisfactory correlation with those obtained in the oxidation (with solar simulator or real sunlight) of appropriate compounds: eugenol and guaiacol (for phenolic lignin degradation products), acetate/butyrate/D glucose (for starch degradation products), and *p*-toluenesulfonic acid (for sulfonated pollutants).

Photocatalytic treatment of bleaching effluent from the pulp mill has been studied by Toor et al. (2007) in a low-cost, nonconcentrating shallow pond slurry reactor using artificial UV light with Degussa P25 TiO_2 as a catalyst. The results obtained with the sunlight for the UV radiation were similar to those obtained under artificial UV light of the same intensity. The degradation of pollutants more than 90%, in terms of COD, has been possible. This research has shown that efficient degradation of pulp and paper mill effluent containing recalcitrant compounds is possible by this method. Experiments under solar radiation yielded results comparable to those obtained indoors under UV lamps, which show that this process can be applied on an industrial scale and its cost may not be prohibitive. Because pulp and paper mills already use holding ponds for microbiological treatment of wastewaters, large-scale shallow pond reactors for solar detoxification may be an option on the front or back end of a combined solar/microbiological treatment system for wastewater.

Heterogeneous photocatalysis and ozone treatment have been successfully used to remove low concentrations of organic and halo-organic contaminants in bleached kraft mill effluents (Torrades et al., 2001). A 20-hour photocatalytic treatment using TiO_2 (Degussa P 25) predominantly anatase (80% anatase and 20% rutile) removed all the color and most of the TOC, adsorbable organic halides (AOX), and COD in a lightly loaded effluent obtained from the D stage of an AOD (A, acid; O, oxygen; D, chlorine dioxide) bleach sequence. For an effluent with a higher contaminant load obtained from the first D stage in a conventional elemental chlorine-free (ECF) sequence, the best treatment is the one that takes advantage of (hydrolysis) a previous treatment with lime and the synergistic effect of simultaneous photocatalysis and ozonation. Similar levels of TOC removal were obtained in the sequences hydrolysis—Ph—O_3 and hydrolysis—O_3—Ph, although for larger reaction times. The TOC, COD, and AOX reductions in the treated effluents were above 80% in all cases, and the effluents were always fully decolorized.

The present treatment costs of photocatalytic systems are slightly higher than those of conventional techniques, but the efforts being made in the design of more efficient systems with improved catalyst usage will establish this technology to be a cleaner and cost-effective alternative.

The effect of several operating factors on the decomposition of 2-chlorophenol in aqueous solution by sonolysis was studied by Ku et al. (2007). Experiments conducted with the purge of Ar/O_2 gas mixture of 2:1 molar ratio into aqueous solution yielded noticeably higher decomposition rate for 2-chlorophenol possibly due to the increased solubility of the gas mixture. Sonochemical decomposition of 2-chlorophenol was found to be more effective for experiments conducted in acidic and neutral solutions than in alkaline solutions (about 85% decomposition at solution pH 3). The sonication rate constant for the decomposition of 2-chlorophenol was increased (0.0006–0.00516 at pH 3; 0.00023–0.00284 at pH 9) with sonication intensity applied between 8 and 50 W/cm^2. The addition of appropriate amounts of ferrous ions could increase the decomposition rate of 2-chlorophenol by sonolysis, suggesting that Fe(II) ions may react with hydroxyl peroxide to prevent the recombination of hydroxyl free radicals.

Although sonolysis is a very attractive possibility to remove hazardous compounds from wastewater, transfer of small-scale studies to a plant scale will require further developments.

Fungal/Enzymatic Treatment

Fungi and their enzymes have tremendous potential in degrading the pulp and paper mill effluent, including the xenobiotic compounds (Bajpai et al., 1999). Different white rot fungal species have been reported to decolorize and detoxify bleach plant effluents from the bleached kraft pulp mill (Nagarathnamma and Bajpai, 1999; Nagarathnamma et al., 1999). A study has indicated that fungi, other than white rot fungi, are also capable of decolorizing extraction stage effluents. *Rhizopus oryzae* (Zygomycetes member) had proved to be superior to *Ceriporiopsis subvermispora* (a white rot). Strains with proved biopulping capabilities, such as *C. subvermispora*, also have the capability to decolorize extraction stage effluents. The mechanism of treatment is not the same for all the fungi, and fungal treatment can be used upstream to the conventional biological treatment system for enhancing the treatability of bleach effluents (Bajpai et al., 2003).

Sorce Inc. Technology uses a combination of fungi and facultative bacteria to degrade the highly cross-linked structure of lignin. This technology was started up on a Southeastern Kraft Pulp Mill with a wastewater flow of 15 million gallons/day. The starting color value of the wastewater averaged 1880 Pt-Co units. After nutrient conditioning and application of the microorganisms to the mill's lagoon, color reduced more than 50% with the anticipation of more than 80% color removal (Sorce Inc., 2003). This technology is called fungal/bacterial sequencing or biogeochemical cycling. Biogeochemical cycling uses specific microorganisms and manipulates their life cycles so that their degrading activities can be predicted and harnessed in a beneficial way. In this case, white rot fungi and its ability to secrete highly oxidative enzymes are used to fragment the lignin structure into smaller compounds. These fragments are mineralized into CO_2 and water with facultative anaerobic bacteria.

Mineralization is accelerated with the use of co-metabolites. The latent phase of the fungal growth is a time of limited food, nutrients, or adverse environmental conditions that results in a decrease in the microbial population. The life-cycle manipulation is the basis of the white rot/facultative bacterial sequencing technology, in other words, keeping the fungi in a latent phase, at the same time keeping facultative bacteria in a prolonged exponential growth phase. Under these conditions the white rot fungi secrete a tremendous amount of enzymes catalyzing the lignin degradation reaction that becomes the prime food source for the bacteria, ultimately mineralizing the degraded lignin fragments and reducing color, toxicity, biological oxygen demand (BOD), COD, etc., of the water to make it suitable for certain applications. This technology seems to be quite effective but requires large land area—tens of hectares.

The potential of using a combined fungal and enzyme system as an internal treatment was investigated for the control of the buildup of detrimental, dissolved, and colloidal substances present in a TMP/newsprint mill process water (Zhang, 2001). The experimental data obtained concerning the composition of a typical TMP process white water provided a better understanding of the influence that the dissolved and colloidal substance components in the recycling white-water system had on the paper properties and also helped in the design of an appropriate treatment technology. The white rot fungus, *Trametes versicolor*, was shown to be able to grow on unsupplemented process waters, while effectively removing white-water organics. The fungus also produced a large spectrum of enzymes during its growth on the different white-water streams, and the fungal enzyme treatments resulted in a significant degradation or modification of various dissolved and colloidal substance components. A combined fungal and enzyme system could possibly be used as an internal treatment "kidney" to remove detrimental organic substances present in a TMP/newsprint mill with a closed water system. A concept flow diagram for the combined fungal and enzymatic treatment system is shown in Fig. 6.6.

Different studies have shown that a combined fungal enzyme system showed promise as one way of decreasing the detrimental substances present within a closed water system, while treatments with different enzyme preparations revealed that

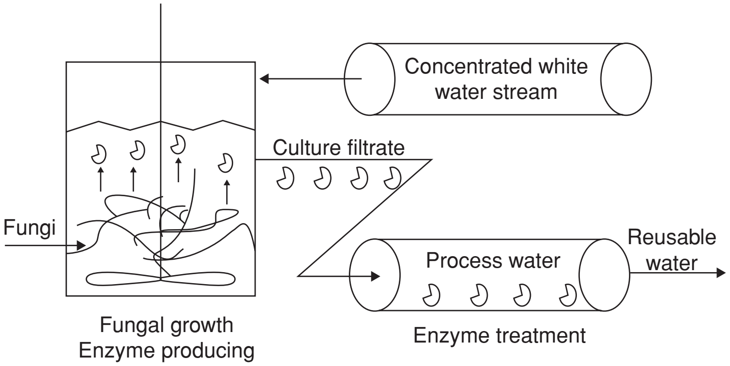

Figure 6.6 The principle of combined fungal and enzyme treatment system. Based on Zhang (2001) .

fungal laccases play an important part in the removal of white-water extractives. Potentials of laccase enzymes to modify model extractive compounds found in TMP/newsprint process waters were investigated by Zhang et al. (2001). The model compounds used were representative of the fatty acids, resin acids, and triglycerides found in mill process waters. It was found that these compounds were significantly degraded or modified by the laccase treatments.

Sequential treatment using fungal process followed by photocatalytical treatment on COD, color removal, degradation of chlorophenolic compounds in bleach effluent has been studied (Pendroza et al., 2007). The overall reduction was 97% in COD, 92% in color, and 99% in chlorophenols. An enzymatic pretreatment has been used to improve the filterability of a process water concentrate obtained by pilot-scale UF of circulation water from a Finnish ground wood mill using spruce as raw material (Lantto et al., 2003).

Sequential Anaerobic/Aerobic Bioprocesses

Most of the soluble components from wood and recycled paper are biodegradable. Biological treatment can be operated to give efficient removal of nutrients. Biological treatment in combination with filtration produces water that is of acceptable quality for the replacement of 20–30% of freshwater without any risk to product or production efficiency. In the production of unbleached grades, the reuse can be extended considerably provided that accumulation of salt can be managed. Biologically treated water does not sustain slime growth; most of the anionic disturbing substances are eliminated and the temperature is typically about 30°C, which also makes it usable in sealing vacuum pumps (Lindholm, 2000). Existing biological treatment plants can and should be utilized in a strategy for replacement of freshwater. Mills without biotreatment are recommended to consider the possibility of water reuse when they decide to build a treatment plant. Biological treatment removes biodegradable organic substances. Generally, an aerobic system gives a higher removal than anaerobic processes measured as residual organic carbon (TOC).

In an anaerobic system, approximately 75% of the carbon is found in the biogas—approximately 65% CH_4 and 35% CO_2, 20% in the effluent; and only 5% forms excess sludge, which is positive. Energy in the biogas must be utilized to fully benefit from the system. Anaerobic treatment is sensitive to certain substances (tannins), and the sulfate in effluent is reduced to sulfide, which also retards activity; whereas in aerobic systems, the organic carbon is equally split between excess sludge and CO_2, and approximately 5% is found in the treated effluent. These values vary depending on composition of the product, but they can nevertheless be used for guidance. In practice, if anaerobic treatment is implemented, it is followed by aerobic polishing.

The development and implementation of high-rate anaerobic treatment systems enormously contributed to the self-sufficiency of polluting industries, not merely as end-of-pipe approach but increasingly as process integration. This particularly has been accomplished in European countries in the recent decades. Anaerobic treatment enables the concept of recovering useful by-products such as energy in the form of biogas, chemicals, and raw materials. Industries increasingly attempt to close water cycles by its implementation with the proper physicochemical and complementary treatments, mainly for reasons of economy and environmental considerations. For example, the wastewater in paper mills contains starch, volatile fatty acids, and cellulose as organics, and thus is very good substrate for anaerobic treatment, if the reduction of the soluble COD is the objective. Sulfate will be reduced in the reactor and can be removed from the process loop by biogas stripping (Lens et al., 1998). In general, an anaerobic treating wastewater from a recycled paper mill degrades up to 80% of the soluble COD (Van Lier et al., 2001). The organic matter is either reduced to methane that can be recovered for steam production inside the mill, or anaerobically oxidized to bicarbonate, which is used in the subsequent stages for calcium removal. A zero-discharge paper mill using the anaerobic–aerobic treatment has been described by Van Lier et al. (2001). Whether the treated water can be reused in the process after the aerobic stage depends on the quality demands in the production line. For packaging and board mill, anaerobic treatment complemented with aerobic treatment and sand filtration suffices. However, for the production of high-quality paper, a tertiary treatment step is required to focus on removal of very fine particles, color, and/or salts.

Anox AB has carried out research to determine the feasibility of a three-stage thermophilic moving bed biofilm reactor for treating printing paper white water (Bengtsson et al., 2003). A 60% removal of dissolved organic compounds could be attained at 57°C. This removal of dissolved organic compounds resulted in a low level of easily biodegradable organic matter in the effluent. The process can be run with very low levels of nutrients in the effluent and can recover quickly from a short disturbance such as sudden pH or temperature drop. The increase in color of the treated water could be a problem and may require further treatment. Ozone treatment could be effective for this purpose.

In Germany, biological wastewater treatment is performed by anaerobic and aerobic processes. Due to degradation products of anaerobic metabolism, the effluents from anaerobic reactors (upflow anaerobic sludge blanket [UASB] reactor and newly developed high-load expanded granular sludge bed [EGSB] reactors) do not have the appropriate qualities to be discharged directly into the receiving water. Therefore, the anaerobic reactor is generally used as a first biological stage, followed by an aerobic stage, mainly activated sludge plants. This kind of wastewater treatment is state-of-the-art in German recycled paper processing mills producing packaging papers such as Testliner, corrugated medium, and cardboard (Schabel and Humm, 2007). This could achieve the COD discharge of about 0.5 kg oxygen per tonne paper to the treated wastewater in the German mills with a production of more than 200,000 t/year each against the COD discharge value of 1.5 kg/t paper with the best available technology levels of the European best available technique reference document pulp and paper industry (BREF). The specific wastewater discharge from these RCF mills also reduced to only 7 m^3/t papers in 2006.

Effective combination of anaerobic–aerobic technologies may prove a powerful tool for treatment of mill effluent, and thus help plants to meet environmental standards. A combination of anaerobic–aerobic processes for effluent treatment of liquor can reduce power consumption by 60% and chemical consumption by 35%, when compared to a purely aerobic approach (Panwar et al., 2004). The treated effluent is used for irrigation purposes. After suitable tertiary treatment, including filters for suspended solids, this effluent can be recycled back to the mill process where water quality requirement is not very stringent. Due to the development of high-rate bioreactors, and increased understanding of microbiology and anaerobes, the new technology is increasingly recognized as a viable alternative.

Internal Circulation Reactor

The anaerobic treatment of wastewaters containing dissolved organics is quite popular using the conventional UASB reactor, which has been applied in hundreds of pulp and paper mill effluent projects over the world. Now, a new reactor concept called the internal circulation (IC) reactor is being tried at different pulp and paper mills. This is a more compact anaerobic reactor compared with UASB as explained below.

IC reactor is based on the proven UASB process, as it is an upflow granular sludge bed system, which is applied as a pretreatment step in effluent treatment to convert 85% of the BOD into methane gas. In fact, the IC reactor consists of two UASB reactor compartments on top of each other, one high loaded in the lower part and one low loaded on top of that. Its special feature is the separation of biogas in two stages within a tall reactor tank. The biogas collected in the first stage drives a gas lift resulting in an internal circulation of wastewater and sludge, which gives the reactor its name.

A Dutch board mill producing 400 t/day of board from the recycled fiber has been operating with a closed water circuit for 20 years. Due to more COD in the raw fiber material as well as more strict requirements with respect to odor in the paper and in the surroundings of the mill, a new treatment plant using anaerobic IC reactor with aeration and sand filtration was commissioned to maintain the closed circuit (Habetes et al., 2000). Earlier with the UASB reactor, the machine backwater had to be cooled before feeding to UASB reactor because in closed circuits the heat losses are minimized and the temperature may increase to 55–60°C. But now, with IC reactor, the cooling has been eliminated with the application of thermotolerant bacteria. The water can be treated in two lines to produce two different qualities of water for reuse. The first line requires six process steps and produces a water quality “A” that is reused by the mill. The second line has only three treatment steps and produces an effluent of lower quality standard (quality “B”), which is suitable for the dilution of the pulp. Equipment-wise, the UASB reactor has been replaced by an IC reactor to cope with higher temperatures, to increase biomass activities, to improve mixing, and to save space. The aeration tanks have been designed with a water level of approximately 10 m, whereas the aeration takes place by externally placed aeration jets that are provided with compressed air.

The plant has a design load of 90 m^3/h of process water to maintain the process water COD at a level of 3000–4000 mg/L. The operating temperature is 55°C. The process water temperature at the Dutch mill was already at 55°C and the water circuit was already closed completely, so there would not be much time available for cultivation of the bacteria. Therefore, thermophilic bacteria were cultivated during 1-year operation in a 70 m^3 pilot reactor at another mill and were transferred to the thermotolerant treatment plant for its successful operation.

FlooBed Bioreactor Process

Eimco Water Technologies is providing an advanced, high-loaded biological treatment method called FlooBed® process. It is a biological treatment of industrial wastewaters. It consists of microorganisms both attached to the carriers and suspended in the water. The FlooBed solution has been the choice for several types of water such as effluent from process industries, landfill leachate, and municipal wastewaters. In the pulp and paper industry, FlooBed has been built into the mill area, for pretreatment of existing activated sludge plants and for new mills with high requirements. FlooBed bioreactor is a suspended carrier biofilm process. It is reliable and easy to operate and has been developed especially for industrial effluent treatment. Compared to conventional methods, FlooBed tolerates higher variations in water quality and flow and still maintains its high treatment efficiency (EIMCO, 2007a). These processes are used to significantly increase the capacity of existing activated sludge systems, and it is also suitable for covering the total effluent treatment of the mill. In contrast to traditional activated sludge processes, most of the microbes grow as biofilm on surface of the freely moving carriers. The plastic carrier elements inside have a large surface area and a structure that is optimized to protect the biofilm from abrasion. This allows a high amount of biomass inside the reactor, and the needed reactor size can be kept small. Savings in civil work costs are remarkable with this process. Carriers are made of plastic, and their density is slightly lower than that of water. Due to that, carriers can be easily mixed through Eimco aeration system, which covers the entire reactor bottom. The process does not require backwashes, which were typical for conventional biofilm processes and took up a lot of energy in addition to interfering with functioning of the process.

The combination of a high-load biofilm-activated sludge (BAS) (FlooBed bioreactor and a low-load activated sludge plant) is an efficient and stable solution for improved industrial effluent treatment. The FlooBed BAS process has already proved its efficiency in several successful full-scale installations. With FlooBed the loading of a treatment process is reduced and peak loads are efficiently managed. This enables stable functioning of the following activated sludge stage and gives good-quality discharge as a final result. Industrial effluents typically have high concentration of organics, and there are significant variations in both flow and concentration. FlooBed BAS utilizes the advantages of conventional biofilm processes and combines them with the best features of activated sludge plants. Many FlooBed systems have been installed all over the world. The installations (of up to 4000 m^3/h effluent volume) in pulp and paper industry as in November 2007 are Brazil two, Finland three, France one, Germany six, Hungary one, Italy two, China one, Poland two, Portugal one, Spain two, Sweden four, Switzerland one, Taiwan one, and Thailand one (EIMCO, 2007b).

With FlooBed the loading of a treatment process is reduced and peak loads are efficiently managed. This enables stable functioning of the following activated sludge stage and gives good-quality discharge as a final result. The compact FlooBed BAS process can easily be installed in both greenfield factories or embedded into existing treatment systems, which are then modified to modern FlooBed BAS processes. Benefits of FlooBed-based processes are good treatment efficiency, resulting in low residual concentrations, stable discharge water quality, a short start-up in the beginning and also after accidental or planned shutdowns, excellent capacity for handling toxic compounds and load variations, low sludge production, and small construction costs. In cases where the capacity of the effluent treatment plant needs to be increased, the existing process can be upgraded with FlooBed RE to function as a modern FlooBed BAS process. Consequently, the need for operation and control of the process will decrease dramatically (EIMCO, 2006). If anaerobic biological treatment precedes the aerobic process, a simple small FlooBed bioreactor will be able to do the satisfactory job. More details on anaerobic treatment of pulp and paper mill wastewaters are available in Bajpai (2000).

Membrane Processes

“Membrane filtration” is a general term used for a number of different separation processes. The semipermeable membrane acts as a filter that allows water to flow through, while removing suspended solids and other substances. Membrane process can be pressure-driven or dependent on electrical potential gradients, concentration gradients, or other driving forces. Pressure-driven membrane processes include MF, UF, NF, and RO. MF and UF are characterized by their ability to remove suspended or colloidal particles via a sieving mechanism based on the size of the membrane pores relative to that of the particulate matter. NF and RO constitute the class of membrane processes that is most often used in applications that require the removal of dissolved contaminants, as in the case of softening or desalination. RO process has also been referred as hyperfiltration and NF is known as loose RO.

Membranes, particularly those with molecular weight cutoffs in the range of 100–500 Da, are very effective for removing salts and organic compounds. Membranes are of different pore size and it is necessary to select membranes of appropriate pore size for specific purpose so that wastewater could be purified and permeate could be recycled a number of times. Biological treatment in combination with membrane filtration and salt removal from a selected amount of treated effluent makes it possible to recycle water completely. Most of the membranes are made from the polymeric materials, except a few of them are made from ceramic materials also. RO membranes presently available include the asymmetric membranes of cellulose acetate (CA), aromatic polyamides (PA-type), and a patented polymer from Osmonics, which is also a PA-type. Also available are the newer thin-film composite membranes, of which aromatic polyamide (PA) on a polysulfone substrate is the best known. UF polymers currently available include polysulfone, CA blends, a fluorinated polymer (VF), and Osmonics' patented polymer (PA-type). MF membrane polymers commercially available are the most numerous, due to the relative ease of achieving the required pore size for MF compared to UF and RO membranes. Polypropylene, acrylonitrile, nylon, and polytetrafluro ethylene (PTFE) are among the more common MF polymers in addition to ceramic materials, and their broad chemical compatibility characteristics make the MF range of membranes the most chemically stable. Other polymers that show some long-term promise are acrylonitrile copolymers and polyethersulfone. The material for the membrane also depends on the chemical nature of the fluid being treated and operating conditions such as temperature and pH. The membrane systems are available in different configurations such as plate and frame, tubular, spiral wound, and cross-rotational (CR) system.

In *cross-flow membrane filtration*, the influent stream is separated into two effluent streams, known as permeate and concentrate. Permeate is that fraction which has passed through the "semipermeable" membrane. The concentrate is that stream which has been enriched in the solutes or suspended solids, which have not passed through the membrane. Membrane is a surface filtration medium, which affects separation in the ionic and molecular range, as well as the macromolecular and particle range. The advantage of this design approach is that the membrane medium is operated in a continuously self-cleaning mode, with solutes and solids swept away by the concentrate stream, which is running parallel to the membrane, hence the term "cross-flow." The advantage of this approach is separation in the micron, submicron, molecular, and ionic range. The feed solution flows under pressure between the two membranes, and as it flows over the membranes, permeate passes through. The rate of permeation per unit of membrane area is known as flux. The concentrated fraction of the stream exits through the same flow channel as the feed enters, carrying away concentrated solutes and particles.

Membrane filtration solutions for water treatment were first employed in the virgin fiber industry in 1999 and in the recovered paper industry in 2002. There have also been pilot tests in nonwoven applications (Hepp et al., 2005). Membrane filtration is often employed as part of a bioreactor that also includes a biological degradation stage. The two configurations are side stream and submerged. Ugchelen Mill of Veiligheidspapierbabriek, Netherlands, polishes bleaching water of cotton raw material and reduces COD by 85% using dissolved air flotation followed by an MBR.

Metso Paper has developed a special type of membrane filter system called OptiFilter CR. It is a plate and frame-type solution, in which flat membranes are fastened on both sides of filter cassettes. They are stacked on top of each other. Between each cassette, there is a rotor that creates turbulence to enhance the filtrate capacity and reduce the fouling effect. This is an advanced device based on fine physical separation on a high molecular level. Protected OptiFilter CR's cross-rotational technique makes it superior for treating water fractions in the pulp and paper industry. Combining OptiFilter CR with other membrane technologies makes it possible to easily control detrimental substances in the paper machine's white-water circulation, thus ensuring paper machine runnability even with low freshwater consumption.

Microfiltration

MF has generally come to be regarded as effecting separation in the 0.02–2.0 μm ranges. Materials small enough to be present in dissolved form will generally permeate the MF membrane, while suspended solids are rejected. In general, MF removes all solids larger than about 0.05 μm. MF membrane materials commercially available are the most numerous, due to the relative ease of achieving the required pore size for MF compared to UF and RO membranes. Polypropylene, acrylonitrile, nylon, PTFE, and ceramics are among the common MF materials, and their broad chemical compatibility characteristics make the MF range of membranes the most chemically stable.

Bench-scale tests were carried out on MF membrane process in the recycling of specific liquid. For old newsprint de-inking effluent, flexographic ink was completely removed and the quality of the permeate was suitable for recycling. Effluent from a paper coating operation was concentrated to a consistency of 16.5%, with 96% of the original water removed (Silva et al., 1998). Very good permeate quality was achieved. MF of effluent from the bleached chemithermomechanical pulp mill retained suspended solids in the effluent, but the permeate contained high levels of total dissolved solids, which were not removed. Treatment of effluent from a board mill using recycled old corrugated container using a submerged MF MBR removed 95% of COD and 99% of BOD, giving acceptable water quality.

Wastewater discharged from a mill producing tissue papers was treated using three types of tubular carbon ceramic UF and MF membranes for reuse as industrial water (Park et al., 2003). The filtration time was fixed at 8 or 16 minutes, while nitrogen-backflushing time (BT) was changed in 0–60 seconds. The short nitrogen-BT could reduce the membrane fouling and recover the permeate flux sufficiently for MF membrane having a large pore size, while longer nitrogen-BT was required to achieve the maximum volume of purified water for UF and MF membranes having a small pore size. Average rejection rates of pollutants were found to be higher than 99% for turbidity and 22.8–59.6% for COD. Rejection rates of total dissolved solids, however, were lower than 8.9%. The purified water acquired in the UF and MF system with periodic nitrogen-backflushing could be used for the paper process.

In the Italian paper mills, utilizing secondary fiber as raw material, the water consumption was still very high in 2004—about 20–30 m^3/t of fine paper—because biological treated water was not adequate for reuse as feed water. Therefore, the final wastewater originating from Lucart Industry in Lucca is cleaned by different membrane technologies, including MF (Pizzichini et al., 2004). Outstanding separation performances were achieved with ceramic MF membrane presenting a cutoff of 0.14 μm that guarantees a productivity of 60–75% of feed water with a low fouling index of the membrane.

Test trials at Hunsfos Paper Mill, situated on the Otra River, close to Kristiansand, Norway, which produces a range of paper on three paper machines and one off-line coater, revealed that a microfilter produced a consistent quality of filtrate of a suitable clarity for reuse, while requiring only a moderation addition of chemicals (Solheim-Olsen and Dewhurst, 2006).

New advances in membrane design and flux maintenance protocols have enabled membranes to meet variable, challenging wastewaters. Different membranes behave differently depending on their ability to resist or handle fouling. Modular membrane trains are easily expandable, and more and more affordable solutions are being offered in pre-engineered, packaged, and mobile designs. Pall Water Processing's Microza hollow-fiber MF membrane is made from a polyvinylidene fluoride polymer and has a uniform construction throughout its thickness (Caothien et al., 2008). The unique symmetrical configuration of the MF membrane means that there is no skin or coating that can delaminate or separate from the substrate under operating stress. The membrane is resistant to surface defects and pinholes.

Now, the MF systems of different configurations and different materials are being used for the treatment of pulp and paper mill wastewaters to remove the fine suspended particles so that the recovered water can be used in the mill. The MF is also used as a pretreatment step before UF and NF basically to reduce the fouling of UF, NF, and RO membranes and improve their permeate flux.

Ultrafiltration

UF separates suspended solids and some colloidal material, depending on the membrane used. UF technology can help in removing colloidal silica from boiler feed water. India's one of the largest board mill at Bhadrachalam, Andhra Pradesh, supplies 250 t/h steam at 62 bar. The presence of high levels of silica in the feed water necessitates frequent blowdowns to clear accumulations, and this causes heat and water wastage. After installation of UF membranes of Koch Membrane, USA (273 mm diameter by 1829 mm long cartridges—44 in numbers), both the suspended silica and the organic impurities are removed (Anonymous, 2008). Triplex Water Engineering, New Delhi, India, has designed and constructed the system. The Targa cartridges comprise of polyester fibers with an internal diameter of 0.035 in. and a pore size of 10,000 Da. The filtration system has reduced the silica content from 35 to 15 ppm. Blowdowns have reduced and the boiler heat transfer efficiency has also increased.

UF membranes can remove the colloidal wood resins from the mechanical pulp filtrates. Metso Paper has specially designed a UF system, called OptiCycle R, for this purpose. OptiCycle R process is a solution for mechanical, chemimechanical, or chemical pulp mills to remove resins (i.e., pitch) from pulping process water without chemicals. Colloidal wood resins are one of the main components to cause problems at paper machine process, paper machine, and even at the printing process. This process is based on OptiFilter CR UF (mentioned earlier), which is a pressure-driven membrane separation process. UF membranes with pore size in the range of 0.01–0.1 μm allow complete separation of suspended solids, colloidal material (pitch), emulsion, bacteria, and large molecules.

OptiCycle R is specially suited for pulping processes with high colloidal resin content. These are typically chemithermomechanical pulp (CTMP), TMP, and groundwood pulping processes with various wood species. It can be utilized at the chemical pulping processes also, if needed (e.g., it has been installed for chemical pulp process at Domsjö Fabriker Ab, Sweden). When the freshwater consumption is decreased in the papermaking process and/or the effluent treatment capacity is limited, the way to minimize problems and investments is to upgrade the mechanical pulp mill water system with OptiCycle R process.

The filtrate from the pulp press is treated with effective pretreatment to recycle valuable fibers back to the process. OptiFilter CR filters are producing 4–5 m^3/t pulp resin-free permeate for pulp washing. Postconcentration is done by similar OptiFilter CR to meet high DS content for burning. Modular design makes OptiCycle R process flexible for different pulping processes. Due to the UF membrane characteristics, the resins are removed but salts penetrate the membrane. This makes the concentrate low salt containing and thus suitable for burning, that is, at a bark boiler. Resin-free permeate is recycled back to the pulping process. Thus, this UF separation process prevents the drifting of harmful resins to the paper machine. It gives both economic and ecological benefits to the papermaking process. These types of UF systems are in use at several pulp and paper mills.

A pilot membrane test was set up by the Markische Fachhochschule at Stora Kabel, Germany, for 21 days (Kothe and Schroth, 1999). Stora's main aim was to reduce its freshwater consumption levels to under 14 m^3/t. It was found that the CR membrane method was economical and environmentally friendly. Freshwater consumption levels were reduced. Stora's total investment costs were DM 237 million, 28% of which were spent on energy and 14% on the CR-membrane equipment. Investment costs were expected to be recovered in 4.9 years and investment profitability was expected to be 21%. UF filtration is used for the purification of paper and board mill's white water also (Hepp et al., 2005; Klepaczka, 2004). Arctic Paper, Munkedals, Sweden, and Papierfabrik Palm, Germany, employ UF membrane separation process for treating the white water to be recycled (Hepp et al., 2005).

UF process of Metso Paper, called OptiCycle W, is an efficient method for paper/board mill's filtrate water treatment. Mills with high freshwater consumption levels can normally achieve good runnability and paper quality without any additional kidneys. However, internal kidneys are needed to increase the runnability when the freshwater consumption level decreases. OptiCycle W (membrane filtration) is installed in the paper mill's filtrate waters (white waters) to purify the water to a level where it can be used as an alternative to freshwater. The quality of the UF filtrate enables trouble-free recycling of the water fraction to the wire and press-section high-pressure showers, some low-pressure showers, chemical final dilutions (e.g., bentonite and wet-end starch), and sealing waters. Concentrate is pumped to the effluent treatment plant. By replacing warm freshwater with ultrafiltered water in the full-scale processes, a freshwater reduction of about 2–4 m^3/t of paper can be achieved.

Feed water to this UF system is generally low-solid-containing "save-all" filtrate (clear filtrate) to minimize the fiber loss. First feed water is prescreened to remove

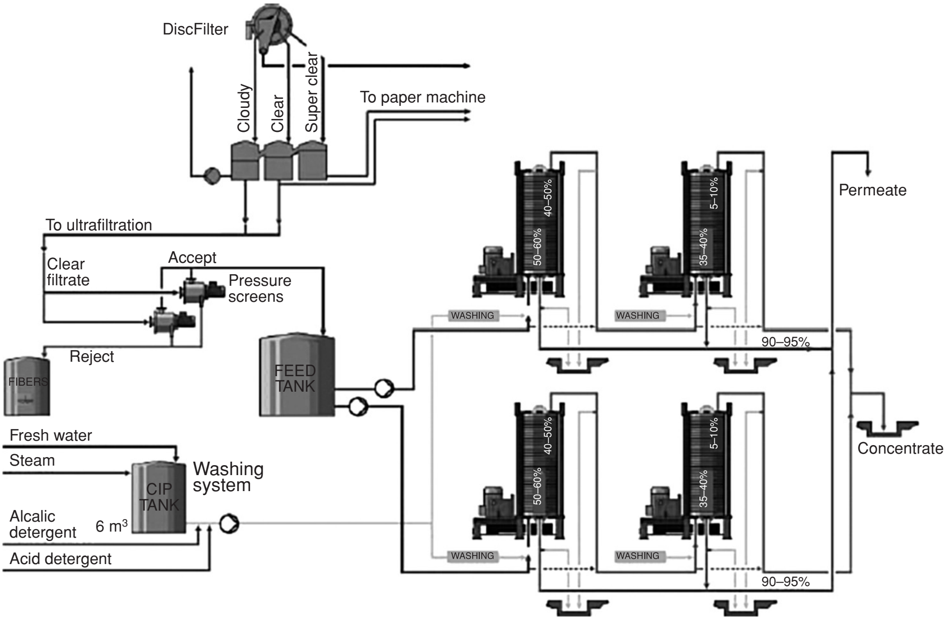

Figure 6.7 OptiCycle W process for paper machine white waters (courtesy Metso Paper).

big particles and long fibers (to minimize the fiber loss). Then, it is pumped through two ultrafilters, connected in series (Fig. 6.7). Permeate (filtrate) is pumped to the paper process where it is required. Final concentrate is led to wastewater treatment. To increase the capacity, the required numbers of UF units are added in parallel. All the filters have common "cleaning in place" system. Ultrafilters need to be washed regularly to keep up constant capacity. Alkaline washing is an automated action, which is normally done once a week for all filters. Acid washing is normally needed once a month.

The ultrafiltered water is free from suspended solids and colloids. For instance, bacteria, latex, and other microstickies are removed. As the anionic trash is cut to approximately half of the original level, the quality of the filtrate enables trouble-free recycling to the process.

Operational costs for OptiCycle W process are normally between €0.2 and €0.4/m^3. Half of it comes from energy and the other half is divided between washing, membranes, and other spare parts. About half of the consumed energy will be gained as heating energy; permeate temperature will be 1–2°C higher than feed. This will help in thermal balance. The advantages of paper machine white-water treatment by UF and recycling are less freshwater requirement, less generation of wastewater, less emission, better machine runnability, better process heat balance, lower energy consumption, less water treatment cost, and short payback time. It provides solution for environmental and economic challenges.

Holmen Paper Papelera Peninsular Mill, Madrid, chose this UF system to decrease the freshwater consumption from 9 to 7 m^3/t of paper. Capacity of the UF unit is 800–900 m^3/day, producing solid- and bacteria-free water, which is then used to replace freshwater at certain applications. It resulted in 100% removal of suspended solids, 100% removal of ash, and 43% reduction in COD (Blanco and Pío, 2007). UPM-Kymmene Tervasaari mill (Valkeakoski, Finland), one of the largest specialty paper mills in the world, started OptiCycle W process in their PM8 in November 2005 to lower the wastewater amounts by increasing internal water recycling (Anonymous, 2007). It has decreased the freshwater consumption about 5 m^3/t (from 11 to 6 m^3/t). Permeate works without any problems at paper machine wire and press-section showers. Paper machine runnability is as good as before, though water circuits are closed to this extent. Capacity is stable. Membrane lifetime is more than 1 year. OptiCycle W has helped the mill to keep up more stable temperature balance. This has major effect on production efficiency. As per Metso Paper's presentation, the other references of OptiCycle W are Metsa-Serla, Kirkniemi, Finland, (installed in 1995, 1996, 1999, and 2002 for magazine/fine/newsprint machine white waters), Modern Karton (in 2008 for old corrugated container white water), Hokuetsu, Niigata, Japan (in 2008 for fine paper machine white water), and an undisclosed mill in Germany (in 2009 for old corrugated container white water).

UF has become one of the main methods for coating effluent treatment, enabling recycling of pigment and chemicals with retention of their functional value and recycling of filtrate water (Mahmood, 2006; Roitto, 2007; Siivonen and Genduso, 2003; Singh et al., 1999; Tizon et al., 2005). Cellier, Activity of ABB France, in cooperation with PALL Corporation has developed a UF system based on the cross-flow filtration technology with ceramic membranes for liquid/solid separation specially for the paper industry and is designed for the treatment of effluents (mainly rinsing water) resulting from the coating process (coating color kitchen and associated equipment) (Tempesta, 2007). It uses Membralox® ceramic elements, which are asymmetric multichannel membranes consisting of a porous alumina support and a filtering layer (alumina or zirconia). The ceramic membranes are fitted with a 316 L stainless steel housing (module). They are resistant to chemical attacks, extreme pH, and temperature values and are compatible with organic solvents. The standard UF range is 20–100 nm. ABB UF systems are composed of several Membralox modules in series and/or in parallel according to the required filtration area. Each system can be extended by adding new modules. The feeding is continuous and the working tank operates at a constant level. The feed stream moves parallel to the membrane filtration surface, and purified liquid passes through the membrane. The separation is driven by the pressure difference from one side of the membrane to the other—referred to as transmembrane pressure. Cross-flow filtration streams are divided into three parts: (1) feed that enters the filtration channels, (2) permeate, a solution that passes through the membrane pores (clear water), and (3) retentate (or concentrate)—the solution retained by the membrane (raw materials).

With the turbulence created by the cross-flow velocity, particles are continually swept away to avoid the clogging up of the membrane surface. The retentate is the

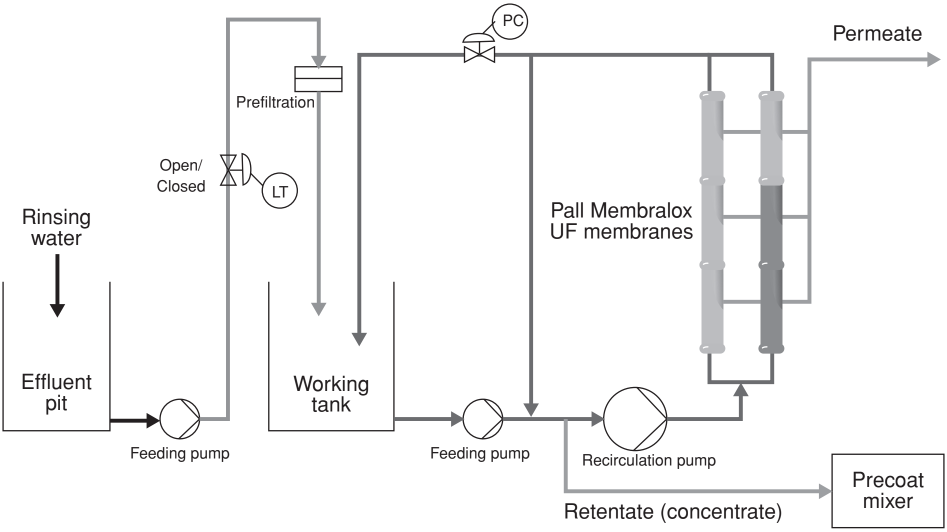

Figure 6.8 Process flow diagram showing filtration loop using Cellier UF membrane (courtesy ABB France).

result of the concentration of the original feed stream. It flows through the channel and is recycled back into the feed stream. A general filtration loop is shown in Fig. 6.8.

The UF stage enables to recycle rinsing water by decreasing the COD value and lower the load of the wastewater treatment plant as well as the relating operating and energy costs. The UF unit also helps to minimize the perturbations in the wastewater treatment plant, such as highly variable effluent flow and concentration rates, and COD peaks, for instance, due to a paper break. Recovered permeate or "clear water" can be used as rinsing or process water in the paper mill. According to the application, solid matters contained in the concentrate slurry can be added as a component to the coating color or precoat directly at the mixing stage. The system has been implemented at Cascades Blendecques S.A., France; Cartiera di Sarego (Burgo Group spa), Italy; Thai Paper Co., Ltd., Thailand; Advance Agro Public Co., Ltd., Thailand; and Suzano de Papele e Celulose S/A, Brazil.

Metso Paper has also developed UF process called OptiCycle C for treatment of coating effluent and recovery of coating color solids.

Nanofiltration

NF lies between RO and UF in terms of separation efficiency. It is sometimes used for further treatment of water from ultrafiltration, where monovalent ions are not separated. NF membranes with pore sizes of 0.001–0.01 μm allow separation of mono-, di-, and oligosaccharides and polyvalent negative ions.

Nanofiltration has been studied for filtering the chelation stage effluent from a TCF pulp process to enable the reuse of wastewater by the total removal of metals and organic compounds to achieve zero liquid effluent operation (Romero et al., 1999). Polymeric NF membranes made from aromatic polyamide were found to be useful in reducing wastewater discharge and reusing process water in pulp and paper mills. The membranes show chemical stability in the process conditions in addition to providing good selectivity and good-quality water.

M-real Kirkniemi, Finland, provides an example of the use of NF along with UF in their PM3 (Siivonen and Genduso, 2003). By nanofiltering the water that has been through a UF unit to replace or supplement a freshwater plant, the consumption of freshwater is about 6 m^3/t, a very low level for a mill with integrated production of mechanical pulp. In fact, NF process is expected to be used as kidney in the mill water circulation system, especially in mills where water source is limited (Nystrom et al., 2005). NF gives very good-quality water that can be used anywhere in a mill. For NF to be effective, it must be operated in conjunction with different kinds of pretreatments to remove the membrane foulants. The best pretreatments include thermophilic aerobic biological treatment, flocculation, pH change, or UF. NF in conjunction with UF has been tried in Papierfabrik Palm GmbH PM6, Germany, which produces lightweight chipboard and fluting (Wirth et al., 2005). The machine featured a closed water loop to reduce freshwater consumption. A process water cleaning plant was installed to combat the expected buildup of chemical and other contaminants. This consisted of anaerobic and aerobic stages and a two-layer sand filter, followed by a membrane filter comprising UF and NF with RO.

In a study, membrane filtration, UF, and NF alone and as part of hybrid processes were considered as means to purify pulp and paper mill process waters suitable for reuse. Thermophilic aerobic biological treatment, pH adjustment, flocculation, and ozonation were tested as pretreatment methods on pilot or on laboratory scale (Nuortila-Jokinen et al., 2003). It has been shown that membrane filtration offers a very competitive option as a “kidney” process in the closed water circuits of integrated pulp and paper mills. Shear enhanced membrane modules offer high fluxes and the compact structure demanded from an internal purification process—the CR filter for the UF and the VSEP filter for NF. Thermophilic aerobic biology assisted the removal of organic material and increased flux significantly. The most cost-effective processes, however, seemed to be a pH-adjusted NF and a flocculation–NF hybrid process, which is understandable due to their significantly lower investment costs compared to, for example, those of biological process. The pH adjustment increased the electrostatic repulsion between negatively charged solutes and membrane, thereby increasing the flux. Flocculation removed the foulants effectively from the feed, and it both increased flux and reduced fouling. Noteworthy benefits were also obtained with UF and ozonation.

Several studies with recommendations of very high potential have been reported about NF in combination with other pretreatments (e.g., pH adjustment, coagulation/flocculation, and MF) and posttreatments such as RO for pulp and paper wastewaters (Manttari and Nystrom, 2006; Puurunen and Vasara, 2007; Richardson et al., 2008; Takaoka, 2007; Zippel, 2003).

Reverse Osmosis

RO is close to an absolute method for separation of ions and molecules from water. RO, sometimes called hyperfiltration, is perhaps the most technically complex class of membranes, effecting separation at the micromolecular and ionic size range. Pore sizes ranging from 5 to 15 Å affect separation of the solutes down to 150 molecular weight and often lower. As with UF, RO has rarely been viable unless used in a cross-flow mode. RO treatment cannot be applied to process effluent from pulp and paper industry without extensive pretreatment. Treatment of a side stream for removal of salt can be implemented (Wirth et al., 2005).

Rigid Paper, Selby, Yorkshire, UK (one of the leading paper packaging mills in the UK, owned by VPK Packaging Group, Belgium), producing approximately 70,000 t/year of corrugating medium from waste paper, has installed RO for the treatment of boiler feed water, which was further given a polishing treatment of ion exchange (Freer, 2005). RO compares very favorably with ion exchange dealkalization in the reduction of hazardous chemical delivery, and handling and operating costs are lower. For Rigid Paper the capital cost of GBP56,000 was expected to be paid back in less than 2 years. Installation of a Compact III packaged RO system from ELGA Process Water took place in 2001. The success of the project may be replicated at other European sites within the Belgian group.

Tertiary wastewater treatment using direct NF and RO membranes is found to generate clean permeate that is easily reused in paper production (Manttari and Nystrom, 2006). Biologically treated discharge waters from pulp and paper mill activated sludge plants were subjected to NF and low-pressure RO, after which the resultant permeate's retention, flux, and quality were evaluated using a high-shear filter. Results show that NF produces permeate with no color and organic compounds but with significant amounts of chloride ions and other inorganic compounds, especially when the discharge waters have high levels of sulfate ions. The presence of high sulfate ions in the discharge waters reduces the retention capability of NF membranes for monovalent anions, resulting in detrimental accumulation of chloride and nitrate ions in permeates. This necessitates the use of RO membranes to achieve excellent process water. RO membranes can retain more than 95% of monovalent ions, but they produce permeate with higher fouling and lower flux than that of NF membranes. NF and RO membranes can retain almost all organic compounds and provide permeate with less than 10 mg/L organic carbon.

Caustic recovery after the treatment of pulp with alkali has also been tried using RO (Suchy et al., 2006). AFC99 thin film polyamide composite membranes were used, and the trials were run at 800 psi pressure. No deterioration in the performance of the membrane was observed over the period of testing (over 50 hours), and the membrane retained its separation and performance characteristics after continuous exposure to sodium hydroxide solution for 7 days. For 1% solution of sodium hydroxide at 800 psi transmembrane pressure and an average temperature of 26°C, the flux values measured about 70 L/h per m^2, with 85% salt rejection.

A new effluent treatment plant installed by Siemens at Albert Kohler GmbH's Gengenbach, Germany, board mill, enables virtually all wastewater to be reused. The system comprises an MBR linked to UF and RO units. Kohler Pappen is the first paper industry to have installed the MBR with integrated RO (Junk et al., 2008). It has shown that the concept allowed average COD to be reduced from 2200 mg/L to less than 150 mg/L, with average BOD levels reduced from 1000 mg/L to 2–3 mg/L. It also reduced effluent water hardness by approximately 40%. The new treatment plant has cut the mill's wastewater volumes by 90%. It also offers significant energy consumption savings as well as lower carbon dioxide emissions. The equipment consists of six container modules (three-stage cascade features sludge clarification, followed by separation based on Siemens Memcor's membrane operating system using Siemens Water Technologies' MemJet feed process, and further treatment by RO), which can be fitted within a 2-month period.

Several pulp and paper mills have tried RO for the treatment of inorganic-rich wastewater streams to reduce the dissolved inorganic solids to enable the recovered water to be used in the process (Duarte et al., 2008; Elliott and Voss, 2002; MacLatchy et al., 2001; Soalheiro, 2006; Whittaker, 2006), whereas dissolved organic solids are removed by biological methods. The concentrate fraction of the RO-treated stream can be further concentrated by evaporation to recover the chemicals or to dispose of as solid waste. RO for recovery of ion exchange regeneration wastes is used with success. The concentrate can be further processed to regenerate the chemicals.

Membrane Bioreactor

MBR combines a conventional activated sludge treatment with a membrane liquid–solid separation process. MBR also called immersed membranes, submerged membranes, or MF is an activated sludge process that utilizes a physical barrier, a membrane, to separate the wastewater solids from the liquid. Membrane MF technology for wastewater treatment is relatively new in the United States; however, it has been in use in Europe and Japan for many years. The most significant difference between other activated sludge processes and the MBR process is that the MBR process does not require a clarifier or settling tank. This eliminates the problems, risks, challenges, and costs associated with operation of most conventional activated sludge treatment plants to maintain a biomass that can consistently settle by gravity. Operation of the MBR plant is significantly simplified and controllable. In addition, the MBR process occupies a relatively small area because the mixed liquor suspended solids (MLSS) of the reactor tank are at a much higher concentration than ordinary activated sludge processes. MBR process is ideally suited for biological nutrient removal applications as coagulated metal salts are easily captured as phosphorous in the waste sludge. Nitrogen removal is inherently provided by the MBR process, which is very important for effluent reclamation and reuse purposes.

Wastewater entering the MBR process is collected in an equalization tank to dampen the surge flows from pump stations etc. and is screened to remove floatable or grit materials of 1/8 in. or larger. A regulated amount of flow is then transferred to an anoxic tank where a recycle stream of flow from the MBR reactor tank is mixed with the influent wastewater that serves three purposes: removes nitrates, recovers lost alkalinity, and improves filterability.

The MBR reactor is essentially a high-concentration MLSS-activated sludge process with an integral (in-tank) solid–liquid separation mechanism—membrane unit. Membrane units are available in two configurations: flat panels or hollow fibers. Flat panel membranes as used in the MBR process have many important advantages over the hollow fiber–type; thus, flat panel-type membranes are recommended. Flat panel membranes are arranged in parallel assemblies called "cassettes." The membranes have an average porosity of 0.4 μm and an effective porosity of 0.1 μm, which is small enough to block virtually all bacteria and viruses. The diffuser case supports the membranes and houses the aeration diffuser equipment. As air bubbles are emitted at the diffuser in the bottom and channeled between each of the membrane panels, the aeration action serves three purposes: to transfer oxygen to the wastewater organisms for biological assimilation, to sweep solids away from the surface of the membranes, and to create a pressure gradient between the top and bottom of the membrane cassette. The membranes are operated at very low transmembrane pressures (0.2 bar typically). The energy consumption is only 0.2 kWh/m^3 for the filtration compared to 4–8 kWh/m^3 for external loop MBRs.

The consumption of water and the production of wastewater can be minimized by purifying and recycling wastewater by MBR technology, which uses a bioreactor and MF or UF for wastewater treatment. The advantages of MBR systems include reduced space utilization, the production of heat, the retention of organisms that would be washed out of conventional systems, the quality of the water produced, and minimal or zero sludge production. There are however higher capital and maintenance costs, and a potential for membrane fouling. In submerged MBR systems, the membrane is immersed into the activated sludge reactor and subjected to a vacuum which draws permeate through. In cross-flow MBR, activated sludge from the MBR is pumped to a pressure-driven tubular UF membrane. Submerged systems use air bubbles to prevent fouling, while cross-flow systems use the generation or turbulence, which increases energy consumption but makes the system less susceptible to fouling. Membranes for submerged systems are cheaper, but cannot be used at temperatures above 55°C. Niederauer Muhle conducted a pilot trial of an MBR for 6 months. From the results, a WinGEMS simulation was carried out of a proposed redesign of the plant. The simulation suggests that considerable savings in water consumption and reductions in total suspended solids (TSS) can be achieved. VHP Security Paper Mill conducted a pilot test of an MBR to recycle the bleaching effluent. Following the pilot study, a full-scale plant was constructed, which has led to savings of €321,000/year (Van Dijk et al., 2003).

A case study of MBR has been reported using the production of graphic paper according to central European practice concerning production capacity, raw material, stock preparation, and specific effluent amount (Helble and Mobius, 2007). The investment and operation costs of the MBR process for this model have been determined, which can be applied for greenfield plants. While the design criteria cost of the MBR process may be higher than a standard system, the higher costs should be balanced against the benefits. The modification into an MBR system of adding an appropriate membrane stage could produce a more economical result.

An MBR has recently been tried in Kohler Pappen mill, Germany, to improve the quality of treated effluent and reduce freshwater consumption in the pulp and paper mills (Junk et al., 2007). The membrane consisted of a polymer-based fiber matrix with a nominal 0.04 μm pore size that removes 99.99% pathogenic microorganisms. Fouling problems due to the high calcium carbonate content of water circuits, particularly with recycled papers, and high lignin levels in pulp production have so far prevented the membrane process being adopted by the paper industry. Pilot trials have shown that membrane cleaning performance is directly proportional to the biomass concentration, resulting in significantly lower COD. Total MBR treatment costs including amortization at Kohler Pappen amounted to €0.50/m^3.

In one study, anaerobic membrane bioreactor was used to investigate the possibility of removing organic substances and contaminants present in white water from paper production with bleached kraft pulp in phase 1 and recycled brown pulp in phase 2 (Loures et al., 2008). The study also compared the performance of this treatment system to that of the conventional anaerobic bioreactor at different hydraulic retention times and different organic loading rates. Parameters studied included COD, BOD, TSS, turbidity, pH, total alkalinity, bicarbonate alkalinity, volatile organic acids, total hardness, calcium hardness, and electrical conductivity. In phase 1, a slight increase in pH and conductivity was observed, which indicates that anaerobic membrane bioreactor had advantage over the conventional anaerobic treatment in terms of treated white-water recovery. However, in phase 2, the white water was found to be unsuitable for the anaerobic treatment, and this was probably a result of the volatile organic acid generation, which makes it impossible to maintain a suitable pH for the microorganisms inside the bioreactor.

Occasionally, a membrane cleaning procedure using bleach solution should be performed to remove fouling and restore optimum transmembrane capacity. The cleaning process is fully automatic and takes only a few hours. Replacement of membranes should be anticipated at approximately 8-year intervals; however, longer service life is possible under some conditions. The purchase cost of membrane units were previously rather high; however, such costs have steadily declined due to higher production quantities and advancements in the manufacturing process. The transmembrane pressure gradient, created by the system, forces water from the MLSS through the membrane into a permeate stream, leaving the solids behind. The permeate (filtered) water is the effluent stream from the plant and is equal to or better than effluent from conventional activated sludge plants with tertiary treatment (sand or fabric filters).

Flow through the plant can be regulated by a flow control valve on the permeate lines and liquid levels in the MBR tanks. The system can be fully automated using programmable logic controllers (PLCs, computers). Another significant advantage of the MBR technology is that increases in treatment capacity can be added in small increments by simply installing additional membrane cassettes in existing tanks. Equipment such as pumps and aeration blowers can be replaced and upsized at specific intervals because they usually have a service life of 10–15 years.

The key benefits of MBR process are recovery of high-quality water, high efficiency and low maintenance of the system, easy to clean, yields 60–80% less sludge than conventional system, compact design, and possibility of direct and indirect water reuse.

Other Techniques

A combination of physicochemical and biological treatments is very common for treating the wastewaters. Biological treatment followed by different membrane processes such as MF/UF/NF/RO (any one or more than one, depending on the requirement) is also being used in various mills for recovery of water. These processes may also be preceded by dissolved air flotation/microflotation, etc. Ion exchange processes for the treatment of boiler water and removing wood-derived metals (Webb, 1997) and evaporation have also been practiced. However, a few new treatment concepts are also being tried/studied for treating the wastewater for recycling.

Combination of Biological and Chemical Processes

A combination of chemical and biological processes leads to greater and more thorough destruction of many organic contaminants in wastewaters. The biodegradability or recalcitrant character of the wastewater often suggests the particular processes and order of treatment to be used. Four types of wastewater have been identified in which a two-step combination of processes should show potential for significant improvement over single processes (Scott and Ollis, 1995). These wastewaters may contain recalcitrant compounds, largely biodegradable compounds requiring subsequent chemical polishing, inhibitory compounds, and intermediate dead-end products.

Pretreatment usually enhances the second process. Initial chemical oxidation can destroy compounds that would otherwise limit the effectiveness of the biological unit and may produce intermediates that are amenable to further degradation. A few examples of adverse effects due to pretreatment have also been identified. These effects may be due to the formation of toxic intermediates or even recalcitrant compounds. Moreover, the chemical removal of compounds, for which biological removal is more efficient, is an ineffective pretreatment of wastewater. Similarly, the biological systems, when utilized as a pretreatment, can favorably affect the subsequent chemical oxidation by removing biogenic compounds that would otherwise compete for the expensive chemical oxidant. Specific microbial degraders could be employed to selectively remove problematic compounds.

Aerobic Cyclic Softening Process

This process enables carbonates to be removed from biologically treated effluents in the paper industry, and this allows treated water to be reused. AZE units can be installed downstream of the activated sludge and postclarification stages. The AZE process removes 70–95% of calcium and 20–40% of chloride, and reduces conductivity, BOD, and volatile organic acid (VOA) contents by 25–40%, 15–30%, and 70–100%, respectively. The process also removes more than 99% of hydrogen sulfide from the exhaust air. Calcium, BOD, and VOA levels can be further reduced by combining the AZE process with Aerocycle's Metha Therm System ahead of the activated sludge stage (Althofer et al., 2007). AZE treatment improves product quality by reducing ash content and also reduces the calcium content in process water to less than 400 mg/L. The reuse of biowater provides cost savings of €1.29–2.34/m^3, increases biological treatment efficiency, and avoids excessive organic sludge formation. The AZE process offers the best available technology and certified emission reduction for paper mills. The new technology has been installed at Propapier's Burg, a German mill, and at a modern Chinese paper mill.

Ozone Treatment in Combination with Other Processes

Research has been carried out to study the effect of combining ozonation with membrane process on the removal of biologically recalcitrant organic compounds of alkaline bleach plant wastewater (Bijan and Mohseni, 2004). A ceramic membrane with nominal cutoff of 1000 Da was used to separate organics, and a bubble column reactor was used for ozonation studies. The research revealed that integration of UF with ozonation resulted in more recalcitrant organic matter removal than ozonation alone, by over 30%, while consuming less ozone. Selective reaction of ozone with color-causing compounds of the alkaline effluent resulted in significant color removal. UF facilitated the overall removal of color from wastewater by almost 30% during ozonation. Reaction of ozone with the organic compounds resulted in significantly decreased pH, indicating the generation of organic acids. In addition, UF advanced selective reaction of ozone with high–molecular-weight organics by providing more concentrated wastewater.

Ozonation and ozone/hydrogen peroxide techniques were reported to be fairly effective methods for removing color and AOX from pulp and paper mill wastewaters with reasonable operational cost, but the efficiency for COD removal was rather limited (Salokannel et al., 2007). While both techniques increased the biodegradability of the treated waters, reflected in the increased BOD values. It can be combined with biological treatment. Ozone treatment followed by a biological treatment will increase the effluent processing capacities of paper mills to reduce COD levels. Ozone is also effective in removing brown discolorations from effluent due to the presence of lignin and unsaturated chemicals. A concept developed by the Paper Technology Institute adds ozone and biofilter stages to one- or two-stage biological effluent treatment plants (Bierbaum and Oller, 2007). Residual COD levels are controlled by adjusting the rate of ozone dosage. Approximately 100 g ozone/m^3 followed by biofiltration was found to reduce COD levels by approximately 50%. A second, less effective concept places the ozone unit between the first and second biological treatment stages, eliminating the need for a biofilter. A third concept for plants with a single biological treatment stage combines the effectiveness of the first with the cost advantages of the second concept. The effluent stream is passed from the biological stage to the ozone unit and then returned for further biological treatment. Controlled ozone addition allows dosage rates to be matched to changing effluent concentrations, allowing annual energy and oxygen costs to be reduced by 20%.

A study was carried out to investigate the impact of ozone oxidation under a different initial pH on transforming high-molecular-weight organics to improve the biodegradability of alkaline bleach plant effluent (Medeiros et al., 2008). The experiments were carried out in a semibatch reactor equipped with a fine bubble diffuser, and the results indicated that ozone could potentially be used as a pretreatment for conventional biological treatment. Approximately 80% of the organics with a molecular weight higher than 5 kDa were converted after applying approximately 20 mmol of ozone per liter of wastewater. The study showed that ozonation under initially neutral conditions was more effective than under alkaline conditions in improving the effluent quality as well as the generation of biodegradable compounds. Another study on combined ozone biological treatment of eucalyptus bleached kraft pulp effluent has also been reported (De Assis et al., 2008). The combination of ozonation and biological treatment was found to give significant increases in the removal of COD, BOD, TOC, lignin, and AOX compared to the effluent without ozone treatment. The study emphasized the need to develop wastewater treatment technologies that are able to degrade high-molecular-mass organic compounds. Such compounds continue to represent a potential risk to aquatic environments.

6.12 BIOTECHNOLOGIES FOR CLEANER PAPER PRODUCTION

In the recent years, the awareness has increased to employ biotechnological processes in pulp and paper manufacturing. These processes can tackle environmental pollution of the paper production process in several ways (Bajpai et al., 1999). Wastewater treatment systems for removal of oxygen-demanding substances and suspended solids, preparing starch using enzymes for paper sizing, have long been part of the industry. Improvement in fiber supply by selection of superior trees is being done by forest product companies. Even the control of slime and deposits on paper machine can be considered as aspects of biotechnology. However, within the past several years, biotechnologists have sought specific applications for microorganisms/enzymes in the pulp and paper industry. The need for sustainable technologies has also brought biotechnology into the realm of pulp and papermaking more than a decade ago. The application of xylanase enzyme in pulp bleaching was essentially a first step in demonstrating that enzymes are efficient technological means and can be introduced into existing plants without big investments. Later on, other enzymes such as lipases or glucanases were tested for large-scale applications. Enzymatic processes as well as fungal processes are being developed to improve the manufacturing process, quality of the products, and quality of wastewater and to purify bleach plant effluents.

While many biotechnological approaches are still in the research and development stage, several new applications have found their way into the paper mill in an unprecedented short period (Bajpai et al., 1999). In addition, some of these new developments in biotechnology, if successful, could have a profound impact on the future technology of the pulp and paper manufacturing process. There are several areas described later where biotechnology has a role to play in cleaner production and energy efficiency in the pulp and paper industry.

Tree Improvement

The first emerging technology is related to trees, the most important raw material for paper production. An attempt is made to change their chemical structure by genetic engineering. More precisely, research is aimed at structural modifications of lignin, the environmentally pernicious component of wood. The role of the genetic engineering for trees could develop into providing the pulp industry with tailor-made fibers. Genetically modified trees are an example of an integrated technology: by substituting the current raw material, the overall process becomes less polluting. The introduction of tailor-made fibers as raw material offers the possibility of simplifying the current process, possibly by eliminating certain parts of it.

The expensive, energy-intensive process of turning wood into paper costs the pulp and paper industries more than US$6 billion a year. Much of that expense involves separating wood's cellulose from lignin, the glue that binds a tree's fibers, by using an alkali solution and high temperatures and pressures. Although the lignin so removed is reused as fuel, wood with less lignin and more cellulose would save the industry millions of dollars a year in processing and chemical costs. Research in United States shows promise of achieving this goal. By genetically modifying aspen trees, researchers have reduced the trees' lignin content by 45–50% and accomplished the first successful dual-gene alteration in forestry science. Their results are described in the *Proceedings of the National Academy of Sciences* (April, 2003). Research shows not only a decrease in lignin but also an increase in cellulose in the transgenic aspens and faster growth of the trees. This is indeed a very good news for the wood, paper, and pulp industries, which do multibillion-dollar business worldwide. Fast-growing, low-lignin trees offer both economic and environmental advantages, because separating lignin from cellulose—using harsh alkaline chemicals and high heat—is costly and environmentally unfriendly. Harvesting such trees, using them as "crops" with desirable traits, would also reduce pressure on existing forests. Four-year field trials of such trees in France and the United Kingdom show that lignin-modified transgenic trees do not have detrimental or unusual ecological impacts in the areas tested. In the previous work, US researchers had successfully reduced lignin in aspens by inhibiting the influence of a gene called 4CL. The current research modifies the expression of both 4CL and a second gene, CAld5H, in the trees. This dual-gene engineering alters the lignin structure, and produces the favorable characteristics of lower and more degradable lignin, higher cellulose and accelerated maturation of the aspens' xylem cells. The research is described in the paper by Zhou et al. (2003). These results are "very significant" and will have dramatic impacts on the future genetic improvement of forest trees for pulp and paper production. The improved tree growth and high cellulose content will increase pulp-yield production, while the reduced lignin content will reduce the pulping cost and energy consumption in the pulping process. The ability to produce high-yield plantations with these desirable characteristics will enable to produce wood more efficiently on less land, allowing natural forests to be managed less intensively—for habitat conservation, aesthetics, and recreational uses.

Wood Pretreatment to Remove Toxic Extractives

The lipophilic extractives in the softwoods and in certain hardwood species such as eucalyptus come out in the effluents during pulping and bleaching process. The major extractive compounds are triglycerides, resin acids, and steryl esters. These are environmentally significant because of their relative persistence and toxicity to fish and are responsible for a large part of acute toxicity of pulp mill effluents (Sunito et al., 1988). Besides being the major contributors to toxicity to aquatic life, these lipophilic extractives (pitch) cause a number of serious problems in the production process. Due to the toxicity of these compounds, it is necessary to have a pretreatment of the raw material (wood chips) or the pulp that reduces the liberation of these compounds. The following two biotechnological approaches can be used to reduce the liberation of toxic extractives.

Use of Fungi

A variety of wood-inhabiting fungi including sapstain fungi, basidiomycetes, and molds are capable of degrading wood extractives (Farrell et al., 1997). It removes extractives by metabolizing them. Cartapip^{TM} marketed by M/s Clariant Ltd. as a dry powder is a colorless strain of *Ophiostoma piliferum*, an ascomycete that often dominates in naturally seasoned piles. It is diluted with water to a 1–3% solids solution and sprayed onto wood chips. It rapidly proliferates and removes pitch/resin from wood chips within 4–10 days. Chip piles show good coverage of fungal growth, with pitch reduction of 50% or more. In general, fungal treatment results in an overall decrease in total fatty acids and total resin acids. Triglycerides are almost completely hydrolyzed. In a thermomechanical pulp mill, using southern yellow pine, a trial was performed comparing a 2-week period using the Cartapip product on their wood chips to a 2-week period without using Cartapip (Farrell et al., 1997). Reductions in extractive content of pulp caused expected reductions in use of alum, a pitch control chemical. Use of Cartapip resulted in 36.9% reduction in bleach usage along with an increase in paper brightness of 0.9% (Table 6.3). In addition, strength properties were increased due to lower extractive content of the paper. A 2-month Cartapip 97 trial at a US thermomechanical pulp mill using southern yellow pine showed significant reduction in the extractives of wood chips and an increase in burst index of the pulp. The free fatty acid content of the Cartapip-treated chips is lower than that of the naturally aged chips, indicating further metabolism and removal of these components by the fungus. To date, the wood species that have been effectively treated for pitch

Table 6.3 The use of a Depitching Organism in a TMP Mill

DCM extractive content of secondary refiner pulp	−37.5%
Alum usage	−31.7%
Bleach usage	−36.9%
Brightness	+0.9%
Tensile index	+5.4%
Tear index	+3.4%
Burst index	+3.3%

Based on data from Farrell et al. (1997).

removal include many different pine species, spruce, birch, eucalyptus, aspen, and mixed tropical hardwoods. The dosage of the fungus product and storage time in the chip pile may vary depending on temperature and wood species. Table 6.4 shows the extractive content of sterile southern yellow pine treated with various basidiomycetes.

Use of Enzymes

Lipase enzymes can also be used for removal of pitch. These enzymes catalyze the hydrolysis of triglycerides that have been identified as one of the key components for pitch troubles. Lipases from *Aspergillus oryzae*, *Candida cylindraceae*, and *Pseudomonas* sp. have been used (Fischer and Messner, 1992; Fischer et al., 1993; Fujita et al., 1992). A few commercial preparations of lipases for pitch removal, for example, Resinase A 2X, are available in the market (Fujita et al., 1992), which

Table 6.4 Extractive Content of Sterile Southern Yellow Pine Treated with Various Basidiomycetes

Fungal species	Control extractives (%)	Treatment extractives (%)	Reduction (%)
Phanerochaete chrysosporium	2.19	1.30	41
Phanerochaete subacida	3.34	2.01	40
Phanerochaete gigantea	3.34	2.03	39
Phlebia tremellosa	1.98	1.21	39
Hyphodontia setulosa	1.98	1.20	39
Coriolus versicolor	1.98	1.28	36
Inonotus rheades	3.34	2.18	34
Trichaptum abietinium	4.70	3.13	33
Ceriporiopsis subvermispora	3.34	2.18	29
Trichaptum biforme	4.70	3.13	24
Schizophylum commune	2.50	2.03	17
Sistotrerma brinkmanii	2.44	2.17	11
Ganoderma collosum	2.29	1.75	23

Based on data from Farrell et al. (1997).

Table 6.5 The Effect of Lipase Treatment on Pitch Deposition

Resinous solid[a] Polar compounds/nonpolar compounds	Pitch-water suspension		Pitch-pulp suspension[b]	
	Control (mg)	Lipase treatment (mg)	Control (mg)	Lipase treatment (mg)
9/1	76	49	30	Trace
7/3	137	53	46	Trace
5/5	204	79	50	Trace

Based on data from Irie and Hata (1990).

[a] Contained 0.6 g of both compounds totally.

[b] Pulp consistency 1%.

have been tried on mechanical, kraft, and sulfite pulps to reduce the pitch content of the pulps to 70–90%. Table 6.5 shows the effect of lipase treatment on pitch deposition and Table 6.6 shows the effect of lipase concentration on hydrolytic rate of triglycerides.

Both the fungal and enzymatic methods are effective in reducing the generation of toxic extractives in effluent (Bajpai and Bajpai, 2001; Bajpai et al., 1999). Resin acids, free fatty acids, triglycerides, etc., which contribute significantly to pulp mill effluent toxicity, are reduced substantially by these methods. Besides reducing toxic extractives and offering ecofriendly and nontoxic technology, these methods offer several other advantages such as improved pulp and paper quality, reduction in bleach chemical consumption, reduction of effluent load, space and cost savings in a mill wood yard by using unseasoned logs. With chemical pulps (sulfite), the application of lipase improves the properties of resins by lowering their adhesiveness.

The principal problem associated with the fungal pitch control method is the relatively long time required for chip pretreatment after fungal inoculation (Bajpai et al., 1999). There is a need to identify/develop fast-growing fungal cultures using classical or genetic engineering techniques, which could do the job in lesser time. With lipase, improvement of agitation system is required to improve the effectiveness of enzyme. This could have a big effect on the saving of the enzyme. A half amount

Table 6.6 The Effect of Lipase Concentration on Hydrolytic Rate of Triglycerides

Lipase concentration (ppm/ 4% pulp slurry)	Hydrolytic rate of triglycerides (%)
5	74.2
3	50.0
1	12.9

Based on data from Irie and Hata (1990).

of the lipase will be enough to get the same effect with effective agitation. To reduce the cost of the enzyme, there is a need to improve the productivity of microorganisms.

Biopulping

The use of white rot fungi for the treatment of wood chips prior to mechanical or chemical pulping is called "biopulping". In "biomechanical" pulping, the aim of using fungi is to replace chemicals in pretreating wood for mechanical pulping, reduce energy demand, and increase paper strength. For chemical pulping, biopulping is intended to reduce the amount of cooking chemicals, to increase the cooking capacity, or to enable extended cooking, resulting in lower consumption of bleaching chemicals. Increased delignification efficiency results in an indirect energy saving for pulping, and reduces pollution (Kirk, 1993; Kirk et al., 1994).

Biomechanical Pulping

Considerable efforts at Swedish Pulp and Paper Research Institute (STFI) were directed toward developing cellulase-less mutants of selected white rot fungi to improve the selectivity of lignin degradation and thus the specificity of biopulping (Johnsrud and Eriksson, 1985). In one study, using spruce and pine wood, up to 23% energy savings and an increase in tensile index were noticed. On a large scale, success was achieved on bagasse (Johnsrud et al., 1987), while the results using wood chips were less encouraging. An energy requirement of 4800 kWh/t for producing chemimechanical pulp (CMP) of 70°SR (Schopper Riegel) according to the Cuba-9 process (6% NaOH treatment at 90°C for 10–20 minutes) was decreased to 1700 kWh/t by pretreating the bagasse with fungi, as shown in Table 6.7. The strength properties of biochemimechanical pulp (BCMP) were better than those of CMP, but there was a small drop in the yield of BCMP due to fungal degradation of bagasse. STFI's work has been summarized in a number of publications on biomechanical pulping and related aspects (Ander and Eriksson, 1975; Eriksson, 1985; Eriksson and Vallander, 1980, 1982; Eriksson et al., 1976, 1980; Johnsrud and Eriksson, 1985; Johnsrud et al., 1987; Kirk, 1993; Setliff et al., 1990). Figure 6.9 shows that biopulping process can be easily fitted into an existing mill's wood handling system.

Table 6.7 Energy Requirement for Chemimechanical Pulp and Biochemimechanical Pulp from Bagasse

	Energy input (kWh/tonne)	
Refining equipment	CMP	BCMP
Defibrator and PFI mill	4800	1700
Disk refiner	3100	2100

Based on data from Johnsrud et al. (1987).

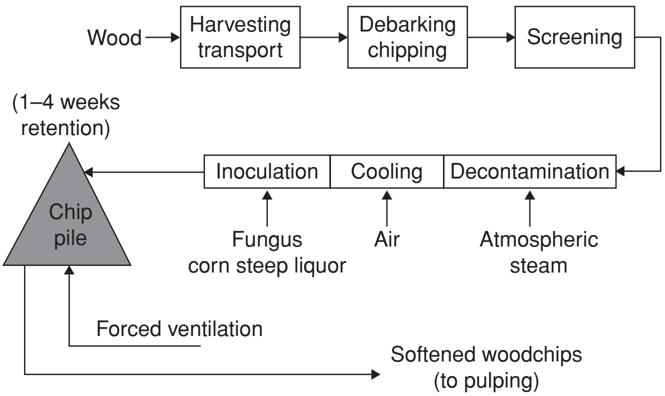

Figure 6.9 Biopulping process can be fitted into an existing mill's wood handling system.

Effluents from mechanical pulping of fungus-treated wood chips were reported to be substantially less toxic (by Microtox method) than effluents from pulping raw chips (Table 6.8) (Sykes, 1994). The Environmental Protection Agency (EPA) toxicity reduced from 33 to 4 (100/EC_{50}). Pollutant loads and toxicity of the effluents from kraft pulping and sulfite pulping of fungal-treated chips are also less than those from untreated chips.

It is well established that waste loads increase as pulp yield decreases, temperature increases, or pulping chemicals are added. Consequently, the waste load produced by biopulping should be considerably lower and more benign than effluents currently produced by commercial mechanical or chemithermomechanical pulp mills. These findings suggest that biopulping is environmentally compatible. Moreover, biopulping saves a substantial amount of electrical energy.

Table 6.8 BOD, COD, and Toxicity of Nonsterile Aspen Chips after Treatment with *C. subvermispora*

Pulp[a]	BOD (g/kg pulp)	COD (g/kg pulp)	EPA toxicity[b] (100/EC_{50})
Raw chips	18	40	33
Control			
No nutrients	10	30	5
Nutrients added	12	33	9
Fungus treated			
No nutrients	10	33	6
Nutrients enriched	11	35	4

Based on data from Sykes (1994).

[a] All pulps incubated for 4 weeks at 27°C, except raw chips.

[b] EC_{50} is a measure of toxicity.

A biopulping process would require inoculum regularly for commercial-scale applications, which would involve additional work and expense. Large-scale production of basidiomycetes is usually difficult. The fungal treatment is lengthy; a minimum 2-week incubation is required to get the desired benefits. At first glance, the long reaction time needed for the fungal process seems to be a great disadvantage. However, considering that wood chips are often stored at the mill for at least 2 weeks, time and space should be available in the pulp mill to introduce this process. Nevertheless, it is desirable to apply classical or molecular genetic methods to improve the effectiveness of the biopulping fungi, leading to shorter reaction treatment times.

Although a chip pile-based biopulping system has been designed and evaluated on a pilot scale, the process requires demonstrated long-term operation at mill scale.

Biochemical Pulping

Fungal pretreatment of wood before chemical pulping has received relatively little attention. However, the fungi that are effective in biomechanical pulping have been tested as pretreatments for both kraft and sulfite pulping in a few studies (Bajpai et al., 2001, 2004a; Messner et al., 1997).

Kraft

Kraft pulps prepared from chips of aspen or red oak pretreated with *Phanerochaete chrysosporium* for 10–30 days cooked faster and gave higher yields at a given kappa number (residual lignin content) than pulps from untreated chips (Oriaran et al., 1990, 1991). The improved cooking properties of the fungus-treated chips were attributed to enhanced penetration of cooking liquor and a lower lignin content. The fungus-pretreated pulps were more responsive to beating and gave higher tensile strength than the control pulps (Oriaran et al., 1990). The environmental consequences of the fungal treatments were not addressed in these studies, but the substantial (up to 17%) wood weight loss during the fungal pretreatment would negate the reported yield improvement, and the darkening of the wood by the fungus would probably require application of more bleaching chemicals.

Pretreatment of mixed hardwood chips with the Cartapip 97 fungus, *O. piliferum*, for 21 days improved kraft pulping efficiency so that kappa number could be decreased by 29% or the active alkali concentration in the pulping liquor could be decreased by 20% (Wall et al., 1996). Pulp yield was unaffected and viscosity, an indicator of pulp strength, was increased. The improvements were attributed to enhanced liquor penetration resulting from removal of ray parenchyma cells, resin deposits, and pit membranes. The Cartapip pretreatment could be used to reduce the environmental impact of kraft pulp production by decreasing bleach chemical usage or by decreasing cooking chemical usage (Wall et al., 1996).

Screening of 283 basidiomycetes for ability to improve the efficiency of kraft pulping of pine chips revealed *Coriolus versicolor*, *Pycnoporus sanguineus*, and *Stereum hirsutum* as the most promising species (Wolfaardt et al., 1996). Pretreatment of the pine chips with *S. hirsutum* for 9 weeks reduced the cooking time required to reach a kappa number of 28, but increased alkali consumption and lowered pulp yield and viscosity. The fungal pretreatment did not seem to give economic or environmental benefits.

Bajpai et al. (2001) observed that extractive content reduced by 17–39% and the AA requirement reduced by 18% when eucalyptus chips treated with the fungus *C. subvermispora* for 2 weeks were subjected to kraft pulping. Brightness and strength properties of biopulps were better than the control, and the pulps were easier to bleach and easier to refine—requiring less energy (by 18–30%). In another study, Bajpai et al. (2004a) observed reduction in extractive content by 44% and reduction in kappa number by 22–27% (at the same alkali charge) when wheat straw treated with the fungus *C. subvermispora* for 1 week was subjected to soda pulping. The alkali charge was found to be reduced by 30 kg/t of the raw material at the comparable kappa number. Biopulps required lesser bleaching chemicals and showed higher brightness and whiteness, and there was no adverse effect on strength properties.

Treatment of birch, maple, oak, sycamore, or pine chips with an enzyme mixture containing cellulase and hemicellulase for 24 hours disrupted the pit membranes, blocking pores between cells, and increased the longitudinal and transverse diffusion rates of sodium hydroxide in the chips (Jacobs et al., 1998). Kraft pulping experiments with enzyme-treated sycamore chips confirmed the expected improvement in delignification; addition of pectinase to the enzyme mixture further lowered kappa numbers without reducing yield (Jacobs-Young et al., 1998). The pulps produced from enzyme-treated chips were easier to bleach with chlorine dioxide than control pulps, and had comparable strength properties. Reduced bleaching chemical use should result in lower effluent BOD, COD, and chloroorganic loadings.

Sulfite

Pretreatment of chips with white rot fungi increases the rate of their delignification in sulfite pulping (Messner et al., 1997). In magnesium-based sulfite pulping, treatment of birch and spruce chips with *Phlebia tremellosa*, *Phanerochaete brevispora*, *Dichomitus squalens*, and especially *C. subvermispora* for 2–4 weeks significantly reduced the pulp kappa number. However the fungal treatments also reduced pulp strength and brightness. Pretreatment of loblolly pine chips with *C. subvermispora* for 2 weeks increased the rates of lignin and yield loss to the same extent in sodium bisulfite pulping, but preferentially enhanced delignification in calcium-acid sulfite pulping, and decreased shives production. The fungal treatment darkened the chips, so that equal amounts of bleaching chemicals were needed to brighten the treated and control pulps. BOD and COD levels were the same in effluents from the fungus treated and control pulps, but the Microtox toxicity in the effluent from the fungus-treated chips was less than half that of the control. The reduced toxicity was attributed to biodegradation of resin and fatty acids by the fungus (Messner et al., 1997). In biochemical pulping, delignification during the fungal treatment partially replaces delignification by the pulping chemicals, without obvious economic or environmental benefit. Pretreatments with non-ligninolytic fungi or enzymes, which can remove toxic extractives and/or impediments to pulping liquor penetration, offer more promise. Fungal delignification is more appropriate to pulp bleaching, where the amounts of lignin are smaller and chemical delignification is more problematic.

Biobleaching of Pulp

In kraft pulping, bleaching is one of the most expensive operations in the pulp mill and therefore a prime target for cost reduction. North American mills have moved toward ECF bleaching, which has increased operating costs even further. In Canada, about 10% of bleached kraft pulp is now manufactured with xylanase treatment to reduce the amount and cost of chlorine dioxide used.

The use of xylanase enzymes to enhance the bleaching of the pulp was first reported in 1986. By 1994, many mills in Canada and Scandinavian countries started using xylanase enzyme. Several reviews on different aspects of xylanase bleaching have been published (e.g., Bajpai, 2004; Bajpai and Bajpai, 1992, 1997). Xylanase bleaching has led to reduction in effluent AOX and dioxin concentrations due to reduced chlorine requirement to achieve a given brightness. It decreases the AOX in proportion to the decrease in chlorine compound usage (Tables 6.9–6.11). The

Table 6.9 The Effect of Xylanase Treatment on Effluent Quality

	Control	Treated
Pretreatment	No	Yes
pH	–	4.8
Xylanase charge (unit/kg pulp)	–	5000
Time (hours)	–	3
Temperature (°C)	–	37
Kappa number	32	31.3
Viscosity (mPa.s)	25.1	30.7
($C_{70}D_{30}$) Stage		
Cl_2 (kg/t pulp)	19.2	15.0
ClO_2 (kg/t pulp)	17.0	13.3
Active Cl_2 (kg/t pulp)	64.0	49.9
(Eo) Stage		
NaOH (kg/t pulp)	35.2	27.0
O_2 (kg/t pulp)	5.0	5.0
Eo kappa number	4.8	4.4
Effluent properties		
Color (kg/t pulp)	155	118
AOX (kg/t pulp)	2.02	1.68
BOD (kg/mt pulp)	15	11
COD (kg/t pulp)	74	62

Based on data from Viikari et al. (1986).

Unbleached kappa number 32.0, viscosity 30.7 mPa.s.

Table 6.10 The Effect of Xylanase Treatment on Effluent Properties of Hardwood Pulp

	Control		Xylanase treated		
Parameter	W(DC)E	W(DC)E	X(DC)E	X(C+D)E	X(CD)E
Kappa factor	0.15	0.20	0.10	0.10	0.10
(DC) E_1DE_2D brightness (% ISO)	89.3	90.0	89.5	89.1	89.3
BOD (mg/L)	261	259	212	283	280
COD (mg/L)	1100	1160	956	906	988
BOD/COD	0.24	0.22	0.22	0.31	0.28
TOC (mg/L)	429	464	385	379	402
Toxicity (% solution)	8.9	8.8	4.9	6.6	4.8
AOX (mg/L)	17.6	25.3	13.3	7.5	7.5

Based on data from Dunlop and Gronberg (1994).
Substitution of chlorine dioxide in the chlorination stage 40%.
Kappa number of control pulp 12.2; kappa number of xylanase-treated pulp 11.6.

BOD-to-COD ratio of the bleach effluent has been found to increase on the use of xylanase enzymes, indicating that the effluent became more amenable to biological degradation in a secondary treatment plant. Because the bleach plant effluent color is dependent on the chlorine usage, a decrease in chlorine compounds also decreases the effluent color. Table 6.12 shows the various benefits obtained by the use of xylanase enzyme.

The most conventional method is to add xylanase to the brown stock 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 the 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 brown stock pulp. The

Table 6.11 The Effect of Xylanase Treatment on Effluent Characteristics

Bleaching sequence	COD (kg/TP)	AOX (kg/TP)
No enzyme treatment, Cl_2 bleaching	58.1	2.6
No enzyme treatment, bleaching with mixture of 90% ClO_2 and 10% Cl_2	55.0	1.0
Enzyme treatment, bleaching with mixture of 90% ClO_2 and 10% Cl_2	40.0	0.6
Enzyme treatment, washing and bleaching with mixture of 90% ClO_2 and 10% Cl_2	40.0	0.6

Based on data from Enso-Gutzeit (1990).

Table 6.12 Advantages of Prebleaching with Xylanase Enzymes

Conventional bleaching	
	Reduction of elemental chlorine and AOX
	Higher pulp brightness
ECF bleaching	
	Reduction of chlorine dioxide and AOX
	Higher pulp brightness
	Increase in productivity when chlorine dioxide is limited
TCF bleaching	
	Higher pulp brightness
	Reduction in chemical consumption
	Unchanged strength properties

latest generation of alkali-tolerant enzymes requires 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 to brown stock pulp. Instances of corrosion problems were seen when acid was incorrectly applied. New xylanases have higher pH optima and function optimally without pH adjustment.

The acid of preference by far has been sulfuric acid. However, with the development of alkaline xylanases, noncorrosive carbon dioxide is an excellent choice and also improves washer performance. The addition of acid prior to the D_o stage in ECF bleaching has also been shown to improve the performance of D_o stage. This is because the higher acidity in the stage prevents decomposition of chlorine dioxide to chlorate and because the chemistry of delignification with chlorine dioxide favors an acidic environment. Typical sites of acidification are also indicated in Fig. 6.10. Acid added to the low-consistency pulp prior to the washer vat provides the benefits of reducing pitch deposits; however, acid charges here tend to be much higher due to the large volume that must be treated. Acid can also be added on the washer shower, the bar shower, or in the repulper discharge section. Experience has shown that prevention of corrosion must be a high priority.

Detailed laboratory work is generally 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 (1000 tonnes pulp (TP)/day) without intermediate pilot stages. It has also been observed that even higher brightness values can be reached on the full scale than those attainable in the laboratory, which is due to the more efficient mixing systems and higher pulp consistencies. No expensive capital investments have generally 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, which is a considerable advantage of this technology.

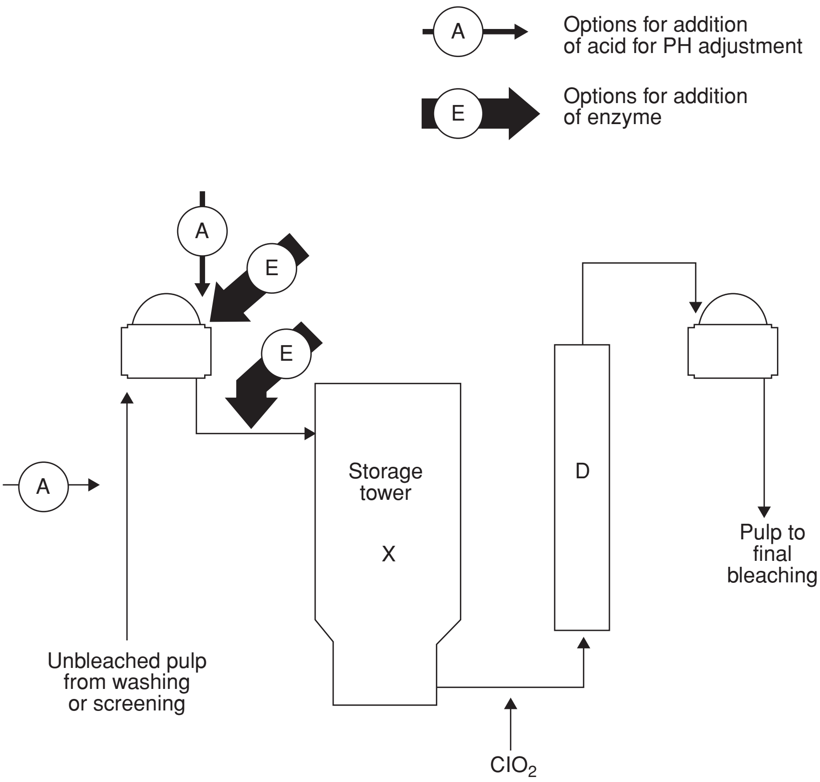

Figure 6.10 Typical xylanase and acidification sites.

Lignin oxidizing enzymes are also being developed (Paice et al., 1995), which will have much impact on reducing the pollution problems related to pulp bleaching. The system 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 softwood and hardwood pulps as well as for annual plant fibers. A repeated enzymatic treatment is possible and results in a 50–70% reduction in the kappa number per treatment step (Tables 6.13 and 6.14). Laccase-mediator system (LMS) is compatible with all other bleaching sequences. The performance of the LMS system has been proved in pilot plant trials. The summary of the results is presented in Table 6.15. Figure 6.11 shows possible mechanism of laccase and mediator action on lignin.

In addition, fungal bleaching is also being studied (Fujita et al., 1991, 1993), which will eliminate the use of any chemical in bleaching and thus the pollution problem (Table 6.16). However, because of very slow process, requiring a few days in place of a few hours for bleaching, this process is not commercially viable at present (Bajpai, 2004; Bajpai et al., 1999).

Table 6.13 Bleaching of Conventional Softwood Kraft Pulp with the Laccase-Mediator System

Treatment	Kappa number	Viscosity (cP)	Brightness (% ISO)
Untreated pulp	28.7	27.5	24.7
Enzyme-treated pulp	11.5	21.6	31.6
Enzyme-treated pulp after TCF sequence	–	15.0	24.0

Based on data from Call and Mücke (1994).

Table 6.14 Bleaching of an Extended Cooked Softwood Kraft Pulp with the Laccase Mediator System

Treatment	Kappa number	Viscosity (mL/g)	Brightness (% ISO)
Untreated pulp	20	970	28.8
Enzyme-treated pulp	10	950	32.8
TCF sequence	–	850	80.0
Enzyme-treated pulp after TCF sequence	–	850	88.0

Based on data from Call and Mücke (1994).

Table 6.15 Summary of Results from the Pilot Plant Trial with the Laccase-Meditor System

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 (minutes)	120	60	30	210
Pressure (bar)	2	–	–	–
Dosage	Enzyme: 2 kg/t Mediator: variable	NaOH	0.2% chelating agent	3% peroxide

Based on data from Call and Mücke (1995).

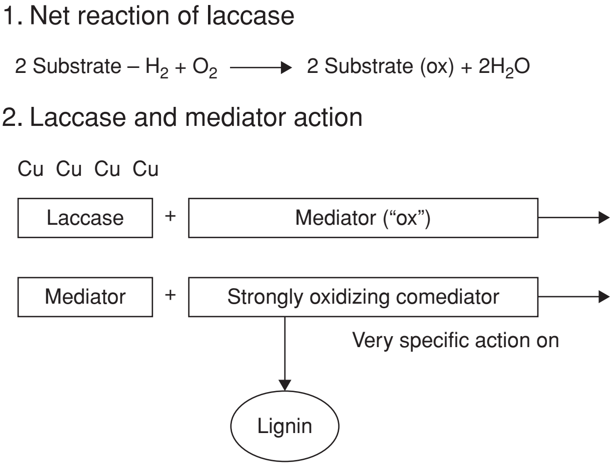

Figure 6.11 Possible mechanism of laccase and mediator action on lignin.

Enzymatic De-inking

Conventional de-inking is a chemical-intensive process and requires extensive wastewater treatment, which is expensive and becoming highly regulated. Enzyme-based de-inking offers a potential means for the reduction of chemical use in the de-inking process and thus reducing the load on the wastewater treatment systems (Bajpai and Bajpai, 1998). Enzymatic approaches of de-inking involve attacking either the ink or the fiber surfaces. Lipases and esterases can degrade vegetable oil-based inks. Pectinases, hemicellulases, cellulases, and ligninolytic enzymes alter the fiber surface or bonds in the vicinity of the ink particles, thereby freeing ink for removal by washing or floatation. The exposure of recovered newsprint to high temperature in closed containers accelerates the oxidation and polymerization of ink particles (summer effect) (Haynes, 2000). Sulfite de-inking has been shown to give relatively better de-inking performance as compared to alkaline de-inking (Chezick

Table 6.16 COD and Total Color Loadings for Conventional Five-Stage Bleaching and Biobleaching Processes

	COD (kg/t of pulp)				
Bleaching sequence	C	E_1	$D_1E_2D_2$	Total	Total color (kg/t of pulp)
CEDED (conventional process)	10.08	17.64	3.07	31.42	38.25
FCED (biobleaching process)	5.03	8.86	1.78	15.94	8.23

Based on data from Fujita et al. (1991).
CEDED (C—chlorination, E—extraction, D—chlorine dioxide, E—extraction, D—chlorine dioxide).
FCED (F—fungal treatment, C—chlorination, E—extraction, D—chlorine dioxide).

et al., 2004) but no improvement in the brightness. However, combining enzymes with sulfite chemistry significantly enhances sulfite de-inking to achieve de-inking of aged newsprint at neutral pH.

Enzymatic de-inking produces a white water with a lower COD than conventional alkaline de-inking process, as reported by many researchers, thus reducing the load on the wastewater treatment systems (Yang and Eriksson, 1995). The enzymatically de-inked pulp displays improved drainage and possesses superior physical properties, higher brightness, and lower residual ink compared to chemically de-inked recycled pulps. Improved drainage results in faster machine speed, which yields significant savings in energy and thus in overall cost (Bajpai, 1999). In addition, more and more recycled fiber will be used in papermaking, reducing the requirement of virgin pulp production and thus resulting in great saving of energy required for pulping, bleaching, refining, etc., which will eventually lead to lower environmental pollution problems and cutting of less number of trees for papermaking.

De-inking with enzymes at acidic to neutral conditions should reduce the overall chemical requirements and minimize yellowing of reclaimed papers normally observed by conventional alkaline de-inking. The use of enzymes could lead to a reduction of the pulping time, thus saving energy and potentially increasing production. Besides the greater decrease in the ink area, the mild alkaline conditions used with enzymes impact positively on stickies problems at mill scale. An additional positive effect can also be expected as a consequence of nonionic surfactant reduction due to its slow biodegradation in the water treatment plant.

The de-inked pulp obtained after de-inking of sorted office waste with hydrolytic enzymes shows higher brightness (1.0–1.5 points) and whiteness (2.7–3.0 points) and lower residual ink as compared to chemically de-inked pulp (Bajpai et al., 2004b). It is possible to obtain pulp of less than 10 ppm dirt count with combination of cellulase and α-amylase enzymes, resulting in reduced chemical consumption (Tables 6.17 and 6.18). COD and color loads were lower in the case of effluents generated during enzymatic de-inking (Table 6.19).

Table 6.17 De-inking of Sorted Office Waste with Different Hydrolytic Enzymes Alone and in Combination

Enzymes	Brightness (% ISO)	CIE whiteness	Dirt count (ppm)	Yield (%)	Ash (%)
Hemicellulase	81.5	71.4	15	70.6	6.0
α-Amylase	80.2	69.1	19	70.8	6.1
Cellulase	81.6	71.5	12	71.0	6.1
Cellulase + α-amylase	81.7	71.5	8	70.9	6.2
Cellulase + hemicellulase	81.3	71.7	13	71.2	6.2
Cellulase + hemicellulase + α-amylase	81.5	71.5	7	70.8	6.2
Chemicals (control)	80.1	69.2	16	71.1	6.3

Based on Bajpai et al. (2004b).

CIE, Commission Internationale de l'Eclairage.

Table 6.18 Chemical Consumption in De-inking of Sorted Office Waste

Chemicals (kg/t)	Chemical de-inking	Enzymatic de-inking
Enzyme	—	0.4
Sodium hydroxide	26.0	16.0 (−10)
Sodium silicate	10.0	Nil (−10)
Hydrogen peroxide	25.0	20.0 (−5)
DTPA	2.0	2.0
Surfactant	2.0	2.0
Coagulating/flocculating agent	3.0	3.0

Based on Bajpai et al. (2004b).

Treatment of 100% multiprint furnish with cellulose and amylase enzymes at pH 7.0–7.5 improved the pulp brightness by 2 ISO points in the laboratory investigation as a part of EUREKA Enzyrecypaper Project (Gill et al., 2007). The ink particles released by treating with amylase enzymes appeared to be more hydrophobic than ink particles released by treating with cellulose. During the mill trial using highly specific amylases, the brightness was significantly improved up to 8 points. The ash content also reduced to a great extent after flotation and washing, resulting in a change of the final pulp characteristics.

Mixed office waste often contains a large variety of dyed papers. The color must be removed to make the pulp suitable for reuse. For this reason, it is frequently underutilized source of waste papers. Usually, several chemical bleaching agents such as ozone, oxygen, hydrogen peroxide, or sodium hydrosulfite have been used to bleach secondary fibers. Now, there is an alternative color stripping process for secondary fibers—the laccase-mediator system. In a study by Arjona et al. (2007), a bleaching sequence included an enzyme stage called the laccase-mediator system stage (L), a hydrogen peroxide stage (P), and a sodium hydrosulfite stage (Y) on a mixture of different colored writing and printing papers (green, yellow, red, and blue). After the application of L–P–Y sequence, a pulp with optical properties near to eucalyptus totally bleached pulp was obtained. The application of L–P sequence resulted in the pulp optical properties near to the final pulp from K–P–Y sequence

Table 6.19 Generation of Pollutants in Different Stages of De-inking of Sorted Office Waste

Parameter	Enzymatic de-inking with same chemicals[a]	Enzymatic de-inking with less chemicals[b]	Chemical de-inking (control)
COD (kg/TP)	39.80	36.80	40.70
TSS (kg/TP)	20.1	20.2	19.9
Color (kg/TP)	7.71	8.57	10.50

Based on Bajpai et al. (2004b).

[a] NaOH 1%; sodium silicate 1%; H_2O_2 0.5%; surfactant 0.2%; soap 0.001%.

[b] Surfactant 0.2%; soap 0.001%.

where K is a stage applied in the same conditions of L stage but without enzyme. The L–P–Y sequence reaches a color removal of 90% and saves chemicals in the final stages.

Fiber Modification

Enzymatic modification of fibers aims at decreased energy consumption in the production of thermomechanical pulps and increased beatability of chemical pulps or improvement of fiber properties (Bajpai et al., 2006; Bhardwaj et al., 1996). The use of enzymes to modify wood pulp is not new. In 1942, a patent claimed that hemicellulase enzymes from *Bacillus* and *Aspergillus* sp. could aid refining and hydration of pulp fibers (Diehm, 1942). Later (Bolaski et al., 1959; Noe et al., 1986; Yerkes, 1968), processes were patented that used cellulase enzymes from *Aspergillus* sp. and white rot fungus to separate and fibrillate pulp. About 20–50% reduction in beating time and improvements in water retention, formation, and tensile strength were obtained. Mixtures of cellulase and hemicellulase have also been tried (Bajpai et al., 2006; Bhardwaj et al., 1996; Mohlin and Pettersson, 2001). About 20–70% reduction in beating time with different hardwood, softwood, and bamboo pulp has been observed.

In mill trials, approximately 15–20% reduction in refining energy with mixture of cellulase and hemicellulase enzymes on different types of papers (glassine, condenser, and thin papers) was observed (Freiermuth et al., 1994; Yamaguchi and Yaguchi, 1996). Another process-scale trial in a mill producing coated papers, using the same enzyme, showed a reduction in refining energy of about 70 kWh/TP in softwood pulps, and 30 kWh/TP in hardwood pulp (Bajpai et al., 2006). A reduction in steam consumption of about 0.5 tonne/t of paper was observed. The use of the enzyme eliminated the debottlenecking of refining in the softwood street and increased production by 12% (Table 6.20). The strength properties were not affected. Process-scale trials in other mills producing writing and printing paper also showed encouraging results (Bajpai et al., 2006). In a mill producing heavy grams per square meter (gsm) base papers, a trial conducted with mixture of cellulase and hemicellulase enzymes led to the bypass of a triple-disk refiner of 180 KWh (Table 6.21).

Table 6.20 The Effect of Enzyme Treatment on Power and Steam Consumption during Coating Base Manufacture–*Process-Scale Trial Results*

Particulars	Power consumption kWh/t pulp Softwood	Power consumption kWh/t pulp Hardwood	Steam tonne/tonne paper
Control	200	150	2.57
Trial	130	120	2.07
Savings	70	30	0.50

Based on data from Bajpai et al. (2005b, 2006).

Conditions: Temperature 40–45°C; pH 6.8–7.0; enzyme dose 100 g/TP (in both the streets).

Table 6.21 The Effect of Enzyme Treatment on Power Consumption during Manufacturing of High gsm Base Papers (Supercoated Art Board 122 gsm and Art Paper 102 gsm)—*Process-Scale Trial Results*

Condition	Normal (control)	Trial
Before refining	16–18	16–18
After refining (1 conical, 1 triple-disk refiner, and 1 DDR)	23–25	25–28
After refining (1 conical and 1 DDR)	—	23–25

Based on data from Bajpai et al. (2005b, 2006).

Conditions: Temperature 40–45°C; pH 6.8–7.0; retention time 1.5 hours; stock consistency 4%; enzyme dose 200 g/TP (dilution 50:50); dosing point, mixing chest.

The strength and other properties were within the specified limits and comparable to those without a trial run. Process-scale trials in a mill producing packaging grade paper during the manufacture of normal extensible sack kraft paper (ESKP) (60% unbleached bamboo long fraction kraft pulp and 40% new double lines kraft cutting) and high-strength ESKP (100% long fraction bamboo pulp) showed reduction in refining energy of 25 kWh/TP due to reduction in double-disk refiner (DDR) (stock and machine) load (Bajpai et al., 2006). There was also reduction in steam consumption of approximately 0.6 tonne/ton paper. The strength properties were not affected by enzyme treatment; in fact, the mill was able to produce high-strength paper having low Gurley porosity without sacrificing other strength properties (Table 6.22). In the case of normal ESKP, stock DDR was bypassed. Saving in power due to reduction in DDR load was 54 kWh/TP (Table 6.23). Saving in steam consumption was observed to be approximately 0.25 tonne/tonne paper, and the strength properties were comparable.

Oxidative enzymes, manganese peroxidase, and laccase-mediator system (Petit-Conil et al., 1998; Wong et al., 1999) also reduced energy requirement in refining. Manganese peroxidase reduced Papperindustriens Forsknings Intitutet (PFI) refining by 25%; laccase-mediator system reduced refinability of high kappa kraft pulp

Table 6.22 The Effect of Enzyme Treatment on Power Consumption during Manufacturing of ESKP High Strength—*Process-Scale Trial Results*

Particulars	Stock DDR (kWh/t)	Machine DDR (kWh/t)	Steam (tonne/tonne paper)
Control (no enzyme)	80.12	50.97	3.18
Trial (with enzyme)	62.34	43.57	2.55
Savings	17.79	7.40	0.63

Based on data from Bajpai et al. (2005b, 2006).

Net savings in refining power: 25.19 kWh/t

Conditions: Temperature 40–45°C; pH 6.8–7.5; enzyme dose 145 mL/TP; dosing point, pit pulper.

Table 6.23 The Effect of Enzyme Treatment on Power Consumption during Manufacturing of ESKP Normal—*Process-Scale Trial Results*

Particulars	Stock DDR (kWh/t)	Machine DDR (kWh/t)	Steam (tonne/tonne paper)
Control (no enzyme)	71.67	35.42	3.15
Trial (with enzyme)	0.00 (bypassed)	52.79	2.90
Savings	71.67	−17.38	0.25

Based on data from Bajpai et al. (2005b, 2006).

Net savings in refining power: 54.29 kWh/t.

Conditions: Temperature 40–55°C; pH 6.8–8.0; enzyme dose 110 mL/TP; dosing point, pit pulper, and Tridyne pulper.

by increasing hand sheet bulk. Kallioinen et al. (2003) reported that enzyme-aided refining is economical and competitive in improving energy economy of mechanical pulping (Kallioinen et al., 2003). Cellulase and hemicellulase enzymes are being used regularly for refining in mills throughout India, China, Indonesia, and North America.

Fibers become more flexible and easy to refine by treatment with enzyme, requiring less energy to fibrillate the fibers. This results in generation of less fines due to better flexibility of fibers (the fibrils/fines are also partially hydrolyzed in the backwater system by endoglucanase component of enzyme). Thus, enzyme action results in two different and opposite effects. One is generation of less fines (better drainability) and second is better fibrillation of fibers (low freeness). This results in an SR value that may or may not be the same as that obtained without enzyme treatment. This behavior varies with the pulp quality. Very often, there is no noticeable change in SR, but there is appreciable improvement in strength properties (due to generation of less fines and better fibrillation). So, refining energy can be reduced to get the desired strength properties without generation of much fines (at lower °SR or higher Canadian standard freeness (CSF) value).

Mixtures of cellulase and hemicellulase enzymes function mainly by partial hydrolysis of the fines, perforation, and brushing of long fibers (D. Ghosh, personal communication). By hydrolyzing fines, the enzyme increases drainage at the paper machine, reduces the vacuum requirement, reduces the steam load, and increases the paper machine speed. A reduction in the number of fines allows an improvement in the sheet strength due to an increase in the percentage of long fibers. Cellulases in the enzyme mixture prefer attaching to fines, rather than long fibers. This protects the long fibers from severe hydrolysis conditions. The other main action of these enzymes is the perforation of the fibers by xylanase action. This improves the fibers' hydration (swelling) and promotes the internal fibrillation and delamination of the fiber, which improves its properties. Brushing of long fibers is another effect (D. Ghosh, personal communication). The long fibers are eventually collided with by cellulases, which damage the bonds on the exposed cellulose chains. This is partial depolymerization of cellulose chains on the fiber surface, causing a weakening (but not a complete cutting) of external microfibers, which allows the fiber to be refined with less energy or to be more easily defibrillated. This defibrillation also facilitates fiber rehydration, internal fibrillation, and fiber swelling.

The directly visible advantages of enzymes are a reduction in the electrical energy requirement for refining the pulp, a reduction in steam consumption, and a reduction in the backwater consistency. Other benefits are possibility of reducing toxic biocides that create problem in ETP and also denature enzyme; ease in operation of backwater clarification/filtration; possibility of reduction in pitch problem due to better dispersion; better biodegradability of machine effluent (due to hydrolysis of fine fiber fibrils by the enzyme); ease in operation of ETP (due to fewer fibrils and smaller amount of biocides); reduction in greenhouse gas emissions associated with the generation of steam and power; and ease in broke repulping—better dispersion—which may also reduce the addition of chemicals for dispersion.

Water removal on the paper machine has been shown to improve as a result of limited hydrolysis of the fibers in recycled paper. A mixture of xylanase and cellulase enzymes at low concentrations has been found to markedly increase the freeness of recycled fibers without substantially reducing yield (Fuentus and Robert, 1988). The lower the initial freeness, the greater the gain following treatment. Many different cellulases and hemicellulases have been found to improve freeness (Bhardwaj et al., 1995, 1997; Pommier et al., 1989, 1990) (Figs. 6.12 and 6.13).

Freeness shows a rapid initial increase, with over half of the observed effect occurring in the first 30 minutes. A relatively small amount of the enzyme is required. While the initial effects are largely beneficial, extending the reaction time with

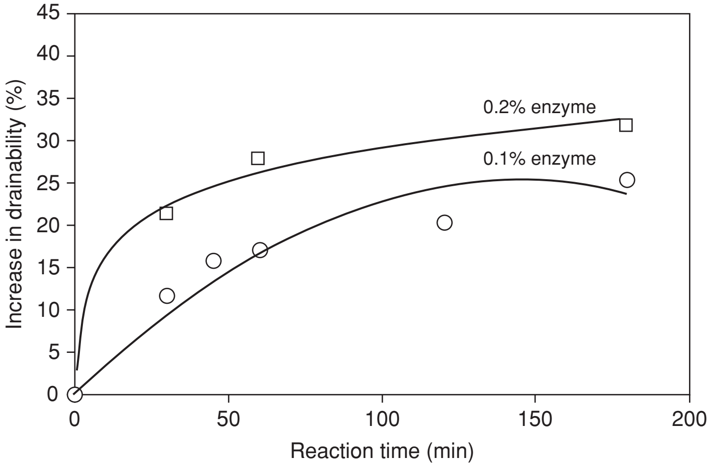

Figure 6.12 The effect of enzyme treatment on drainability of low-freeness (490 mL CSF) recycled pulp. Based on Bhardwaj et al. (1995).

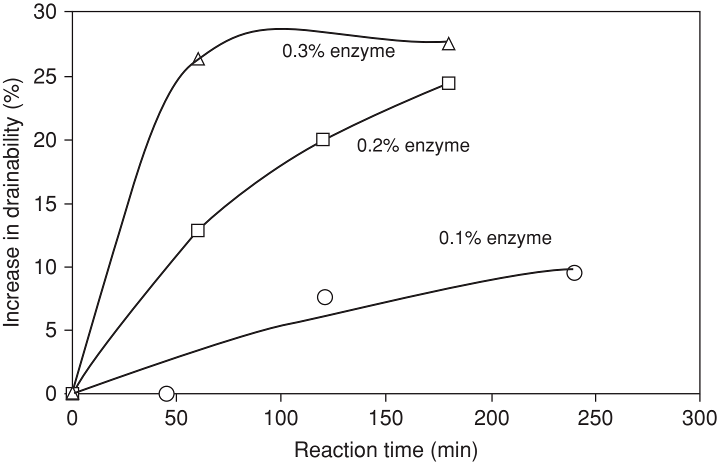

Figure 6.13 The effect of enzyme treatment on drainability of high-freeness (620 mL CSF) recycled pulp. Based on Bhardwaj et al. (1995).

large concentrations of enzyme is detrimental. Unfortunately, crude enzyme mixtures also reduce strength properties. Mill trials have been carried out successfully using a commercial *Trichoderma reesei* enzyme called Pergalase A40 (Pommier et al., 1990). Mixed xylanases and cellulases peel the surface of the fibers. If treatment is limited, the enzymes only remove elements that have a great affinity for water but which contribute little to interfiber binding potential. By selectively removing these surface components, pulp water interactions are reduced and drainage increases without noticeable changes in the final mechanical strength properties of the pulp. If the treatment is extended, however, fibrillation becomes pronounced and drainage decreases. If large quantities of crude enzymes are used, the average fiber length is reduced, fines disappear, and the strength properties of the fibers are lost. Therefore, an optimum level of enzyme treatment is required. It has been reported that the drainability of mechanical pulp can also be enhanced by the addition of hemicellulases (Karsila et al., 1990). The authors claim that xylanase improves the freeness of de-inked recycled pulp while having no detrimental effect on fiber tensile strength properties. By comparison, the tear indices of recycled pulps treated with cellulase decreased (Karsila et al., 1990). These findings suggested that xylanases might be much more effective than cellulases or crude xylanase–cellulase mixtures. Xylanases, however, remove hemicelluloses that promote interfiber bonding. This effect can also lead to poor paper properties.

The degree of polymerization of pulp treated with cellulase-free xylanase was found to increase, apparently due to the selective removal of xylan, which has a lower degree of polymerization (Clark et al., 1989; Puls and Poutanen, 1989). Thus, treatment of pulps with xylanases has been shown to increase their viscosities. However, even low cellulase activities in the enzyme preparation result in decreased viscosity.

Stickies Control

One of the major consequences of fiber recycling is dealing with stickies that are natural components of the recycled fiber used by the mills. Stickies can cause runnability and quality problems if recycled fiber and their variable nature make them difficult to control. A new approach to stickies control has been developed that uses esterase-type enzymes to break down the stickies into smaller and less tacky particles (Fitzhenry et al., 2000; Jones, 2005; Jones and Fitzhenry, 2003; Van Haut, 2003; Zimmermann, 2004).

Stickies are tacky, hydrophobic, and pliable organic material found in recycled paper systems. They exhibit a broad range of melting points and different degrees of tackiness depending on their composition. Stickies are composed of a variety of materials including adhesives, styrene–butadiene latex, rubber, vinyl acetate, and hot melts. Variable nature of stickies and the variability of the composition of recycled fiber used by paper and board mills make them more difficult to control.

Enzymes are highly specific in nature; they exhibit a very specific action when applied. A specific enzyme will catalyze a specific type of chemical reaction, meaning that enzymes can be used to target specific areas. This also means that the enzyme used to control stickies will not affect fiber or other papermaking additives. The trick is to find the enzyme that will break down stickies.

A study of the chemical composition of stickies reveals that most contain a number of ester-type chemical bonds that link the basic building blocks of the stickies together. A number of esterase-type enzyme mixtures have been studied to find the one that had the ability to break down the stickies. Breaking the ester bonds reduces the size of the sticky by breaking it into smaller components. A key advantage of this approach is that once broken down, the chance of the particles reagglomerating further along the process is greatly reduced. Another important effect on the stickies is the enzyme modification of the surface of the stickies. This change results in less tacky stickies (Jones, 2005). These enzymes have been proved to reduce downtime, decrease cleaning chemical costs, and increase machine-clothing life better than historical stickies control technologies.

By treatment of old newsprints and old magazines with esterase-type enzyme in a mill trial, a dramatic reduction in the size of the sticky particles is observed (Jones and Fitzhenry, 2003), as shown in Fig. 6.14. The stickies content of all the sizes and the total stickies were much less on enzyme treatment as compared to those without enzyme (pretrial results). The bigger sized stickies are totally absent in the recycled fiber treated with enzyme.

When the recycled fiber from mixed office waste (MOW) was treated with esterase enzyme in a mill trial, the total stickies content came down appreciably (Jones and Fitzhenry, 2003). Without enzyme treatment of MOW, it was not possible to increase the recycled fiber content in the final furnish beyond 50%. Even then, the total stickies were more than 250 ppm (Table 6.24). However, by treating the recycled fiber from MOW with enzyme, total stickies content could

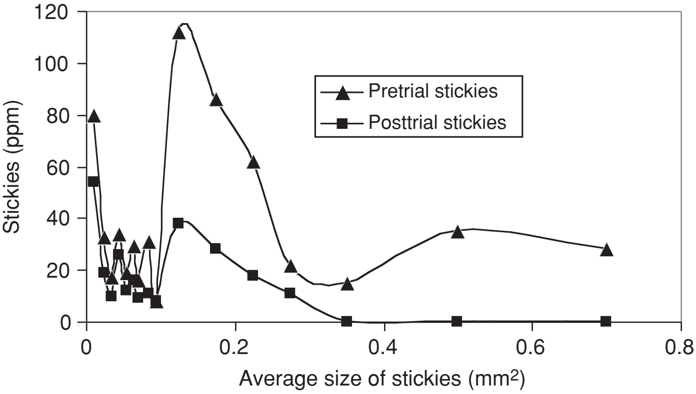

Figure 6.14 Size distribution of stickies in finished stock—plant trial with Optimyze^{TM} of Buckman on old newsprints and old magazines. Based on Jones and Fitzhenry (2003).

be reduced to about 100 ppm that too with higher content (60%) of recycled fiber.

In another MOW mill, the recovered fiber was treated with enzyme to reduce the percentage of high brightness virgin pulp in the final furnish without compromising on brightness of the finished stock. With addition of 35% high bright pulp, the normal brightness gain from coarse screen to finish stock was only 12–14 points when no enzyme treatment was given to the recovered fiber (Jones and Fitzhenry, 2003). However, after esterase enzyme (Optimyze of Buckman) treatment of MOW-recovered fiber, it became possible to get a brightness gain of more than 15 points even when the high bright pulp content was 15–20% only.

Table 6.24 Results of Esterase Enzyme (Optimyze) Evaluation in a Mill Using MOW Furnish—Stickies Content versus Recycled Fiber Content in Furnish

Day and time	Recycled fiber content (%)	Total stickies (ppm)
Day 1		
9 AM (pretrial: no enzyme)	50	250
11 AM	60	420
2:30 PM (enzyme addition)	60	1200
4:30 PM	60	906
5:45 PM	60	390
Day 2		
2 PM	60	110
3:30 PM	60	30
5:30 PM	60	110

Based on Jones and Fitzhenry (2003).

Decolorization and Detoxification of Bleached Kraft Effluent

Several methods have been attempted for decolorization and detoxification of bleached kraft effluents. These include physicochemical and biotechnological methods. The problems underlying the physicochemical treatments are those associated with cost and reliability. Coagulation and precipitation produce a voluminous sludge, which is very difficult to dewater. Usually, an extreme pH range is used for optimum treatment, and the pH needs to be readjusted to neutral before discharge. Oxidation using ozone and hydrogen peroxide is costly and oxidation using chlorine species generates secondary pollutants such as chlorinated organics. The membrane techniques require pretreatment and a large capital investment. Membrane fouling is also a problem with the membrane technique. Biotechnological methods have the potential to eliminate/reduce the problems associated with physicochemical methods. These methods may be bacterial treatment (aerobic as well anaerobic), fungal treatment, or enzymatic treatment (Bajpai and Bajpai, 1994). The bacterial processes are not very effective due to the limitation that they cannot degrade the high-molecular-weight chlorolignin compounds and enzymatic processes are not cost-effective (Bajpai and Bajpai, 1996; Bajpai et al., 1999). Among the biological methods tried so far, the method using white rot fungi is quite effective in decolorizing, dechlorinating, and detoxifying bleach plant effluents.

One of the drawbacks associated with the fungal treatment has been the requirement of easily metabolizable cosubstrate such as glucose for the growth and development of ligninolytic activity (Eriksson and Kirk, 1985; Kirk and Farrell, 1987). To make the fungal treatment method economically feasible, there is a need to reduce the requirement of cosubstrate or identify a cheaper cosubstrate. Hence, effort should be made to identify the strains that show good decolorization with less or no cosubstrate and can utilize industrial waste as a cosubstrate. Efforts should be also made to utilize the spent fungal biomass for preparing the culture medium required in the synthesis of active fungal biomass. If successful, the cost of treatment may be further reduced. As the lignin-degrading system of white rot fungus has a high oxygen requirement, use of oxygen instead of air as fluidizing media should be explored. Increasing the oxygen concentration in the culture atmosphere is expected to have a dual effect: it would lead to an increased titer of the lignin-degrading system and to an increased stability of the existing system.

The use of white rot fungi can serve as a pretreatment method to bacterial treatment and to enhance the bacterial ability to remove organic chlorine and to degrade the relatively higher-molecular-weight chlorolignins. This process can be used as an alternative to internal process modifications (e.g., modified cooking, oxygen bleaching, high-level chlorine dioxide substitution) and conventional biological treatment.

Because the majority of AOX and color is in high-molecular-weight chlorolignins, the priority of research should concentrate on the fate of high-molecular-weight chlorolignins in biological treatment or in the natural environment. Because bacteria degrade significantly only those chloroorganics with molecular weights lower than 800–1000 Da, research is needed to decrease the chlorolignin molecular weight or to remove high-molecular-weight chlorolignins before biological treatment is applied to enhance the biotreatability of bleaching effluents.

Biofiltration of Exhaust Gases

People living in or near a kraft pulp mill often complain of the odor nuisance associated with the mill's operations. These complaints are directly related to the production of odorous compounds during the cooking of wood chips with white liquor and subsequent points of gaseous release to the atmosphere. Even when pure sodium hydroxide is used to treat wood and straw, odors are produced. The cause of these odors is to be found in the residual sulfur-containing protoplasm, which reacts with the alkali to form mercaptans and organic sulfides during the digestion phase. It was found that the mercaptans are formed by the saponification of lignin methoxyl groups by sulfide ions.

The evil smelling gases emitted from the kraft process include H_2S, methyl mercaptan (CH_3SH), and various organic sulfides such as dimethyl sulfide (DMS) ($CH_3—S—CH_3$), and dimethyl disulfide (DMDS) ($CH_3—S—S—CH_3$), collectively referred to as TRS. They are formed during kraft pulping by reaction of sulfides with methoxy groups of lignin via nucleophilic substitution reactions. The major source of TRS emissions include digester blow and relief gases, multiple-effect evaporator vents and condensates, the recovery furnace with direct-contact evaporators, smelt dissolving tank and slacker vents, brown stock washers and seal tank vents, and the limekiln exit vents. Typical characteristics of the gaseous emissions are shown in Table 6.25 (Andersson et al., 1973; Environmental Pollution Control Pulp and Paper Industry, 1976).

The principal difficulty with TRS emission is their nauseous odor, which is detected by the human nose at very low concentrations. Table 6.25 lists the odor threshold (odor detectable by 50% of the subjects) concentrations of the principal TRS compounds emitted by kraft mills, which are only few parts per billion by volume (Springer and Courtney, 1993). At low concentrations, TRS is more of a nuisance than a serious health hazard. Thus, odor control is one of the main air pollution problems in a kraft mill (Table 6.26).

A number of methods are available to eliminate odorous components from gaseous emissions. A broad spectrum of compounds can usually be converted with chemical method, but energy consumption is relatively high. Consumption of chemicals (oxidants) is another disadvantage of these methods. Physical methods, such as absorption in liquids and adsorption on solids, have the disadvantage that the pollutants are not converted, and that the sorbents have to be regenerated. In this way, a new polluted mass flow is often created although these methods, sometime, offer the possibility of recovering valuable components. On the other hand, the biological methods generally have the specific advantage that the pollutants are not concentrated in another phase, but are converted to harmless or much less harmful oxidation products (e.g., CO_2 and H_2O). These processes do not generally give rise to new

Table 6.25 Typical Off-gas Characteristics of the Kraft Pulp Mill

Emission source	Off-gas flow rate (m^3/t pulp)	Concentration (ppm by volume)			
		H_2S	CH_3SH	CH_3SCH_3	CH_3SSCH_3
Digester batch					
Blow gases	3–6,000	0–1,000	0–10,000	100–45,000	10–10,000
Relief gases	0.3–100	0–2,000	10–5,000	100–60,000	100–60,000
Digester, continuous	0.6–6	10–300	500–10,000	1,500–7,500	500–3,000
Washer hood vent	1,500–6,000	0–5	0–5	0–15	0–3
Washer seal tank	300–1,000	0–2	10–50	10–700	1–150
Evaporator hotwell	0.3–12	600–9,000	300–3,000	500–5,000	500–6,000
BLO tower exhaust	500–1,500	0–10	0–25	10–500	2–95
Recovery furnace	6,000–12,000	(after direct-contact evaporator)			
		0–1,500	0–200	0–100	2–95
Smelt dissolving tank	500–1,000	0–75	0–2	0–4	0–3
Limekiln exhaust	1,000–1,600	0–250	0–100	0–50	0–20
Lime slacker vent	12–30	0–20	0–1	0–1	0–1

Based on data from Andersson et al. (1973) and Environmental Pollution Control Pulp and Paper Industry (1976).

environmental problems, or if they do, these problems are minimal. An exhaust air problem should preferably not become a solid waste or wastewater problem. Another advantage of biological treatment is the possibility of carrying out the process at normal temperature and pressure. Moreover, the process is reliable and relatively cheap, while the process equipment is simple and generally easy to operate.

As microorganisms need a relatively high water activity, these reactions generally take place in the aqueous phase and as a consequence the compounds to be degraded

Table 6.26 Odor Threshold Concentration of TRS Pollutants

Reduced sulfur compound	Odor threshold concentration (ppb)
Hydrogen sulfide (H_2S)	8–20
Methyl mercaptan ($CH_3{-}SH$)	2.4
DMS ($CH_3{-}S{-}CH_3$)	1.2
DMDS ($CH_3{-}S{-}S{-}CH_3$)	15.5

Based on data from Springer and Courtney (1993).

as well as the oxygen required for their oxidation first have to be transferred from the gas phase to the liquid phase. The microbial population can either be freely dispersed in the water phase or is immobilized on a packing or carrier material. The first-mentioned operation is carried out in bioscrubbers, the second one in trickling filters and biofilters. Bioscrubbers and tricking filters are more energy-intensive than biofilters as water circulation in these two systems requires relatively much more energy than gas transport through a biofilter. Also, the reliability of operation of bioscrubbers is relatively low due to possible washing away of active microorganisms. Whereas the presence of a large amount of packing material with a buffering capacity diminishes the sensitivity of biofilters to different kinds of fluctuations. Therefore, biofiltration technology is receiving a significant attention (Singhal et al., 1996).

Biofilters are reactors in which a humid polluted air stream or contaminated exhaust gas is passed through a porous packed bed on which pollutant-degrading microbial cultures are naturally immobilized on compost/peat/mixture of natural and synthetic packing materials. Biofilters excel in two main domains: in the removal of odoriferous compounds and in the elimination of volatile organic chemicals, primarily solvents, from air. Under optimum conditions, the pollutants are fully biodegraded without the formation of aqueous effluents. As gases pass through a biofilter, odorous compounds are removed by processes thought to include sorption (absorption/adsorption) and bio-oxidation. The odorous gases adsorb onto the surface of the biofilter medium and/or are absorbed into the moisture film on the biofilter particles. Given a sufficient rate of biological activity in the filter, the sorbed compounds are then oxidized (degraded) by microorganisms. End products from the complete bio-oxidation of the air contaminants are CO_2, water, mineral salts, and microbial biomass. The elimination of a gaseous pollutant in a biofilter is the result of a complex combination of different physicochemical and biological phenomena.

Different types of representative microorganisms/cultures used by various investigators have been shown in Table 6.27. Soil and compost contain a large variety of indigenous microorganisms, which degrade the odorous compounds in air. The common soil bacteria, *Bacillus cereus* var. *mycoides*, and strains of *Streptomyces* are most frequently identified in the soil samples. Autotrophic bacteria such as *Thiobacillus* are also present in the soil, which grow on thiosulfate medium. But the counts of heterotrophic bacteria are much higher. They have been demonstrated to reduce the sewage odors, especially by eliminating the hydrogen sulfide present in the waste air stream (Bohn and Bohn, 1988; Carlson and Leiser, 1966; van Lith et al., 1997). Following bacteria and microfungi—*Actinomyces globisporus*, *Penicillium* sp., *Cephalosporium* sp., *Mucor* sp., *Micromonospora albus*, *Micrococcus albus*, *Ovularia* sp., etc.—are the most frequently occurring microorganisms in the compost cultures. Compost has been a common choice of microbial source in biofiltration (Bohn, 1975; Leson and Wikener, 1991; Pomeroy, 1982; van Lith et al., 1997). In addition to the source of microorganisms, the soil and compost provide a physical support for the microorganisms, and these materials also provide water-holding capacity and some amount of minor and trace nutrients. Aerobically digested sludge of night soil has also been used as a source of microbial cultures in the biofilters for the removal of H_2S, DMS, and methanethiol (Hirai et al., 1990; Lee and Shoda, 1989).

Table 6.27 Microbial Cultures Used for Degradation of Pollutants

Culture	Pollutants
Soil (indigenous microbes)	Sewage odors—H_2S
Compost (indigenous microbes)	Various volatile organic compounds
Aerobically digested sludge of night soil	Sulfur compounds (H_2S, DMS, methanethiol)
Peat (indigenous microbes)	H_2S
Sludge from sewage treatment	H_2S, C_2H_5SH, $(C_2H_5)_2NH$, C_4H_9CHO
Thiobacillus sp. strain MS_1	Methyl sulfides (DMS, DMDS)
Thiobacillus thioparus TK-m	H_2S, DMS, DMDS, methanethiol
Thiobacillus thioparus strain E_6	DMDS
Hyphomicrobium sp. strain S	DMS, DMSO
Hyphomicrobium sp. strain EG	Methylated sulfur compounds
Pseudomonas fluorescens (DSM50 090)	Methanol, isopropanol, butanol, etc.
Bacterial consortium consisting of *Pseudomonas*, *Methylomonas*, *Aeromonas*, *Achromobacter*, *Flavobacterium*, *Alcaligenes*	Methanol

Based on data from Leson and Wikener (1991), van Lith et al. (1997), Bohn (1975), Pomeroy (1982), Hirai et al. (1990), Lee and Shoda (1989), Furusawa et al. (1984), Ottengraph and Van Denoever (1983), Sivela and Sundman (1975), Kanagawa and Kelly (1986), Kanagawa and Mikami (1989), Smith and Kelly (1988a,b), DeBont et al. (1981), Suylen et al. (1986), Suylen et al. (1987), Kirchner et al. (1987), Shareefdeen et al. (1993).

The digested sludge of night soil is supposed to contain several types of microorganisms, useful in bio-oxidation of air pollutants. The indigenous microorganisms in the peat have been tried for bio-oxidation of H_2S in a biofilter (Furusawa et al., 1984). In a few cases, sludge from sewage treatment works is used as the source of microorganisms (Ottengraph and Van Denoever, 1983). Classical microbiological techniques have revealed the presence of mixed populations of bacteria, yeast, fungi, and higher organisms in the biofilters. Bacterial species of *Thiobacillus* and *Hyphomicrobium* degrade many sulfur compounds such as H_2S, methyl sulfide, DMS, DMDS, dimethyl sulfoxide (DMSO), and methanethiol (DeBont et al., 1981; Kanagawa and Kelly, 1986; Kanagawa and Mikami, 1989; Sivela and Sundman, 1975; Smith and Kelly, 1988a,b; Suylen et al., 1986, 1987). For methanol bio-oxidation, *Pseudomonas fluorescens* (Kirchner et al., 1987) and a bacterial consortium (Shareefdeen et al., 1993) consisting of *Methylomonas*, *Aeromonas*, *Achromobacter*, *Flavobacterium*, *Alcaligenes*, and *Pseudomonas* have been used.

Because biofilters compete with incineration and carbon adsorption in many situations, they are attractive in terms of not having to deal with landfilling costs or regeneration headaches. This has already been recognized in Europe, and some biofilter technology has found its way to the United States (Anonymous, 1991). Thought of not simply transferring contaminants from one medium to another is particularly appealing. The biofilter creates a truly destructive process.

The use of microbial filter techniques in the treatment of air effluents containing organic pollutants can offer a number of advantages. They are inexpensive, work efficiently at ambient temperature, self-generating, maintenance free with low running cost, long life, kind to the environment, and oxidize most common volatile organic compounds to carbon dioxide and water producing virtually no by-products. The microbial flora survives a fairly long period during which the filter bed is not loaded (periods of a fortnight are easily spanned with hardly any loss of microbial activity). This is important in view of the dynamic behavior of filter bed at discontinuous operation, and means a very short starting time after longer periods of not operating the filter bed. Moreover, the presence of a large amount of packing material with a buffering capacity diminishes the sensitivity of biofilters to different kinds of fluctuations.

Biofiltration technology for purification of exhaust gases from pulp and paper industry has a great potential. Very little information directly related to the industry is available although reasonably good information is available on the biofiltration of organic compounds similar to those found in the exhaust gases of pulp and paper industry. More studies are needed to obtain a better understanding of the heat transfer, mass transfer, and reaction processes, occurring within the biofilter beds. Comprehensive long-term studies of full-scale biofilter systems would also be valuable in improving our understanding of biofilters used to remove volatile organic compounds from off-gases generated in the paper industry. Extended studies of transient behavior of biofilters are also needed to provide the basic empirical knowledge necessary for plant design, scale-up, and performance evaluation under real conditions.

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Glossary and Abbreviations

Achievable level When using a particular technique or combination of techniques, achievable level means that a certain emission level may be expected to be achieved over a substantial period in a well-designed, well-maintained, and well-operated installation or process using those techniques.

Acute toxicity Toxicity that causes a rapid adverse effect (e.g., death) in a living organism following short-term exposure.

Aerobic A process that occurs in the presence of air or oxygen.

Anaerobic Conditions where oxygen is lacking; organisms not requiring oxygen for respiration.

Best available technique (BAT) A technique that an institution determines, after examination for efficacy under field conditions and not solely under laboratory conditions, to be the best available (taking cost into consideration). BAT is a requirement under the EU Directive on Integrated Pollution Prevention and Control.

Bioaccumulation A general term describing a process by which chemical substances are accumulated by aquatic organisms from water, either directly or through consumption of food containing the chemicals.

Biological oxidation The way bacteria and microorganisms feed on and decompose complex organic materials. It is used in self-purification of water bodies and in activated sludge wastewater treatment.

Biological oxygen demand (BOD) A measure of the amount of oxygen consumed in biological processes that breaks down organic matter in water. The greater the BOD, the higher the degree of pollution.

Biological treatment A treatment technology that uses bacteria to consume waste. The treatment breaks down organic materials.

Biomass All materials that are produced by photosynthesis and potentially useful for the production of organic chemicals or as energy sources.

Black liquor The liquor that exits the digester with the cooked chips at the end of the kraft cook. It is a mixture of the cooking chemicals and dissolved wood material that remains after sulfate cooking; it is recovered during pulp washing, concentrated by evaporation, and burned in the recovery boiler to regenerate the cooking chemicals and energy.

Bleaching The process of brightening the fiber by removal or decolorization of the colored substance.

Bleaching efficiency Some of the oxidizing power of a bleaching agent is always wasted in side reactions. Some bleaching agents are more prone than others to undergo wasteful reactions; conversely, some use their oxidizing power more efficiently than others. Efficiency is a measure of the degree to which a bleaching agent's oxidizing power is used in desirable kappa reducing reactions.

Brightness The reflectance or brilliance of the paper when measured under a specially calibrated blue light. Not necessarily related to color or whiteness, brightness is expressed in % ISO.

Environmentally Friendly Production of Pulp and Paper, by Pratima Bajpai

Brightness reversion Decrease of brightness of a sheet of pulp or paper due to aging.

Broke Paper that has been discarded anywhere in the process of manufacture.

Brown stock The suspension of unbleached pulp.

Buffer A solution containing a weak acid and its conjugate weak base, the pH of which changes only slightly on the addition of acid or alkali.

Buffer capacity Amount of acid and/or base that a buffer solution can neutralize and still maintain an essentially constant pH. A measure of the relative sensitivity of a solution to pH changes on the addition of acids or base.

Carbohydrates A large group of polymer compounds synthesized by plants containing carbon, hydrogen, and oxygen, in which the latter two elements are usually in the 2:1 proportion of water. Cellulose, sugars, and starches are all carbohydrates.

Carcinogen A substance that induces cancer in a living organism.

Catalyst An agent that speeds up a chemical reaction by changing the reaction mechanism to one of lower activation energy.

Cationic The characteristic behavior or property of an ion with a positive charge. Cations move to the cathode in electrolysis.

Causticizing This is a process by which green liquor separated from the smelt produced in the recovery boiler is converted to white liquor with the help of quicklime, thus allowing the cooking chemicals to be reused.

Cellulose A high-molecular-weight linear polymer of repeating β-D-glucopyranose units. It is the chief structural element and major constituent of the cell wall of trees and plants.

Chelating agent A multidentate ligand simultaneously attaches to two or more positions in the coordination sphere of a central metal ion. Chelants or chelating agents such as ethylenediamine tetraacetic acid and diethylenetriamine pentaacetic acid are applied because of good sequestering properties, that is, their ability to suppress the activity of dissolved transition metal ions without precipitation.

Chemical oxygen demand (COD) A measure of the oxygen required to oxidize all compounds in water, both organic and inorganic. COD is more widely used as it is a simple procedure and includes the effects of nonbiodegradable organic matter, which can account for up to half of the material discharged.

Chemical pulp A generic term that describes pulp produced by chemical (as opposed to mechanical) processes. These chemical processes include kraft (sulfate) and sulfite processes.

Chemical recovery The process of burning concentrated black liquor in a recovery boiler to derive the usable chemicals and to extract the heat energy from the used liquor.

Chemimechanical pulp The pulp of lignocellulose materials that have been treated with chemical reagents, obtained by defibration at atmospheric pressure.

Chemithermomechanical pulp (CTMP) A category of pulp produced by a process in which wood chips are treated with chemicals prior to heating and refining. Unbleached CTMP is mainly used in integrated paper mills. Bleached CTMP, dried and sold as market pulp, has grown significantly in importance and is now widely used in the production of many grades of paper, including woodfree papers.

Chronic Lingering or continuing for a long time, often for several weeks to years. This can be used to define either the exposure of an aquatic species or its response to an exposure (effect). Chronic exposure typically includes a biological response of relatively slow progress and long continuance, often affecting a life stage.

Chronic toxicity Toxicity that results in adverse physiological effects in exposed organisms, which appear slowly and persist for long periods following frequent, prolonged, repeated, or continuous exposure to a toxicant.

Closed-cycle A mill or industrial plant that has little or no process effluent.

Consistency The weight percent of air dry (or oven dry) fibrous material in a stock or stock suspension. Typical ranges are low consistency (3–5%, LC), medium consistency (10–15%, MC), and high consistency (30–50%, HC).

Contaminant Biological (e.g., bacterial and viral pathogens) and chemical introductions capable of producing an adverse response (effect) in a biological system, seriously injuring structure, function, or producing death.

Corrosion Deterioration of surfaces through erosion processes such as the conversion of metals to oxides and carbonates.

Daily production capacity The weight of products (air dry mass) an installation can produce during 1 day.

Defoamer Any product that is added to the water–pulp mixture during the manufacture of pulp in a mill to prevent the production of foam or reduce the amount of foam that would otherwise be produced.

De-inking The process of removing ink from printed waste papers, but also involving general removal of other undesirable materials.

Delignification The removal of lignin–-the material that binds wood fibers together–-during the chemical pulping process.

Detection limit The smallest concentration or amount of a substance that can be reported as present with a specified degree of certainty by definite complete analytical procedures.

Dioxins The term used to describe the families of chemicals known as chlorinated dibenzo-*p*-dioxins and dibenzo-*p*-furans. These families consist of 75 chlorinated dibenzo-*p*-dioxins and 135 chlorinated dibenzo-*p*-furans. These molecules can have from one to eight chlorine atoms attached to a planar carbon skeleton. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF) are two of the most toxic members of this family of compounds. If dioxins are detected in releases from bleaching processes that expose unbleached pulp to elemental chlorine, the dioxins are most likely to be TCDD and TCDF.

Disperging Mechanical treatment of waste paper fibers to disperse ink particles.

Dissolved oxygen The oxygen freely available in water. Dissolved oxygen is vital to fish and other aquatic life and for the prevention of odors. Traditionally, the level of dissolved oxygen has been accepted as the single most important indicator of a water body's ability to support desirable aquatic life. Secondary and advanced waste treatments are generally designed to protect dissolved oxygen in waste-receiving waters.

Dissolved solids Disintegrated organic and inorganic material contained in water. Excessive amounts make water unfit to drink or use in industrial processes.

Dregs The solids that settle on in the clarifiers in the causticizing process.

Dry-end Part of the papermaking process after formation of the paper web.

Effluent A complex waste material (e.g., liquid industrial discharge or sewage) that may be discharged into the environment.

Elemental chlorine-free (ECF) A bleaching process that uses chlorine dioxide as opposed to elemental chlorine gas. ECF papers are made exclusively from pulp that uses chlorine dioxide rather than elemental chlorine gas as a bleaching agent. This virtually eliminates the discharge of detectable dioxins in the effluent of pulp-manufacturing facilities.

Environmental impact or effect Change in one or several components of the natural environment that may occur as a result of a particular human activity.

Enzyme A substance containing protein that catalyzes biological reaction.

***Eucalyptus* spp.** The genus *Eucalyptus* belongs to the family Myrtaceae. Worldwide, Myrtaceae comprises some 140 genera and 3000 species.

Eutrophication The overfertilization of lakes due to pollution by sewage, runoff from the land, and industrial wastes (inorganic phosphates and nitrates). These compounds act as nutrients, stimulating algal growth to produce huge blooms. Their subsequent decomposition reduces the oxygen content in the water, and this leads to the death of the algae themselves and proliferation of bacteria that do not require oxygen and kills most aquatic life.

Evaporation plant This is the pulp mill department where spent cooking liquor is concentrated to make it suitable for burning and chemical recovery.

Extractives Compounds extractable from wood with organic solvents. From a physiological standpoint, they can be classified into the following groups:

1. Food reserves (fats, fatty acids)
2. Protectants (terpenes, resin acids, phenols)
3. Plant hormones (phytosterols)

Fate Disposition of a material in various environmental compartments (e.g., soil or sediment, water, air, and biota) as a result of transport, transformation, and degradation.

Fats Triglycerides in which saturated fatty acid components predominate.

Fillers Papermaking additives, usually mineral clays or calcium carbonates.

Fines Small particle-sized material in papermaking usually defined as material below 75 μm.

Flue gas A mixture of gases resulting from combustion and emerging from chimney or stack.

Fossil fuels Petroleum, natural gas, and coal. These fuels are derived from plants and animal life of millions of years ago.

Furan The type of organochlorine compound that occurs naturally and is produced in a wide variety of oxidation processes.

Furnish A mixture of various materials that are blended in the stock suspension from which paper or board is made. The chief constituents are the fibrous material (pulp), fillers, sizing agents, wet-strength, or other additives and dyes.

Grammage The real mass of the paper/board, usually expressed as g/m^2.

Green liquor It is produced by means of dissolving the cooking chemicals digested in the recovery boiler. It is regenerated into white liquor by using lime. White liquor is a cooking solution of pulp.

Green liquor and dregs Molten inorganic salts, referred to as "smelt," collect in a char bed at the bottom of the recovery furnace. Smelt is drawn off and dissolved in weak wash water in the smelt dissolving tank to form a solution of carbonate salts, called "green liquor," which is primarily Na_2S and Na_2CO_3. Green liquor also contains insoluble unburned carbon and inorganic impurities, called "dregs," which are removed in a series of clarification tanks.

Habitat The place where a population (e.g., humans, animals, plants, and microorganisms) lives and its surroundings, both living and nonliving.

Hardness The concentration of all metallic cations, except those of the alkali metals, present in water. In general, hardness is a measure of the concentration of calcium and magnesium ions in water and is frequently expressed as mg/L calcium carbonate equivalent.

Hardwood Pulpwood from broad-leaved dicotyledonous deciduous trees such as aspen, beech, birch, and eucalyptus.

Head box Pulp feed to the paper machine starts here.

Hemicelluloses Short-chain polysaccharides having a DP (degree of polymerization) of 15 or less, mainly polymers of sugars other than glucose. Principal hemicelluloses are xylan in hardwoods and glucomannan in softwoods.

Hexenuronic acids Approximately 75% of the hemicelluloses in hardwoods consist of xylan (4-*O*-methyl glucuronoarabinoxylan). Under the kraft pulping conditions, xylan generates hexenuronic acid (HexA) groups, which form a considerable part of the residual oxidizable material after pulping (measured by the kappa number). Hardwood kraft pulps, and especially eucalypt kraft pulps, may contain high amounts of HexA, contrary to softwood kraft pulps. HexA has adverse effects in bleaching. The most important ones are increased consumption of bleaching agents such as chlorine dioxide (ClO_2) and ozone (O_3) to reach target brightness, increased brightness reversion, and contribution to formation and scaling of oxalates in bleaching equipment.

Hydraulic retention time (HRT) The average length of time liquid and soluble compounds remain in a reactor. Increasing the HRT allows more contact time between substrate and bacteria but requires slower feeding and/or a larger reactor volume.

Hydrophilic Having an affinity for water, readily absorbs water.

Hydrophobic Having little or no affinity for water, repels or does not absorb water.

Ion Electrically charged species consisting of a single atom or a group of atoms. It is formed when a neutral atom or group of atoms either gains or loses electrons.

Ion exchange A process in which ions in solution are exchanged for corresponding ions held on the surface of an ion exchange material.

Isothermal cooking (ITC) This process was developed by Kvaerner and expands on extended modified continuous cooking (EMCC) with an additional circulation loop and a fifth white liquor addition point. The ITC circulation is very high volume and requires a special type of screen to handle the flow. The screens are equipped with backflushing valves that reduce blinding.

Kappa factor Ratio between the first-stage bleaching chemical charge and the kappa number. If the first bleaching stage is D, the kappa factor is usually expressed as active chlorine.

Kappa number A measure of residual lignin content in unbleached pulp, determined after pulping and prior to bleaching. The lower the kappa number, the less associated the lignin.

Kraft process This process is the world's predominant chemical pulping process because of the strength of pulp it produces. The process involves cooking (digesting) wood chips in an alkaline solution, where the active cooking agent is a mixture of sodium hydroxide and sodium sulfide. The dissolved lignin is later removed, leaving behind the cellulose fibers. The term "kraft" is interchangeable with "sulfate" and is derived from a German word which means "strong."

Kraft pulp A chemical pulp produced by combining wood chips and chemicals in huge vats known as digesters. The effect of the heat and the chemicals dissolves the lignin that binds the cellulose fibers together, without breaking the wood fibers, creating a strong pulp product.

Landfills Land disposal sites for solid wastes where the waste is spread in layers, compacted to the smallest practical volume, and cover material applied.

Leachate Water that has passed through a soil and that contains soluble material removed from that soil.

Leaching A hydrometallurgical process in which a metal is dissolved in aqueous solution and then deposited from it after purification.

Lignin Structural constituent of wood and (to a lesser extent) other plant tissues, which encrusts the cell walls and cements the cells together. It is not fermentable.

Limekiln It is used to reburn lime sludge ($CaCO_3$) to form calcium oxide (CaO), which can be reused in causticizing.

Lipids Several naturally occurring substances (e.g., fats and oils) sharing the property of solubility in solvents of low polarity.

Lipophilic Hydrophobic.

Lo-solids cooking This pulping process uses multiple extractions and split wash water additions to minimize the concentration of dissolved solids in the bulk and final phase of delignification. Dissolved solids in digester cooking liquor can cause a decrease in pulp strength and viscosity, increased cooking chemicals and a decrease in bleachability. In Lo-solids cooking, spent liquor is extracted at different locations to purge the dissolved solids that have a negative impact on pulp strength and chemical consumption. Makeup water addition and makeup cooking chemical addition are necessary to satisfy the system hydraulic requirements and subsequent cooking.

Magnefite Magnesium-based sulfite pulping process.

Market pulp Pulp produced for sale to the open market and not used for the manufacture of paper and/or board at the same site.

Mechanical pulp Mass of fibers separated from wood chips by mechanical energy during refining. It contains cellulose, hemicelluloses, and lignin.

Mechanical vapor recompression (MVR) Evaporators reuse the energy from the steam they create, thus eliminating the need for an outside source of heat and cooling. A compressor is used to boost the pressure of steam from the evaporator so that it will condense at a higher temperature. This boost enables the latent heat in the steam to be returned to the evaporator, thus generating more steam. Therefore, the same heat is continuously reused. With power being the only utility, the major operating expense of an MVR evaporator is the mechanical energy required to operate the compressor.

Microtox The Microtox system is a bioassay to test the acute toxicity on environmental samples and pure compounds based on the natural bioluminescence of the marine bacteria *Vibrio fischeri*; in presence of pollutant agents, the natural bioluminescence of *V. fischeri* is reduced and the toxicity is expressed as the agent concentration, which produces a 50% reduction of the initial luminescence (EC50). Nowadays, Microtox is a widespread screening toxicity test for its characteristics of sensitivity, discriminant power, reproducibility, and easy application for organic and inorganic pollutants.

Modified continuous cooking (MCC) process In the MCC process, the cooking zone in the digester is divided into two zones: a cocurrent zone and a countercurrent zone. The charge of white liquor is split between the two zones. The purpose of the modification is to decrease the initial alkali concentration, keep an even concentration of alkali during the cooking process, and a low concentration of the dissolved lignin in the final part of the cooking. EMCC process was developed on the basis of the MCC process. The difference is that in the EMCC process, white liquor is also charged to the washing zone to extend delignification in the digester.

Monosaccharides The simplest repeating units of carbohydrates, also known as sugars or saccharides (glucose and fructose are monosaccharides).

Nonintegrated production An installation in which the production of paper and/or board is not directly connected with the production of pulp. Either pulp or paper and/or board is produced.

Nonprocess elements Elements that can accumulate when closing up the water circuits in pulp mills. They include Al, Si, Ca, Ma, and Mn.

Not detectable Below the limit of detection of a specified method of analysis.

Oils Triglycerides in which unsaturated fatty acid components predominate.

Oligosaccharides Carbohydrates that hydrolyze to yield 2–10 molecules of a monosaccharide (maltose and sucrose are disaccharides).

Organochlorines The group name for organic compounds containing chlorine, both those occurring naturally and those formed during bleaching with chlorinated compounds.

Osmosis Diffusion of a solvent through a semipermeable membrane into a more concentrated solution, tending to equalize the concentrations on both sides of the membrane.

Oxidation The combination of oxygen with a substance, or the removal of hydrogen from it or, more generally, any reaction in which an atom loses electrons.

Oxidation/reduction The process in which electrons are lost or gained and the oxidation state (valence) of some atoms increases or decreases. The substance containing atoms whose oxidation states increase is oxidized. The substance containing atoms whose oxidation states decrease is reduced.

Oxidizing agent An agent that makes possible an oxidation process by itself becoming reduced.

Paper A sheet of fibers with a number of added chemicals. According to the basic weight, it can be distinguished as follows: paper < 150 g/m^2 $<$ paperboard (or board) < 250 g/m^2 $<$ cardboard.

Particulate A small, discrete mass of solid or liquid matter that remains individually dispersed in gas or liquid emissions. Particulates take the form of aerosol, dust, fume, mist, smoke, or spray. Each of these forms has different properties.

Particulate emissions Fine liquid or solid particles discharged with exhaust gases. Usually measured as grains per cubic foot or pounds per million Btu input.

Phenols Phenol is a benzene ring with one —OH radical replacing hydrogen. Phenols are compounds that contain additional chemical groups bound to this basic structure (each replacing hydrogen).

Photosynthesis The process by which green plants convert carbon dioxide (CO_2) dissolved in water to sugars and oxygen in the presence of chlorophyll using sunlight for energy. Photosynthesis is essential in producing a lake's food base and is an important source of oxygen.

Pitch Resinous material in virgin pulps.

Pollution Generally, the presence of matter or energy whose nature, location, or quantity produces undesired environmental effects.

Polysaccharides Carbohydrates that hydrolyze to yield more than 10 molecules of a monosaccharide (cellulose and starch are glucose polymers).

Primary treatment Physical treatment of wastewater to reduce settleable and floatable solids.

Protocol A formally agreed method and procedure for measuring an indicator; it defines the sampling, sample handling procedures, and sample analysis.

Pulping The process of converting raw fiber (e.g., wood) or recycled fiber to a pulp usable in papermaking.

Reactivity Reactivity may be defined in terms of the fraction of the residual oxidizable material that a bleaching agent is capable of removing (i.e., delta kappa/delta bleaching agent).

Recovery boiler It is used to burn black liquor from sulfate pulping for recovery of inorganic chemicals as well as for energy production.

Recycled fiber pulp Fibrous material that has already passed through paper and/or board production.

Refinability The ease with which paper or pulp can be treated in a refiner as measured in kWh/ODt or MJ/kg.

Refining A process of mechanically treating fibers to develop strength.

Resin and fatty acids (RFAs) These are predominantly components of coniferous trees having the natural function of protecting against microbial damage. These compounds are released from wood during the pulping process and a fraction reaches the wastewater treatment system. RFAs are acutely toxic to aquatic organisms at concentrations of the order of parts per million, and their presence has been linked to toxicity outbreaks in receiving waters following process upsets.

Salt cake The chemical, generally sodium sulfate, added to black liquor to make up for soda loss.

Saponification The hydrolysis of a triglyceride by a strong base. The products are glycerol and soap.

Save-all An apparatus used for reclaiming fibers and fillers from white water. It usually operates on a filtration, sedimentation, flocculation, or flotation principle.

Secondary treatment Biological treatment of wastewater to reduce BOD and toxicity; it normally reduces TSS also.

Sediment Unconsolidated mineral and organic particulate materials that settle to the bottom of aquatic environment.

Selectivity Selectivity is the degree to which a pulping or bleaching agent can lower the kappa number without dissolving or damaging the other components of the fiber (cellulose and hemicellulose). Selectivity can be loosely defined as the ratio of attack on lignin to attack on carbohydrates.

Smelt The molten ash that flows out of the recovery furnace as a white hot liquid.

Soaps The salts of fatty acids, for example, $RCOO\text{-}Na^+$, where the R group is a hydrocarbon chain containing from 3 to 21 carbon atoms.

Softwood Wood obtained from evergreen cone-bearing species of trees such as pines and spruces that are characterized by having needles.

Stickies Materials that stick together; adhesive contaminants in recovered paper.

Stock The mixed suspension of fiber and other materials used to form paper.

Stripper Equipment used to carry out stripping (desorption).

Stripping (desorption) A unit operation in which a volatile component of a liquid mixture is transferred into a gas.

Sulfite pulp Chemical pulp where various sulfites or bisulfites are used as main cooking chemicals.

Sulfite pulping Pulp produced with sulfur dioxide and calcium, magnesium, ammonium, or sodium bases. The pulp can be produced at different pH levels. The higher the pH, the stronger the pulp produced. At pH 14, the strength of sulfite pulp equals that of kraft pulp.

Supercalendered paper Calendered groundwood paper made using alternating chrome and fiber rollers, which produce a very smooth, thin sheet of paper, known as supercalendered paper. Supercalendered paper is typically used in magazines, catalogs, and directories.

Suspended solids Small particles of solid pollutants that float on the surface or are suspended in sewage or other liquids.

Thermomechanical pulp (TMP) A high-yield pulp produced from wood chips that have been exposed under pressure to superheated steam. The heat softens the lignin, which allows fiber separation with less damage than in purely mechanical pulping.

TMP processes The use of a refiner that consists of one or two rotating serrated disks to separate the fiber in wood chips. TMP processes reduce the energy requirement of the refining process and increase the strength of the pulp. Typical pulp yields range from 90% to 95%.

Total reduced sulfur This parameter is a measure of the amount of odorous sulfur compounds.

Total reduced sulfur compounds Mix of organic compounds that cause the odor associated with kraft pulp mills. These compounds include hydrogen sulfide, dimethyl sulfide, dimethyl disulfide, and methyl mercaptan.

Total suspended solids A measure of the suspended solids in wastewater, effluent, or water bodies, determined by using tests for total suspended nonfilterable solids. They can eventually settle on the bottom of a mill's receiving water and affect the habitat of bottom-living organisms. Well-operated treatment systems remove most of these solids. Concern remains, however, because heavy metals, dioxins, and other non-chlorinated compounds can be adsorbed into the remaining suspended solids.

Totally chlorine-free Bleaching process that uses no chlorine products.

Tonne (metric tonne) This measure of weight is equal to 2000 lb (907.18 kg). It is also equal to 0.907 metric tonne.

Total reduced sulfur This parameter is a measure of the amount of odorous sulfur compounds.

Toxicity The inherent potential or capacity of a material to cause adverse effects in a living organism.

Transition metals Transition metals consist of the 38 elements in groups 3–12 of the periodic table of the elements. As with all metals, the transition elements are both ductile and malleable, and conduct electricity and heat. One interesting aspect of transition metals is that their valence electrons, or the electrons they use to combine with other elements, are present in more than one shell. Consequently, they often exhibit several common oxidation states. A partial list of transition metals includes titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), molybdenum (Mo), silver (Ag), cadmium (Cd), tantalum (Ta), tungsten (W), platinum (Pt), gold (Au), and mercury (Hg). Transition metals of interest in chemical pulp bleaching are Mn, Fe, and Cu because they catalyze the decomposition of hydrogen peroxide. Transition metals of interest for their environmental impact are Cd and Hg because of their poisoning effect.

Triglycerides Esters of glycerol (1,2,3-propanetriol) with long-chain monocarboxylic (fatty) acids.

Turpentine A mixture of terpenes, principally pinene, obtained by the steam distillation of pine gum recovered from the condensation of digester relief gases from the cooking of softwoods by the kraft pulping process.

UASB Upflow anaerobic sludge blanket reactor/process.

Viscosity Measured by dissolving pulp fibers in cupric ethylene diamine and observing the time taken for the solution to pass through a standard capillary (TAPPI Test Method T230 om-94).

Viscosity is expressed in centipoises (cP) or millipascal seconds (mPa.s), which are numerically the same. It is related to cellulose molar mass (the degree of polymerization) and indirectly to fiber strength.

Volatile organic compounds (VOCs) Organic compounds, such as ethylene, propylene, benzene, and acetone, which evaporate readily. VOCs embrace both hydrocarbons and compounds of carbon and hydrogen, which contain other elements such as oxygen, nitrogen, and chlorine.

Wet end Part of the papermaking process prior to formation of the paper web.

White liquor It consists of caustic soda (NaOH) and sodium sulfate (Na_2S), and is used as cooking solution of sulfate pulp.

White water A general term for all waters of a paper mill that have been separated from the stock or pulp suspension, either on the paper machine or accessory equipment, such as thickeners, washers, save-alls, and from pulp grinders. It carries a certain amount of fiber and may contain varying amounts of fillers and dyestuffs

Wood-containing paper and/or board Paper and board having considerable part of noncellulosic compounds (more than 5%) as an essential constituent of its fiber composition.

Woodfree paper and/or board Paper and board having in principle only chemical pulp in its fiber composition; in practice, however, it may contain a small amount of other fibers or pulps (less than 5% noncellulosic compounds).

Yankee cylinder A large single cylinder used mainly to dry tissue/towels.

Yield The amount of useful fiber after pulping and/or bleaching expressed as a percentage of the raw fiber on an oven-dry basis

ABBREVIATIONS

AOX	Adsorbable organic halides
AQ	Anthraquinone
BAT	Best available technology
BFR	Bleach filtrate recycle
BOD	Biological oxygen demand (mg/L)
BREF	BAT reference document
CEPI	Confederation of European Paper Industries
CMP	Chemimechanical pulp
COD	Chemical oxygen demand (mg/L)
CP	Cleaner production
CTMP	Chemithermomechanical pulp
DAF	Dissolved air flotation
DIP	De-inking plant/de-inked pulp
DTPA	Diethylenetriamine pentaacetic acid
ECF	Elemental chlorine-free
EDTA	Ethylenediamine tetraacetic acid
EFM	Effluent-free mill
EGSB	Expanded granular sludge bed
EPA	Environmental Protection Agency
ETP	Effluent treatment plant
ISO	International Organization for Standardization
ITC	Isothermal cooking
LWC	Lightweight coated
MCC	Modified continuous cooking/medium-consistency cooking
MBR	Membrane biological reactor
MF	Microfiltration
MLSS	Mixed liquor suspended solids
MVR	Mechanical vapor recompression
NCASI	National Council for Air and Stream Improvements (USA)
NCG	Noncondensable gases
NF	Nanofiltration
NSSC	Neutral sulfite semichemical
PEO	Polyethylene oxide
ppm	Parts per million
PTFE	Polytetrafluoroethylene (Teflon)
RO	Reverse osmosis
SS	Suspended solids (mg/L)

TCDF	Tetrachlorodibenzofurans
TCF	Totally chlorine-free
TMP	Thermomechanical pulp
TOC	Total organic carbon
TRS	Total reduced sulfur
TSS	Total suspended solids (mg/L)
UASB	Upflow anaerobic sludge blanket
UF	Ultrafiltration
UNEP	United Nations Environment Programme
VOA	Volatile organic acids
VSEP	Vibrating shear-enhanced process

Subject Index

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